Notes

Cationic Rhodium Complex Catalyzed Highly Selective Hydrosilylation of Propargylic Amine Derivatives

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Summary: Hydrosilylation of N-propargyl sulfonamides in the presence of a catalytic amount of $[Rh(COD)_2]BF_4$ *and* PPh_3 *(P/Rh = 2) proceeded at room temperature to give N-[(E)-3-silyl-2-propenyl] sulfonamides with high selectivities in excellent yields.*

Introduction

Hydrosilylation of alkynes[1] is the most convenient method for the preparation of vinylsilanes, which are useful synthetic intermediates.[2] However, the reaction has a selectivity problem due to the difficulty in controlling regio- and stereoselectivity. Generally, hydrosilylation of 1-alkynes gives regio- and stereoisomers, i.e., (*E*)-1-silyl-1-alkene, (*Z*)-1-silyl-1-alkene, and 2-silyl-1-alkene.[3] We could overcome the selectivity problem by using a cationic rhodium complex as a catalyst.[4] Cationic rhodium complex catalyzed hydrosilylation of 1-alkynes was found to be highly selective to give (*E*)-1-silyl-1-alkenes. Another unique feature of cationic rhodium complex catalysis is its opposite stereoselectivity compared to that given by neutral rhodium complex catalysis.[5]

Regio- and stereocontrolled hydrosilylation of alkynes bearing a functional group is an important and useful route to a vinylsilane bearing a functional group.[6] The effectiveness of our cationic rhodium complex catalysis is demonstrated for the synthesis of (*E*)-γ-silyl allylic alcohols, which are useful building blocks.[4a] (*E*)-γ-Silyl allylic alcohols could be obtained in excellent yields by cationic rhodium complex catalyzed highly selective hydrosilylation of propargylic alcohols. We extend this chemistry to propargylic amines and their derivatives. A few examples of hydrosilylation of propargylic amines were reported.[7] The reaction using Speier's catalyst gave the corresponding product in a moderate yield. However, rhodium complex catalyzed hydrosilylation of propargylic amines and their derivatives has not been reported. Here, we describe cationic rhodium complex catalyzed highly selective hydrosilylation of propargylic amine derivatives.

Results and Discussion

First, we examined cationic rhodium complex catalyzed hydrosilylation of propargylamine and *N*,*N*-dimethylpropargylamine with diethylmethylsilane (**2a**). While the starting materials were consumed, no hydrosilylation product was obtained. Reactions resulted in polymerization of an alkyne.[8] Uncharacterized polymeric material was obtained. Hydrosilylation of *N*-propargylbenzamide (**1a**) with diethylmethylsilane (**2a**) in the presence of a catalytic amount of $[Rh(COD)_2]BF_4$ and PPh_3 (P/Rh = 2) under refluxing 1,2-dichloroethane for 15 h gave the corresponding products in 54% yield. The ratio of **3a**/**4a**/**5a** was 81/6/13. *E*-isomer **3a** was obtained as a major product. Hydrosilylation product could be obtained by introduction of an electron-withdrawing group on a nitrogen atom. To obtain a hydrosilylation product in a high yield, we examined the hydrosilylation of *N*-propargylsulfonamides, where a strong electron-withdrawing group was substituted on a nitrogen atom. Hydrosilylation of *N*-propargylmethanesulfonamide (**1b**) with diethylmethylsilane (**2a**) at room temperature for 2 h gave *N*-[(*E*)-3-(diethylmethylsilyl)-2-propenyl]methanesulfonamide (**3ba**) in 93% yield, eq 1. Neither stereo- nor regioisomer was obtained. Similarly, *N*-propargyl-*p*-toluenesulfonamide (**1c**) was also hydrosilylated at room temperature for 2 h. *N*-[(*E*)-3-(Diethylmethylsilyl)-2-propenyl]-*p*-toluenesulfonamide (**3c**) was obtained in 95% yield. $[Rh(COD)_2]BF_4$ and PPh_3 (P/Rh = 2) were found to be an efficient catalyst system for the hydrosilylation of *N*-propargylsulfonamide. The nature of the catalyst precursor affected the reaction markedly. The results are summarized in Table 1. Reactions catalyzed by a cationic rhodium complex and PPh_3 proceeded at room temperature to give **3ba**, *E*-isomer exclusively, irrespective of the counteranion (entries 1−4). However, a neutral rhodium complex gave a different result. Reactions were less selective and gave a low yield of products, even under refluxing 1,2-dichloroethane (entries 5 and 6). Speier's catalyst is known as the most active and widely used

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(2) For a review, see: (a) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375. (b) Fleming, I.; Dunogues, J.; Smithers, R. H. *Org. React.* **1989**, *37*, 57. (c) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988; p 7.

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(4) (a) Takeuchi, R.; Nitta, S.; Watanabe, D. *J. Org. Chem.* **1995**, *60*, 3045. (b) Takeuchi, R.; Nitta, S.; Watanabe, D. *J. Chem. Soc., Chem. Commun.* **1994**, 1777. (c) Takeuchi, R.; Tanouchi, N. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2909. (d) Takeuchi, R.; Tanouchi, N. *J. Chem. Soc., Chem. Commun.* **1993**, 1319.

(5) Neutral rhodium complex catalyzed hydrosilylation of 1-alkynes is (*Z*)-selective, see: Ojima, I; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127.

(6) For example, see: Takeuchi, R.; Sugiura, M. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1031.

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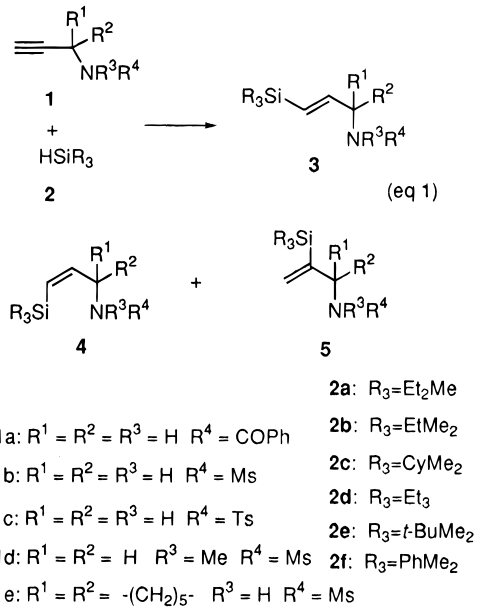
Table 1. Effect of Catalyst on Hydrosilylation of 1b with 2a[a]

entry	catalyst	conditions	yield/%[b]	ratio[c] **3ba:4ba:5ba**
1[d]	$[Rh(COD)_2]BF_4/PPh_3$	room temperature, 2 h	93	100:0:0
2	$[Rh(COD)_2]ClO_4/PPh_3$	room temperature, 2 h	90	100:0:0
3	$[Rh(COD)_2]PF_6/PPh_3$	room temperature, 2 h	94	100:0:0
4	$[Rh(COD)_2]OTf/PPh_3$	room temperature, 2 h	92	100:0:0
5[e]	$RhCl(PPh_3)_3$	83 °C, 45 h	30	79:3:18
6[f]	$[Rh(COD)Cl]_2/PPh_3$	83 °C, 26 h	36	80:9:11
7[g]	$H_2PtCl_6{\cdot}6H_2O$	room temperture, 3 h	60	60:1:39
8[h]	$[Rh(COD)_2]BF_4$/dppe	83 °C, 5 h	52	92:0:8
9	$[Rh(COD)_2]BF_4/P(OPh)_3$	83 °C, 19 h	35	72:7:21
10	$[Rh(COD)_2]BF_4/P(n\text{-}Bu)_3$	83 °C, 5 h	50	77:9:14

[a] A mixture of **1b** (2 mmol), **2a** (2.4 mmol), catalyst (0.004 mmol), ligand (P/Rh = 2), and $ClCH_2CH_2Cl$ (3 mL) was stirred under argon. [b] Isolated yield based on **1b**. [c] Determined by NMR. [d] **1b** (4 mmol), **2a** (4.8 mmol), catalyst (0.008 mmol), PPh_3 (0.016 mmol), and $ClCH_2CH_2Cl$ (6 mL). [e] Catalyst (0.02 mmol). [f] Catalyst (0.01 mmol), PPh_3 (0.04 mmol). [g] $H_2PtCl_6{\cdot}6H_2O$ (0.004 mmol), *i*-PrOH (50 μL). [h] dppe = 1,2-Bis(diphenylphosphine)ethane.



hydrosilylation catalyst.[9] Although the reaction using Speier's catalyst proceeded at room temperature, three products were obtained (entry 7). A cationic rhodium complex gave a better result than Speier's catalyst and a neutral rhodium complex. The effect of the phosphorus ligand was also examined at the ratio of P/Rh = 2 (Table 1). Of the ligands surveyed, PPh_3 was found to be the most efficient ligand (entry 1). Using other phosphorus ligands in place of PPh_3 required heating to give the product and decreased the yield and the selectivity (entries 8−10).

It is well-known that a substituent on the silicon atom has a considerable effect on the selectivity of hydrosilylation, e.g., chemo-, regio-, and stereoselectivity.[10] We examined the effect of hydrosilanes on the reaction of

Table 2. Effect of Hydrosilanes[a]

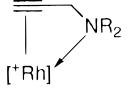
entry	hydrosilane (**2**)	product	yield/%[b]	ratio[c] **3:4:5**
1	$HSiEt_2Me$ (**2a**)	**3ba:4ba:5ba**	94	100:0:0
2	$HSiMe_2Et$ (**2b**)	**3bb:4bb:5bb**	91	100:0:0
3	$HSiCyMe_2$ (**2c**)	**3bc:4bc:5bc**	100	100:0:0
4[d]	$HSiEt_3$ (**2d**)	**3bd:4bd:5bd**	88	98:2:0
5[e]	$HSi(t\text{-}Bu)Me_2$ (**2e**)	**3be:4be:5be**	35	92:0:8[f]
6[f]	$HSiPhMe_2$ (**2f**)	**3bf:4bf:5bd**	82	100:0:0

[a] A mixture of **1b** (4 mmol), **2** (4.8 mmol), $[Rh(COD)_2]BF_4$ (0.008 mmol), PPh_3 (0.016 mmol), and $ClCH_2CH_2Cl$ (6 mL) was stirred under argon at room temperature for 2 h. [b] Isolated yield based on **1b**. [c] Determined by NMR. [d] At 50 °C for 2 h. [e] Refluxing for 24 h. [f] Determined by GLC. [g] **1b** (2 mmol), **2f** (2.4 mmol), $[Rh(COD)_2]BF_4$ (0.01 mmol), PPh_3 (0.02 mmol), and $ClCH_2CH_2Cl$ (3 mL), at room temperature for 3 h.

1b. The results are summarized in Table 2. The structure of the hydrosilanes affected the selectivity slightly. Reactions with diethylmethylsilane (**2a**), ethyldimethylsilane (**2b**), cyclohexyldimethylsilane (**2c**), and dimethylphenylsilane (**2f**) gave the corresponding *E*-isomer exclusively (entries 1−3 and 6). When triethylsilane (**2d**) and *tert*-butyldimethylsilane (**2e**) were used, the selectivities of the corresponding *E*-isomer were 98% and 92%, respectively (entries 4 and 5). The reaction with a bulky silane such as **2e** at room temperature gave no hydrosilylation product. Starting materials were recovered. The reaction with **2e** under refluxing 1,2-dichloroethane gave the corresponding product in a decreased yield.

N-Propargylsulfonamides **1d** and **1e** could be hydrosilylated with various hydrosilanes. The results are summarized in Table 3. In all cases, the corresponding *E*-isomers were obtained exclusively. Reactions of **1d** with diethylmethylsilane (**2a**) and ethyldimethylsilane (**2b**) gave an excellent yield of product (entries 1 and 2). When triethylsilane (**2d**) was used, the yield was somewhat decreased (entry 3). Cyclic sulfonamide **1e** also underwent hydrosilylation (entries 4−6). The reaction required a longer time and heating for completion.

As mentioned above, hydrosilylation of propargylamine and *N*,*N*-dimethylpropargylamine resulted in polymerization. Coordination of a nitrogen atom on a propargylic position to a rhodium center might retard hydrosilylation. The results described here show that



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(8) Polymerization of arylalkynes in the presence of hydrosilane has been reported, see: (a) Goldberg, Y.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1994**, 1209. (b) Yamamoto, H.; Mondoh, K.; Fuchikami, T. *Tetrahedron Lett.* **1994**, *35*, 4137. Rhodium complex catalyzed polymerization of alkynes, see: (c) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1994**, *116*, 12131. (d) Amer, I.; Schumann, H.; Ravindar, V.; Baidossi, W.; Goren, N.; Blum, J. *J. Mol. Catal.* **1993**, *85*, 163.

(9) (a) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (b) Reference 1a, p 41.

(10) Reference 1a, p 160.

Table 3. Hydrosilylation of 1d and 1e[a]

entry	substrate	hydrosilane	conditions	product	yield/%[b]	ratio[c] 3:4:5
1	**1d**	**2a**	room temperature, 2 h	**3da**:**4da**:**5da**	90	100:0:0
2	**1d**	**2b**	50 °C, 2 h	**3db**:**4db**:**5db**	91	100:0:0
3	**1d**	**2e**	50 °C, 15 h	**3de**:**4de**:**5de**	68	100:0:0
4[d]	**1e**	**2a**	50 °C, 15 h	**3ea**:**4ea**:**5ea**	94	100:0:0
5[d]	**1e**	**2b**	50 °C, 15 h	**3eb**:**4eb**:**5eb**	97	100:0:0
6[d]	**1e**	**2e**	50 °C, 15 h	**3ee**:**4ee**:**5ee**	67	100:0:0

[a] A mixture of sulfonamide **1** (2 mmol), hydrosilane **2** (2.4 mmol), catalyst (0.004 mmol), PPh_3 (0.008 mmol), and $ClCH_2CH_2Cl$ (3 mL) was stirred under argon. [b] Isolated yield based on **1**. [c] Determined by NMR. [d] Catalyst (0.01 mmol), PPh_3 (0.02 mmol).

a sulfonyl group or a benzoyl group on a nitrogen atom is necessary for hydrosilylation. The strong electron-withdrawing nature of these groups would retard the coordination of a nitrogen atom to a rhodium center by decreasing a electron density of a nitrogen atom.

In conclusion, a cationic rhodium complex was an efficient catalyst for hydrosilylation of *N*-propargylsulfonamides. A sulfonyl group on a nitrogen atom was necessary for the highly selective hydrosilylation.

Experimental Section

Materials. All reagents were dried and purified before use by the usual procedures. $[Rh(COD)_2]BF_4$,[11] $RhCl(PPh_3)_3$,[12] and $[Rh(COD)Cl]_2$[13] were prepared by literature methods. $H_2PtCl_6 \cdot 6H_2O$ was purchased. *N*-Propargylic benzamide was prepared by the reaction of *N*-propargylic amine with benzoyl chloride. *N*-Propargylic sulfonamides were prepared by the reaction of the corresponding propargylic amines with methanesulfonyl chloride. The propargylic amines were purchased.

General Methods. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL-EX-270 spectrometer. Samples were dissolved in $CDCl_3$ solutions, and the chemical shift values were expressed relative to Me_4Si as an internal standard. Compound **3bf** was dissolved in benzene-d_6. GC analyses were performed on a Shimadzu GC-14A with 3-mm × 2-m glass columns packed with either 20% SE-30 on 60/80 mesh chromosorb w, AW-DMCS, or 5% OV-17 on 60/80 mesh chromosorb w, AW-DMCS. Column chromatography was carried out on 70−230 mesh silica gel (Merk, Silica Gel 60). Elemental analyses were performed at the Microanalytical Center of Kyoto University. Samples for elemental analysis were purified by a preparative gas chromatography.

General Procedure for Hydrosilylation of Propargylic Amine Derivatives. A typical procedure is described for hydrosilylation of **1b** with **2a**. A two-necked flask equipped with a magnetic stirring bar was charged with sulfonamide **1b** (533 mg, 4 mmol), $[Rh(COD)_2]BF_4$ (3.2 mg, 0.008 mmol), and PPh_3 (4.2 mg, 0.016 mmol). The reactor was evacuated and filled with argon. 1,2-Dichloroethane (6 mL) was added to the flask. The mixture was stirred for 5 min. Diethylmethylsilane **2a** (491 mg, 4.8 mmol) was added via a syringe. The progress of the reaction was monitored by GLC. After the reaction was completed, the solution was concentrated in vacuo. The product **3ba** was isolated by column chromatography (*n*-hexane/EtOAc = 85/15). The yield was 93% (876 mg).

***N*-[(*E*)-3-(Diethylmethylsilyl)-2-propenyl]benzamide (3a):** ^1H NMR δ 0.0 (s, 3H), 0.53 (q, 4H, J = 7.3 Hz), 0.90 (t, 6H, J = 7.3 Hz), 4.06−4.11(m, 2H), 5.80 (dt, 1H, J = 18.8, 1.7 Hz), 6.09 (dt, 1H, J = 18.8, 5.0 Hz), 7.01 (br, 1H), 7.34−7.49 (m, 3H), 7.78−7.84 (m, 2H). ^{13}C NMR δ −6.2, 5.1, 7.1, 44.4, 126.9, 128.2, 128.5, 131.1, 134.3, 142.4, 167.2. Anal. Calcd for $C_{15}H_{23}NOSi$: C, 68.91; H, 8.87; N, 5.36; O, 6.12; Si, 10.74. Found: C, 68.81; H, 9.12; N, 5.41.

***N*-[(*Z*)-3-(Diethylmethylsilyl)-2-propenyl]benzamide (4a).** Compound **4a** could not be isolated in pure form. The ^1H-NMR spectra was same as that of **3**, except δ 5.68 (dt, 1H, J = 14.2, 1.3 Hz), 6.40 (dt, 1H, J = 14.2, 5.2 Hz).

***N*-[2-(Diethylmethylsilyl)-2-propenyl]benzamide (5a).** Compound **5a** could not be isolated in pure form. The ^1H-NMR spectra was same as that of **3**, except δ 5.41−5.42 (m, 1H), 5.75−5.76 (m, 1H).

***N*-[(*E*)-3-(Diethylmethylsilyl)-2-propenyl]methanesulfonamide (3ba):** ^1H NMR δ 0.03 (s, 3H), 0.56 (q, 4H, J = 7.9 Hz), 0.92 (t, 6H, J = 7.9 Hz), 2.95 (s, 3H), 3.80 (t, 2H, J = 5.3 Hz), 4.76 (br, 1H), 5.90 (d, 1H, J = 18.5 Hz), 6.04 (dt, 1H, J = 18.8, 4.6 Hz). ^{13}C NMR δ −6.3, 5.0, 7.1, 40.6, 47.5, 130.5, 141.4. Anal. Calcd for $C_9H_{21}NO_2SSi$: C, 45.92; H, 8.99; N, 5.95; O, 13.59; S, 13.62; Si, 11.93. Found: C, 45.75; H, 9.02; N, 5.79.

***N*-[(*Z*)-3-(Diethylmethylsilyl)-2-propenyl]methanesulfonamide (4ba):** Compound **4ba** could not be isolated in pure form. The ^1H-NMR spectra was same as that of **3ba**, except δ 5.73 (dt, 1H, J = 14.2, 1.3 Hz), 6.34 (dt, 1H, J = 14.2, 6.9 Hz).

***N*-[2-(Diethylmethylsilyl)-2-propenyl]methanesulfonamide (5ba).** Compound **5ba** could not be isolated in pure form. The ^1H-NMR spectra was same as that of **3ba**, except δ 5.47−5.49 (m, 1H), 5.87−5.89 (m, 1H).

***N*-[(*E*)-3-(Ethyldimethylsilyl)-2-propenyl]methanesulfonamide (3bb):** ^1H NMR δ 0.05 (s, 6H), 0.54 (q, 2H, J = 7.9 Hz), 0.93 (t, 3H, J = 7.9 Hz), 2.96 (s, 3H), 3.80 (t, 2H, J = 5.0 Hz), 4.56 (br, 1H), 5.92 (d, 1H, J = 18.8 Hz), 6.04 (dt, 1H, J = 18.8, 4.6 Hz). ^{13}C NMR δ −3.9, 6.9, 7.1, 40.6, 47.5, 131.7, 140.9. Anal. Calcd for $C_8H_{19}NO_2SSi$: C, 43.40; H, 8.65; N, 6.33; O, 14.45; S, 14.48; Si, 12.69. Found: C, 43.33; H, 8.72; N, 6.29.

***N*-[(*E*)-3-(Cyclohexyldimethylsilyl)-2-propenyl]methanesulfonamide (3bc):** ^1H NMR δ 0.02 (s, 6H), 0.62 (tt, 1H, J = 12.2, 3.3 Hz), 0.99−1.20 (m, 5H), 1.63−1.72 (m, 5H), 2.96 (s, 3H), 3.80 (t, 2H, J = 5.3 Hz), 4.55 (br, 1H), 5.90 (d, 1H, J = 18.5 Hz), 6.02 (dt, 1H, J = 18.5, 4.6 Hz). ^{13}C NMR δ −5.5, 25.2, 26.6, 27.1, 27.7, 40.5, 47.5, 130.8, 141.2. Anal. Calcd for $C_{12}H_{25}NO_2SSi$: C, 52.32; H, 9.15; N, 5.08; O, 11.62; S, 11.64; Si, 10.20. Found: C, 52.09; H, 9.35; N, 5.14.

***N*-[(*E*)-3-(Triethylsilyl)-2-propenyl]methanesulfonamide (3bd):** ^1H NMR δ 0.58 (q, 6H, J = 7.9 Hz), 0.93 (t, 9H, J = 7.9 Hz), 2.95 (s, 3H), 3.81 (t, 2H, J = 5.0 Hz), 4.96 (br, 1H), 5.88 (d, 1H, J = 18.8 Hz), 6.05 (dt, 1H, J = 18.8, 5.0 Hz). ^{13}C NMR δ 3.2, 7.1, 40.7, 47.7, 129.5, 141.7. Anal. Calcd for $C_{10}H_{23}NO_2SSi$: C, 48.15; H, 9.29; N, 5.62; O, 12.83; S, 12.85; Si, 11.26. Found: C, 48.10; H, 9.52; N, 5.72.

***N*-[(*Z*)-3-(Triethylsilyl)-2-propenyl]methanesulfonamide (4bd).** Compound **4bd** could not be isolated in pure form. The ^1H-NMR spectra was same as that of **3bd**, except δ 5.70 (d, 1H, J = 14.2 Hz), 6.37 (dt, 1H, J = 14.2, 6.6 Hz).

***N*-[(*E*)-3-(*tert*-Butyldimethylsilyl)-2-propenyl]methanesulfonamide (3be):** ^1H NMR δ 0.03 (s, 6H), 0.87 (s, 9H), 2.96 (s, 3H), 3.82 (t, 2H, J = 4.6 Hz), 4.56 (br, 1H), 5.93 (d, 1H, J = 18.8 Hz), 6.05 (dt, 1H, J = 18.8, 4.6 Hz). ^{13}C NMR δ −6.2, 16.4, 26.3, 41.0, 47.7, 130.5, 141.7. Anal. Calcd for $C_{10}H_{23}NO_2SSi$: C, 48.15; H, 9.29; N, 5.62; O, 12.83; S, 12.85; Si, 11.26. Found: C, 47.86; H, 9.59; N, 5.55.

***N*-[2-(*tert*-Butyldimethylsilyl)-2-propenyl]methanesulfonamide (5be).** Compound **5be** could not be isolated in

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pure form. The ^{1}H-NMR spectra was same as that of **3be**, except δ 5.46−5.47 (m, 1H), 5.90−5.91 (m, 1H).

***N*-[(*E*)-3-(Dimethylphenylsilyl)-2-propenyl]methanesulfonamide (3bf):** ^{1}H NMR δ 0.28 (s, 6H), 2.35 (s, 3H), 3.41 (dd, 2H, J = 6.6, 3.3 Hz), 4.52 (br, 1H), 5.82 (dt, 1H, J = 18.8, 3.3 Hz), 5.90 (d, 1H, J = 18.8 Hz), 7.18−7.28 (m, 3H), 7.42−7.51 (m, 2H). ^{13}C NMR δ −2.6, 40.3, 47.5, 128.2, 129.5, 130.2, 134.2, 138.3, 143.3. Anal. Calcd for $C_{12}H_{19}NO_2SSi$: C, 53.49; H, 7.11; N, 5.20; O, 11.88; S, 11.90; Si, 10.42. Found: C, 53.19; H, 7.29; N, 5.15.

***N*-[(*E*)-3-(Diethylmethylsilyl)-2-propenyl]toluenesulfonamide (3c):** ^{1}H NMR δ −0.09 (s, 3H), 0.45 (q, 4H, J = 7.5 Hz), 0.84 (t, 6H, J = 7.5 Hz), 2.41 (s, 3H), 3.63 (t, 2H, J = 5.0 Hz), 5.21 (t, 1H, J = 6.0 Hz), 5.70 (d, 1H, J = 18.8 Hz), 5.84 (dt, 1H, J = 18.8, 5.0 Hz), 7.29 (d, 2H, J = 7.9 Hz), 7.77 (d, 2H, J = 7.9 Hz). ^{13}C NMR δ −6.4, 5.0, 7.0, 21.3, 47.6, 127.0, 129.5, 130.1, 137.2, 140.8, 143.1. Anal. Calcd for $C_{15}H_{25}NO_2SSi$: C, 57.84; H, 8.09; N, 4.50; O, 10.27; S, 10.29; Si, 9.02. Found: C, 57.56; H, 8.26; N, 4.59.

***N*-[(*E*)-3-(Diethylmethylsilyl)-2-propenyl]-*N*-methylmethanesulfonamide (3da):** ^{1}H NMR δ 0.04 (s, 3H), 0.57 (q, 4H, J = 7.9 Hz), 0.93 (t, 6H, J = 7.9 Hz), 2.81 (s, 3H), 2.82 (s, 3H), 3.80 (d, 2H, J = 4.6 Hz), 5.90 (d, 1H, J = 18.8 Hz), 5.99 (dt, 1H, J = 18.8, 4.6 Hz). ^{13}C NMR δ −6.3, 5.1, 7.1, 34.0, 35.9, 54.9, 133.0, 140.3. Anal. Calcd for $C_{10}H_{23}NO_2SSi$: C, 48.15; H, 9.29; N, 5.62; O, 12.83; S, 12.85; Si, 11.26. Found: C, 48.09; H, 9.17; N, 5.69.

***N*-[(*E*)-3-(Ethyldimethylsilyl)-2-propenyl]-*N*-methylmethanesulfonamide (3db):** ^{1}H NMR δ 0.06 (s, 6H), 0.55 (q, 2H, J = 7.9 Hz), 0.93 (t, 6H, J = 7.9 Hz), 2.81 (s, 3H), 2.82 (s, 3H), 3.80 (d, 2H, J = 4.0 Hz), 5.91 (d, 1H, J = 18.5 Hz), 5.99 (dt, 1H, J = 18.5, 4.0 Hz). ^{13}C NMR δ −3.8, 7.0, 7.2, 34.1, 35.9, 54.8, 134.2, 139.8. Anal. Calcd for $C_9H_{21}NO_2SSi$: C, 45.92; H, 8.99; N, 5.95; O, 13.59; S, 13.62; Si, 11.93. Found: C, 45.90; H, 9.28; N, 5.83.

***N*-[(*E*)-3-(Triethylsilyl)-2-propenyl]-*N*-methylmethanesulfonamide (3dd):** ^{1}H NMR δ 0.59 (q, 6H, J = 7.9 Hz), 0.94 (t, 9H, J = 7.9 Hz), 2.81 (s, 3H), 2.82 (s, 3H), 3.80 (d, 2H, J = 5.0 Hz), 5.87 (d, 1H, J = 18.5 Hz), 6.00 (dt, 1H, J = 18.5, 5.3 Hz). ^{13}C NMR δ 3.0, 7.0, 33.9, 35.7, 54.9, 131.6, 140.6. Anal. Calcd for $C_{11}H_{25}NO_2SSi$: C, 50.15; H, 9.56; N, 5.32; O, 12.15; S, 12.17; Si, 10.66. Found: C, 50.41; H, 9.56; N, 5.37.

***N*-1-[(*E*)-2-(Diethylmethylsilyl)ethenyl]cyclohexylmethanesulfonamide (3ea):** ^{1}H NMR δ 0.05 (s, 3H), 0.58 (q, 4H, J = 7.9 Hz), 0.95 (t, 6H, J = 7.9 Hz), 1.26−1.92 (m, 10H), 2.94 (s, 3H), 5.13 (br, 1H), 5.92 (d, 1H, J = 19.5 Hz), 6.08 (d, 1H, J = 19.5 Hz). ^{13}C NMR δ −6.3, 5.1, 7.1, 21.7, 25.3, 36.0, 43.5, 59.4, 127.8, 150.1. Anal. Calcd for $C_{14}H_{29}NO_2SSi$: C, 55.40; H, 9.63; N, 4.61; O, 10.54; S, 10.56; Si, 9.25. Found: C, 55.16; H, 9.86; N, 4.53.

***N*-1-[(*E*)-2-(Ethyldimethylsilyl)ethenyl]cyclohexylmethanesulfonamide (3eb):** ^{1}H NMR δ 0.08 (s, 6H), 0.57 (q, 2H, J = 7.9 Hz), 0.94 (t, 3H, J = 7.9 Hz), 1.26−1.92 (m, 10H), 2.93 (s, 3H), 4.99 (br, 1H), 5.94 (d, 1H, J = 19.5 Hz), 6.07 (d, 1H, J = 19.5 Hz). ^{13}C NMR δ −3.8, 7.1, 7.2, 21.7, 25.3, 36.0, 43.6, 59.4, 129.1, 149.7. Anal. Calcd for $C_{13}H_{27}NO_2SSi$: C, 53.93; H, 9.40; N, 4.84; O, 11.05; S, 11.07; Si, 9.70. Found: C, 54.21; H, 9.69; N, 4.87.

***N*-1-[(*E*)-2-(Triethylsilyl)ethenyl]cyclohexylmethanesulfonamide (3ed):** ^{1}H NMR δ 0.61 (q, 6H, J = 7.9 Hz), 0.95 (t, 9H, J = 7.9 Hz), 1.27−1.86 (m, 10H), 2.95 (s, 3H), 4.78 (br, 1H), 5.90 (d, 1H, J = 19.5 Hz), 6.08 (d, 1H, J = 19.5 Hz). ^{13}C NMR δ 3.3, 7.3, 21.9, 25.4, 36.3, 43.9, 59.8, 127.1, 150.3. Anal. Calcd for $C_{15}H_{31}NO_2SSi$: C, 56.73; H, 9.84; N, 4.41; O, 10.08; S, 10.10; Si, 8.84. Found: C, 56.59; H, 10.13; N, 4.39.

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