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[Rh(COD)Cl]$_2$/PPh$_3$-Catalyzed Dehydrogenative Silylation of Styrene Derivatives with NBE as a Hydrogen Acceptor

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Cite This: https://dx.doi.org/10.1021/acs.organomet.0c00242 Read Online

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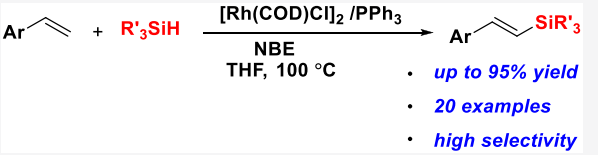
ABSTRACT: Direct synthesis of arylalkenylsilanes by [Rh(COD)Cl]$_2$/PPh$_3$-catalyzed dehydrogenative silylation of styrene derivatives with R$_3$SiH (R = alkyl, alkoxy, aryl) was realized, in which norbornene (NBE) and PPh$_3$ play a key role in achieving excellent selectivity in the formation of dehydrogenative silylation products. Moreover, this high-yielding transformation exhibits a broad substrate scope and good functional group tolerance.



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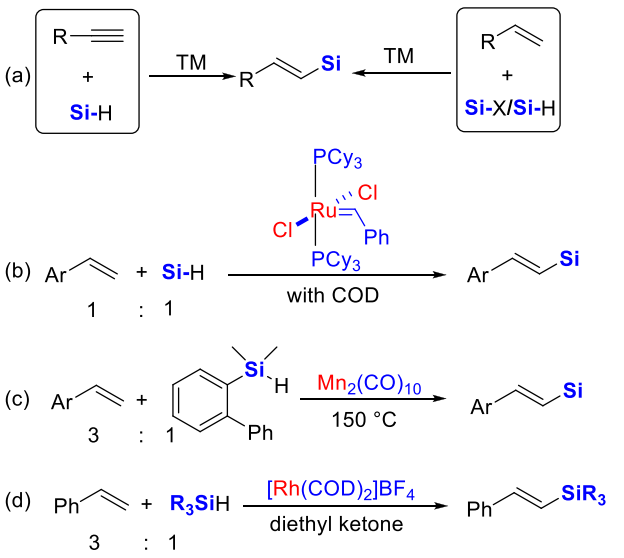
INTRODUCTION

Alkenylsilanes are versatile synthetic intermediates and building blocks in numerous materials science/polymer applications.[1,2] Diverse transformations of alkenylsilanes were also achieved to give various useful building blocks, including allylic alcohols, allylic amines, and alkenyl halides.[2e] Accordingly, effective approaches for preparing alkenylsilanes are highly desirable. A variety of procedures are extant for the preparation of alkenylsilanes, including the silyl-Heck reaction,[3] alkyne hydrosilylation,[4] and dehydrogenative silylation of alkenes (Scheme 1a). Direct dehydrogenative silylation of alkenes is a more favorable access because alkenes are inexpensive and readily available (Scheme 1a).[5,6] Most catalysts for the dehydrogenative silylation of alkenes rely on precious metals such as rhodium, iridium, ruthenium, platinum, and palladium.[5] For example, Falck and Hartwig reported the *Z*-selective dehydrogenative silylation of terminal aliphatic alkenes catalyzed by iridium complexes and nitrogen ligands, respectively.[5c,d] Examples with earth-abundant metal catalysts including iron, cobalt, nickel, copper, and manganese catalytic systems also have been reported recently.[6] Chirik and co-workers developed a bis(imino)pyridine cobalt-catalyzed dehydrogenative silylation of alkyl alkenes to generate allylsilanes.[6d] Xu and co-workers developed a synergistic combination of photoredox, hydrogen atom transfer, and cobalt catalysis to synthesize allylsilanes from methacrylic acid derivatives.[6e] In spite of the significant progress in the direct dehydrogenative silylation of alkenes, there have only been a few reports on the highly selective dehydrogenative silylation of arylalkenes. Jeon demonstrated the dehydrogenative silylation of vinylarenes catalyzed by ruthenium alkylidenes with the addition of cyclooctadiene as the sacrificial hydrogen acceptor (Scheme 1b).[5f] Wang and co-workers achieved Mn$_2$(CO)$_{10}$-catalyzed dehydrogenative silylation of aryl olefins with special hydrosilanes (Scheme 1c).[6j] Lu and co-workers reported a imidazoline iminopyridine cobalt complex catalyzed dehydrogenative silylation of vinylarenes.[6f]

Although there have been some reports on rhodium/PPh$_3$-catalyzed dehydrogenative silylation of alkenes since the early 1980s, only a few catalytic systems have shown high selectivity. Takeuchi and co-workers reported a [Rh(COD)$_2$]BF$_4$/PPh$_3$-catalyzed highly selective dehydrogenative silylation of styrene with tertiary hydrosilanes, but the selectivity was strongly

Scheme 1. Common Approaches to Vinylsilanes



Received: April 5, 2020

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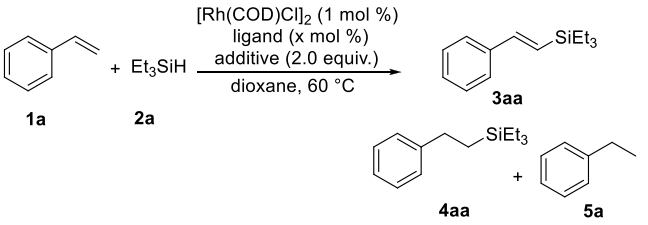
dependent on the reaction temperature, the molar ratio of styrene to hydrosilane, and the steric bulkiness of the hydrosilane (Scheme 1d).[7a] In the dehydrogenative silylation reactions of alkenes with hydrosilanes, the generation of alkenylsilanes is always accompanied by the formation of metal hydrogen species which may result in side reactions, such as isomerization and reduction of alkenes and further reduction of dehydrogenative silylation products.[8,9] Therefore, the prompt consumption of the hydrogen species is crucial for achieving dehydrogenative silylation product in good yield and selectivity. The hydrogen species may be transferred to H_2 which escapes from the reaction system[6e] or be absorbed by large excess of the alkene substrates as sacrificial hydrogen acceptors.[7a] In addition, adding extra hydrogen acceptors is an important approach to consume the hydrogen species, which may suppress the reduction of alkenes and improve the selectivity for the dehydrogenative silylation.[5f] Herein, we report a rhodium/PPh_3-catalyzed dehydrogenative silylation of styrene derivatives with NBE as a hydrogen acceptor to give alkenylsilanes in an effective and highly selective way.

RESULTS AND DISCUSSION

The Wilkinson catalyst showed good reactivity and selectivity for the dehydrogenative silylation of the terminal alkenes of 1,5-dienes.[7b,10] Therefore, we examined the dehydrogenative silylation of styrene **1a** and 2 equiv of Et_3SiH (**2a**) with $RhCl(PPh_3)_3$ or $[Rh(COD)Cl]_2/PPh_3$ as the catalyst. The reaction catalyzed by the Wilkinson catalyst gave the hydrosilylation product **4aa** as the main product in 67% yield, the dehydrogenative silylation product **3aa** in only 15% yield, and the reduction product **5a** in 18% yield (Table 1, entry 1). When $[Rh(COD)Cl]_2$ was used as the precatalyst and 4 equiv of PPh_3 was used as the ligand, the ratio of products obviously changed. The yield of the hydrosilylation product **4aa** decreased, but the yield of the reduction product **5a** increased (Table 1, entry 2). We attempted to add the extra hydrogen acceptor in the dehydrogenative silylation to inhibit the formation of the saturated (reduction) products **4aa** and **5a**. Norbornene (NBE), which coordinates easily with late transition metals and is not prone to react with hydrosilanes in the presence of terminal alkenes, was used first as the sacrificial hydrogen acceptor. The reduction of styrene (**1a**) was inhibited completely in both $RhCl(PPh_3)_3$ and $[Rh(COD)Cl]_2/PPh_3$ catalytic systems (Table 1, entries 3 and 4). In the $[Rh(COD)Cl]_2/PPh_3$ catalytic system, the selectivity of dehydrogenative silylation over hydrosilylation was obviously improved and the catalytic system showed high regioselectivity to generate (*E*)-alkenylsilanes (Table 1, entries 2 and 4). In the case where dicyclopentadiene with a ring strain similar to that of NBE was tested as the hydrogen acceptor, the yield of **3aa** was increased to 58% (Table 1, entry 8). When cyclohexene without a similar ring strain was used, the yield of **3aa** was hardly increased (Table 1, entry 6). The addition of cyclodienes, for example, *cis*-1,5-cyclooctadiene (cod) and 2,5-norbornadiene (NBD), led to no conversion of styrene (Table 1, entries 5 and 7), indicating that a more stable competitive coordination of cyclodienes with the catalyst suppressed the coordination of styrene. Therefore, NBE, a cycloalkene with ring strain, was the best sacrificial hydrogen acceptor in the dehydrogenative silylation of styrene. Then the effect of ligands in the dehydrogenative silylation of styrene with NBE as the hydrogen acceptor was explored. Reducing the loading of PPh_3 resulted in a decrease in the selectivity of dehydrogenative silylation over hydrosilylation. The reaction with 2 mol % of PPh_3 gave the hydrosilylation product **4aa** as the main product (Table 1, entry 10). Gratifyingly, when the loading of PPh_3 was increased, the selectivity of dehydrogenative silylation improved significantly (Table 1, entries 11−16). When 10 mol % of PPh_3 was used in the catalytic system, a 95% yield of **3aa** was obtained within 4 h (Table 1, entry 13).

Moreover, when the loading of PPh_3 was increased to 20 mol %, the activity and selectivity of the reaction were well maintained (Table 1, entry 16).[7a] The electronic nature and steric hindrance of ligands affected the activity and selectivity of the catalytic system significantly. When phosphine ligands with electron-donating groups, P(*p*-tolyl)$_3$ and (4-$MeOC_6H_4)_3P$, were used, the selectivity of dehydrogenative silylation and the activity decreacsed (Table 1, entries 17 and 19). Using a ligand with steric hindrance also led to a decreased selectivity of dehydrogenative silylation (Table 1, entry 17 vs 18). $PPh_2(C_6F_5)$ and diphosphine ligands were inferior for the dehydrogenative silylation (Table 1, entries 20 and 21).

Table 1. Optimization of Reaction Conditions[a]



			yield (%)[b]		
entry	ligand (*x* (mol %))	additive (equiv)	3aa	4aa	5a
1[c]			15	67	18
2	PPh_3 (4)		23	30	40
3[c]		NBE	27	73	0
4	PPh_3 (4)	NBE	78	22	0
5	PPh_3 (4)	NBD			
6	PPh_3 (4)	cyclohexene	36	55	8
7	PPh_3 (4)	COD			
8	PPh_3 (4)	dicyclopentadiene	58	28	0
9		NBE	32	68	0
10	PPh_3 (2)	NBE	34	66	0
11	PPh_3 (6)	NBE	92	6	1
12	PPh_3 (8)	NBE	93	4	2
13	PPh_3 (10)	NBE	95	3	2
14	PPh_3 (12)	NBE	96	3	1
15	PPh_3 (15)	NBE	96	3	1
16	PPh_3 (20)	NBE	95	3	2
17	P(*p*-tol)$_3$ (10)	NBE	88	8	4
18	P(*o*-tol)$_3$ (10)	NBE	70	30	0
19	P(4-MeOPh)$_3$ (10)	NBE	51	10	6
20	$P(C_6F_5)Ph_2$ (10)	NBE	3	4	0
21	Dppp (5)	NBE			
22[d]	PPh_3 (10)	NBE	95	3	2
23[e]	PPh_3 (10)	NBE	96	3	1

[a]Reaction conditions unless stated otherwise: $[Rh(COD)Cl]_2$ (4.9 mg, 1 mol %), ligand, additive (2 equiv), **1a** (104.2 mg, 1 mmol), **2a** (232.6 mg, 2 mmol), dioxane (4 mL), 60 °C, 4 h. [b]Conversion, selectivity, and yields were determined by ^1H NMR or GC analysis (1,2,4,5-tetramethylbenzene as an internal standard). [c]$RhCl(PPh_3)_3$ (18.5 mg, 2 mol %). [d]THF (4 mL), 60 °C, 4 h. [e]THF (4 mL), 100 °C, 1 h.

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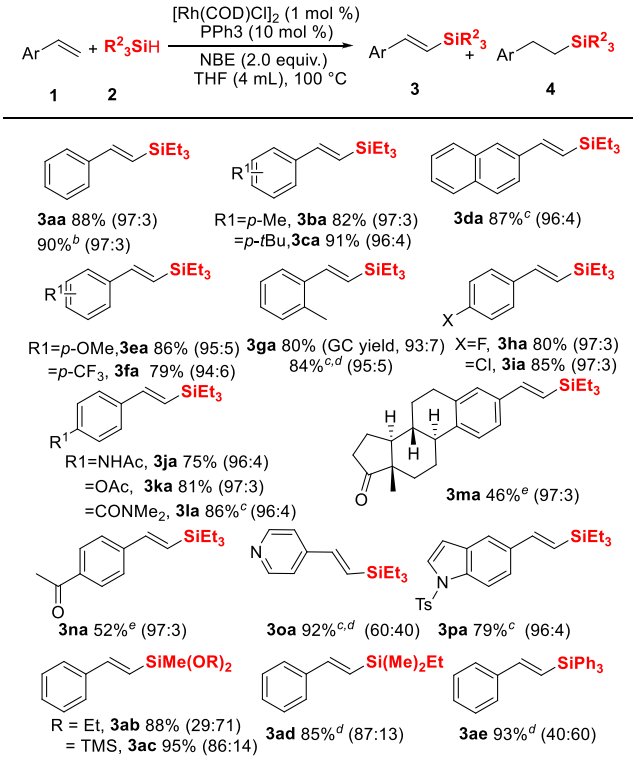
We next screened the solvents and reaction temperature of the dehydrogenative silylation, and the results are shown in Table S1. Ethereal solvents, such as dioxane (Table 1, entry 13) and THF (Table 1, entry 22), were crucial for high activity and selectivity. DCE and CH_3CN (Table S1, entries 3 and 4) were poor solvents, while toluene and DMF (Table S1, entries 1 and 5) slightly reduced the selectivity. Decreasing the reaction temperature resulted in a lower activity (Table S1, entries 8 and 9). When the reaction temperature was increased to 100 °C, the activity was increased and the high selectivity was maintained (Table S1, entries 10−12). The conversion of styrene was complete within 1 h at 100 °C, and the yield of **3aa** was 96% (Table 1, entry 23). Moreover, reducing the amount of Et_3SiH resulted in a decreased conversion of styrene, and reducing the amount of NBE led to a slightly increased yield of the reduction product **5a**. Therefore, the optimized reaction conditions for the dehydrogenative silylation of alkenylarenes were 1 mol % of $[Rh(COD)Cl]_2$ as precatalyst, 10 mol % of PPh_3 as ligand, 2.0 equiv of silane, 2.0 equiv of NBE as additive, THF as solvent, and 100 °C. In the dehydrogenative silylation reaction of styrene and Et_3SiH, our catalytic system ($[Rh(COD)Cl]_2/PPh_3$/NBE) displayed comparable selectivity and higher activity (>99% yield, **3aa**:**4aa**:**5a** = 96:3:1, within 1 h) in comparison to the reported $[Rh(COD)_2]BF_4/PPh_3$ catalytic system (72% yield, **3aa**:**4aa** = 97:3, within 18 h)[7a] and better selectivity and activity in comparison to those of the reported ruthenium alkylidene catalysts (77% conversion, **3aa**:**4aa**:**5a** = 1:6:4, within 8 h).[5f]

The scope of Rh/PPh_3/NBE-catalyzed selective dehydrogenative silylation of styrene derivatives **1** with tertiary silanes **2** was further examined (Table 2). Dehydrogenative silylation with the catalytic system led to the efficient formation of a number of (*E*)-vinylsilanes **3** in good yields with good to excellent selectivities. The nature of the substituents displayed an obvious effect on the reactive activity of vinylarenes, and the results are shown in Figure S2a,b. The reactive rate of *p*-methoxystyrene (**1e**) decreased slightly, and complete conversion was achieved within 1 h to give the corresponding alkenylsilane **3ea** in 86% yield and good selectivity (**3ea**:**4ea** = 95:5). However, the reactive rate of vinylarenes with an electron-withdrawing group, for example, *p*-(trifluoromethyl)-styrene (**1f**), obviously decreased. The conversion of **1f** was accomplished within 2 h to give the corresponding alkenylsilane **3fa** in 86% yield with good selectivity (**3fa**:**4fa** = 94:6). The decreased reactive activity may be ascribed to the fact that the electron-withdrawing groups reduce the coordination ability of vinylarenes with the active catalyst. The alkyl-substituted styryl silanes **3ba** and **3ca** were generated in 82−91% yields with excellent selectivities. For bulkier vinylarenes, an increase in the loading of PPh_3 and a prolonged reaction time were needed to achieve full conversion to give the corresponding alkenylsilanes in good yield and selectivity. For example, the reaction of *o*-methylstyrene (**1g**) with 20 mol % of PPh_3 gave the alkenylsilane **3ga** in a ratio of 95:5 (**3ga**:**4ga**) and 84% yield in 10 h. For an even bulkier substrate, *α*-methylstyrene, the reaction did not occur at all. The catalytic system tolerated diverse functional groups, including halogen, ester, amide, and aromatic heterocycles. The reactions of 4-vinylphenyl acetate (**1k**) and *N*,*N*-dimethyl-4-vinylbenzamide (**1l**) proceeded smoothly to give the corresponding alkenylsilanes **3ka** and **3la** in 81% yield (97:3 selectivity) and 86% yield (96:4 selectivity), respectively. However, the reaction of 4-acetylstyrene (**1n**) and an alkenylarene with an estrone skeleton, **1m**, gave the corresponding alkenylsilanes in moderate yields, because the carbonyl group was partially reduced in the dehydrogenative silylation. 2-Vinylnaphthalene (**1d**) reacted well to generate the alkenylsilane **3da** in 87% yield and with a **3da**:**4da** ratio of 96:4 in 10 h. However, in the case of 4-vinylpyridine **1o** as the substrate, a decreased selectivity of dehydrogenative silylation was observed, even when the loading of PPh_3 was increased to 20 mol %.

The selectivity of dehydrogenative silylation was also affected by the structure of the hydrosilanes. The reactions of styrene (**1a**) with dimethylethylsilane (**2d**) also gave good yields and high selectivities for the dehydrogenative silylation. However, when triphenylsilane **2e** was used, the selectivity of dehydrogenative silylation over hydrosilylation was decreased to 40:60. The bulky alkoxysilane **2c** was reacted with styrene to give the dehydrogenative silylation product **3ac** as the main product; however, decreasing the steric hindrance of alkoxysilanes led to the hydrosilylated species as the major products (**3ab**:**4ab** = 29:71). Unfortunately, the catalytic system was incompatible with alkenylarenes possessing amino, hydroxyl, formyl, nitro, cyano, and bromo groups or aliphatic alkenes. When allylbenzene was used as the reaction substrate, we could only get the olefin isomerization product **1q′** instead of the dehydrogenative silylation product (see the Supporting Information).

Table 2. Substrate Scope for Dehydrogenative Silylation of Alkenylarenes with Tertiary Silanes[a]



[a]Reaction conditions unless stated otherwise: $[Rh(COD)Cl]_2$ (4.9 mg, 1 mol %), PPh_3 (26.2 mg, 10 mol %), **1** (1.0 mmol), **2** (2.0 mmol), NBE (188.3 mg, 2 mmol), THF (4 mL), 100 °C, 2 h. Isolated yields are given, and the ratios of the products **3** and **4** are given in parentheses; the ratio of **3** and **4** was determined by ^1H NMR spectroscopy or GC. [b]**1a** (1041.5 mg, 10 mmol), 100 °C. [c]10 h. [d]PPh_3 (52.5 mg, 20 mol %). [e]4 h.

https://dx.doi.org/10.1021/acs.organomet.0c00242
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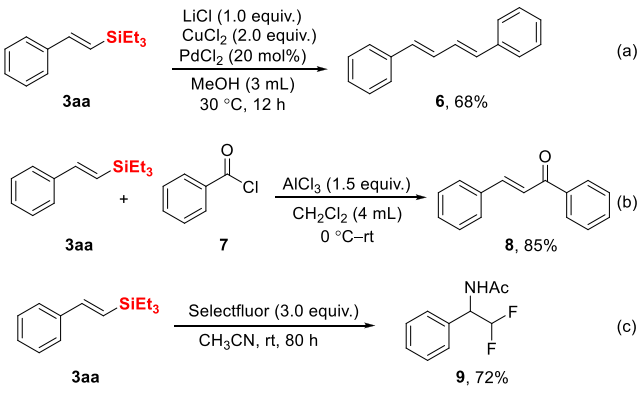
Furthermore, the reaction was easily scaled up to a 10 mmol scale of **1a** under the optimized conditions ($[Rh(COD)Cl]_2$ (1 mol %), PPh_3 (10 mol %), **1a** (10 mmol), **2a** (20 mmol), NBE (20 mmol), THF (40 mL), 100 °C). The conversion of styrene (**1a**) was accomplished within 2 h, and the dehydrogenative silylation product **3aa** was isolated in 90% yield. Alkenylsilanes, the dehydrogenative silylation products, are powerful synthetic intermediates for organic syntheses (Scheme 2). The palladium-catalyzed homocoupling reaction

Scheme 2. Synthetic Applications



of alkenylsilanes **3aa** afforded the conjugated diene **6** in 68% yield (Scheme 2a).[11a] With $AlCl_3$ as the catalyst, the acylation of the styryl silane **3aa** with benzoyl chloride (**7**) occurred selectively at the carbon−carbon double bonds to generate chalcone **8** in 85% yield (Scheme 2b).[11b] Moreover, fluorine-containing compounds may show unique bioactive features. The alkenylsilanes **3aa** can be converted to difluoromethyl-substituted amides **9** in moderate yield using Selectfluor (1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis-(tetrafluoroborate)) in CH_3CN (Scheme 2c).[11c]

To further understand the role of PPh_3 and NBE in the catalytic system, the profiles for the reactions of styrene **1a** with triethylsilane (**2a**) catalyzed by Rh/PPh_3 systems in THF were monitored by GC at 60 °C (Figure 1) and 100 °C (Figure S1). When a combination of 1 mol % of $[Rh(COD)Cll_2$ and 4 mol % of PPh_3 was used as the catalytic system at 60 °C (Figure 1a), the dehydrogenative silylation product **3aa** was observed accompanied by the hydrosilylation product **4aa** and the reduction byproduct **5a** as the major byproducts. The conversion of styrene **1a** was accomplished within 4 h to give the product **3aa** in 68% yield with the generation of **4aa** in 7% yield and **5a** in 25% yield, and then the decay of **3aa** occurred. After 8 h, the yield of **3aa** decreased to 57%, and the yield of **4aa** increased to 18%. When the reaction was carried out at 100 °C (Figure S1a), the conversion of styrene (**1a**) was accomplished within 30 min, but the yield of hydrosilylation product **4aa** increased to 26%. Similarly, a decreased yield of **3aa** was observed after 30 min. These results indicated that the Rh/PPh_3 catalytic system cannot completely inhibit the formation of the reduction product **5a** and hydrosilylation product **4aa** and the dehydrogenative silylation product **3aa** may be reduced to **4aa** in the catalytic system.

When norbornene was added as the sacrificial hydrogen acceptor in the catalytic system of 1 mol % of $[Rh(COD)Cll_2$ and 4 mol % of PPh_3 (Figure 1b), the conversion of styrene was complete within 4 h, and the reduction of styrene (**1a**) was suppressed significantly, but the reduction of **3aa** to **4aa** was

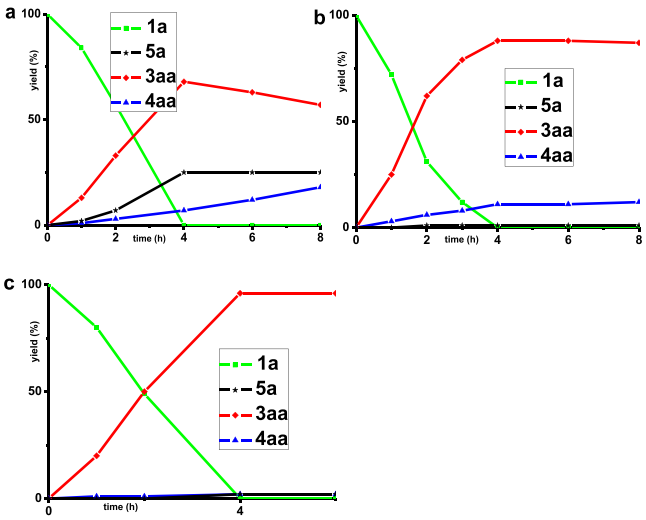


Figure 1. Profiles for the reactions of styrene (**1a**) with triethylsilane (**2a**) catalyzed by Rh/PPh_3 systems. Reaction conditions: (a) $[Rh(COD)Cl]_2$ (4.9 mg, 1 mol %), PPh_3 (10.5 mg, 4 mol %), **1a** (104.2 mg, 1.0 mmol), **2a** (232.6 mg, 2.0 mmol), THF (4 mL), 60 °C, in six sealed tubes; (b) $[Rh(COD)Cl]_2$ (4.9 mg, 1 mol %), PPh_3 (10.5 mg, 4 mol %), **1a** (104.2 mg, 1.0 mmol), **2a** (232.6 mg, 2.0 mmol) and NBE (188.3 mg, 2.0 mmol), THF (4 mL), 60 °C, in six sealed tubes; (c) $[Rh(COD)Cl]_2$ (4.9 mg, 1 mol %), PPh_3 (26.2 mg, 10 mol %), **1a** (104.2 mg, 1.0 mmol), **2a** (232.6 mg, 2.0 mmol) and NBE (188.3 mg, 2.0 mmol), THF (4 mL), 60 °C, in six sealed tubes.

also observed after 4 h. These results demonstrated that NBE was more active than styrene and **3aa** in the reactions with the generated rhodium hydride complex. Moreover, the selectivity of the dehydrogenative silylation obviously improved to give **3aa** in 88% yield. When the reaction temperature was improved, the conversion of styrene **1a** was accomplished within 30 min, and a similar variation tendency was observed (Figure S1b). Therefore, in the Rh/PPh_3/NBE catalytic system, the increased selectivity of **3aa** may result from the coordination of NBE with the catalyst or the higher reactivity of NBE in the reaction with the generated rhodium hydride complex which promoted the dehydrogenative silylation.[12]

Furthermore, when the loading of PPh_3 was increased to 10 mol % in the Rh/PPh_3/NBE catalytic system (Figure 1c), the activity of the catalytic system was retained; moreover, the selectivity of dehydrogenative silylation over hydrosilylation was obviously improved. Styrene **1a** was selectively converted to (*E*)-triethyl(styryl)silane (**3aa**) in 95% yield within 4 h, and no decrease in the yield of **3aa** was observed after 4 h. The reduction of dehydrogenative silylation product **3aa** was substantially inhibited. Even when the reaction was carried out at 100 °C, the high selectivity was retained and the reduction of dehydrogenative silylation product **3aa** was not observed (Figure S1c and entries 11−13 in Table S1). These results suggested that free PPh_3 could compete with the product **3** and hydrosilane **2** to coordinate with the catalyst to suppress the reduction of **3** and hydrosilylation of styrene.

On the basis of our experimental results, a plausible mechanism of Rh/PPh_3/NBE-catalyzed dehydrogenative silylation of styrene derivatives and tertiary silanes is shown in Scheme 3.[13a] $[RhCl(COD)]_2$ was dissociated by PPh_3 to form the intermediate **A**, and then oxidative addition of **A** and hydrosilane **2** gave the rhodium hydride complex **B**.[13b] The presence of rhodium hydride species was detected in our

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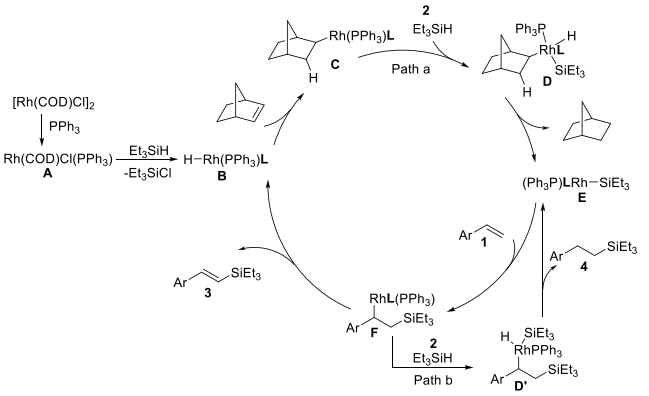
Scheme 3. Proposed Mechanism



catalytic system by ^{1}H NMR spectroscopy (see the Supporting Information for details). Then NBE was inserted preferentially into the rhodium hydride **A** to give alkyl rhodium complex **C** (the structure was also detected in the reaction by ^{1}H NMR spectroscopy; see the Supporting Information for details), because NBE with ring strain is in comparison with styrene derivative **1** or the dehydrogenated silylation products **3** more easily coordinates with the metal catalyst (path a).[13c] The reaction of alkyl rhodium complex **C** with hydrosilane **2** to generate the key intermediate **E** and norbornane was observed by GC-MS. Next, the insertion of styrene derivative **1** into the rhodium silane species **E** formed another alkyl rhodium complex **F**, which either underwent β-H elimination to afford the dehydrogenated silylation product **3** and regenerate the rhodium hydride complex **B**, or reacted with hydrosilane **2** to generate the intermediate **D′**, which underwent reductive elimination to afford hydrosilylation product **4** and rhodium silane species **E** (path b).

CONCLUSIONS

In summary, we have disclosed a rhodium-catalyzed regioselective dehydrogenative silylation of styrene derivatives with tertiary silanes using readily available PPh_3 as the ligand and NBE as the additive. The reactions of various alkenylarenes with tertiary silanes selectively provided (*E*)-alkenylsilanes in good to excellent selectivity and yields. This catalytic protocol showed good functional group tolerance of halogens, aromatic heterocycles, amides, and esters. Further functionalization of the alkenylsilanes renders the useful building blocks under mild conditions.

EXPERIMENTAL SECTION

General Information. Commercial reagents were purchased from commercial sources unless otherwise noted, and all solvents were dried and distilled before use according to the standard methods. Unless otherwise noted, all reactions were performed using standard Schlenk techniques under an atmosphere of nitrogen. Analytical thin-layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Visualization on TLC was achieved with UV light (254 nm) and potassium permanganate as visualization methods. ^{1}H NMR spectra were recorded on a 400 MHz or a 500 MHz instrument. Chemical shifts are quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ shift), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double of doublets, ddd = doublet of doublets of doublets, dt = doublet of triplets, td = triplet of doublets), integration, coupling constant (Hz), and assignment. ^{13}C NMR spectra were recorded on a 100 MHz or a 125 MHz instrument. Chemical shifts are reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-d or a heptet at 39.5 ppm of dimethyl sulfoxide-d_6. Coupling constants (J) are reported in Hz and refer to apparent peak multiplications. HRMS were obtained on an ESI (or EI)-TOF mass spectrometer.

***N,N*-Dimethyl-4-vinylbenzamide (1l).**[14] 4-Vinylbenzoic acid (1.48 g, 10 mmol, 1.0 equiv) was added at 0 °C to thionyl chloride (2.38 g, 20 mmol, 2 equiv) in small portions in 40 mL of CH_2Cl_2. The reaction mixture was warmed to room temperature and stirred for 2 h. The remaining thionyl chloride was removed in vacuo, and the residue was transferred to a solution of *N*,*N*-dimethylamine (2 M in THF, 25 mL, 50 mmol, 5 equiv) in Et_2O (25 mL) at 0 °C. The reaction mixture was stirred at room temperature for 2 h, before water (20 mL) was added. Organic components were extracted with DCM (3 × 20 mL) and dried over $MgSO_4$. The combined organic layers were dried over $MgSO_4$, and the solvent was removed in vacuo. The product was isolated after purification by column chromatography (petroleum ether/ethyl acetate 1/1) as a colorless solid (1.29 g, 74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 6.71 (dd, J = 17.5, 11.0 Hz, 1H), 5.79 (d, J = 18.0 Hz, 1H), 5.30 (d, J = 11.0 Hz, 1H), 3.09 (s, 3H), 2.98 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.2, 138.6, 135.9, 135.3, 127.3, 125.9, 115.0, 39.4, 35.2.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]-phenanthren-17-one (1m).[15] A 100 mL flask was flame-dried and charged with estrone (1.35 g, 5 mmol, 1.0 equiv), CH_2Cl_2 (20 mL), and Et_3N (1.01 g, 10 mmol, 2.0 equiv). The mixture was cooled in a 0 °C ice−water bath, and Tf_2O (1.55 g, 5.5 mmol, 1.1 equiv) was added over 10 min. The mixture was warmed to room temperature and stirred at room temperature under nitrogen for 3 h. The resulting brown mixture was diluted with CH_2Cl_2 and washed with saturated NH_4Cl, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, and the filtrate was concentrated. A threaded tube was charged with the above product, potassium vinyltrifluoroborate (0.74 g, 5.5 mmol, 1.1 equiv), and $PdCl_2$ (17.7 mg, 0.1 mmol, 0.02 equiv), and the tube was brought into a N_2-filled glovebox. PPh_3 (78.6 mg, 0.3 mmol, 0.06 equiv), Cs_2CO_3 (4.89 g, 15 mmol, 3.0 equiv), and THF (18 mL) were added, and the tube was sealed and removed from the glovebox. A 2 mL portion of H_2O was added, and the mixture was stirred at 85 °C for 19 h. The resulting dark brown mixture was cooled to room temperature, diluted with CH_2Cl_2, and washed with H_2O. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, and the filtrate was concentrated. The crude product was purified by column chromatography (petroleum ether/ethyl acetate 10/1) to afford 1.05 g of a white solid (75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27−7.25 (m, 1H), 7.23−7.20 (m, 1H), 7.14 (s, 1H), 6.67 (dd, J = 17.6, 10.8 Hz, 1H), 5.70 (d, J = 17.6 Hz, 1H), 5.19 (d, J = 10.8 Hz, 1H), 2.94−2.90 (m, 2H), 2.51 (dd, J = 19.2, 8.8 Hz, 1H), 2.46−2.41 (m, 1H), 2.34−2.27 (m, 1H), 2.19−2.16 (m, 1H), 2.10−2.01 (m, 2H), 1.98−1.95 (m, 1H), 1.68−1.59 (m, 2H), 1.57−1.40 (m, 4H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 220.8, 139.5, 136.5, 135.1, 126.8, 125.5, 123.5, 113.1, 50.5, 47.9, 44.4, 38.1, 35.8, 31.5, 29.3, 26.5, 25.7, 21.5, 13.8.

General Procedures for Dehydrogenative Silylation of Alkenylarenes. In an oven-dried 25 mL sealed tube containing a stirring bar were placed $[Rh(COD)Cl]_2$ (4.9 mg, 1 mol %), PPh_3 (26.2 mg, 10 mol %), NBE (188.3 mg, 2.0 mmol), and THF (4 mL). The solution was stirred at room temperature for 10 min. Then, the olefin (1 mmol) and R_3SiH (2.0 mmol) were added to the above mixture. The initial color of the mixture pf $[Rh(COD)Cl]_2$, PPh_3, and NBE in THF was pale yellow, and there was no color change observed following the addition of olefin, R_3SiH, and NBE. The Schlenk tube was sealed and heated to 100 °C for 2−10 h; after the reaction, the resulting red-brown mixture was cooled to room temperature and then the solvent was concentrated. The crude product was purified by column chromatography with petroleum ether as eluent to afford the products **3** and **4**.

https://dx.doi.org/10.1021/acs.organomet.0c00242
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*(E)-Triethyl(styryl)silane (**3aa**).*[6h] Purified by column chromatography on silica gel with petroleum ether. Colorless oil (**3aa**:**4aa** = 97:3). Yield: 192 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.2 Hz, 2H), 7.32 (t, J = 7.2 Hz, 2H), 7.26−7.21 (m, 1H), 6.89 (d, J = 19.2 Hz, 1H), 6.42 (d, J = 19.2 Hz, 1H), 0.99 (t, J = 8.0 Hz, 9H), 0.66 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 138.5, 128.4, 127.8, 126.3, 125.7, 7.4, 3.6.

*(E)-Triethyl(4-methylstyryl)silane (**3ba**).*[6h] Purified by column chromatography on silica gel with petroleum ether. Colorless oil (**3ba**:**4ba** = 97:3). Yield: 190 mg, 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 7.2 Hz, 2H), 7.19 (d, J = 7.2 Hz, 2H), 6.94 (d, J = 19.2 Hz, 1H), 6.42 (d, J = 19.2 Hz, 1H), 2.40 (s, 3H), 1.06 (t, J = 8.0 Hz, 9H), 0.72 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 137.7, 135.9, 129.2, 126.2, 124.5, 21.2, 7.4, 3.6.

*(E)-(4-(tert-Butyl)styryl)triethylsilane (**3ca**).*[6h] Purified by column chromatography on silica gel with petroleum ether. Colorless oil (**3ca**:**4ca** = 96:4). Yield: 249 mg, 91%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40−7.34 (m, 4H), 6.87 (d, J = 19.6 Hz, 1H), 6.37 (d, J = 19.2 Hz, 1H), 1.32 (s, 9H), 0.98 (t, J = 8.0 Hz, 9H), 0.65 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 144.7, 135.9, 126.1, 125.4, 124.7, 34.5, 31.3, 7.4, 3.6.

*(E)-Triethyl(2-(naphthalen-2-yl)vinyl)silane (**3da**).*[16] Purified by column chromatography on silica gel with petroleum ether. Colorless oil (**3da**:**4da** = 96:4). Yield: 233 mg, 87%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82−7.77 (m, 4H), 7.70−7.68 (m, 1H), 7.47−7.41 (m, 2H), 7.06 (d, J = 19.2 Hz, 1H), 6.55 (d, J = 19.2 Hz, 1H), 1.01 (t, J = 8.0 Hz, 9H), 0.70 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 135.9, 133.6, 133.3, 128.11, 128.06, 127.6, 126.5, 126.4, 126.1, 125.9, 123.3, 7.4, 3.6.

*(E)-Triethyl(4-methoxystyryl)silane (**3ea**).*[6h] Purified by column chromatography on silica gel with petroleum ether. Colorless oil (**3ea**:**4ea** = 95:5). Yield: 213 mg, 86%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.37 (m, 2H), 6.87−6.81 (m, 3H), 6.25 (d, J = 19.2 Hz, 1H), 3.80 (s, 3H), 0.98 (t, J = 8.0 Hz, 9H), 0.65 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 144.2, 131.6, 127.5, 123.0, 113.8, 55.3, 7.4, 3.6.

*(E)-Triethyl(4-(trifluoromethyl)styryl)silane (**3fa**).*[17] Purified by column chromatography on silica gel with petroleum ether. Colorless oil (**3fa**:**4fa** = 94:6). Yield: 226 mg, 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 19.2 Hz, 1H), 6.55 (d, J = 19.2 Hz, 1H), 0.99 (t, J = 8.0 Hz, 9H), 0.68 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 141.7 (d, J = 1.1 Hz), 129.7, 129.6 (q, J = 32.1 Hz), 125.4 (q, J = 3.8 Hz), 124.2 (q, J = 270.2 Hz), 7.3, 3.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.5.

*(E)-Triethyl(2-methylstyryl)silane (**3ga**).*[18] Purified by column chromatography on silica gel with petroleum ether. Colorless oil (**3ga**:**4ga** = 95:5). Yield: 195 mg, 84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52−7.50 (m, 1H), 7.20−7.12 (m, 4H), 6.30 (d, J = 19.2 Hz, 1H), 2.37 (s, 3H), 1.00 (t, J = 8.0 Hz, 9H), 0.66 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 138.0, 135.1, 130.2, 127.8, 127.6, 126.1, 125.3, 19.6, 7.4, 3.6.

*(E)-Triethyl(4-fluorostyryl)silane (**3ha**).*[6h] Purified by column chromatography on silica gel with petroleum ether. Colorless oil (**3ha**:**4ha** = 97:3). Yield: 189 mg, 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.38 (m, 2H), 7.04−6.98 (m, 2H), 6.84 (d, J = 19.2 Hz, 1H), 6.32 (d, J = 19.2 Hz, 1H), 0.98 (t, J = 8.0 Hz, 9H), 0.65 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 161.3, 143.5, 134.7 (d, J = 3.3 Hz), 127.8 (d, J = 8.0 Hz), 125.6 (d, J = 2.2 Hz), 115.3 (d, J = 21.5 Hz), 7.4, 3.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −114.3.

*(E)-(4-Chlorostyryl)triethylsilane (**3ia**).*[6h] Purified by column chromatography on silica gel with petroleum ether. Colorless oil (**3ia**:**4ia** = 97:3). Yield: 214 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.34 (m, 2H), 7.30−7.27 (m, 2H), 6.83 (d, J = 19.2 Hz, 1H), 6.40 (d, J = 19.2 Hz, 1H), 0.98 (t, J = 8.0 Hz, 9H), 0.66 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 137.0, 133.5, 128.6, 127.5, 126.9, 7.4, 3.5.

*(E)-N-(4-(2-(Triethylsilyl)vinyl)phenyl)acetamide (**3ja**).* Purified by column chromatography on silica gel with 5/1 petroleum ether/ethyl acetate. Colorless solid (**3ja**:**4ja** = 96:4). Yield: 206 mg, 75%. Mp: 139.6−141.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.8 Hz, 2H), 7.17 (br, 1H), 6.84 (d, J = 19.2 Hz, 1H), 6.34 (d, J = 19.2 Hz, 1H), 2.18 (s, 3H), 0.98 (t, J = 8.0 Hz, 9H), 0.65 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 143.9, 137.5, 134.7, 126.9, 125.0, 119.6, 24.6, 7.4, 3.5. HRMS-ESI (m/z): calculated for $C_{16}H_{26}NOSi$ (M + H)$^+$ 276.1784, found 276.1790.

*(E)-4-(2-(Triethylsilyl)vinyl)phenyl Acetate (**3ka**).*[6h] Purified by column chromatography on silica gel with 10/1 petroleum ether/ethyl acetate. Colorless oil (**3ka**:**4ka** = 97:3). Yield: 224 mg, yield 81%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.8 Hz, 2H), 7.05 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 19.2 Hz, 1H), 6.37 (d, J = 19.2 Hz, 1H), 2.28 (s, 3H), 0.98 (t, J = 8.0 Hz, 9H), 0.65 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 150.2, 143.7, 136.3, 127.2, 126.2, 121.5, 21.0, 7.3, 3.4.

*(E)-N,N-Dimethyl-4-(2-(triethylsilyl)vinyl)benzamide (**3la**).* Purified by column chromatography on silica gel with 2/1 petroleum ether/ethyl acetate. Colorless oil (**3la**:**4la** = 96:4). Yield: 249 mg, 86% ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 6.89 (d, J = 19.2 Hz, 1H), 6.49 (d, J = 19.2 Hz, 1H), 3.05 (s, s, 6H), 0.99 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 143.8, 139.6, 135.4, 127.8, 127.4, 126.1, 39.5, 35.3, 7.3, 3.4. HRMS-ESI (m/z): calculated for $C_{17}H_{28}NOSi$ (M + H)$^+$ 290.1940, found 290.1942.

*(8R,9S,13S,14S)-13-Methyl-3-((E)-2-(triethylsilyl)vinyl)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17-(14H)-one (**3ma**).* Purified by column chromatography on silica gel with 10/1 petroleum ether/ethyl acetate. Colorless solid (**3ma**:**4ma** = 97:3). Yield: 181 mg, 46%. Mp: 87.3−89.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27−7.23 (m, 2H), 7.18 (s, 1H), 6.84 (d, J = 19.2 Hz, 1H), 6.37 (d, J = 19.6 Hz, 1H), 2.94−2.91 (m, 2H), 2.50 (dd, J = 18.8, 8.4 Hz, 1H), 2.47−2.40 (m, 1H), 2.33−2.27 (m, 1H), 2.19−2.10 (m, 1H), 2.09−1.94 (m, 3H), 1.68−1.58 (m, 2H), 1.56−1.41 (m, 4H), 0.97 (t, J = 8.0 Hz, 9H), 0.91 (s, 3H), 0.65 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 220.8, 144.5, 139.6, 136.5, 136.2, 126.9, 125.5, 125.0, 123.7, 50.5, 48.0, 44.4, 38.2, 35.8, 31.6, 29.4, 26.5, 25.7, 21.6, 13.8, 7.4, 3.5. HRMS-ESI (m/z): calculated for $C_{26}H_{39}OSi$ (M + H)$^+$ 395.2770, found 395.2768.

*(E)-1-(4-(2(Triethylsilyl)vinyl)phenyl)ethanone (**3na**).*[19] Purified by column chromatography on silica gel with 20/1 petroleum ether/ethyl acetate. Colorless oil (**3na**:**4na** = 97:3). Yield: 135 mg, 52%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 19.6 Hz, 1H), 6.59 (d, J = 19.2 Hz, 1H), 2.60 (s, 3H), 0.99 (t, J = 8.0 Hz, 9H), 0.68 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 143.5, 142.7, 136.2, 130.1, 128.6, 126.3, 26.5, 7.3, 3.4.

*(E)-4-(2-(Triethylsilyl)vinyl)pyridine (**3oa**).*[19] Purified by column chromatography on silica gel with 5/1 petroleum ether/ethyl acetate. Colorless oil (**3oa**:**4oa** = 60:40). Yield: 201 mg, 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, J = 6.0 Hz, 2H), 7.29 (d, J = 6.0 Hz, 2H), 6.83 (d, J = 19.2 Hz, 1H), 6.70 (d, J = 19.6 Hz, 1H), 0.99 (t, J = 8.0 Hz, 9H), 0.68 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 145.3, 142.3, 132.6, 120.7, 7.3, 3.3.

*(E)-1-Tosyl-5-(2-(triethylsilyl)vinyl)-1H-indole (**3pa**).* Purified by column chromatography on silica gel with 20/1 petroleum ether/ethyl acetate. Pale blue oil (**3pa**:**4pa** = 96:4). Yield: 325 mg, 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.8 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.56 (s, 1H), 7.53 (d, J = 3.6 Hz, 1H), 7.44 (d, J = 8.8 Hz, 1H), 7.19 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 19.2 Hz, 1H), 6.63 (d, J = 3.2 Hz, 1H), 6.38 (d, J = 19.2 Hz, 1H), 2.32 (s, 3H), 0.97 (t, J = 8.0 Hz, 9H), 0.65 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 144.6, 135.2, 134.6, 134.2, 131.1, 129.8, 126.9, 126.7, 125.1, 123.0, 119.3, 113.5, 109.3, 21.5, 7.4, 3.5. HRMS-ESI (m/z): calculated for $C_{23}H_{30}NO_2Si$ (M + H)$^+$ 412.1767, found 412.1762.

*(E)-Prop-1-en-1-ylbenzene (**1q'**),.*[20] The reaction of allylbenzene with a conversion of 100% gave the olefin isomerization product as a colorless oil. Yield: 108.7 mg, 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.26 (m, 4H), 7.20−7.16 (m, 1H), 6.40 (d, J = 15.8 Hz, 1H), 6.28−6.19 (m, 1H), 1.88 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 131.0, 128.4, 126.7, 125.8, 125.7, 18.5.

https://dx.doi.org/10.1021/acs.organomet.0c00242
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(E)-Ethyldimethyl(styryl)silane (**3ab**).[21] Purified by column chromatography on silica gel with petroleum ether. Colorless oil (**3ab**:**4ab** = 29:71). Yield: 208 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47−7.45 (m, 2H), 7.36−7.22 (m, 3H), 6.89 (d, J = 19.2 Hz, 1H), 6.31 (d, J = 19.6 Hz, 1H), 3.83 (q, J = 6.8 Hz, 4H), 1.26 (t, J = 6.8 Hz, 6H), 0.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 137.8, 128.52, 128.50, 126.7, 122.4, 58.4, 18.4, −4.2.

(E)-1,1,1,3,5,5,5-Heptamethyl-3-styryltrisiloxane (**3ac**).[5f] Purified by column chromatography on silica gel with petroleum ether. Colorless oil (**3ac**:**4ac** = 86:14). Yield: 308 mg, 95%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, J = 7.5 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.28−7.25 (m, 1H) 6.96 (d, J = 19.0 Hz, 1H), 6.26 (d, J = 19.5 Hz, 1H), 0.18 (s, 3H), 0.13 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.0, 138.2, 128.5, 128.2, 126.63, 126.57, 1.9, 0.01.

(E)-Ethyldimethyl(styryl)silane (**3ad**). Purified by column chromatography on silica gel with petroleum ether. Colorless oil (**3ad**:**4ad** = 87:13). Yield: 162 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 7.6 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.28−7.26 (m, 1H), 6.89 (d, J = 19.2 Hz, 1H), 6.48 (d, J = 19.2 Hz, 1H), 0.99 (t, J = 8.0 Hz, 3H), 0.63 (q, J = 8.0 Hz, 2H), 0.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 138.4, 128.5, 128.3, 127.9, 126.3, 7.4, 3.6. HRMS-EI (m/z): calculated for $[C_{12}H_{18}Si]^+$ 190.1178, found 190.1175.

(E)-Triphenyl(styryl)silane (**3ae**).[22] Purified by column chromatography on silica gel with petroleum ether. Colorless solid (**3ae**:**4ae** = 40:60). Yield: 337 mg, 93%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59−7.50 (m, 6H), 7.49−7.47 (m, 2H), 7.45−7.41 (m, 3H), 7.40−7.38 (m, 6H), 7.34−7.26 (m, 3H), 6.98 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8, 138.0, 136.0, 135.6, 134.4, 129.6, 128.5, 127.9, 126.7, 122.9.

(1E,3E)-1,4-Diphenylbta-1,3-diene (**6**).[11a] Purified by column chromatography on silica gel with petroleum ether. Colorless oil. Yield: 140 mg, 68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45−7.43 (m, 4H), 7.35−7.31 (m, 4H), 7.25−7.21 (m, 2H), 6.99−6.92 (m, 2H), 6.71−6.64 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3, 132.8, 129.2, 128.6, 127.5, 126.4.

(E)-Chalcone (**8**).[23] Purified by column chromatography on silica gel with petroleum ether and ethyl acetate. Pale yellow solid. Yield: 177 mg, 85%. Mp: 56.6−58.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03−8.01 (m, 2H), 7.81 (d, J = 12.8 Hz, 1H), 7.65−7.63 (m, 2H), 7.60−7.49 (m, 4H), 7.43−7.40 (m, 3H), 7.34−7.26 (m, 3H), 6.98 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5, 144.8, 134.8, 132.7, 130.5, 128.9, 128.6, 128.5, 128.4, 122.0.

N-(2,2-Difluoro-1-phenylethyl)acetamide (**9**).[24] Purified by column chromatography on silica gel with petroleum ether and ethyl acetate. Colorless solid. Yield: 143 mg, 72%. Mp: 104.5−105.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42−7.34 (m, 5H), 6.18−5.89 (m, 2H), 5.47−5.36 (m, 1H), 2.09 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.8, 133.9 (d, J = 4.4 Hz), 128.9, 128.8, 127.8, 116.2, 114.6 (t, J = 244.9 Hz), 113.0, 54.7 (t, J = 21.8 Hz), 23.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ −125.4 (d, J = 280.9 Hz, 1F), −127.3 (d, J = 280.5 Hz, 1F).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00242.

^{1}H, ^{13}C, and ^{19}F NMR spectra of all isolated alkenylarenes (PDF)

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Notes

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■ ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China for financial support. This paper is dedicated to Prof. Pierre H. Dixneuf for his outstanding contribution to organometallic chemistry and catalysis.

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