Synthesis of Functionalized 1-Substituted Alkenylsilanols and Establishment of Conditions for Their Palladium-Catalyzed Cross-Coupling Reactions To Afford 1-Substituted Styrene Derivatives

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An efficient method for the quantitative conversion of 1-substituted alkenyl(phenyl)silanes into the corresponding alkenylsilanols has been developed and used in their palladium(0)-catalyzed, tetrabutylammonium fluoride-promoted cross-coupling reaction with aryl iodides. Copper(I) chloride modulated the reactivity of TBAF in such a way that it virtually eliminated the protiodesilylation of alkenylsilanols, thus favoring the formation of *ipso*-coupled products.

Introduction

Styrene derivatives with substitution at the 1-position are important intermediates in the pharmaceutical industry. The chiral 1-arylmethyl unit derivable from 1-substituted styrene is common in many nonsteroidal anti-inflammatory drugs.[1] Such types of substituted styrenes with functionalized alkyl groups could be easily further transformed into biologically active β-aryl-γ-aminobutyric acid (GABA) derivatives[2] and related molecules.[3] Although these classes of compounds are accessible through metal-catalyzed cross-coupling reactions of alkenyl Mg, Zn, B, Al, Sn, and Zr compounds,[4] the requirement for inert and anhydrous conditions as well as the toxicity of the by-products produced during the reaction are major concerns. Some of these metals limit the inbuilt functionalities on the alkenyl group. Of late, organosilicon compounds[5] have also emerged as suitable partners in these couplings to provide a practical solution to these problems, with additional features for chemical manipulations of the intermediates. In this regard, Hiyama[6] has reported the synthesis of 1-butyl-substituted styrenes by the use of alkenylfluorosilane, and Denmark[7] has described the preparation of 1-methyl-substituted styrenes from alkenylsilacyclobutane.

Our interest was to expand the scope of this coupling reaction through the presence of additional functionalities in the alkenylsilane units, which would in turn provide functionalized 1-substituted styrene derivatives. Here we report a general method for the preparation of 1-substituted alkenylsilanols bearing additional functionalities and their application in the palladium-catalyzed cross-coupling reaction with various aryl iodides to furnish 1-substituted functionalized styrenes.

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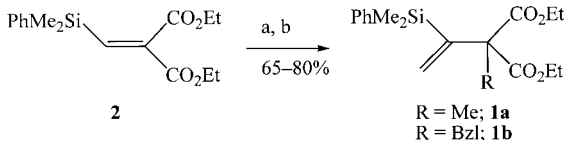
Results and Discussion

1. Preparation of Alkenylsilanols

For the cross-coupling reactions to proceed, the alkenylsilanes should generally have a heteroatom or a heteroatomic group on silicon. In this context, alkenyl(fluoro)silanes or alkenylsilanes with an oxygen functionality, such as OH or OR, are very common. Although terminally substituted alkenylsilanols[8] are easily available, no general procedure for the synthesis of 1-substituted alkenylsilanols has been reported. Recently, we have reported[9] a general method for the preparation of 1-substituted alkenyl(phenyl)silanes **1a** and **1b** from 2-silylalkylidene derivative **2**[10] (Scheme 1), and so we decided to convert these silanes into the corresponding silanols **3a** and **3b**.



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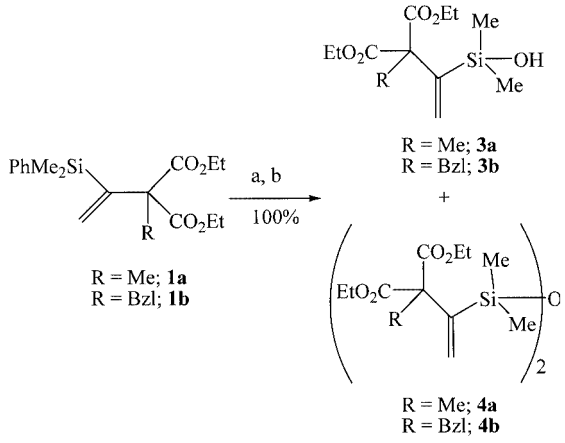
R = Me; **1a**
R = Bzl; **1b**

Scheme 1. Reagents and conditions: (a) Me_3SI, Na-dimsylate, DMSO/THF; (b) MeI or BzlBr

A $PhMe_2Si$ group in alkenylsilanes is known to be convertible into a Me_2SiOH group by a nucleophilic attack on silicon by a strong base such as *t*BuOK/18-crown-6 in the presence[11] or absence[12] of DMSO. Unfortunately, these methods did not provide the desired silanols with silanes **1a** and **1b**. An alternative option to this problem was a selec-

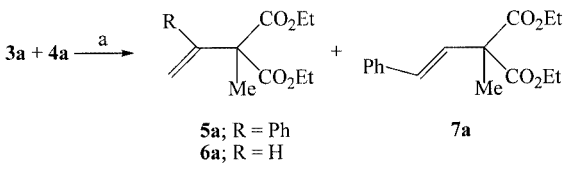
tive aryl-protiodesilylation, as the reactivity of the substituents at silicon decreases in the order allyl > aryl > vinyl.[13] We were delighted to find that brief treatment of the alkenylsilane **1a** with 5.5 equiv. of CF_3SO_3H in CH_2Cl_2 at −2 °C remarkably gave a mixture of the desired alkenylsilanol **3a** and its dehydrated dimer, disiloxane **4a** (**3a**/**4a**, 25:75) through an exclusive aryl-protiodesilylation in quantitative yield (Scheme 2). An explanation for the driving force behind this highly selective dearylation could be the fact that protonation on the double bond would produce a primary carbocation, which is energetically less favored than protonation on the aromatic ring. This method has also been used for the preparation of silanol **3b** and disiloxane **4b** (**3b**/**4b** = 1:1), again in quantitative yield, from silane **1b** (Scheme 2). It was not necessary to separate the silanol and disiloxane prior to coupling, since disiloxanes and silanols[14] are known to be equally reactive partners in the cross-coupling reaction.



Scheme 2. Reagents and conditions: (a) CF_3SO_3H, CH_2Cl_2, −10 to −2 °C; (b) aq. NH_3

2. Cross-Coupling Reactions of Alkenylsilanols

Our exploratory studies of the cross-coupling reaction between a mixture of **3a** and **4a** and iodobenzene were performed with $[Pd(all)Cl]_2$/$Pd(dba)_2$ as catalyst and tetrabutylammonium fluoride (TBAF) as promoter in various solvents (THF, DMSO, DMF, NMP, MeCN, Et_2O). Disappointingly, the target 1-substituted styrene **5a** was formed in poor yields (< 25%) in association with variable amounts of protiodesilylated olefin **6a** and the *cine*-coupled styrene derivative **7a** (Scheme 3). It was found that $[Pd(all)Cl]_2$ was superior to $Pd(dba)_2$ and that DMF was the best solvent. The low yield of the desired coupling product **5a** was presumably due to poor coupling reactivity of the silanol **3a**/disiloxane **4a**, thus allowing its rapid degradation by protiodesilylation. When a mild promoter such as CsF[15] or Ag_2O[16] was used, the coupling reaction was sluggish even at 60 °C and many unidentified side products were formed.



Scheme 3. Reagents and Conditions: (a) PhI, TBAF, Pd catalyst, solvent, room temp., 17 h

Tetrabutylammonium hydroxide (TBAOH) has been introduced[17] as a promoter in the silanol-based cross-coupling reaction to alleviate the problem of protiodesilylation.[18] When TBAF was replaced with TBAOH (40% in water) in this coupling, however, protiodesilylated olefin **6a** (49%) was found to be the major product, in association with a trace amount (3%) of the *cine*-coupled product **7a**. Unchanged starting materials (**3a** + **4a**) (48%) could also be seen in the ^1H NMR spectrum of the crude product. To improve the coupling yield, we next decided to use a combination of TBAF and TBAOH. Unfortunately, variation of the quantities of these reagents did not improve the formation of the desired product **5a**; in all cases, in fact, preferential formation of the unusual *cine*-coupled product took place, as can be seen in Figure 1.

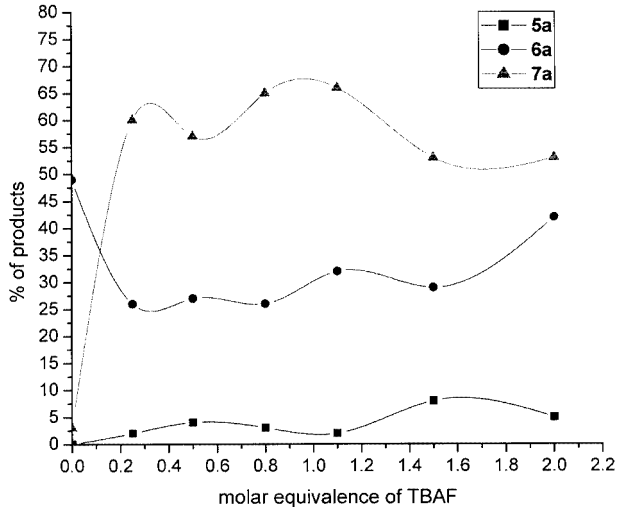


Figure 1. Effect of variation of TBAF equivalence on the product ratios in the presence of 1 equivalent of TBAOH

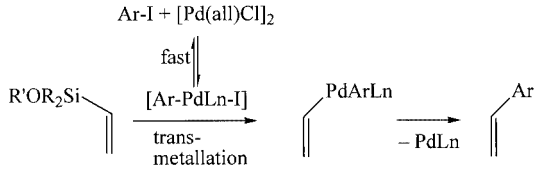
3. Investigation of the *cine*-Coupling Mechanism

The preferential formation of the *cine*-coupled product could not be easily explained in terms of alkenylsilane cross-coupling mechanisms,[6b] although exclusive formation of this type of unusual *cine*-coupled product from direct cross-coupling of alkenylsilanols with aryl iodides has been reported by Anderson et. al.,[19] but without any evidence of the direct participation of the alkenylsilanols. The alternative possibility could be initial protiodesilylation of silanols to the corresponding alkene followed by a normal Heck process[20] to give the *cine*-coupled product. To confirm this, we first carried out the protiodesilylation of **3a** + **4a** with TBAF in DMF and subsequently treated the derived product **6a** with Pd catalyst, TBAOH, and iodobenzene, which gave the *cine*-coupled product **7a** (42%) along with the unchanged alkene **6a** (**7a**/**6a**, 7:3). In addition to

this we also carried out a time course study of the coupling reaction between the pure disiloxane **4a** and iodobenzene. The progress of the reaction was monitored by ^{1}H NMR at different time intervals, and the ratio of the components was judged by integration of the individual olefinic protons. There was no generation of any of the cross-coupled products after the first 2.5 h; only the protiodesilylated olefin **6a** and a small amount (ca. 25%) of starting material were present. After 5.5 h, the *cine*-coupled product **7a** had been formed to the extent of 18%, while after 24 h, olefin **6a** and *cine*-coupled product **7a** were found in a 57:43 ratio. This further confirmed that the *cine*-coupled product did indeed arise from Heck coupling between protiodesilylation product **6a** and iodobenzene and not from the cross-coupling of disiloxane **4a**.

4. Optimization of Conditions for *ipso*-Coupling

At this juncture we were keen to improve the yield of the cross-coupling reaction affording the desired *ipso*-coupled product, and prevention of the formation of protiodesilylated product was essential for this. A glance at the mechanism of silanol cross-coupling reveals that the rate-determining step is the transmetallation of ArPdLnX complex with the alkenylsilanol/siloxane (Scheme 4). Were we able to facilitate this transmetallation step, the rate of coupling would also increase, and so we searched for additives that might suppress protiodesilylation and probably also accelerate the transmetallation.



Scheme 4. Mechanism of Pd^0-catalyzed cross-coupling of alkenylsilanol with iodoarenes

Many research groups[21] have employed copper(I) salts as promoters for the cross-coupling of aryl and alkenylsilanes to obviate the use of fluoride, copper(I) salts have been used as co-catalysts in palladium-catalyzed cross-coupling reactions to accelerate the reaction and product yield,[22] and they have also been used to suppress the formation of *cine*-coupled products in Stille and Suzuki coupling reactions of sterically hindered organometalloids.[23] It has been proposed[22b][23b] that Cu^I generates a metalloid (RCu) that is more reactive than the initial organostannane/organosilane, and this subsequently undergoes an easy transmetallation with aryl-palladium complex, thus improving the yield and specificity of the reaction. In anticipation that Cu^I salts should have a similar influence on our coupling reaction, we used varying amounts of CuCl in conjunction with TBAF (2 equiv.) and Pd catalyst in 5% aqueous DMF[24] at 45 °C. We were gratified to note that there was a significant increase in the amount of desired product **5a** with the increasing amount of CuCl. The results are presented in Figure 2.

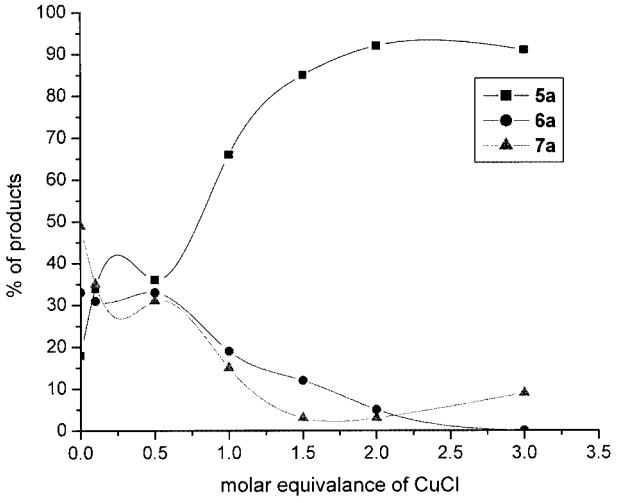
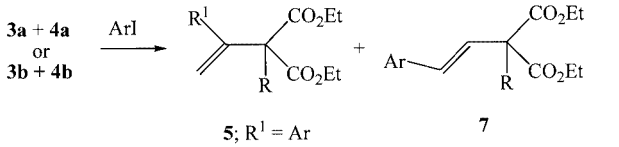


Figure 2. Effect of variation of CuCl equivalence on the product ratios in the presence of 2 equiv. of TBAF

The optimum conditions involved the use of 2 equiv. of CuCl in addition to 2 equiv. of TBAF, 0.05 equiv. of $[Pd(all)Cl]_2$ and 1.5 equiv. of iodobenzene in 5% aqueous DMF at 45 °C.[25] Any further increase in CuCl reduced the yield of the coupling products, due to a reduced rate of cross-coupling. We carried out this coupling reaction between **3a** + **4a** and iodobenzene in the presence of 2 equiv. of CuBr or CuI and found these salts to be inferior to CuCl. The scope of this coupling reaction with silanols **3a** and **3b** was examined under the optimum condition using various aryl iodides, and the results are summarized in Table 1.

Table 1. Coupling of silanols with various aryl iodides in the presence of TBAF and CuCl



5; R^1 = Ar
6; R^1 = H
7

Entry	Ar, R	Products	5[a][b]	6[a]	7[a]
1	Ph-, Me	**5a**, **6a**, **7a**	92 (78)	5	3
2	4-MeO-C_6H_4-, Me	**5b**, **6a**, **7b**	96 (76)	0	4
3	2-MeO-4-Me-C_6H_3-, Me	**5c**, **6a**, **7c**	83 (74)	13	4
4	1-Np-, Me	**5d**, **6a**,**7d**	87 (77)	9	4
5	4-AcNH-C_6H_4-, Me	**5e**, **6a**, **7e**	96 (92)	0	4
6	4-MeO-C_6H_4-, Bn	**5f**, **6b**, **7f**	93 (76)[c]	0	7
7	4-AcNH-C_6H_4-, Bn	**5g**, **6b**, **7g**	93 (80)[c]	0	7
8	4-CF_3-C_6H_4-, Me	**5h**, **6a**, **7h**	88 (84)	12	0

[a] Proportion obtained by ^{1}H NMR. [b] The values in parentheses are the % isolated yields of **5**. [c] Reaction carried out with 2 equiv. of CuBr instead of CuCl.

As can be seen from the results summarized in Table 1, the *ipso*-coupled product was almost exclusively formed in all the cases, contaminated with a trace amount of *cine*-coupled product. In the coupling between **3b** + **4b** and 4-iodoanisole (Table 1, Entry 6) or 4-acetamidoiodobenzene (Table 1, Entry 7), CuBr was found to be a better additive than CuCl. The *ipso*-coupled products **5f** or **5g** were formed along with 7% of the *cine*-isomers **7f** or **7g**, respectively. The formation of the latter was possibly due to rate retardation of *ipso*-coupling by steric congestion in **3b/4b**. This allowed the competitive protiodesilylation, subsequently resulting in the formation of *cine*-coupled product **7f** or **7g** through the normal Heck coupling[20] with iodoarenes.

5. Scrutiny of the Role of CuCl

Experiments were carried out with **3a** + **4a** to ascertain the role of CuCl, with omission of Pd catalyst and TBAF, respectively. No coupling products were obtained in either case. These results testified that CuCl neither played the role of a catalyst nor acted as a sole promoter in this reaction. Also, we do not have any evidence for transmetallation from silicon to copper. When the coupling reaction was performed with disiloxane **4a** and benzyl bromide in the presence of CuCl and TBAF with omission of the palladium catalyst, we did not obtain the desired benzylated product; only the protiodesilylated olefin **6a** was formed. Formation of alkenylcopper species[22g−22i] from the alkenylsilane prior to coupling could not therefore be confirmed but in the presence of TBAF and palladium catalyst its involvement cannot be ruled out. It has been noticed that silanols/disiloxanes **3a**, **3b/4a**, and **4b** undergo complete protiodesilylation within a few min when treated with 2 equiv. of TBAF in DMF. Therefore, in our case Cu^I salts played a significant role by modulating the reactivity of TBAF, in turn inhibiting the protiodesilylation and thus enabling the cross-coupling reaction to proceed to provide the *ipso*-coupled product.

Conclusions

In conclusion, we have developed a very simple method for the quantitative conversion of 1-substituted alkenylsilanes into the corresponding disiloxanes/silanols, which are otherwise difficult to prepare. These silanols possessed poor reactivity towards palladium-catalyzed cross-coupling under the usual conditions. In addition, they undergo a rapid fluoride-assisted protiodesilylation. Extensive optimization of the cross-coupling reaction identified conditions suitable to make the reaction efficient and high-yielding through the use of Cu^I salts as additives. Although the role of copper is not clear, the mechanism might involve transmetallation from Si to Cu prior to transmetallation to Pd. This development significantly expands the range of compatible alkenylsilanols/disiloxanes in cross-coupling reactions, which are otherwise prone to protiodesilylation under the usual coupling conditions. We have shown that the unusual *cine*-substitution product is formed through a conventional Pd^0-catalyzed Heck reaction of the protiodesilylated product and aryl iodides in the presence of TBAF. It is also worth noting that these disiloxanes are more versatile as they bear additional functionalities for further synthetic maneuvers. These styryl products could be further transformed into biologically important molecules such as 1,1-disubstituted amino acids, substituted GABA and related molecules.

Experimental Section

General Remarks: All reactions were performed in oven-dried (120 °C) or flame-dried glass apparatus under dry N_2 or argon. The solvents were dried and distilled from the indicated drying agents: CH_2Cl_2 and $CHCl_3$ from P_2O_5, THF and Et_2O from sodium/benzophenone, toluene, benzene and hexanes from sodium, and DMSO and DMF from CaH_2. Tetrabutylammonium fluoride trihydrate was obtained from Fluka. Compounds **1a**, **1b**,[9] **2**,[10b] $Pd(dba)_2$,[4g] $[Pd(all)Cl]_2$,[26] 4-acetamidoiodobenzene,[27] and 1-iodo-2-methoxy-4-methylbenzene[27] were prepared by literature procedures.

^1H NMR and ^{13}C NMR spectra were recorded with a Bruker 200 MHz spectrometer. Spectra were referenced to residual chloroform (^1H NMR: δ = 7.25 ppm., ^{13}C NMR: δ = 77.00 ppm). Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quadruplet), quint (pentet), m (multiplet), and br (broad). Coupling constants (*J*) are reported in Hertz. Mass spectra were recorded with a Fisons VG Quatro II mass spectrometer (EI, 70 V; CI 30 V. ESI 3.5 KV). Infrared spectra (IR) were recorded with a Nicolet Impact 410 FT IR spectrophotometer in NaCl cells or in KBr discs; peaks are reported in cm^{-1}. Melting points (m.p.) were determined with a Fischer John's melting point apparatus and are uncorrected. Analytical thin-layer chromatography was performed on home-made silica gel plates (0.5 mm).

Disiloxane 4a: Trifluoromethanesulfonic acid (5.3 mL, 60.6 mmol, 5.3 equiv.) was rapidly added at −2 °C (bath) to a stirred solution of the alkenylsilane **1a** (3.8 g, 11.38 mmol, 1 equiv.) in dichloromethane (80 mL). The reaction mixture was stirred under those conditions for 10 min and poured into ice-cold ammonia solution (30% aqueous solution, 350 mL). The organic layer was separated, and the aqueous phase was extracted with chloroform. The combined organic extracts were dried ($MgSO_4$) and evaporated to give a mixture of disiloxane **4a** and silanol **3a** (**4a/3a**, 75:25) (3 g, 100%). The disiloxane **4a** and the silanol **3a** were easily separable by column chromatography. For the cross-coupling reaction the separation was not required.

Data for 4a: R_f = 0.39 (hexane/EtOAc, 92:8). IR (neat): ṽ = 3052, 1732, 1600, 1258, 1050 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.23 (s, 12 H), 1.25 (t, *J* = 7.2 Hz, 12 H), 1.59 (s, 6 H), 4.00−4.30 (m, 8 H), 5.61 (s, 2 H), 5.64 (s, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 2.44 (4 C), 13.88 (4 C), 21.98 (2 C), 59.96 (2 C), 61.20 (4 C), 126.75 (2 C), 150.84 (2 C), 171.52 (4 C) ppm. ESI MS: *m/z* (%) = 553 (100) $[M + 23]^+$, 548 (36) $[M + 18]^+$, 333 (80). $C_{24}H_{42}O_9Si_2$ (530.8): calcd. C 54.31, H 7.98; found C 54.11, H 8.23.

Data for 3a: R_f = 0.34 (hexane/EtOAc, 85:15). IR (neat): ṽ = 3650−3200 (br), 3053, 1731, 1258, 863 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.26 (s, 6 H), 1.26 (t, *J* = 7.2 Hz, 6 H), 1.60 (s, 3 H), 4.20 (q, *J* = 7.2 Hz, 4 H), 5.61 (s, 1 H), 5.69 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.39 (2 C), 13.92 (2 C), 21.76, 59.80,

61.68 (2 C), 126.85, 150.90, 172.33 (2 C) ppm. ESI MS: *m/z* (%) = 297 (15) $[M + 23]^+$, 257 (100) $[M - 17]^+$.

Disiloxane 4b: Trifluoromethanesulfonic acid (1.2 mL, 13.4 mmol, 5.5 equiv.) was rapidly added at −10 °C (bath) to a stirred solution of the alkenylsilane **1b** (1 g, 2.439 mmol, 1 equiv.) in dichloromethane (19 mL). The reaction mixture was stirred under those conditions for 15 min and poured into ice-cold ammonia solution (30% aqueous solution; 80 mL). The organic layer was separated, and the aqueous phase was extracted with chloroform. The combined organic extracts were dried ($MgSO_4$) and evaporated to give a mixture of disiloxane **4b** and silanol **3b** (**4b**/**3b**, 1:1) (0.831 g, 100%). The disiloxane **4b** and the silanol **3b** were easily separable by column chromatography. The former is a waxy solid. For the cross coupling reaction separation of disiloxane **4b** and silanol **3b** was not required.

Data for 4b: M.p. 43−44 °C; R_f = 0.38 (hexane/EtOAc, 92:8). IR ($CHCl_3$): $\tilde{\nu}$ = 3085, 1732, 1252, 1038 cm^{-1}. ^1H NMR(200 MHz, $CDCl_3$): δ = −0.06 (s, 12 H), 1.18 (t, *J* = 8 Hz, 12 H), 3.40 (s, 4 H), 4.00−4.22 (m, 8 H), 5.96 (d, *J* = 1.2 Hz, 2 H), 6.03 (d, *J* = 1.2 Hz, 2 H), 7.09−7.17 (m, 10 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 2.06 (4 C), 13.68 (4 C), 42.82 (2 C), 61.04 (4 C), 64.42 (2 C), 126.54 (2 C), 127.68 (4 C), 130.21 (2 C), 130.41 (4 C), 136.23 (2 C), 149.79 (2 C), 170.50 (4 C) ppm. ESI MS: *m/z* (%) = 705 (100) $[M + 23]^+$, 700 (14) $[M + 18]^+$, 333 (62). $C_{36}H_{50}O_9Si_2$ (683.0): calcd. C 63.31, H 7.38; found C 63.02, H 7.50.

Data for 3b: R_f = 0.34 (hexane/EtOAc, 87:13). IR (neat): $\tilde{\nu}$ = 3650−3200 (br), 3087, 1732, 1605, 1251, 863 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.08 (s, 6 H), 1.19 (t, *J* = 7.2 Hz, 6 H), 3.42 (s, 2 H), 4.00−4.20 (m, 4 H), 5.90 (s, 1 H), 5.95 (s, 1 H), 7.00−7.20 (m, 5 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 0.96 (2 C), 13.61, 13.77, 42.82, 61.45 (2 C), 64.73, 126.78, 127.86 (2 C), 129.68, 130.28 (2 C), 136.06, 149.95, 170.99 (2 C) ppm. ESI MS: *m/z* (%) = 333 (100) $[M - 17]^+$, 259 (44), 91 (12), 77 (3).

Typical Procedure for Palladium-Catalyzed Cross-Coupling between 3a/4a and Iodobenzene in the Presence of TBAF and TBAOH in DMF: Tetrabutylammonium hydroxide (40% solution in water) (0.33 mL, 0.5 mmol) was added under argon atmosphere to a stirred solution of a mixture of silanol **3a** and disiloxane **4a** (0.5 mmol based on silanol, 1 equiv.) in DMF (1.5 mL) in a Schlenk flask. The reaction vessel was evacuated and filled with argon (3 times). Iodobenzene (0.75 mmol, 1.5 equiv.) and $[Pd(allyl)Cl]_2$ (9 mg, 0.025 mmol, 0.05 equiv.) were added, followed by the required amount of TBAF (1 M in DMF). The reaction mixture was stirred at room temperature for 40 h, diluted with hexane/dichloromethane, and washed with water. The organic extract was dried ($MgSO_4$), and the solvents were evaporated. The residue was purified by chromatography to give the styrene derivative.

Ethyl (*E*)-2-Ethoxycarbonyl-2-methyl-4-phenyl-3-butenoate (7a): Compound **7a** was obtained in 42% yield from the reaction between **3a** + **4a** and iodobenzene under the indicated conditions (1.1 molar equivalent of TBAF) after purification by column chromatography. In addition, ethyl 2-ethoxycarbonyl-2-methyl-3-butenoate (**6a**) was isolated in 23% yield.

Data for 7a: R_f = 0.37 (hexane/EtOAc, 95:5). IR (neat): $\tilde{\nu}$ = 1731, 967 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.2 Hz, 6 H), 1.66 (s, 3 H), 4.22 (q, *J* = 7.2 Hz, 4 H), 6.48 (d, *J* = 16.4 Hz, 1 H), 6.69 (d, *J* = 16.4 Hz, 1 H), 7.23−7.42 (m, 5 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.98 (2 C), 20.31, 55.63, 61.64 (2 C), 126.57 (2 C), 127.64, 127.84, 128.52 (2 C), 130.72, 136.50, 171.10 (2 C) ppm. EI MS: *m/z* (%) = 277 (3) $[M + 1]^+$, 276 (21) $[M]^+$, 204 (10), 203 (21), 175 (5), 158 (14), 147 (28), 131 (32), 129 (100), 128 (23), 115 (19), 91 (7), 77 (5). $C_{16}H_{20}O_4$ (276.3): calcd. C 69.55, H 7.30; found C 69.30, H 7.52.

Data for 6a: R_f = 0.25 (hexane/EtOAc, 98:2). IR (neat): $\tilde{\nu}$ = 3091, 1738, 1640, 994, 928 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.2 Hz, 6 H), 1.54 (s, 3 H), 4.18 (q, *J* = 7.2 Hz, 4 H), 5.18 (d, *J* = 17 Hz, 1 H), 5.25 (d, *J* = 10.4 Hz, 1 H), 6.29 (dd, *J* = 10.4, 17 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.92 (2 C), 19.49, 56.11, 61.52 (2 C), 115.96, 135.97, 170.94 (2 C) ppm. EI MS: *m/z* (%) = 201 (0.5) $[M + 1]^+$, 155 (7), 128 (39), 127 (56), 100 (68), 99 (100), 85 (15), 82 (37), 55 (15).

Typical Procedure for the Palladium-Catalyzed Cross-Coupling of Silanols/Disiloxanes with Aryl Iodides in the Presence of TBAF and CuCl in DMF: Water (0.125 mL) was added under argon atmosphere to a stirred solution of disiloxane and silanol (0.5 mmol based on silanol, 1 equiv.) in DMF (0.9 mL) in a Schlenk flask, and the solution was degassed under vacuum. Cuprous chloride (100 mg, 1 mmol, 2 equiv.) and $[Pd(allyl)Cl]_2$ (10 mg, 0.027 mmol, 0.05 equiv.) were introduced into the reaction pot, followed by the addition of aryl iodide (0.75 mmol, 1.5 equiv.) and TBAF (1 mL, 1 M in DMF, 1 mmol, 2 equiv.). The reaction mixture was stirred at 45 °C for 40 h, brought to room temperature, and diluted with water. The reaction mixture was extracted with 1:1 hexane/dichloromethane. The organic extract was dried ($MgSO_4$), and the solvents were evaporated. The residue was purified by chromatography to give the styrene derivatives.

Ethyl 2-Ethoxycarbonyl-2-methyl-3-phenyl-3-butenoate (5a): Compound **5a** was obtained in 78% yield from the reaction between **3a** + **4a** and iodobenzene under the indicated conditions after purification by column chromatography. R_f = 0.32 (hexane/EtOAc, 95:5). IR (neat): $\tilde{\nu}$ = 3084, 1732, 1625, 862 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.20 (t, *J* = 7.1 Hz, 6 H), 1.59 (s, 3 H), 4.18 (q, *J* = 7.1 Hz, 4 H), 5.33 (s, 1 H), 5.34 (s, 1 H), 7.26 (br. s, 5 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.77 (2 C), 22.20, 59.96, 61.55 (2 C), 117.97, 127.29, 127.77 (2 C), 128.16 (2 C), 140.66, 147.70, 171.27 (2 C) ppm. EI MS: *m/z* (%) = 276 (0.5) $[M]^+$, 231 (0.5) $[M - 45]^+$, 203 (100), 185 (11), 175 (89), 147 (15.6), 129 (64.4), 115 (33.3), 91 (26.6). $C_{16}H_{20}O_4$ (276.3): calcd. C 69.55, H 7.30; found C 69.42, H 7.60.

Ethyl 2-Ethoxycarbonyl-2-methyl-3-(4-methoxyphenyl)-3-butenoate (5b): Compound **5b** was obtained in 76% yield from the reaction between **3a** + **4a** and 4-iodoanisole under the indicated conditions after purification by column chromatography. R_f = 0.33 (hexane/EtOAc, 93:7). IR (neat): $\tilde{\nu}$ = 3094, 1737, 1608, 837 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.21 (t, *J* = 7.1 Hz, 6 H), 1.58 (s, 3 H), 3.78 (s, 3 H), 4.17 (q, *J* = 7.1 Hz, 4 H), 5.27 (s, 1 H), 5.30 (s, 1 H), 6.79 (d, *J* = 8.6 Hz, 2 H), 7.18 (d, *J* = 8.6 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.80 (2 C), 22.14, 55.11, 60.08, 61.52 (2 C), 113.08 (2 C), 117.25, 129.34 (2 C), 133.00, 147.22, 158.81, 171.37 (2 C) ppm. EI MS: *m/z* (%) = 307 (2.5) $[M + 1]^+$, 306 (2.5) $[M]^+$, 261 (1.9), 233 (100), 205 (79.5), 187 (10.7), 177 (25.2), 159 (45.5), 145 (17), 115 (20.8), 91 (19.6). $C_{17}H_{22}O_5$ (306.4): calcd. C 66.65, H 7.24; found C 66.79, H 7.33.

Ethyl 2-Ethoxycarbonyl-3-(2-methoxy-4-methylphenyl)-2-methyl-3-butenoate (5c): Compound **5c** was obtained in 74% yield from the reaction between **3a** + **4a** and 1-iodo-2-methoxy-4-methylbenzene under the indicated conditions after purification by column chromatography. R_f = 0.27 (hexane/EtOAc, 93:7). IR (neat): $\tilde{\nu}$ = 3089, 1733, 1625, 1605, 864 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.2 Hz, 6 H), 1.39 (s, 3 H), 2.26 (s, 3 H), 3.67 (s, 3 H), 4.10−4.30 (m, 4 H), 5.34 (s, 1 H), 5.41 (s, 1 H), 6.68 (d, *J* = 8.2 Hz,

1 H), 6.99 (s, 1 H), 7.02 (d, J = 8.2 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.92 (2 C), 20.35, 20.95, 55.06, 59.41, 61.35 (2 C), 109.86, 120.53, 129.12 (2 C), 129.61, 131.67, 145.12, 154.28, 171.66 (2 C) ppm. EI MS: m/z (%) = 321 (3) $[M + 1]^+$, 320 (15) $[M]^+$, 247 (100), 229 (9), 219 (50), 201 (17), 189 (14), 173 (31), 159 (16), 158 (17), 128 (9), 115 (12). $C_{18}H_{24}O_5$ (320.4): calcd. C 67.48, H 7.5; found C 67.32, H 7.75.

Ethyl 2-Ethoxycarbonyl-2-methyl-3-(1-naphthyl)-3-butenoate (5d): Compound **5d** was obtained in 77% yield from the reaction between **3a** + **4a** and 1-iodonaphthalene under the indicated conditions after purification by column chromatography. R_f = 0.3 (hexane/EtOAc, 96:4). IR (neat): ṽ = 3089, 1732, 1634, 863 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.12−1.34 (m, 6 H), 1.50 (s, 3 H), 4.00−4.32 (m, 4 H), 5.43 (s, 1 H), 5.80 (s, 1 H), 7.37−7.49 (m, 4 H), 7.75−7.85 (m, 2 H), 8.01−8.09 (m, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.70 (2 C), 21.60, 60.40, 61.52 (2 C), 121.55, 124.81, 125.54, 125.73, 125.79, 126.26, 127.53, 127.92, 132.56, 133.42, 138.30, 144.04, 171.25 (2 C) ppm. EI MS: m/z (%) = 327 (9) $[M + 1]^+$, 326 (29) $[M]^+$, 253 (31), 252 (61), 225 (29), 223 (13), 207 (28), 206 (32), 179 (100), 178 (32), 165 (44), 153 (28), 152 (29), 128 (14). $C_{20}H_{22}O_4$ (326.4): calcd. C 73.60, H 6.79; found C 73.35, H 7.10.

Ethyl 3-(4-Acetamidophenyl)-2-ethoxycarbonyl-2-methyl-3-butenoate (5e): Compound **5e** was obtained in 92% yield from the reaction between **3a** + **4a** and 4-acetamidoiodobenzene under the indicated conditions after purification by column chromatography. R_f = 0.28 (hexane/EtOAc, 55:45). IR (neat): ṽ = 3366, 3306, 3184, 3108, 3047, 1729, 1695, 1673, 1596, 1527, 848 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.22 (t, J = 7.2 Hz, 6 H), 1.59 (s, 3 H), 2.17 (s, 3 H), 4.18 (q, J = 7.2 Hz, 4 H), 5.31 (s, 1 H), 5.33 (s, 1 H), 7.22 (d, J = 8.4 Hz, 2 H), 7.30 (s, broad, 1 H), 7.42 (d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.80 (2 C), 22.13, 24.40, 59.99, 61.66 (2 C), 117.83, 119.11 (2 C), 128.73 (2 C), 136.36, 137.33, 147.04, 168.67, 171.36 (2 C) ppm. EI MS: m/z (%) = 334 (0.6) $[M + 1]^+$, 333 (3) $[M]^+$, 260 (100), 232 (92), 214 (9), 186 (12), 162 (10), 144 (69), 130 (31), 118 (26), 106 (17), 77 (8), 43 (44). $C_{18}H_{23}NO_5$ (333.4): calcd. C 64.85, H 6.95, N 4.20; found C 64.62, H 7.17, N 4.26.

Ethyl 2-Benzyl-2-ethoxycarbonyl-3-(4-methoxyphenyl)-3-butenoate (5f): Compound **5f** was obtained in 75% yield from the reaction between **3b** + **4b** and 4-iodoanisole under the indicated conditions after purification by column chromatography. R_f = 0.37(hexane/EtOAc, 92:8). IR (neat): ṽ = 3087, 1736, 1608, 837 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.08 (t, J = 7.2 Hz, 6 H), 3.46 (s, 2 H), 3.79 (s, 3 H), 4.04 (q, J = 7.2 Hz, 4 H), 5.37 (s, 1 H), 5.40 (s, 1 H), 6.81 (d, J = 8.6 Hz, 2 H), 7.19 (br. s, 5 H), 7.20 (d, J = 8.6 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.68 (2 C), 41.73, 55.20, 61.34 (2 C), 64.77, 113.21 (2 C), 120.05, 126.75, 127.77 (2 C), 129.10 (2 C), 130.54 (2 C), 133.93, 136.57, 145.23, 158.84, 169.87 (2 C) ppm. EI MS: m/z (%) = 383 (0.4) $[M + 1]^+$, 382 (1) $[M]^+$, 336 (1.5), 333 (2.5), 299 (2.5), 292 (3.5), 309 (2.5), 291 (19), 245 (5.5), 235 (11), 218 (9.5), 217 (100), 189 (12), 161 (6), 149 (14), 145 (26), 135 (27), 121 (20), 91 (51). $C_{23}H_{26}O_5$ (382.5): calcd. C 72.23, H 6.85; found C 72.24, H 7.21.

Ethyl 3-(4-Acetamidophenyl)-2-benzyl-2-ethoxycarbonyl-3-butenoate (5g): Compound **5g** was obtained in 80% yield from the reaction between **3b** + **4b** and 4-acetamidoiodobenzene under the indicated conditions after purification by column chromatography. M.p. 104−105 °C; R_f = 0.32 (hexane/EtOAc, 6:4). IR ($CHCl_3$): ṽ = 3400−3200 (br), 3179, 3103, 3060, 3034, 1741, 1678, 1595, 1522, 837 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.08 (t, J = 7 Hz, 6 H), 2.16 (s, 3 H), 3.47 (s, 2 H), 4.04 (q, J = 7 Hz, 4 H), 5.40 (s, 1 H), 5.44 (s, 1 H), 7.18−7.26 (m, 8 H), 7.42 (d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.63 (2 C), 24.39, 41.80, 61.40 (2 C), 64.55, 119.07 (2 C), 120.21, 126.83, 127.81 (2 C), 128.33 (2 C), 130.38 (2 C), 136.32, 137.12, 137.40, 145.28, 168.64, 169.76 (2 C) ppm. ESI MS: m/z (%) = 433 (27) $[M + 24]^+$, 432 (100) $[M + 24]^+$, 410 (5) $[M + 1]^+$. $C_{24}H_{27}NO_5$ (409.5): calcd. C 70.40, H 6.65, N 3.42; found C 70.35, H 6.75, N 3.40.

Ethyl 2-Ethoxycarbonyl-2-methyl-3-(4-trifluoromethylphenyl)-3-butenoate (5h): Compound **5h** was obtained in 84% yield from the reaction between **3a** + **4a** and 1-iodo-4-trifluoromethylbenzene under the indicated conditions after purification by column chromatography. R_f = 0.29 (hexane/EtOAc, 95:5). IR (neat): ṽ = 3099, 1732, 1615, 1327, 854 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.19 (t, J = 7.1 Hz, 6 H), 1.62 (s, 3 H), 4.17 (q, J = 7.1 Hz, 4 H), 5.38 (s, 1 H), 5.44 (s, 1 H), 7.40 (d, J = 8.1 Hz, 2 H), 7.54 (d, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.75 (2 C), 22.19, 59.77, 61.74 (2 C), 119.35, 124.08 (q, J = 270 Hz), 124.76 (2 C), 128.68 (2 C), 129.47 (q, J = 32.1 Hz), 144.57, 146.74, 170.96 (2 C) ppm. EI MS: m/z (%) = 345 (0.03) $[M + 1]^+$, 344 (0.03) $[M]^+$, 325 (3), 299 (1), 271 (77), 243 (100), 225 (10), 197 (24), 177 (16), 159 (17), 129 (21), 128 (25). $C_{17}H_{19}F_3O_4$ (344.3): calcd. C 59.30, H 5.56; found C 59.06, H 5.78.

Supporting Information: ^{1}H and ^{13}C NMR spectra of **3a** and **3b**; **4a** and **4b**; **5a**−**5h**; **6a** and **7a** (29 pages) (see also the footnote on the first page of this article.

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