Palladium-catalyzed cross-coupling reaction using alkenyldimethyl(2-thienyl)silanes

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Abstract: Alkenyldimethyl(2-thienyl)silanes underwent the cross-coupling reaction with organic halides mediated by tetrabutylammonium fluoride and a palladium catalyst under extremely mild conditions to afford alkenyl-coupled products in good to excellent yields. Starting from 1,2-bissilylated alkenes, 1,2-disubstituted olefins were also synthesized and successfully applied to the cross-coupling reaction.

Key words: Cross-coupling; organosilicon compounds; 2-thienyl group; palladium catalyst.

Introduction. The cross-coupling reaction is an essential method for making bonds between sp^2 carbons and employs organometallic reagents and organic halides (or triflates) and transition metal catalysts (eq. [1]).¹⁾ The straightforward strategy when applied to synthesis of complex target molecules needs to use organometallic reagents that are easily prepared and react smoothly with high selectivity and stereospecificity. In addition, such organometallic reagents should be commercially available especially in case of industrial applications. Prior to our studies, such organometallic reagents applicable to the cross-coupling reaction were limited to those derived from Mg,²⁾ B,³⁾ Al,⁴⁾ Zn,⁵⁾ Sn,⁶⁾ or Cu.⁷⁾ Most of these reagents indeed react efficiently but some are less accessible.

In contrast, organosilicon compounds are readily available, stable against moisture and air, and endowed with high selectivities. However they are in general much less reactive compared with other organometallic reagents, owing to the less polarized carbon-silicon bond. Fortunate enough, activation of a carbon-silicon bond is possible by means of a nucleophilic fluoride ion that forms pentacoordinate silicates.⁸⁾ Such highly coordinated silicates behave like main group organo-

metallics to undergo transmetalation with Pd(II) complexes and thus achieve the cross-coupling reaction as we disclosed in 1988.⁹⁾

The silicon-based cross-coupling reaction has advantages in view of high chemoselectivity, lack of homocoupling byproducts, structural variations of accessible organosilicon compounds, and toxicity much less than other metals. In addition, many of organosilicon compounds are readily prepared from commercially available chlorosilanes. Accordingly, use of organosilicon compounds for the carbon-carbon bond forming strategy is decisively beneficial.

Over a decade we have been studying the palladium catalyzed cross-coupling reaction of organohalosilanes (halogen = F, Cl) using a fluoride ion as the activator.⁹⁾ The success of the reaction totally owes to the activation of C-Si bonds through forming silicate anions. An electron-withdrawing heteroatom on the tetracoordinated silicon makes the silicon acidic enough to accept F^- .⁸⁾ Recently, Denmark reported that alkenylsilacyclobutanes couple efficiently with organic halides, the reactivity of organosilanes being improved dramatically,¹⁰⁾ due possibly to the formation of silanols.¹¹⁾ The cross-coupling reaction of organo-alkoxysilanes¹²⁾ or organosilanols¹³⁾⁻¹⁵⁾ with organic halides are independently documented. Thus, the presence of at least one heteroatom on the silicon of alkenylsilanes is essential for the reaction to proceed. Herein, we report that alkenyldimethyl(2-thienyl)silanes act as a coupling partner with organic halides (Scheme 1).¹⁶⁾ The coupling reaction proceeds under extremely mild conditions ever

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reported for any organosilicon compounds.

The advantages of the 2-thienyl group as an activating group as well as a dummy ligand are demonstrated by alkenyldimethyl(2-thienyl)silanes **2** that are much more stable against moisture, acid and base, compared to the corresponding halosilanes or other heteroatom-substituted silanes. Alkenyldimethyl(2-thienyl)silanes **2** can be readily accessible by hydrosilylation of alkynes with dimethyl(2-thienyl)silane (**1**), abbreviated as HSiMe_2Th , that is readily available by treatment of chlorodimethylsilane with 2-thienyllithium.

Scheme 1

Results and discussion. *Preparation of alkenyldimethyl(2-thienyl)silanes.* First, we selectively prepared (*E*)- and (*Z*)-1-octenyldimethyl(2-thienyl)silanes as shown in eq. [2]. Hydrosilylation of 1-octyne with **1** in the presence of Pt or Rh catalyst¹⁷⁾ afforded (*E*)- or (*Z*)-1-octenyldimethyl(2-thienyl)silanes ((*E*)-**2a** or (*Z*)-**2a**), respectively. The *E/Z* selectivity of hydrosilylation could be controlled by the catalyst employed. The optimization of hydrosilylation of 1-octyne with **1** disclosed that both H_2PtCl_6 (Speier's catalyst) and $\text{Pt}(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}$ ($\text{Pt}[\text{DVDS}]$) did not show satisfactory selectivity, but with *t*- $\text{Bu}_3\text{P}/\text{Pt}[\text{DVDS}]$,¹⁸⁾ (*E*)-1-octenyldimethyl(2-thienyl)silane ((*E*)-**2a**) and α -adduct (α -**3**) were obtained in a ratio of 99/1. On the other hand, the selectivity for (*Z*)-1-octenyldimethyl(2-thienyl)silane ((*Z*)-**2a**) was lower in the reaction catalyzed by $\text{RhCl}(\text{PPh}_3)_3$ or $[\text{RhI}(\text{cod})_2]$ (75:25 or 83:17, respectively). Finally, with $\text{NaI}/\text{RhCl}(\text{PPh}_3)_3$, the (*Z*)-/(*E*)-**2a** ratio was raised up to 88/12.¹⁹⁾ Both (*E*)- and (*Z*)-**2a** are quite stable against moisture, acid (acetic acid, silica gel), and base (1 M NaOH aq., basic alumina).

Optimization of the cross-coupling reaction conditions. We next optimized the conditions for the cross-coupling reaction of (*E*)-**2a** with 4-iodobenzotrifluoride (**4a**) using a palladium catalyst and tetrabutylammonium fluoride (TBAF) as a fluoride source (eq. [3]). Cross-coupling of **4a** with (*E*)-**2a** (1.2 equiv.) in the presence of $\text{Pd}(\text{PPh}_3)_4$ (5 mol%) and TBAF (2.4 equiv.) took place at 60 °C in 4 h to afford the desired alkenylarene (*E*)-**5a** in 72% yield. Using $\text{Pd}(\text{OAc})_2$, the reaction proceeded smoothly at room temperature (25 °C) to give (*E*)-**5a** in a quantitative yield. Taking into account that the silicon-mediated cross-coupling reaction requires normally elevated temperatures,²⁰⁾ the reactivity is enhanced significantly in this system. Ligandless catalyst $\text{Pd}_2(\text{dba})_3$ completed the reaction in 0.5 h to afford (*E*)-**5a** in quantitative yield. Because of the ease in handling, we chose $\text{Pd}(\text{OAc})_2$ as the standard catalyst. Use of TBAF and (*E*)-**2a** in a 1:1 molar ratio resulted in slow down of the reaction as compared with that in a 2:1 ratio. Accordingly, TBAF was used in 2 molar equiv. to (*E*)-**2a**, i.e., 2.4 equiv. to **4a**. When we introduced two 2-thienyl groups on silicon, the reactivity was enhanced further, and the reaction was completed in 0.5 h (>99% yield). Unlike TBAF, the use of anhydrous $[(\text{Et}_2\text{N})_3\text{S}][\text{Me}_3\text{SiF}_2]^-$ (TASF) or KF as a fluoride salt resulted in no reaction at room temperature. Meanwhile 2 M aqueous KF or NaOH gave (*E*)-**5a** in a small amount (4% or 35%, respectively). Here it should be noted that the THF solution of TBAF contains several % of water (~5 wt. % in a reagent purchased from Aldrich).

On the reaction pathways. Very recently, Yoshida and Itami disclosed the cross-coupling reaction of alkenyldimethyl(2-pyridyl)silanes.²¹⁾ The coupling reaction is considered to proceed through alkenyldimethylsilanol formation followed by transmetalation, pyridine being detected spectrometrically. Shown in Scheme 2 are the possible reaction pathways for the reaction of **2** with **4**. We also observed that thiophene was released gradually when the coupling of (*E*)-**2a** and **4a** was monitored by ^1H NMR. Furthermore, when TBAF was added to (*E*)-**2a**, we confirmed the production of (*E*)-1-octenyldimethylsilanol and bis[(*E*)-1-

octenyldimethyl]disiloxane by GC-MS (eq. [4]). Thus, even under the conditions for (*E*)-**2a**, milder than those for 2-pyridylsilanes, the 2-thienyl group on the silicon appears to be cleaved. Accordingly, the penta-coordinated silicate **A** may be formed prior to the transmetalation. In this case, the effect of 2-thienyl group may be speculated as, (1) electronegative 2-thienyl group may accelerate the formation of the reactive penta-coordinated silicate (**A** or **B**), or (2) released thiophene may promote the coupling reaction itself. Direct transmetalation from penta-coordinated silicate **A** remains to be another possibility though. In this case, (3) 2-thienyl group may coordinate to arylpalladium(II) complex to promote transmetalation.²²⁾

Scope and limitations. The scope of the coupling reaction was examined under the optimal conditions. Various types of alkenylsilanes and organic halides are applicable to the coupling reaction (Table I). The coupling products are available from aryl iodides having electron-donating groups (entries 3 and 4) as well as electron-withdrawing groups (entries 1 and 2). Aryl iodide **4f** having a sterically crowded substituent also couples smoothly to afford the corresponding alkenylarene in a quantitative yield (entry 5). Aryl bromides **4g**, **4h** also couple with the alkenylsilanes at room temperature (entries 6 and 7). Aryl chloride **4i** couples under the milder conditions than the previous coupling systems although phosphine ligand and elevated temperatures are required (entry 8).^{23,24)} Halidess of 1-naphthyl, 3-pyridyl, alkenyl, and alkynyl were successfully applicable to the coupling reaction (entries 9–13). The (*Z*)-isomer of **2a** (*Z/E* = 88/12) gave the corresponding alkenylarene

Table I. Cross-coupling of alkenyldimethyl(2-thienyl)silanes **2** with various organic halides **4**^a

Entry	Organosilane (%) ^{b)}	Organic halide	Time (h)	Yield of 5 (%) ^{c)}
1	<i>n</i> -C ₆ H ₁₃ SiMe ₂ Th (<i>E</i>)- 2a (<i>E/α</i> = 99/1)		0.5	5b (96)
2	(<i>E</i>)- 2a		0.5	5c (94)
3	(<i>E</i>)- 2a		0.25	5d (78)
4	(<i>E</i>)- 2a		0.5	5e (97)
5	(<i>E</i>)- 2a		3	5f (99)
6	(<i>E</i>)- 2a		5	5g (96)
7 ^{d)}	(<i>E</i>)- 2a		24	5h (91)
8 ^{d), e)}	(<i>E</i>)- 2a		6	5i (99)
9	(<i>E</i>)- 2a (<i>E/α</i> = 91/9)		0.5	5j (97)
10	(<i>E</i>)- 2a		5	5k (64)
11	(<i>E</i>)- 2a		6	5l (98)
12	(<i>E</i>)- 2a		0.5	5m (56)
13 ^{d)}	(<i>E</i>)- 2a		40	5n (41)
14	<i>n</i> -C ₆ H ₁₃ SiMe ₂ Th (<i>Z</i>)- 2a (<i>Z/E</i> = 88/12)	4a	1	(<i>Z</i>)- 5a (98) (<i>Z/E</i> = 89/11)
15	 2b	4a	0.5	5o (90)
16	PhSiMe ₂ Th (85) 2c (<i>E/α</i> = 99/1)	4a	1	5p (98) (<i>E/α</i> = 99/1)
17	<i>t</i> -BuSiMe ₂ Th (87) 2d (<i>E/α</i> = 99/1)	4a	5	5q (97) (<i>E/α</i> = 99/1)
18	EtSiMe ₂ Th (82) 2e	4a	3	5r (86)
19	Me ₃ SiSiMe ₂ Th (72) 2f (<i>E/α</i> = 96/4)	4a	1	5s (95) (<i>E/α</i> = 96/4)
20	NC(CH ₂) ₃ SiMe ₂ Th (77) 2g (<i>E/α</i> = 75/25)	4a	1	5t (90) (<i>E/α</i> = 81/19)
21	OHSiMe ₂ Th (85) 2h (<i>E/α</i> = 86/14)	4a	24	5u (71) (<i>E/α</i> = 99/1)

^{a)}All the reactions were performed using alkenyldimethyl(2-thienyl)silane **2** (0.6 mmol), **4** (0.5 mmol), Pd(OAc)₂ (5 mol%), and TBAF (1.2 mmol) in THF at room temperature.

^{b)}Yields and isomer ratios of the hydrosilylation are given in parentheses. ^{c)}Isolated yields. The isomer ratios were determined by ¹H and ¹⁹F NMR. ^{d)}PCy₃ (10 mol%) was added. ^{e)}The reaction was carried out at 60 °C. ^{f)}Pd(OAc)₂ (10 mol%) and PCy₃ (20 mol%) were added.

(*Z*)-**5a** maintaining the *Z/E* ratio of 89/11 (entry 14). Mono-substituted vinylsilane **2b**, di-substituted alkenylsilanes **2c**, **2d**, and tri-substituted alkenylsilane **2e** all coupled smoothly with **4a** (entries 15–18). Bissilylated alkene **2f** reacted completely at dimethyl(2-thienyl)silyl moiety with a trimethylsilyl site being unaffected (entry 19). Chemoselectivity is as good as previous organosilicon-based coupling reactions.¹⁰⁾ For example, the reaction gives the coupled product from alkenylsilanes with nitrile and hydroxyl functional groups (entries 20 and 21). Yields were still high and no other byproducts were detected.

Double cross-coupling for the synthesis of 1,2-disubstituted olefins. We examined one-pot sequential synthesis of di-substituted olefins as shown in eq. [5]. Like entry 18 in Table I, a solution of (*E*)-trimethylsilyl[dimethyl(2-thienyl)silyl]ethene was coupled with **4a** at the dimethyl(2-thienyl)silyl moiety in the presence of TBAF. TASF was next added as an alternative fluoride source, together with ethyl 4-iodobenzoate, palladium catalyst, and triethyl phosphite cocatalyst to afford the (*E*)-di-substituted olefin, stereoselectively.¹⁰⁾ Thus, by the choice of the fluoride source, both silyl groups could be utilized for the coupling in a stepwise manner. Also, we prepared the 1,2-bis[dimethyl(2-thienyl)silyl]ethene stereoselectively by bissilylation of ethyne with 1,2-di(2-thienyl)-1,1,2,2-tetramethyldisilane in the presence of Pd(OAc)₂ and 1,1,3,3-tetramethylbutyl isocyanide (Scheme 3).²⁵⁾ With this bis-silylated ethene, a double coupling reaction proceeded to form the (*Z*)-di-substituted olefin in a single step.

Scheme 3

Conclusion. Here we have demonstrated alkenyldi-methyl(2-thienyl)silanes are excellent coupling partners with organic halides in the TBAF promoted palladium-catalyzed cross-coupling reactions. The 2-thienyl group acts as an activating group as well as a dummy ligand. The reaction proceeds under very mild conditions and can be tolerant of a variety of functional groups.

Experimental. *General.* NMR spectra were taken with a Varian Mercury 200 (¹H, 200 MHz) spectrometer using CDCl₃ as a solvent. Chemical shifts of ¹H NMR are expressed in parts per million downfield relative to an internal tetramethylsilane (δ = 0 ppm) or chloroform (δ = 7.26 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet. ¹³C NMR spectra were measured on a Varian Mercury 200 (¹³C, 200 MHz) spectrometer with tetramethylsilane as an internal standard (δ = 0 ppm). Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Kyoto University Elemental Analysis Center. GC analyses were carried out on a SHIMADZU GC-14B. TLC analyses were performed by means of Merck Kieselgel 60 F and column chromatography was carried out using Wakogel C-200. THF and diethyl ether were distilled from benzophenone and sodium under an argon atmosphere. Butyllithium was purchased from Sigma-Aldrich Co. Inc., Milwaukee, U.S.A. All reactions were carried out under an argon atmosphere. Cooling a reaction vessel at –78 °C was effected using methanol with dry ice.

Dimethyl(2-thienyl)silane (1). To a dry ice cooled solution of chlorodimethylsilane (7.9 g, 84 mmol) in diethyl ether (30 mL) was added 2-thienyllithium, prepared from *n*-butyllithium (70 mmol) and 2-bromothiophene (13.7 g, 84 mmol) in diethyl ether (50 mL) so slowly that the temperature was kept at –30 °C. The resulting solution was allowed to warm up to room temperature overnight. The solvent was concentrated under reduced pressure, and hexane was added to the residue. Filtration of the precipitate, followed by concentration of the filtrate, gave a brown oil. Distillation at 45 °C (20 mmHg) afforded **1** as a colorless oil (7.9 g, 80%): ¹H NMR δ 0.38 (s, 3 H), 0.40 (s, 3 H), 4.54–4.61 (m, 1 H), 7.19 (dd, *J* = 3.2, 4.6 Hz, 1 H), 7.32 (d, *J* = 3.2 Hz, 1 H), 7.61 (d, *J* = 4.6 Hz, 1 H). ¹³C NMR δ 2.8, 111.1, 128.2, 131.0, 135.1. HRMS Calcd for C₆H₁₀SiS: *M*, 142.0272; Found: *m/z* 142.0261.

(*E*)-1-Octenyldimethyl-(2-thienyl)silane ((*E*)-2a**).** A mixture of 1-octyne (0.55 g, 5.0 mmol), Pt(CH₂=CHSiMe₂)₂O (0.5 mL, 0.005 mmol, 0.01 M in hexane), *t*-Bu₃P (1 mg, 0.005 mmol) and **1** (0.78 g, 5.5

mmol) was placed in a sealed screw tube at 0 °C. An exothermic reaction occurred in a few minutes, and the reaction mixture stirred at 0 °C for 2 h. The reaction was monitored by ^1H NMR. After completion of the reaction, this material was distilled at 85 °C (0.6 mmHg) to afford (*E*)-**2a** as a colorless oil (1.15 g, 91%): ^1H NMR δ 0.37 (s, 6 H), 0.89 (m, 3 H), 1.29–1.44 (m, 8 H), 2.15 (q, J = 6.4 Hz, 2 H), 5.76 (d, J = 18.6 Hz, 1 H), 6.18 (dt, J = 6.4, 18.6 Hz, 1 H), 7.19 (dd, J = 3.2, 4.6 Hz, 1 H), 7.27 (d, J = 3.2 Hz, 1 H), 7.61 (d, J = 4.6 Hz, 1 H). ^{13}C NMR δ –1.2, 14.0, 22.6, 28.4, 28.8, 31.7, 36.7, 126.9, 128.0, 130.6, 134.4, 149.8. Calcd for $\text{C}_{14}\text{H}_{24}\text{SSi}$: C, 66.60; H, 9.58. Found: C, 66.64; H, 9.73.

(*Z*)-1-Octenyldimethyl(2-thienyl)silane ((*Z*)-**2a**). A mixture of 1-octyne (0.55 g, 5.0 mmol), $\text{RhCl}(\text{PPh}_3)_3$ (4.6 mg, 0.005 mmol), NaI (1 mg, 0.25 mmol) and dimethyl(2-thienyl)silane (0.78 g, 5.5 mmol) was placed in a sealed screw tube at 0 °C. An exothermic reaction occurred in a few minutes, and the reaction mixture stirred at 0 °C for 2 h. The reaction was monitored by ^1H NMR. After completion of the reaction, this material was distilled at 85 °C (0.6 mmHg) to afford (*Z*)-**2a** as a colorless oil (1.01 g, 79%): ^1H NMR δ 0.42 (s, 6 H), 0.86 (m, 3 H), 1.23–1.35 (m, 8 H), 2.09 (q, J = 7.4 Hz, 2 H), 5.62 (d, J = 14.0 Hz, 1 H), 6.42 (dt, J = 7.4, 14.0 Hz, 1 H), 7.16 (dd, J = 3.2, 4.6 Hz, 1 H), 7.28 (d, J = 3.2 Hz, 1 H), 7.57 (d, J = 4.6 Hz, 1 H). ^{13}C NMR δ 0.4, 14.0, 22.5, 28.9, 29.4, 31.7, 33.7, 126.1, 128.0, 130.5, 134.4, 151.5. Calcd for $\text{C}_{14}\text{H}_{24}\text{SSi}$: C, 66.60; H, 9.58. Found: C, 66.35; H, 9.84.

(*E*)-*n*- $\text{C}_2\text{H}_5\text{CH}=\text{C}(\text{n}-\text{C}_2\text{H}_5)\text{SiMe}_2\text{Th}$ (**2e**): bp 90 °C (1.5 mmHg). ^1H NMR δ 0.41 (s, 6 H) 0.89 (t, J = 7.6 Hz, 3 H), 1.01 (t, J = 7.6 Hz, 3 H), 2.12 (q, J = 7.6 Hz, 2 H), 2.16 (q, J = 7.0, 7.6 Hz, 2 H), 5.82 (t, J = 7.0 Hz, 1 H), 7.17 (dd, J = 3.4, 4.6 Hz, 1 H), 7.25 (d, J = 3.4 Hz, 1 H), 7.58 (d, J = 4.6 Hz, 1 H). ^{13}C NMR δ –1.4, 14.0, 14.8, 21.6, 22.4, 127.9, 130.5, 134.6, 139.5, 144.0. Calcd for $\text{C}_{12}\text{H}_{20}\text{SSi}$: C, 64.22; H, 8.98. Found: C, 63.93; H, 9.08.

(*E*)- $\text{NC}(\text{CH}_3)_3\text{CH}=\text{CHSiMe}_2\text{Th}$ (**2g**): bp 110 °C (0.5 mmHg). ^1H NMR δ 0.38 (s, 6 H), 1.69–1.88 (m, 2 H), 2.23–2.43 (m, 4 H), 5.86 (d, J = 18.4 Hz, 1 H), 6.08 (dt, J = 5.4, 18.4 Hz, 1 H), 7.19 (dd, J = 3.2, 4.6 Hz, 1 H), 7.27 (d, J = 3.2 Hz, 1 H), 7.61 (d, J = 4.6 Hz, 1 H). ^{13}C NMR δ –1.4, 16.3, 24.1, 35.0, 119.4, 128.1, 130.1, 130.7, 134.5, 146.0. Calcd for $\text{C}_{12}\text{H}_{17}\text{NSSi}$: C, 61.22; H, 7.28. Found: C, 61.11; H, 7.28.

(*E*)- $\text{H}_3\text{CC}(\text{OH})(\text{CH}_3)\text{CH}=\text{CHSiMe}_2\text{Th}$ (**2h**): bp 130 °C (1.5 mmHg). ^1H NMR δ 0.39 (s, 6 H), 1.30 (s, 6 H), 1.59 (br, 1 H), 5.95 (d, J = 18.8 Hz, 1 H), 6.27 (d, J = 18.8 Hz, 1 H), 7.18 (dd, J = 3.2, 4.4 Hz, 1 H), 7.26 (d, J = 3.2 Hz, 1 H), 7.60 (d, J = 4.4 Hz, 1 H). ^{13}C NMR δ 0.18, 128.1,

130.6, 130.8, 134.9, 138.6, 151.0. Calcd for $\text{C}_{11}\text{H}_{18}\text{OSSi}$: C, 58.35; H, 8.01. Found: C, 58.46; H, 8.10.

Cross-coupling reaction of alkenyldimethyl(2-thienyl)-silanes with organic halides. A typical procedure. To a solution of **4a** (0.5 mmol) and (*E*)-**2a** (0.6 mmol) in THF, were added TBAF (1.20 mmol, 1 M in THF) and $\text{Pd}(\text{OAc})_2$ (5 mol%) at room temperature. The mixture was stirred at room temperature for 1 h, poured into saturated aq NaHCO_3 solution, and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over magnesium sulfate. Removal of the solvent under reduced pressure, followed by purification by silica-gel column chromatography (hexane-EtOAc = 50:1), afforded cross-coupled product (*E*)-**5a**: ^1H NMR δ 0.89 (m, 3 H), 1.28–1.53 (m, 9 H), 2.24 (m, 2 H), 6.25–6.46 (m, 2 H), 7.42 (d, J = 8.4 Hz, 2 H), 7.54 (d, J = 8.4 Hz, 2 H). ^{13}C NMR δ 14.0, 22.6, 28.9, 29.1, 31.7, 33.0, 125.2, 125.3, 125.4, 125.5, 125.9, 128.5, 134.1. Calcd for $\text{C}_{15}\text{H}_{19}\text{F}_3$: C, 70.29; H, 7.47. Found: C, 70.42; H, 7.45.

5c: ^1H NMR δ 0.89 (m, 3 H), 1.30–1.50 (m, 9 H), 1.39 (t, J = 7.0 Hz, 3 H), 2.22 (m, 2 H), 4.37 (q, J = 7.0 Hz, 2 H), 6.27–6.47 (m, 2 H), 7.38 (d, J = 8.6 Hz, 2 H), 7.97 (d, J = 8.6 Hz, 2 H). ^{13}C NMR δ 14.0, 14.3, 22.5, 28.8, 29.0, 31.6, 33.1, 60.7, 125.6, 128.5, 128.9, 129.7, 134.1, 142.3, 166.5. HRMS Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_2$: M, 260.1776; Found: m/z 260.1735.

5k: ^1H NMR δ 0.88 (m, 3 H), 1.25–1.50 (m, 8 H), 2.20 (m, 2 H), 6.20–6.40 (m, 2 H), 7.19 (dd, J = 4.2, 7.8 Hz, 1 H), 7.64 (d, J = 7.8 Hz, 1 H), 8.41 (d, J = 4.2 Hz, 1 H), 8.54 (br, 1 H). ^{13}C NMR δ 14.0, 22.5, 28.8, 29.0, 31.6, 33.1, 123.3, 126.1, 132.3, 133.4, 133.7, 147.8, 147.9. HRMS Calcd for $\text{C}_{13}\text{H}_{19}\text{N}$: M, 189.1517; Found: m/z 189.1511.

5q: ^1H NMR δ 1.13 (s, 9 H), 6.34 (s, 2 H), 7.44 (d, J = 8.6 Hz, 2 H), 7.54 (d, J = 8.6 Hz, 2 H). ^{13}C NMR δ 29.4, 33.5, 123.5, 125.2, 125.3, 125.4, 125.5, 126.1, 144.5. Calcd for $\text{C}_{13}\text{H}_{15}\text{F}_3$: C, 68.41; H, 6.62. Found: C, 68.33; H, 6.53.

5r: ^1H NMR δ 0.97 (t, J = 7.4 Hz, 3 H), 1.07 (t, J = 7.4 Hz, 3 H), 2.25 (q, J = 7.4 Hz, 2 H), 2.52 (q, J = 7.4 Hz, 2 H), 5.70 (t, J = 7.4 Hz, 1 H), 7.44 (d, J = 8.8 Hz, 2 H), 7.55 (d, J = 8.8 Hz, 2 H). ^{13}C NMR δ 11.7, 12.5, 20.0, 20.9, 123.1, 123.2, 123.3, 123.4, 124.7, 125.8, 130.2. HRMS Calcd for $\text{C}_{13}\text{H}_{15}\text{F}_3$: M, 228.1126; Found: m/z 228.1161.

5s: ^1H NMR δ 0.17 (s, 9 H), 6.60 (d, J = 19.2 Hz, 1 H), 6.90 (d, J = 19.2 Hz, 1 H), 7.52 (d, J = 9.0 Hz, 2 H), 7.58 (d, J = 9.0 Hz, 2 H). ^{13}C NMR δ –1.3, 125.4, 125.5, 126.4, 133.1, 142.0. Calcd for $\text{C}_{12}\text{H}_{15}\text{F}_3\text{Si}$: C, 58.99; H, 6.19. Found: C, 58.95; H, 6.49.

5t: ^1H NMR δ 1.78–1.96 (m, 2 H), 2.34–2.50 (m, 4 H), 6.24 (dt, $J = 6.8, 16.2$ Hz, 1 H), 6.52 (d, $J = 16.2$ Hz, 1 H), 7.43 (d, $J = 8.4$ Hz, 2 H), 7.56 (d, $J = 8.4$ Hz, 2 H). ^{13}C NMR δ 16.4, 24.7, 31.6, 125.3, 125.4, 125.5, 125.6, 126.1, 126.3, 130.4, 130.7 Calcd for $\text{C}_{13}\text{H}_{12}\text{F}_3\text{N}$: C, 65.27; H, 5.06. Found: C, 65.55; H, 5.22.

One-pot sequential coupling of (E)-trimethylsilyl[di-methyl(2-thienyl)silyl]ethane (2f) with aryl halides. To a solution of **4a** (0.1 mmol) and **2f** (0.1 mmol) in THF, were added TBAF (0.2 mmol, 1 M in THF) and allylpalladium chloride dimer (2.5 μmol) at room temperature. The mixture was stirred at room temperature for 2 h, until the consumption of **4a** was confirmed by GC analysis. Next, TASf (0.2 mmol, 1 M in THF) was added, together with ethyl 4-iodobenzoate (0.2 mmol), allylpalladium chloride dimer (2.5 μmol), and triethyl phosphite (0.01 mmol). The reaction mixture was allowed to warm up to 60 °C and stirred for 48 h, cooled down to room temperature, poured into sat aq NH_4Cl , and extracted with EtOAc. The combined organic layers were washed with brine, and then dried over MgSO_4 . Concentration in vacuo and purification by silica-gel column chromatography (hexane-EtOAc = 10:1) afforded (*E*)-1-(4-ethoxycarbonyl)-phenyl-2-(4-trifluoromethyl)phenylethene (45%): ^1H NMR δ 1.41 (t, $J = 7.2$ Hz, 3 H), 4.38 (q, $J = 7.2$ Hz, 2 H), 7.21 (s, 2 H), 7.58 (d, 8.6 Hz, 2 H), 7.62 (m, 4 H), 8.05 (d, $J = 8.6$ Hz, 2 H). ^{13}C NMR δ 14.3, 61.0, 125.6, 125.7, 126.5, 126.8, 129.4, 129.9, 130.6, 140.2, 140.9, 166.2. HRMS Calcd for $\text{C}_{18}\text{H}_{15}\text{F}_3\text{O}_2$: M, 320.1024; Found: m/z 320.0986.

Double cross-coupling of (Z)-1,2-bis[dimethyl(2-thienyl)-silyl]ethene. To a solution of ethyl 4-iodobenzoate (0.2 mmol) and (*Z*)-1,2-bis[dimethyl(2-thienyl)silyl]ethene (0.1 mmol) in THF, were added TBAF (0.2 mmol, 1 M in THF) and $\text{Pd}_2(\text{dba})_3$ (2.5 μmol) at room temperature. The mixture was stirred at 60 °C for 24 h. Work-up as mentioned above followed by purification by silica-gel column chromatography (hexane-EtOAc = 10:1) afforded (*Z*)-1,2-bis[(4-ethoxycarbonyl)phenyl]ethene (52%, Z/E = 99/1), mp 124.4–124.6 °C; lit. (purity unknown)²⁶ 130–131 °C). ^1H NMR δ 1.41 ($J = 7.1$ Hz, 6 H), 4.39 (q, $J = 7.1$ Hz, 4 H), 7.23 (s, 2 H), 7.59 (d, $J = 8.4$ Hz, 4 H), 8.05 (d, $J = 8.4$ Hz, 4 H); ^{13}C NMR δ 14.3, 61.0, 126.5, 129.8, 129.97, 130.3, 141.1, 166.3. HRMS Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_4$: M^+ , 324.1362; Found: 324.1382.

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