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Synthesis and cross-coupling reaction of alkenyl[(2-hydroxymethyl)phenyl]dimethylsilanes

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Abstract

Highly stable alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes are prepared by stereo- and regioselective hydrosilylation of alkynes catalyzed either by a platinum or ruthenium catalyst using protected [2-(hydroxymethyl)phenyl]dimethylsilanes. Cyclic silyl ether, 1,1-dimethyl-2-oxa-1-silaindan, also serves as a starting material for the alkenylsilanes by the ring-opening reaction with alkenyl Grignard reagents. The resulting alkenylsilanes undergo cross-coupling reaction with various aryl and alkenyl iodides under reaction conditions employing K_2CO_3 as a base at 35–50 °C in highly regio- and stereospecific manners. The reaction tolerates a diverse range of functional groups including silyl protections. The silicon residue is readily recovered and reused on a gram-scale synthesis. Intramolecular coordination of a proximal hydroxyl group is considered to efficiently form pentacoordinate silicates having a transferable group possibly at an axial position and, thus, responsible for the cross-coupling reaction under conditions significantly milder than those reported for the silicon-based reactions.

Keywords: Palladium; Cross-coupling; Silicon; Aryl iodide; Alkenyl iodide

1. Introduction

The metal-catalyzed cross-coupling reactions of main-group alkenylmetals with organic halides provide a regio- and stereochemically well-defined access to a range of substituted ethenes including conjugated arylethenes and dienes that are ubiquitous functionalities in organic materials and natural products [1]. Among many protocols, a silicon-based one is gaining increasing importance and interest in view of high stability and non-toxicity of silicon reagents [2]. Another beneficial aspect of the transformation is well-established metal-catalyzed alkyne-hydrosilylation chemistry that makes a variety of alkenylsilanes readily available in regio-, stereo-, and chemoselective manners [3]. However, the silicon-based protocol has rarely been the choice for synthetic chemists irrespective of these attractive properties of organosilicon compounds. Since the pioneering work by Hiyama and Hatanaka [4], in situ formation of pentacoordinate silicates by use of alkenyl(halo)silanes or alkenyl(alkoxy)silanes in the presence of a fluoride activator has been the standard strategy in the silicon-based cross-coupling protocol [2]. However, halosilanes and alkoxysilanes suffer from drawbacks like sensitivity to heat, moisture, base, and/or acid. A recent breakthrough in this filed has been initiated independently by Mori/Hiyama [5] and Denmark [6], who have used alkenylsilanols as the coupling agents. Silanols are relatively stable compared with halosilanes and alkoxysilanes and allow the cross-coupling reaction to proceed even at room temperature, significantly milder reaction conditions ever reported. Furthermore, recent developments in highly stable tetraorganosilicon reagents, so-called ''masked alkenylsilanols'' that have a labile silacyclobutyl [7], 2-pyridyl [8], 2-thienyl [9], electron-poor aryl [10], benzyl [11], or even phenyl [12] group, have raised the synthetic potential of alkenylsilanes as the cross-coupling reagents for synthesis

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of organic materials and complex natural products [13]. They form alkenylsilanols in situ upon treatment with TBAF or $KOSiMe_3$ to undergo cross-coupling reaction under mild conditions. Thus, the remaining synthetic problem in the silicon-based protocol is the use of fluoride activators, which are relatively expensive and incompatible with several functional groups including common silyl protectors. Fluoride-free cross-coupling reactions of alkenylsilanes are available, but the number is limited. Herein the activation is achieved with NaOH [14], $KOSiMe_3$ [12,15], or stoichiometric amount of transition-metal promoters [5] particularly for alkenyl(halo)silanes, alkenyl(alkoxy)silanes, or alkenylsilanols.

A clue to an ideal activation of alkenylsilane reagents has recently been recorded by Takeda and coworkers who employed alkenyl(trimethyl)silanes having a proximal hydroxyl group *cis* to the silyl group to effect smooth transmetallation from silicon to copper without fluoride activation (Fig. 1) [16]. The resulting alkenylcopper reagents undergo cross-coupling reaction with aryl iodides in the presence of a palladium catalyst. Shindo also demonstrated a similar effect of a carboxyl group in a fluoride-free cross coupling reaction of alkenyl(trimethyl)silanes [17]. These examples clearly show that intramolecular coordination by a negatively charged oxygen nucleophile accelerates transmetallation from silicon to a late transition-metal in highly efficient manners. However, these precedents are restricted to alkenylsilanes that have a transferable group always containing the oxygen-based activating functionality. Accordingly, we have embarked on design of stable tetraorganosilicon reagents that have an activating organofunctional group and an independent transferable group to allow delivery of various organic groups. Indeed, a prototype of our alkenylsilane design has been suggested by Hudrlik and coworkers. They showed that allyl- or benzyl[2-(hydroxymethyl)phenyl]dimethylsilanes could transfer the allyl or benzyl group to carbonyl compounds [18]. We envisioned that upon treatment with a certain base alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes would form penta-coordinate silicate intermediates having a rather electron-withdrawing alkenyl group at an axial position and, thus, selectively transfer the alkenyl group among four different organic substituents. The reagent makes a variety of alkenyl groups transferable to electrophiles, as the activating group can function irrespective of the transferred group [19]. This reagent design has been found to work well as expected. Reported herein are the details [20].

2. Results and discussion

2.1. Preparation of alkenyl[2-(hydroxymethyl)phenyl]-dimethylsilanes

Key synthetic precursors of alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes are readily prepared from 2-bromobenzyl alcohol (Scheme 1). Dimethyl[2-(2-tetrahydro-2*H*-pyranoxymethyl)phenyl]silane (**1**) was obtained by lithiation of THP-protected 2-bromobenzyl alcohol followed by trapping with chloro(dimethyl)silane. Attempted deprotection of **1** to obtain an unprotected hydrosilane failed but gave cyclic silyl ether **2**, which turned out to be another versatile starting silicon reagent for the alkenylsilanes (*vide infra*). Treatment of **2** with $LiAlH_4$ followed by in situ acetylation using acetyl chloride afforded acetyl-protected hydrosilane **3**, a reagent complementary to THP-protected hydrosilane **1**.

With the key starting silicon reagents in hand, we then examined hydrosilylation of alkynes using hydrosilane **1** or **3** to prepare alkenyl[2-(hydroxymethyl)phenyl]dimethyl-

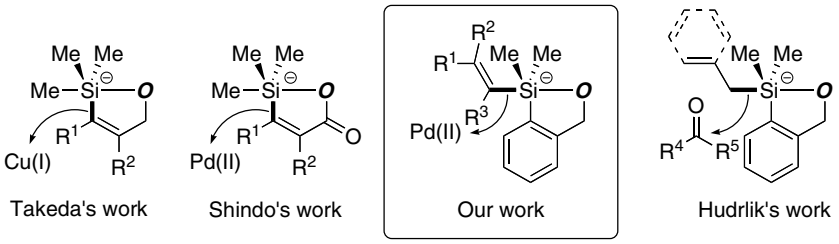
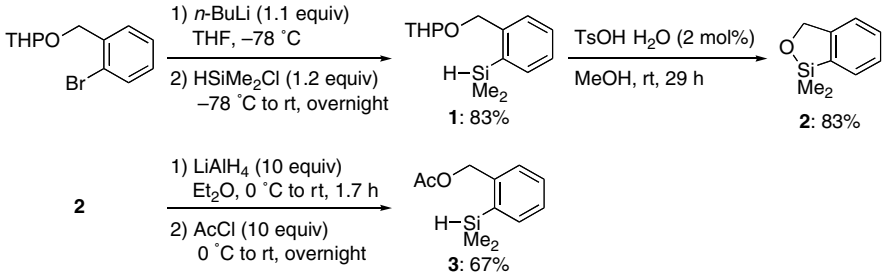
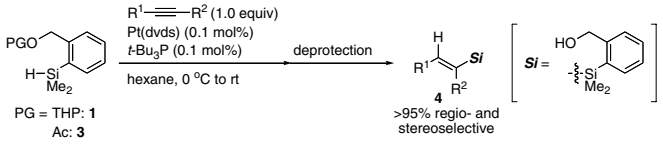


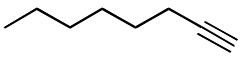
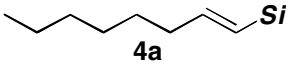
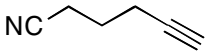
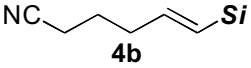
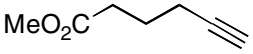
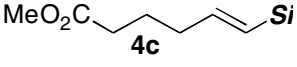
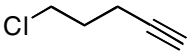
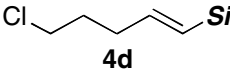
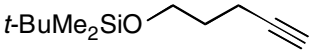
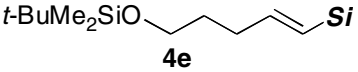
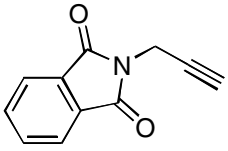
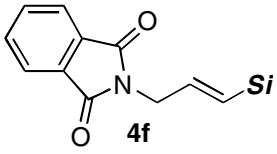
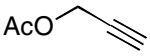
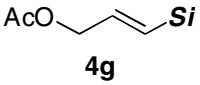
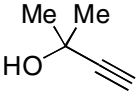
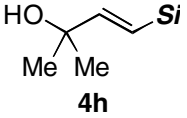
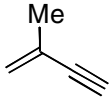
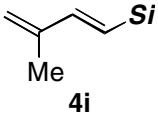
Fig. 1. Organic group transfer from silicon to an electrophile assisted by an intramolecular attack of a negatively charged oxygen.



Scheme 1.

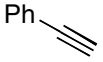
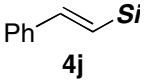
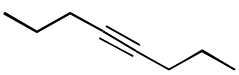
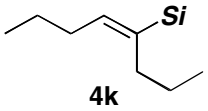
Table 1
Preparation of alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes via hydrosilylation of alkynes catalyzed by Pt/*t*-Bu_3P using hydrosilane **1** or **3** followed by deprotection[a]



Entry	Alkyne	Hydrosilane	Time (h)	Alkenylsilane	Yield[b] (%)
1		**1**	2	 **4a**	81
2		**3**	4		82
3		**1**	22[c]	 **4b**	84
4		**1**	22	 **4c**	68
5		**1**	3	 **4d**	71
6		**3**	3	 **4e**	93
7		**1**	3	 **4f**	72
8		**1**	3	 **4g**	27[d]
9		**1**	5	 **4h**	43
10		**1**	24	 **4i**	57

(*continued on next page*)

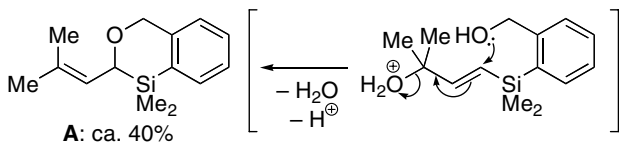
Table 1 (*continued*)

Entry	Alkyne	Hydrosilane	Time (h)	Alkenylsilane	Yield[b] (%)
11		**1**	2	 **4j**	84
12		**1**	18[e]	 **4k**	81

[a] The reaction was carried out using an alkyne (1.0 equiv), a hydrosilane (1.0 equiv), Pt(dvds) (0.1 mol%), and P(*t*-Bu)$_3$ (0.1 mol%) in hexane at 0 °C to room temperature. Deprotection was carried out using *p*-toluenesulfonic acid monohydrate (2 mol%) in MeOH at room temperature for 2–12 h (for **1**) or K_2CO_3 (20 equiv) in MeOH–H_2O (1:1) at 50 °C for 24–60 h (for **3**).
[b] Isolated yields.
[c] Hydrosilylation was carried out at room temperature for 19 h then at 50 °C for 3 h.
[d] Deacetylated product was also obtained in 49% yield.
[e] Hydrosilylation was carried out at rt for 4 h then at 50 °C for 14 h.

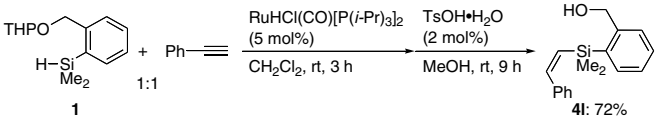
silanes (Table 1). At the onset, we envisaged that protected hydrosilanes **1** and **3** would act in a manner similar to phenyl(dimethyl)silane, a hydrosilane frequently used for hydrosilylation of alkynes. Indeed, the equimolar reaction of hydrosilane **1** with 1-octyne in the presence of 0.1 mol% of platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane [Pt(dvds)] and P(*t*-Bu)$_3$ in hexane at 0 °C to room temperature gave (*E*)-[2-(hydroxymethyl)phenyl]dimethyl-(1-octenyl)silane (**4a**) in 81% yield after deprotection under acidic conditions regio- and stereoselectively (entry 1). The same hydrosilylation procedure with **3** followed by deprotection under basic conditions also afforded **4a** in 82% yield (entry 2). Thus, one can choose either of the hydrosilane reagent, **1** or **3**, depending on the functional group involved in a target alkenylsilane. Fair stability of the silicon reagents toward an acid or base is demonstrated by the facts that **4a** can be purified by silica gel column chromatography without any decomposition and that **4a** can be quantitatively recovered after treatment with a stoichiometric amount of an aqueous 1 M HCl or 1 M NaOH solution in THF at 50 °C for 24 h.

Under the standard conditions, alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes (**4b–4f**) having a functional group such as cyano, ester, chloro, silyloxy, or *N*-phthalimide were prepared in good yields (entries 3–7), whereas an acetoxy-bearing one (**4g**) was obtained in only 27% yield due to formation of a significant amount of deacetylated product during the THP deprotection (entry 8). Hydrosilylation of 1-methyl-3-butyn-2-ol gave the corresponding alkenylsilane (**4h**) in 43% yield and an allylsilane **A** (ca. 40% yield), possibly derived from an intramolecular S_N2' type attack of the hydroxymethyl group assisted by an acid catalyst (entry 9 and Scheme 2) [21]. Conjugated butadienylsilane **4i** and (*E*)-styrylsilane **4j** were prepared in good yields from 2-methyl-1-buten-3-yne and phenylacetylene, respectively (entries 10 and 11). An internal alkyne, 4-octyne, also underwent the present hydrosilylation stereoselectively to give (*E*)-4-octenylsilane **4k** (entry 12).



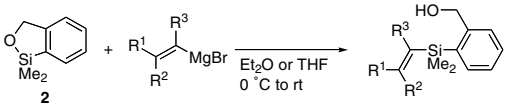
Scheme 2.

Ruthenium-catalyzed hydrosilylation has recently emerged as a unique tool for preparation of (*Z*)-alkenylsilanes via *trans*-addition of hydrosilanes across alkynes [10,22]. Employing the protocol reported by Ozawa and coworkers [10], we prepared (*Z*)-styrylsilane **4l** in 72% yield by the hydrosilylation of phenylacetylene with **1** in the presence of a ruthenium catalyst followed by acidic deprotection (Eq. (1)).



(1)

Ring-opening reactions of cyclic silyl ether **2** with alkenyl Grignard reagents represent another way to prepare various alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes (Eq. (2)). The procedure is straightforward and useful particularly when the corresponding Grignard reagents and/or alkenyl halides are readily available from commercial sources.



$R^1 = R^2 = R^3 = H$: **4m** (81%)
$R^1 = R^3 = H$; $R^2 = Me$: **4n** [94%, *Z*:*E* = 94:6]
$R^1 = R^2 = H$; $R^3 = Me$: **4o** (89%)
$R^1 = R^2 = H$; $R^3 = Ph$: **4p** (56%)
$R^1 = R^2 = Me$; $R^3 = H$: **4q** (71%)

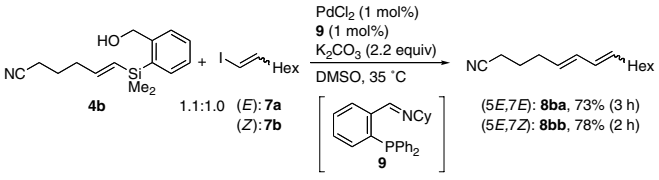
(2)

2.2. Cross-coupling reaction of alkneyl[2-(hydroxymethyl)phenyl]dimethylsilanes with aryl and alkenyl iodides

To prove the viability of our reagent design, we first examined the reaction of (*E*)-1-octenylsilane **4a** (0.39 mmol) with 4-cyanoiodobenzene (**5a**: 0.30 mmol) in the presence of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (0.5 mol%), tri-2-furylphosphine (2.0 mol%), and a metal carbonate (0.78 mmol) at 35 °C (Table 2). Among the bases we examined, use of inexpensive K_2CO_3 in a polar DMSO solvent turned out satisfactory and gave (*E*)-1-(4-cyanophenyl)-1-octene (**6aa**) quantitatively (entry 3), whereas relatively more basic Cs_2CO_3 was best in THF (entry 4). Na_2CO_3 was completely ineffective for the present coupling reaction even in DMSO (entry 1). Stronger bases like NaOH and *n*-BuLi were also effective in THF (entries 5 and 6), showing base flexibility to tune a base depending on substrate structures.

We further found that $PdCl_2$ was equally effective as $[(\eta^3\text{-}C_3H_5)PdCl]_2$ on a larger scale (entry 1 of Table 3), and then extended the reaction of alkneyl[2-(hydroxymethyl)phenyl]dimethylsilanes (1.1 mmol) to various aryl iodides (1.0 mmol) under the optimized conditions employing mild and inexpensive K_2CO_3 as a base (Table 3). Aryl iodides having electron-withdrawing or -donating functional groups such as ester, keto, formyl, nitro, chloro, and methoxy also underwent the reaction in good yields (entries 2–7). It is worth noting that both silyl-protected and unprotected hydroxyl groups tolerated the present protocol (entries 8 and 9). *ortho*-Substituents did not affect the reaction (entries 10 and 11); such heteroaryl iodides as 3-iodopyridine and 2-iodothiophene both reacted in good yields (entries 12 and 13). Functional groups in alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes are also compatible with the present conditions (entries 14–20); arylethene having an allyl acetate moiety **6gb** may find further applications as a substrate for rich chemistry of π-allylpalladium (entry 19). Vinylsilane **4m** and other mono- and disubstituted alkenylsilanes **4i–4q** also reacted with ethyl 4-iodobenzoate (**5b**) in stereo- and regiospecific manners giving the desired arylethenes in good yields (entries 21–30). Especially, regiospecific reaction of **4p** with both activated and unactivated aryl iodides is remarkable in view that the corresponding coupling of fluorosilanes results in *cine*-substitution to some extent (entries 28 and 29) [23].

The cross-coupling reactions of **4b** with (*E*)- and (*Z*)-1-iodo-1-octene (**7a** and **7b**) also proceeded stereospecifically to give 1,4-disubstituted 1,3-diene products **8ba** and **8bb** in 73% and 78% yields, respectively (Eq. (3)). Use of *N*-(2-diphenylphosphinobenzylidene)cyclohexylamine (**9**) as a ligand rather than tri(2-furyl)phosphine was found effective for the present diene formation [24].

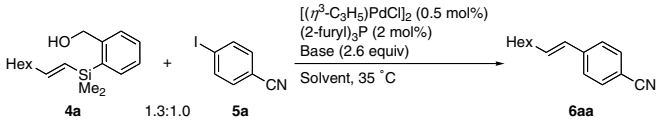


(3)

A gram-scale synthesis was examined using 9.1 g (33 mmol) of **4a** and 8.3 g (30 mmol) of **5b** under the identical conditions. Cyclic silyl ether **2** was recovered by distillation in 62% yield based on the aryl iodide; the residue was chromatographed to give the desired coupling product **6ab** in 97% yield (Eq. (4)). As demonstrated above (Scheme 1 and Table 1), the silyl residue **2** is the starting reagent for the synthesis of the alkenylsilanes. Namely, the metal residue of the cross-coupling is demonstrated for the first time to be reused for the next coupling.

(4)

Table 2
Cross-coupling reaction of (*E*)-[2-(hydroxymethyl)phenyl]dimethyl(1-octenyl)silane (**4a**) with 4-cyanoiodobenzene (**5a**)[a]



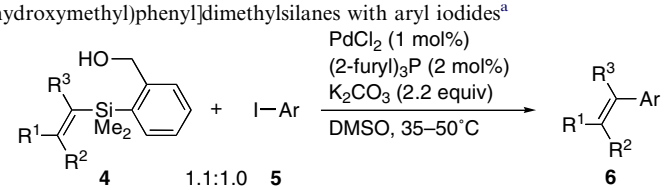
Entry	Base	Solvent	Time (h)	Yield[b] (%)
1	Na_2CO_3	DMSO	31	<5
2	K_2CO_3	THF	48	44
3	K_2CO_3	DMSO	5	100
4	Cs_2CO_3	THF	19	88
5	10 M NaOH aq.	THF	5	93
6[c]	*n*-BuLi	THF	1.5	96

[a] The reaction was carried out using **4a** (0.39 mmol), **5a** (0.30 mmol), a base (0.78 mmol), $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (1.5 μmol), and $(2\text{-furyl})_3P$ (6.0 μmol) in a solvent (0.75 mL) at 35 °C.

[b] Estimated by GC using pentadecane as an internal standard.

[c] **4a** was treated with *n*-BuLi (0.39 mmol) in THF at 0 °C to room temperature before addition of **5a**, $PdCl_2$, and $(2\text{-furyl})_3P$.

Table 3
Cross-coupling reaction of alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes with aryl iodides[a]



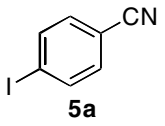
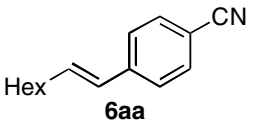
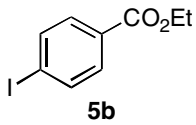
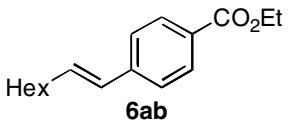
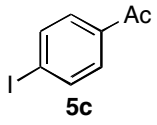
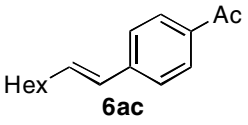
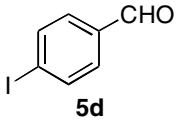
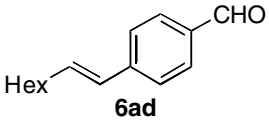
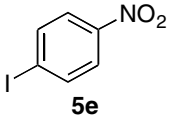
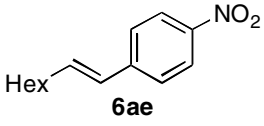
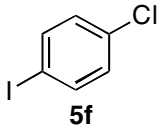
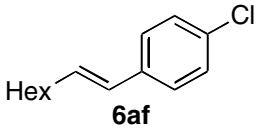
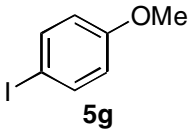
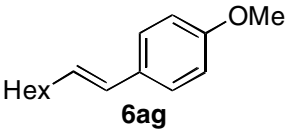
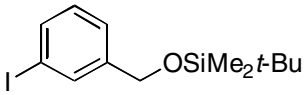
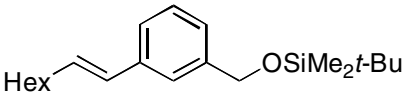
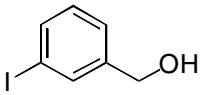
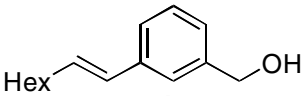
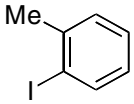
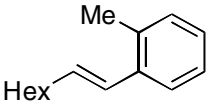
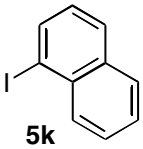
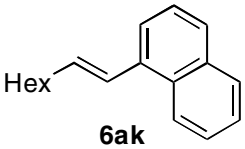
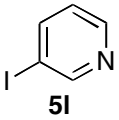
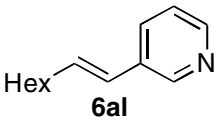
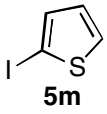
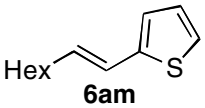
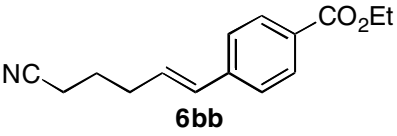
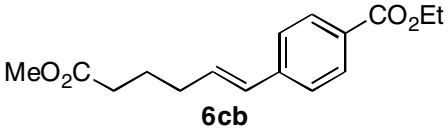
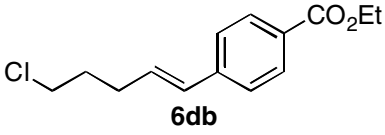
Entry	Alkenylsilane	I–Ar	Time (h)	Product	Yield[b] (%)
1	**4a**	 **5a**	20	 **6aa**	93
2	**4a**	 **5b**	18	 **6ab**	96
3	**4a**	 **5c**	17	 **6ac**	94
4	**4a**	 **5d**	20	 **6ad**	94
5	**4a**	 **5e**	26	 **6ae**	99
6	**4a**	 **5f**	19	 **6af**	93
7	**4a**	 **5g**	40	 **6ag**	89

Table 3 (*continued*)

Entry	Alkenylsilane	I–Ar	Time (h)	Product	Yield[b] (%)
8	**4a**	 **5h**	23	 **6ah**	98
9	**4a**	 **5i**	47	 **6ai**	88
10	**4a**	 **5j**	47	 **6aj**	94
11	**4a**	 **5k**	23	 **6ak**	91
12	**4a**	 **5l**	23	 **6al**	80
13	**4a**	 **5m**	23	 **6am**	99
14	**4b**	**5b**	19	 **6bb**	95
15	**4c**	**5b**	18	 **6cb**	92
16	**4d**	**5b**	50	 **6db**	92

(*continued on next page*)

Table 3 (*continued*)

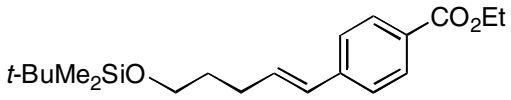
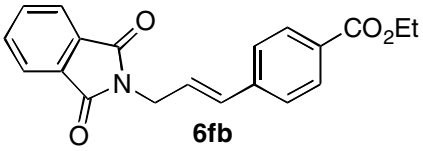
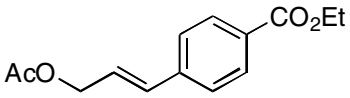
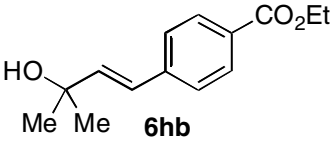
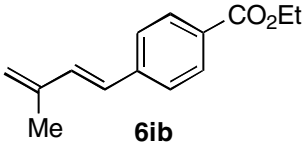
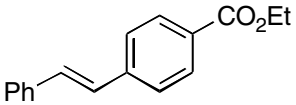
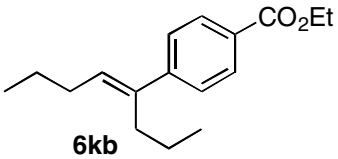
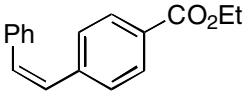
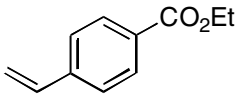
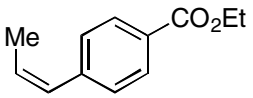
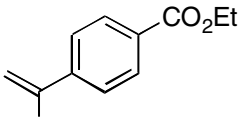
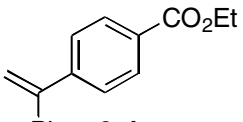
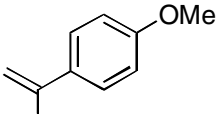
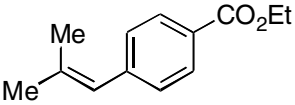
Entry	Alkenylsilane	I–Ar	Time (h)	Product	Yield[b] (%)
17	**4e**	**5b**	31	 **6eb**	90
18	**4f**	**5b**	24	 **6fb**	93
19[c]	**4g**	**5b**	25	 **6gb**	93
20[d,e]	**4h**	**5b**	72	 **6hb**	92
21	**4i**	**5b**	25	 **6ib**	93
22	**4j**	**5b**	19	 **6jb**	88
23[d]	**4k**	**5b**	29	 **6kb**	92
24	**4l**	**5b**	11	 **6lb**	92

Table 3 (*continued*)

Entry	Alkenylsilane	I–Ar	Time (h)	Product	Yield[b] (%)
25	**4m**	**5b**	19	 **6mb**	87
26	**4n**	**5b**	19	 **6nb**	91[f]
27	**4o**	**5b**	24	 **6ob**	96
28	**4p**	**5b**	25	 **6pb**	95
29[c,d]	**4p**	**5g**	12	 **6pg**	80[g]
30	**4q**	**5b**	25	 **6qb**	96

[a] The reaction was carried out using an alkenylsilane (1.1 mmol), an aryl iodide (1.0 mmol), K_2CO_3 (2.2 mmol), $PdCl_2$ (10 μmol), and (2-furyl)$_3$P (20 μmol) in DMSO (2.5 mL) at 35 °C.
[b] Isolated yields.
[c] 1.3 mmol of the alkenylsilane was used.
[d] The reaction was carried out at 50 °C.
[e] $PdCl_2$ (50 μmol) and (2-furyl)$_3$P (0.10 mmol) were used.
[f] Z:E = 94:6 estimated by GC.
[g] *cine*-Product was found at best in 4% yield.

3. Conclusion

A new silicon-based cross-coupling protocol is demonstrated that employs alkenyl[2-(hydroxymethyl)phenyl]-dimethylsilanes under mild conditions employing K_2CO_3 as a base. Highly chemoselective transformations of the highly stable alkenylsilane reagents presented herein certainly allow convenient preparation of a wide range of functionalized conjugated arylethenes and dienes through the silicon-based cross-coupling reaction, and, thus, will find a widespread synthetic applications both in academia and industry. Current efforts are also directed to other metal-catalyzed reactions using these reagents.

4. Experimental

4.1. General remarks

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere. Flush column chromatography was performed using Merck silica gel 60 (40–63 μm), Kanto Chemical silica gel (spherical, 40–50 μm), or Merck aluminium oxide 90 neutral (20–63 μm). Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F_{254} (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Varian Mercury 400 (^{1}H NMR, 400 MHz; ^{13}C NMR, 101 MHz) spectrometer with solvent resonance as the internal standard (^{1}H NMR, $CHCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, br = broad, m = multiplet), coupling constants (Hz), and integration. GC analyses were performed on a Shimadzu GC 2010 equipped with a DB-5 column (30 m × 0.53 mm, pressure = 31.7 kPa, detector = FID, 290 °C) with helium gas as a carrier. Melting points were determined using a YANAKO MP-500D. Mass spectra were obtained with a JEOL JMS-700 (EI at 70 eV unless otherwise stated or CI) or JEOL JMS-HX110A (FAB) spectrometer. Unless otherwise noted, reagents were commercially available and were used without purification. THF and diethyl ether were distilled from sodium/benzophenone ketyl right before use. Anhydrous DMSO was purchased from Aldrich and used without further purification. *N*-(2-Diphenylphosphinobenzylidene)cyclohexylamine (**9**) [25] and $RuHCl(CO)[P(i\text{-}Pr)_3]_2$ [26] were prepared according to the reported procedures.

4.2. Preparation of dimethyl[2-(2-tetrahydro-2*H*-pyranoxymethyl)phenyl]silane (*1*)

To a mixture of 2-bromophenylmethanol (34 g, 0.180 mol) and 3,4-dihydro-2*H*-pyran (18.2 g, 0.22 mol) were added 10 drops of concentrated hydrochloric acid, and the resulting mixture was stirred at rt overnight. The mixture was diluted with diethyl ether, neutralized with a saturated NH_4Cl aqueous solution, dried over anhydrous $MgSO_4$, and concentrated in vacuo to give 2-(2-tetrahydro-2*H*-pyranoxymethyl)bromobenzene, which was dissolved in THF (450 mL). To the solution was added a 1.6 M *n*-BuLi solution in hexane (124 mL, 0.20 mol) over 40 min at −78 °C, and the resulting solution was stirred for 50 min before the addition of chlorodimethylsilane (20 g, 0.22 mol) at −78 °C. The mixture was warmed gradually at rt overnight and quenched with H_2O. After evaporation of the solvents, the residue was extracted with diethyl ether, and the combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. Distillation under vacuum gave **1** (38 g, 83%) as a colorless oil, bp 135 °C (1.0 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 7.2, 1.4 Hz, 1H), 7.44 (dd, J = 7.5, 0.5 Hz, 1H), 7.37 (td, J = 7.5, 1.5 Hz, 1H), 7.29 (td, J = 7.3, 1.3 Hz, 1H), 4.86 (d, J = 11.9 Hz, 1H), 4.73 (t, J = 3.6 Hz, 1H), 4.59 (d, J = 11.7 Hz, 1H), 4.56–4.51 (m, 1H), 3.98–3.89 (m, 1H), 3.60–3.52 (m, 1H), 1.94–1.45 (m, 6H), 0.364 (d, J = 3.7 Hz, 3H), 0.360 (d, J = 3.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 136.5, 134.7, 129.4, 128.3, 127.0, 98.1, 69.1, 62.1, 30.6, 25.5, 19.3, −3.0, −3.1; IR (neat) 2943, 2124, 1250, 1202, 1119, 1080, 1055, 1026, 974, 885, 837, 752 cm^{-1}; MS (EI) *m*/*z* (%) 250 (M^+, 0.1), 164 (12), 163 (14), 150 (17), 149 (100), 85 (22). Anal. Calc. for $C_{14}H_{22}O_2Si$: C, 67.15; H, 8.86. Found: C, 67.44; H, 8.91%.

4.3. Preparation of 1,1-dimethyl-2-oxa-1-silaindan (*2*)

p-Toluenesulfonic acid monohydrate (1.14 g, 6.0 mmol) was added portionwise to **1** (75 g, 0.30 mol) dissolved in MeOH (500 mL) at rt, and the mixture was stirred for 16 h before concentration in vacuo. The residue was distilled to give **2** (41 g, 83%) as a colorless oil, bp 45 °C (2.0 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, J = 7.1, 0.4 Hz, 1H), 7.42–7.37 (m, 1H), 7.33–7.28 (m, 1H), 7.23 (dd, J = 7.5, 0.7 Hz, 1H), 5.16 (s, 2H), 0.40 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 135.0, 131.0, 129.5, 126.8, 121.6, 71.5, 0.6; IR (neat) 3360, 3057, 2953, 2897, 2860, 1701, 1593, 1445, 1350, 1252, 1200, 1134, 1067, 1051, 1024, 858, 829, 791, 748, 692, 652 cm^{-1}; MS (EI) *m*/*z* (%) 165 (M^+, 9), 164 (58), 163 (26), 151 (13), 150 (45), 149 (100), 105 (15). Anal. Calc. for $C_9H_{12}OSi$: C, 65.80; H, 7.36. Found: C, 65.60; H, 7.34%.

4.4. Preparation of dimethyl[2-(2-acetoxymethyl)phenyl]silane (*3*)

To a suspension of $LiAlH_4$ (0.38 g, 10.0 mmol) in diethyl ether (30 mL) was added **2** (1.64 g, 10.0 mmol) at 0 °C, and the resulting mixture was stirred at rt for 100 min before addition of acetyl chloride (7.1 mL, 100 mmol) at 0 °C. Stirring was continued at rt overnight, and the mixture was filtered through a Celite and then through a silica gel pad. The residue was purified by flash chromatography on silica gel to give **3** (1.39 g, 67%) as a colorless oil, R_f 0.30 (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.0 Hz, 1H), 7.42–7.32 (m, 3H), 5.20 (s, 2H), 4.58–4.51 (m, 1H), 2.10 (s, 3H), 0.37 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 140.9, 137.2, 135.0, 129.6, 129.1, 127.8, 66.6, 21.1, −3.1; IR (neat) 2959, 2127, 1742, 1437, 1379, 1362, 1236, 1130, 1080, 1026, 966, 887, 839, 756 cm^{-1}; MS (EI) *m*/*z* (%) 208 (M^+, 6), 207 (37), 194 (14), 193 (81), 165 (59), 163 (24), 152 (25), 151 (98), 150 (29), 149 (100), 148 (24), 147 (27), 145 (12), 135 (27), 134 (12), 133

(55), 131 (11), 123 (14), 121 (14), 119 (13), 117 (38), 105 (20), 91 (34), 75 (46). Anal. Calc. for $C_{11}H_{16}O_2Si$: C, 63.42; H, 7.74. Found: C, 63.48; H, 7.74%.

4.5. Preparation of (E)-alkenyl[2-(hydroxymethyl)-phenyl]dimethylsilanes by platinum-catalyzed hydrosilylation using **1**

4.5.1. (E)-[2-(Hydroxymethyl)phenyl]dimethyl(1-octenyl)silane (**4a**)

To a solution of hydrosilane **1** (10.0 g, 0.040 mol) and 1-ocytne (4.4 g, 0.040 mol) in hexane (4 mL) were added a 10% hexane solution of *t*-Bu_3P (80 mg, 0.040 mmol) and a 0.01 M hexane solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (4.0 mL, 0.040 mmol) at 0 °C. The resulting mixture was stirred at rt for 2 h, filtered through a Florisil pad, and concentrated in vacuo. The residue was dissolved in MeOH (140 mL) and treated with *p*-toluenesulfonic acid monohydrate (152 mg, 0.80 mmol) at rt for 4 h. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel to give the title compound (9.0 g, 81%) as a colorless oil, R_f 0.25 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, $J = 7.3$, 1.3 Hz, 1H), 7.46 (dd, $J = 7.5$, 0.7 Hz, 1H), 7.40 (td, $J = 7.5$, 1.5 Hz, 1H), 7.28 (td, $J = 7.3$, 1.3 Hz, 1H), 6.15 (dt, $J = 18.7$, 6.4 Hz, 1H), 5.83 (dt, $J = 18.7$, 1.5 Hz, 1H), 4.74 (s, 2H), 2.17–2.12 (m, 2H), 1.63 (br s, 1H), 1.42–1.25 (m, 8H), 0.90–0.83 (m, 3H), 0.39 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 146.4, 137.1, 135.1, 130.0, 128.2, 128.0, 127.0, 65.4, 36.8, 31.7, 28.9, 28.5, 22.6, 14.1, −1.2; IR (neat) 3329, 2957, 2926, 2855, 1614, 1466, 1435, 1248, 1126, 1078, 991, 841, 783, 746, 687 cm^{-1}; MS (EI) *m*/*z* (%) 276 (M^+, 0.1), 261 (32), 243 (14), 199 (12), 177 (13), 173 (11), 166 (27), 165 (66), 164 (51), 163 (44), 160 (11), 159 (42), 151 (25), 150 (30), 149 (100), 148 (27), 147 (50), 146 (16), 145 (51), 137 (12), 135 (31), 133 (14), 131 (22), 129 (18), 105 (16), 91 (18), 75 (32), 61 (39), 59 (13), 55 (11). Anal. Calc. for $C_{17}H_{28}OSi$: C, 73.85; H, 10.21. Found: C, 73.86; H, 10.42%.

4.5.2. (E)-5-Cyano-1-pentenyl[2-(hydroxymethyl)-phenyl]dimethylsilane (**4b**)

Following the procedure for **4a**, the reaction using hydrosilane **1** (1.25 g, 5.0 mmol) and 5-hexynenitrile (0.46 g, 5.0 mmol) gave **4b** (1.09 g, 84%) as a colorless oil, R_f 0.30 (hexane–ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, $J = 7.2$ Hz, 1H), 7.46 (d, $J = 7.2$ Hz, 1H), 7.40 (td, $J = 7.4$, 1.2 Hz, 1H), 7.29 (td, $J = 7.4$, 1.2 Hz, 1H), 6.06 (dt, $J = 18.5$, 6.0 Hz, 1H), 5.95 (d, $J = 18.4$ Hz, 1H), 4.73 (s, 2H), 2.33 (q, $J = 7.2$ Hz, 4H), 1.79 (quint, $J = 7.2$ Hz, 2H), 1.60 (br s, 1H), 0.40 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 145.6, 136.2, 135.0, 131.2, 129.7, 127.7, 126.9, 119.5, 65.1, 35.2, 24.0, 16.4, −1.3; IR (neat) 3443, 2953, 2249, 1618, 1433, 1250, 1124, 1078, 991, 910, 827, 733 cm^{-1}; MS (EI) *m*/*z* (%) 259 (M^+, 0.3), 244 (33), 242 (18), 226 (24), 165 (39), 164 (44), 163 (22), 150 (15), 149 (100), 147 (25), 145 (20), 135 (11). Anal. Calc. for $C_{15}H_{21}NOSi$: C, 69.45; H, 8.16. Found: C, 69.68; H, 8.15%.

4.5.3. Methyl (E)-6-([2-(hydroxymethyl)phenyl]-dimethylsilyl)-5-hexenoate (**4c**)

Following the procedure for **4a**, the reaction using hydrosilane **1** (2.5 g, 10.0 mmol) and methyl 5-hexynoate (1.26 g, 10.0 mmol) gave **4 c** (2.0 g, 68%) as a colorless oil, R_f 0.38 (hexane–ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, $J = 7.4$, 1.4 Hz, 1H), 7.47 (d, $J = 7.1$ Hz, 1H), 7.40 (td, $J = 7.4$, 1.5 Hz, 1H), 7.28 (td, $J = 7.5$, 1.3 Hz, 1H), 6.10 (dt, $J = 18.7$, 6.2 Hz, 1H), 5.87 (dt, $J = 18.7$, 1.5 Hz, 1H), 4.74 (s, 2H), 3.65 (s, 3H), 2.31 (t, $J = 7.5$ Hz, 2H), 2.19 (td, $J = 7.4$, 6.2 Hz, 2H), 1.76 (quint, $J = 7.4$ Hz, 2H), 1.66 (bs, 1H), 0.39 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 147.6, 146.5, 136.7, 135.1, 129.8, 129.7, 127.9, 127.0, 65.3, 51.5, 35.9, 33.4, 23.7, −1.2; IR (neat) 3447, 2951, 1738, 1616, 1437, 1250, 1202, 1078, 991, 839, 750 cm^{-1}. Anal. Calc. for $C_{16}H_{24}O_3Si$: C, 65.71; H, 8.27. Found: C, 65.66; H, 8.12%.

4.5.4. (E)-5-Chloro-1-pentenyl[2-(hydroxymethyl)-phenyl]dimethylsilane (**4 d**)

The procedure for **4a** was applied to the reaction of hydrosilane **1** (2.5 g, 10.0 mmol) and 5-chloro-1-pentyne (1.03 g, 10.0 mmol) to give the title compound (1.91 g, 71%) as a colorless oil, R_f 0.15 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, $J = 7.3$, 1.3 Hz, 1H), 7.47 (dd, $J = 7.5$, 0.6 Hz, 1H), 7.40 (td, $J = 7.5$, 1.3 Hz, 1H), 7.29 (td, $J = 7.3$, 1.5 Hz, 1H), 6.10 (dt, $J = 18.7$, 6.2 Hz, 1H), 5.92 (dt, $J = 18.5$, 1.5 Hz, 1H), 4.74 (s, 2H), 3.53 (t, $J = 6.6$ Hz, 2H), 2.31 (tdd, $J = 6.6$, 6.2, 1.5 Hz, 2H), 1.89 (quint, $J = 6.6$ Hz, 2H), 1.59 (bs, 1H), 0.40 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 146.4, 136.7, 135.1, 130.2, 129.7, 128.0, 127.0, 65.4, 44.4, 33.7, 31.3, −1.2; IR (neat) 3369, 2955, 1614, 1435, 1250, 1124, 1078, 991, 839, 750, 650 cm^{-1}. Anal. Calc. for $C_{14}H_{21}ClOSi$: C, 62.54; H, 7.87. Found: C, 62.31; H, 7.70%.

4.5.5. (E)-N-[3-([2-(Hydroxymethyl)phenyl]-dimethylsilyl)-2-propenyl]phthalimide (**4f**)

Following the procedure for **4a**, the reaction using hydrosilane **1** (2.5 g, 10.0 mmol) and *N*-propargylphthalimide (1.85 g, 10.0 mmol) gave **4f** (2.5 g, 72%) as a colorless solid (mp = 88.6–89.2 °C), R_f 0.10 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.82 (m, 2H), 7.75–7.69 (m, 2H), 7.49 (dd, $J = 7.3$, 1.3 Hz, 1H), 7.46 (d, $J = 7.0$ Hz, 1H), 7.38 (td, $J = 7.3$, 1.3 Hz, 1H), 7.26 (td, $J = 7.3$, 1.3 Hz, 1H), 6.12 (dt, $J = 18.6$, 4.5 Hz, 1H), 6.00 (dt, $J = 18.6$, 1.4 Hz, 1H), 4.69 (s, 2H), 4.37 (dd, $J = 4.5$, 1.3 Hz, 2H), 1.79 (bs, 1H), 0.38 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 146.6, 140.0, 135.9, 135.0, 134.0, 132.0, 131.0, 129.8, 128.2, 126.9, 123.4, 65.1, 42.0, −1.5; IR (KBr) 3518, 2930, 1767, 1705, 1423, 1393, 1337, 1250, 1082, 1038, 993, 935, 841, 816, 779, 745, 727, 530 cm^{-1}. Anal. Calc. for $C_{20}H_{21}NO_3Si$: C, 68.35; H, 6.02. Found: C, 68.41; H, 6.12%.

4.5.6. (*E*)-3-([2-(Hydroxymethyl)phenyl]dimethylsilyl)-2-propenyl acetate (**4g**)

Following the procedure for **4a**, the reaction using hydrosilane **1** (2.5 g, 10.0 mmol) and propargyl acetate (0.98 g, 10.0 mmol) gave **4g** (0.71 g, 27%) and (*E*)-[2-(hydroxymethyl)phenyl](3-hydroxypropenyl)dimethylsilane, a deacetylated product (1.08 g, 49%). **4g** was a colorless oil and showed R_f 0.18 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.3 Hz, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.41 (td, J = 7.4, 1.1 Hz, 1H), 7.29 (td, J = 7.4, 1.1 Hz, 1H), 6.14 (s, 2H), 4.72 (s, 2H), 4.63 (dd, J = 1.7, 0.7 Hz, 2H), 2.09 (s, 3H), 1.64 (bs, 1H), 0.43 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 146.5, 141.0, 135.9, 135.1, 131.7, 129.9, 128.1, 127.1, 66.6, 65.3, 20.9, −1.4; IR (neat) 3427, 2953, 1744, 1624, 1435, 1379, 1236, 1126, 1078, 1028, 839, 785, 750 cm^{-1}; HRMS (FAB+) Calcd for $C_{14}H_{21}O_3Si$: $[M+H]^+$, 265.1260. Found: m/z 265.1257. (*E*)-[2-(Hydroxymethyl)phenyl](3-hydroxypropenyl)dimethylsilane was a colorless solid (mp = 65.2–65.7 °C) and showed R_f 0.25 (hexane–ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 7.4, 0.6 Hz, 1H), 7.43 (d, J = 7.5 Hz, 1H), 7.39 (td, J = 7.5, 1.7 Hz, 1H), 7.28 (td, J = 7.3, 1.3 Hz, 1H), 6.26 (dt, J = 18.8, 4.2 Hz, 1H), 6.12 (dt, J = 18.8, 1.3 Hz, 1H), 4.71 (s, 2H), 4.17 (dt, J = 4.0, 0.8 Hz, 2H), 2.19 (bs, 2H), 0.41 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 146.3, 136.3, 135.0, 129.8, 128.2, 128.1, 127.0, 65.2, 65.1, −1.4; IR (neat) 3308, 3194, 2949, 2899, 1624, 1429, 1342, 1250, 1200, 1128, 1074, 1026, 1009, 997, 847, 826, 791, 766, 739, 637, 463, 426 cm^{-1}; HRMS (FAB–) Calcd for $C_{12}H_{17}O_2Si$: $[M-H]^-$, 221.0998. Found: m/z 221.0998.

4.5.7. (*E*)-3-Hydroxy-3-methyl-1-butenyl[2-(hydroxymethyl)phenyl]dimethylsilane (**4h**)

The procedure for **4a** was successfully applied to the reaction of hydrosilane **1** (2.5 g, 10.0 mmol) and 2-methyl-3-butyn-2-ol (0.84 g, 10.0 mmol), and **4h** (1.08 g, 43%) was isolated as a colorless oil, R_f 0.25 (hexane–ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 7.3, 1.3 Hz, 1H), 7.46 (d, J = 7.1 Hz, 1H), 7.40 (td, J = 7.3, 1.1 Hz, 1H), 7.29 (td, J = 7.3, 1.3 Hz, 1H), 6.24 (d, J = 18.8 Hz, 1H), 6.04 (d, J = 19.0 Hz, 1H), 4.71 (s, 2H), 2.04 (s, 1H), 1.68 (s, 1H), 1.31 (s, 6H), 0.41 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 146.4, 136.4, 135.0, 129.7, 128.2, 126.9, 123.6, 71.9, 65.0, 29.1, −1.3; IR (neat) 3323, 2964, 1611, 1433, 1375, 1259, 1215, 1022, 826, 750 cm^{-1}. Anal. Calc. for $C_{14}H_{22}O_2Si$: C, 67.15; H, 8.86. Found: C, 67.28; H, 8.88%.

4.5.8. (*E*)-[2-(Hydroxymethyl)phenyl]dimethyl(3-methyl-1,3-butadienyl)silane (**4i**)

Following the procedure for **4a**, the reaction using hydrosilane **1** (2.5 g, 10.0 mmol) and 2-methyl-1-buten-3-yne (0.66 g, 10.0 mmol) gave **4i** (1.31 g, 57%) as a colorless oil, R_f 0.20 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.3 Hz, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.41 (td, J = 7.4, 1.1 Hz, 1H), 7.30 (t, J = 7.3 Hz, 1H), 6.70 (d, J = 18.8 Hz, 1H), 6.01 (dt, J = 18.7 Hz, 1H), 5.10 (s, 1H), 5.03 (s, 1H), 4.74 (s, 2H), 1.86 (s, 3H), 1.58 (bs, 1H), 0.45 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 146.4, 143.2, 136.5, 135.1, 129.7, 127.9, 127.7, 127.0, 118.0, 65.3, 17.9, −1.3; IR (neat) 3333, 2955, 1574, 1435, 1248, 1202, 1124, 1078, 988, 893, 835, 748 cm^{-1}. Anal. Calc. for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67. Found: C, 72.27; H, 8.50%.

4.5.9. (*E*)-[2-(Hydroxymethyl)phenyl]dimethyl(2-phenylethenyl)silane (**4j**)

Following the procedure for **4a**, the reaction using hydrosilane **1** (0.55 g, 2.2 mmol) and phenylacetylene (0.20 g, 2.0 mmol) gave **4j** (0.45 g, 84%) as a colorless oil, R_f 0.20 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 7.4, 1.3 Hz, 1H), 7.51–7.41 (m, 4H), 7.37–7.27 (m, 4H), 6.97 (d, J = 19.2 Hz, 1H), 6.67 (d, J = 19.2 Hz, 1H), 4.79 (s, 2H), 1.67 (br s, 1H), 0.52 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 145.2, 138.0, 136.4, 135.3, 130.0, 128.6, 128.3, 127.9, 127.8, 127.1, 126.5, 65.4, −1.2; IR (neat) 3444, 3055, 2955, 2359, 1605, 1572, 1495, 1447, 1435, 1248, 1198, 1124, 1076, 1028, 991, 847, 831, 812, 777, 748, 691 cm^{-1}; MS (EI) m/z (%) 268 (M^+, 0.5), 253 (11), 235 (15), 165 (14), 164 (29), 163 (19), 150 (15), 149 (100), 147 (13), 137 (35), 135 (10), 105 (11), 104 (25), 103 (12), 91 (24). Anal. Calc. for $C_{17}H_{20}OSi$: C, 76.07; H, 7.51. Found: C, 75.73; H, 7.55%.

4.5.10. (*E*)-[2-(Hydroxymethyl)phenyl]dimethyl(4-octen-4-yl)silane (**4k**)

Following the procedure for **4a**, the reaction using hydrosilane **1** (0.55 g, 2.2 mmol) and 4-octyne (0.22 g, 2.0 mmol) gave **4k** (0.45 g, 81%) as a colorless oil, R_f 0.25 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 7.2, 1.2 Hz, 1H), 7.47 (dd, J = 7.2, 1.2 Hz, 1H), 7.40 (td, J = 7.3, 1.4 Hz, 1H), 7.30–7.26 (m, 1H), 5.80 (t, J = 7.2 Hz, 1H), 4.70 (s, 2H), 2.12–2.06 (m, 4H), 1.60 (br s, 1H), 1.38 (m, 2H), 1.28–1.18 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H), 0.83 (t, J = 7.2 Hz, 3H), 0.40 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 142.8, 140.2, 136.7, 135.3, 129.6, 128.0, 126.9, 65.2, 32.1, 30.8, 23.4, 22.6, 14.5, 14.0, −1.2; IR (neat) 3319, 2957, 2930, 2870, 1611, 1466, 1435, 1377, 1248, 1124, 1078, 1015, 833, 816, 770, 750, 687 cm^{-1}; MS (EI) m/z (%) 276 (M^+, 0.1), 261 (19), 166 (15), 165 (100), 164 (15), 163 (24), 151 (22), 150 (12), 149 (79), 148 (13), 147 (61), 145 (30), 135 (19), 91 (11), 75 (14), 61 (19), 59 (10), 55 (10). Anal. Calc. for $C_{17}H_{28}OSi$: C, 73.85; H, 10.21. Found: C, 73.67; H, 10.06%.

4.6. Alternative preparation of (*E*)-alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes using **3**

4.6.1. (*E*)-[2-(Hydroxymethyl)phenyl]dimethyl(1-octenyl)silane (**4a**)

A 1.0 M solution of 1-octyne in hexane (0.50 mL, 0.50 mmol) was added dropwise to a mixture of **3**

(104 mg, 0.50 mmol), *t*-Bu_3P (10% hexane solution, 10.0 mg, 5.0 μmol), and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (0.01 M hexane solution, 0.50 mL, 5.0 μmol) at 0 °C. The resulting mixture was stirred at rt for 4 h, filtered through a Florisil pad, and concentrated in vacuo. The residue was dissolved in MeOH (2.5 mL) and water (2.5 mL) and treated with K_2CO_3 (1.38 g, 10.0 mmol) at 50 °C for 24 h. The mixture was extracted with diethyl ether, and the combined organic layers were washed with water and brine and dried over anhydrous $MgSO_4$; the residue was purified by flash chromatography on silica gel to give **4a** (113 mg, 82%).

4.6.2. (*E*)-5-tert-Butyldimethylsiloxy-1-pentenyl[2-(hydroxymethyl)phenyl]dimethylsilane (*4e*)

The above procedure for **4a** was applied to the reaction of hydrosilane **3** (1.48 g, 7.0 mmol) and 5-*tert*-butyldimethylsilyloxy-1-pentyne (1.39 g, 7.0 mmol) to give **4e** (2.4 g, 93%) as a colorless oil, R_f 0.40 (hexane–ethyl acetate = 4:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, $J = 7.3$ Hz, 1H), 7.46 (d, $J = 7.7$ Hz, 1H), 7.40 (td, $J = 7.5$, 1.3 Hz, 1H), 7.31–7.26 (m, 1H), 6.15 (dt, $J = 18.5$, 6.2 Hz, 1H), 5.86 (d, $J = 18.5$ Hz, 1H), 4.74 (s, 2H), 3.61 (t, $J = 6.5$ Hz, 2H), 2.20 (td, $J = 6.5$, 6.2 Hz, 2H), 1.63 (quint, $J = 6.5$ Hz, 2H), 1.57 (bs, 1H), 0.87 (s, 9H), 0.39 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 146.4, 136.9, 135.1, 129.6, 128.7, 128.0, 127.0, 65.4, 62.5, 33.0, 31.7, 26.0, 18.3, −1.2, −5.3; IR (neat) 3358, 2953, 2930, 2856, 1616, 1472, 1254, 1105, 837, 777 cm^{-1}. Anal. Calc. for $C_{20}H_{36}O_2Si_2$: C, 65.87; H, 9.95. Found: C, 65.98; H, 9.65%.

4.7. Preparation of (*Z*)-[2-(hydroxymethyl)phenyl]-dimethyl(2-phenylethenyl)silane (*4l*) by ruthenium-catalyzed hydrosilylation using *1* [10]

A mixture of hydrosilane **1** (1.25 g, 5.0 mmol), phenylacetylene (0.51 g, 5.0 mmol), and $RuHCl(CO)[P(i\text{-}Pr)_3]_2$ (0.122 g, 0.25 mmol) in CH_2Cl_2 (25 mL) was stirred at rt for 3 h before filtration through a silica gel pad and concentration in vacuo. The residue was dissolved in MeOH (15 mL) and treated with *p*-toluenesulfonic acid monohydrate (18.8 mg, 0.100 mmol) at rt for 9 h. After removal of the solvents in vacuo, the residue was purified by flash chromatography on silica gel to give **4l** (0.97 g, 72%) as a colorless oil, R_f 0.20 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, $J = 7.1$, 1.1 Hz, 1H), 7.46 (dd, $J = 15.0$ Hz, 1H), 7.43–7.36 (m, 2H), 7.30 (td, $J = 7.1$, 2.0 Hz, 1H), 7.17–7.09 (m, 5H), 6.08 (d, $J = 15.2$ Hz, 1H), 4.69 (s, 2H), 1.54 (br s, 1H), 0.33 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 146.1, 138.9, 137.4, 134.6, 131.2, 129.7, 128.2, 127.9, 127.8, 127.6, 127.1, 65.5, −0.3; IR (neat) 3331, 3055, 2959, 1591, 1568, 1493, 1435, 1250, 1124, 1078, 1028, 814, 758, 698 cm^{-1}. Anal. Calc. for $C_{17}H_{20}OSi$: C, 76.07; H, 7.51. Found: C, 75.80; H, 7.59%.

4.8. Preparation of alkenyl[2-(hydroxymethyl)phenyl]-dimethylsilanes by the reaction of the Grignard reagents with *2*

4.8.1. [2-(Hydroxymethyl)phenyl]dimethyl(vinyl)silane (*4m*)

To a solution of **2** (2.5 g, 15.0 mmol) in THF (30 mL) was added a 1.0 M solution of vinylmagnesium bromide in THF (16.5 mL, 16.5 mmol) at 0 °C, and the resulting mixture was stirred at rt overnight. The mixture was diluted with diethyl ether, washed with a saturated NH_4Cl aqueous solution, water, and brine, and dried over anhydrous $MgSO_4$. After removal of the solvents in vacuo, the residue was purified by flash chromatography on silica gel to give **4m** (2.3 g, 81%) as a colorless oil, R_f 0.30 (hexane–ethyl acetate = 7:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, $J = 7.3$, 1.3 Hz, 1H), 7.46 (dd, $J = 7.1$, 0.7 Hz, 1H), 7.41 (td, $J = 7.4$, 1.5 Hz, 1H), 7.30 (td, $J = 7.3$, 1.5 Hz, 1H), 6.39 (dd, $J = 20.3$, 14.6 Hz, 1H), 6.08 (dd, $J = 14.6$, 3.7 Hz, 1H), 5.79 (dd, $J = 20.3$, 3.7 Hz, 1H), 4.74 (s, 2H), 1.71 (br s, 1H), 0.43 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 139.0, 136.2, 135.2, 132.8, 129.8, 128.0, 127.0, 65.3, −1.6; IR (neat) 3321, 3051, 2957, 1404, 1250, 1078, 1009, 820, 775, 754 cm^{-1}. Anal. Calc. for $C_{11}H_{16}OSi$: C, 68.69; H, 8.39. Found: C, 68.43; H, 8.36%.

4.8.2. (*Z*)-[2-(Hydroxymethyl)phenyl]dimethyl(propenyl)silane (*4n*)

A solution of (*Z*)-propenylmagnesium bromide in THF (70 mL) [prepared from (*Z*)-1-bromopropene (6.0 g, 50 mmol) and Mg turnings (1.71 g, 50 mmol)] [27] was added to a THF (20 mL) solution of **2** (5.8 g, 35 mmol) at 0 °C, and the resulting mixture was stirred at rt overnight. The mixture was diluted with diethyl ether and filtered to remove unreacted magnesium metal; the filtrate was washed with a saturated NH_4Cl aqueous solution, water, and brine and dried over anhydrous $MgSO_4$. After removal of the solvents in vacuo, the residue was purified by flash chromatography on silica gel to give **4n** [6.8 g, 94% as a (*Z*):(*E*) = 94:6 mixture as estimated by GC analysis] as a colorless oil, R_f 0.26 (hexane–ethyl acetate = 7:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, $J = 7.3$, 1.5 Hz, 1H), 7.47 (d, $J = 7.6$ Hz, 1H), 7.41 (td, $J = 7.5$, 1.5 Hz, 1H), 7.29 (td, $J = 7.3$, 1.3 Hz, 1H), 6.52 (dq, $J = 13.9$, 7.0 Hz, 1H), 5.76 (dq, $J = 13.9$, 1.5 Hz, 1H), 4.72 (s, 2H), 1.79 (br d, $J = 4.9$ Hz, 1H), 1.64 (dd, $J = 6.8$, 1.6 Hz, 3H), 0.45 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 145.1, 137.5, 134.7, 129.7, 129.3, 128.2, 127.0, 65.4, 19.1, −0.2; IR (neat) 3319, 3055, 2961, 2910, 1609, 1435, 1248, 1200, 1124, 1078, 1034, 826, 777, 746, 696, 658 cm^{-1}; MS (EI) *m/z* (%) 206 (M^+, 0.1), 191 (12), 173 (29), 166 (10), 165 (62), 164 (37), 163 (18), 150 (15), 149 (100), 148 (11), 147 (39), 145 (48), 135 (16), 131 (14), 105 (11), 91 (11), 75 (43), 61 (19). Anal. Calc. for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79. Found: C, 69.82; H, 8.81%.

4.8.3. [2-(Hydroxymethyl)phenyl]dimethyl(propen-2-yl)silane (**4o**)

To a solution of **2** (7.5 g, 46 mmol) in THF (50 mL) was added a 0.5 M solution of 2-propenylmagnesium bromide in THF (100 mL, 50 mmol) at 0 °C, and the resulting mixture was stirred at rt for 9 h. The mixture was diluted with diethyl ether, washed sequentially with a saturated NH_4Cl aqueous solution, water, and brine, and then dried over anhydrous $MgSO_4$. After removal of the solvents in vacuo, the residue was distilled under vacuum to give **4o** (8.4 g, 89%) as a colorless oil, bp 75 °C (0.4 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, $J = 7.4$, 1.2 Hz, 1H), 7.48 (ddd, $J = 7.7$, 1.3, 0.5 Hz, 1H), 7.42 (td, $J = 7.5$, 1.5 Hz, 1H), 7.30 (td, $J = 7.3$, 1.5 Hz, 1H), 5.71 (dq, $J = 3.1$, 1.6 Hz, 1H), 5.37 (dq, $J = 3.1$, 1.3 Hz, 1H), 4.72 (s, 2H), 1.92 (br s, 1H), 1.82 (dd, $J = 1.6$, 1.3 Hz, 3H), 0.44 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 146.6, 135.4, 135.3, 129.7, 127.9, 126.9, 126.6, 65.1, 22.5, −2.1; IR (neat) 3329, 2951, 1435, 1248, 1126, 1078, 1034, 924, 835, 818, 775, 754, 696, 662 cm^{-1}; MS (EI) *m*/*z* (%) 206 (M^+, 0.3), 191 (26), 189 (14), 173 (39), 166 (17), 165 (100), 164 (17), 163 (23), 150 (13), 149 (75), 148 (17), 147 (78), 146 (12), 145 (61), 135 (18), 131 (14), 105 (10), 75 (30). Anal. Calc. for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79. Found: C, 69.82; H, 8.56%.

4.8.4. [2-(Hydroxymethyl)phenyl]dimethyl(1-phenylethenyl)silane (**4p**)

To a solution of 1-phenylethenylmagnesium bromide in THF (18 mL), prepared from α-bromostyrene (4.3 g, 24 mmol) and Mg turnings (0.60 g, 25 mmol) [28], was added a THF (10 mL) solution of **2** (3.5 g, 21 mmol) at rt, and the resulting mixture was stirred at rt for 4.5 h. The mixture was diluted with diethyl ether and filtered to remove unreacted magnesium; the filtrate was washed with a saturated NH_4Cl aqueous solution, water, and brine and dried over anhydrous $MgSO_4$. After removal of the solvents in vacuo, the residue was purified by flash chromatography on silica gel to give **4p** (3.2 g, 56%) as a colorless oil, R_f 0.28 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, $J = 7.4$, 1.3 Hz, 1H), 7.48 (dd, $J = 7.6$, 0.8 Hz, 1H), 7.43 (td, $J = 7.4$, 1.3 Hz, 1H), 7.31 (td, $J = 7.3$, 1.5 Hz, 1H), 7.25–7.15 (m, 3H), 7.13–7.08 (m, 2H), 6.04 (d, $J = 1.4$ Hz, 1H), 5.71 (d, $J = 1.4$ Hz, 1H), 4.73 (s, 2H), 1.55 (br s, 1H), 0.48 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 146.5, 143.6, 135.8, 135.3, 129.9, 128.8, 128.2, 128.1, 127.1, 126.72, 126.65, 65.2, −0.8; IR (neat) 3339, 3055, 2955, 1597, 1489, 1439, 1408, 1250, 1200, 1124, 1078, 1028, 934, 831, 812, 781, 754, 708, 633 cm^{-1}; MS (EI) *m*/*z* (%) 268 (M^+, 0.2), 253 (6), 235 (25), 209 (10), 166 (15), 165 (100), 163 (22), 149 (32), 148 (11), 147 (60), 145 (23), 137 (22), 135 (12), 104 (20). Anal. Calc. for $C_{17}H_{20}OSi$: C, 76.07; H, 7.51. Found: C, 76.31; H, 7.48%.

4.8.5. [2-(Hydroxymethyl)phenyl]dimethyl(2-methylpropenyl)silane (**4q**)

A 0.5 M THF solution of 2-methylpropenylmagnesium bromide (100 mL, 50 mmol) was added to a solution of **2** (7.5 g, 46 mmol) in THF (50 mL) at 0 °C, and the resulting mixture was stirred at rt overnight before dilution with diethyl ether. The mixture was washed with a saturated NH_4Cl aqueous solution, water, and brine and dried over anhydrous $MgSO_4$. After removal of the solvents in vacuo, flash chromatography of the residue on neutral aluminium oxide (activity grade III) gave **4q** (7.1 g, 71%) as a colorless oil, R_f 0.26 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, C_6D_6) δ 7.57 (d, $J = 7.3$ Hz, 1H), 7.45 (d, $J = 7.7$ Hz, 1H), 7.22 (t, $J = 7.4$ Hz, 1H), 7.13 (d, $J = 7.4$ Hz, 1H), 5.41 (s, 1H), 4.63 (d, $J = 5.9$ Hz, 2H), 1.78 (t, $J = 5.9$ Hz, 1H), 1.66 (s, 3H), 1.46 (s, 3H), 0.37 (s, 6H); ^{13}C NMR (101 MHz, C_6D_6) δ 153.4, 147.3, 137.5, 134.9, 129.7, 128.0, 127.0, 123.8, 65.3, 29.3, 23.2, 0.0; IR (neat) 3238, 2953, 2907, 1620, 1437, 1371, 1246, 1123, 1076, 1036, 858, 833, 816, 800, 773, 745, 700, 644, 459 cm^{-1}; MS (EI) *m*/*z* (%) 220 (M^+, 0.04), 205 (10), 165 (28), 164 (32), 163 (17), 150 (14), 149 (100), 148 (10), 147 (25), 145 (30), 135 (10), 105 (10), 75 (27), 61 (16). Anal. Calc. for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15. Found: C, 70.83; H, 9.23%.

4.9. Cross-coupling of alkenyl[2-(hydroxymethyl)phenyl]-dimethylsilanes with aryl or alkenyl iodides. A general procedure

To a mixture of K_2CO_3 (0.30 g, 2.2 mmol), a ligand [(2-furyl)$_3$P, 4.6 mg, 0.020 mmol; **9**, 3.7 mg, 0.010 mmol], and $PdCl_2$ (1.8 mg, 0.010 mmol) in DMSO (2.5 mL) were added an alkenylsilane (1.10 mmol) and an aryl or alkenyl iodide (1.00 mmol) sequentially, and the resulting mixture was stirred at 35 °C. After the time specified in Table 3 and Eq. (3), the mixture was diluted with diethyl ether, washed with water and brine, and dried over anhydrous $MgSO_4$. Concentration in vacuo followed by flash chromatography on silica gel afforded the corresponding coupling product in a yield listed in Table 3 and Eq. (3).

4.9.1. (*E*)-1-(4-Cyanophenyl)-1-octene (**6aa**)

A colorless oil, R_f 0.31 (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 6.38–6.35 (m, 2H), 2.24–2.20 (m, 2H), 1.50–1.42 (m, 2H), 1.40–1.25 (m, 6H), 0.92–0.86 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 135.5, 132.2, 128.3, 126.3, 119.1, 109.8, 33.1, 31.6, 28.9, 28.8, 22.5, 14.0; IR (neat) 2955, 2928, 2855, 2226, 1649, 1605, 1502, 1466, 1412, 1175, 966, 856, 733, 552 cm^{-1}; MS (EI) *m*/*z* (%) 213 (M^+, 18), 143 (11), 142 (34), 130 (19), 129 (100), 116 (14), 115 (11). Anal. Calc. for $C_{15}H_{19}N$: C, 84.46; H, 8.98. Found: C, 84.37; H, 8.96%.

4.9.2. (*E*)-1-(4-Ethoxycarbonylphenyl)-1-octene (**6ab**)

A colorless oil, R_f 0.40 (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 7.0$ Hz, 2H), 6.45–6.32 (m, 2H), 4.37 (q, $J = 7.2$ Hz, 2H), 2.23 (q, $J = 7.2$ Hz, 2H), 1.53–1.28 (m, 11H), 0.94–0.86 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

166.5, 142.4, 134.2, 129.8, 129.0, 128.5, 125.7, 60.8, 33.2, 31.7, 29.1, 28.9, 22.6, 14.3, 14.1; IR (neat) 2957, 2928, 2855, 1715, 1607, 1466, 1412, 1366, 1275, 1177, 1107, 1020, 968, 957, 864, 762, 696 cm^{-1}; MS (EI) *m/z* (%) 261 (M^++1, 14), 260 (M^+, 76), 215 (37), 177 (16), 176 (100), 161 (11), 148 (45), 145 (23), 132 (10), 131 (55), 129 (16), 128 (13), 118 (10), 117 (86), 116 (23), 115 (49), 91 (18). Anal. Calc. for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.45; H, 9.41%.

4.9.3. (*E*)-1-(4-Acetylphenyl)-1-octene (**6ac**)

A colorless oil, R_f 0.30 (hexane–ethyl acetate = 20:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 6.43–6.33 (m, 2H), 2.57 (s, 3H), 2.23 (q, $J = 6.4$ Hz, 2H), 1.52–1.42 (m, 2H), 1.40–1.25 (m, 6H), 0.92–0.86 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 142.6, 135.3, 134.5, 128.8, 128.7, 125.8, 33.1, 31.7, 29.1, 28.9, 26.5, 22.6, 14.0; IR (neat) 2957, 2926, 2855, 1682, 1603, 1410, 1358, 1267, 1180, 966, 592 cm^{-1}; MS (EI) *m/z* (%) 231 (M^++1, 12), 230 (M^+, 73), 216 (11), 215 (72), 148 (10), 147 (15), 146 (56), 145 (11), 134 (11), 131 (100), 128 (11), 117 (19), 116 (12), 115 (36). Anal. Calc. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.72; H, 9.74%.

4.9.4. (*E*)-1-(4-Formylphenyl)-1-octene (**6ad**)

A colorless oil, R_f 0.30 (hexane–ethyl acetate = 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.80 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 6.64–6.42 (m, 2H), 2.28–2.22 (m, 2H), 1.53–1.44 (m, 2H), 1.40–1.25 (m, 6H), 0.92–0.86 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 144.1, 135.4, 134.8, 130.1, 128.9, 126.3, 33.2, 31.7, 29.0, 28.9, 22.6, 14.1; IR (neat) 2955, 2926, 2855, 1697, 1603, 1568, 1304, 1213, 1167, 966, 851, 802 cm^{-1}; MS (EI) *m/z* (%) 216 (M^+, 43), 133 (14), 132 (100), 131 (39), 117 (62), 116 (11), 115 (29), 91 (19). Anal. Calc. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.40; H, 9.37%.

4.9.5. (*E*)-1-(4-Nitrophenyl)-1-octene (**6ae**)

A colorless oil, R_f 0.17 (hexane–ethyl acetate = 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, $J = 8.8$ Hz, 2H), 7.44 (d, $J = 8.8$ Hz, 2H), 6.46–6.42 (m, 2H), 2.30–2.20 (m, 2H), 1.54–1.42 (m, 2H), 1.40–1.24 (m, 6H), 0.93–0.87 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 144.4, 136.7, 128.0, 126.3, 123.9, 33.2, 31.6, 28.91, 28.87, 22.6, 14.0; IR (neat) 2955, 2928, 2855, 1649, 1597, 1518, 1466, 1342, 1109, 968, 955, 860, 824, 745, 689 cm^{-1}; MS (EI) *m/z* (%) 234 (M^++1, 11), 233 (M^+, 67), 151 (12), 150 (40), 149 (100), 137 (29), 129 (13), 128 (17), 119 (22), 117 (19), 116 (79), 115 (70), 103 (13), 91 (11), 55 (11); HRMS (FAB+) Calcd for $C_{14}H_{20}NO_2$: $[M+H]^+$, 234.1494. Found: *m/z* 234.1497.

4.9.6. (*E*)-1-(4-Chlorophenyl)-1-octene (**6af**)

A colorless oil, R_f 0.60 (hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 4H), 6.33 (dt, $J = 15.5$, 1.2 Hz, 1H), 6.21 (dt, $J = 15.5$, 6.8 Hz, 1H), 2.20 (q, $J = 6.8$ Hz, 2H), 1.52–1.42 (m, 2H), 1.40–1.23 (m, 6H), 0.94–0.88 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 132.2, 132.0, 128.54, 128.49, 127.1, 33.0, 31.7, 29.2, 28.9, 22.6, 14.1; IR (neat) 2957, 2926, 2855, 1709, 1491, 1466, 1404, 1092, 1013, 964, 845, 820, 802, 735 cm^{-1}; MS (EI) *m/z* (%) 224 (M^++2, 15), 222 (M^+, 44), 153 (29), 152 (12), 151 (88), 140 (31), 139 (10), 138 (100), 129 (10), 125 (17), 117 (11), 116 (36), 115 (46); HRMS (EI) Calcd for $C_{14}H_{19}Cl$: M^+, 222.1175. Found: *m/z* 222.1172.

4.9.7. (*E*)-1-(4-Methoxyphenyl)-1-octene (**6ag**)

A colorless oil, R_f 0.36 (hexane–ethyl acetate = 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, $J = 8.7$ Hz, 2H), 6.84 (d, $J = 8.7$ Hz, 2H), 6.33 (d, $J = 15.7$ Hz, 1H), 6.09 (dt, $J = 15.7$, 7.0 Hz, 1H), 3.81 (s, 3H), 2.19 (q, $J = 7.5$ Hz, 2H), 1.50–1.42 (m, 2H), 1.40–1.26 (m, 6H), 0.93–0.88 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 130.8, 129.1, 129.0, 126.9, 113.9, 55.2, 33.0, 31.8, 29.5, 28.9, 22.6, 14.1; IR (neat) 2955, 2926, 2855, 1609, 1510, 1466, 1248, 1175, 1038, 964, 841 cm^{-1}; MS (EI) *m/z* (%) 218 (M^+, 39), 148 (12), 147 (100), 134 (14), 121 (15), 91 (10). Anal. Calc. for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.52; H, 9.98%.

4.9.8. (*E*)-1-[3-(tert-Butyldimethylsiloxymethyl)phenyl]-1-octene (**6ah**)

A colorless oil, R_f 0.35 (hexane–ethyl acetate = 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 1H), 7.25–7.13 (m, 3H), 6.37 (d, $J = 15.7$ Hz, 1H), 6.22 (dt, $J = 15.7$, 6.9 Hz, 1H), 4.72 (s, 2H), 2.20 (q, $J = 7.7$ Hz, 2H), 1.50–1.42 (m, 2H), 1.38–1.26 (m, 6H), 0.95 (s, 9H), 0.39 (t, $J = 6.9$ Hz, 3H), 0.10 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 137.8, 131.2, 129.7, 128.3, 124.49, 124.47, 123.5, 64.9, 33.0, 31.7, 29.3, 28.9, 26.0, 22.6, 18.4, 14.1, −5.2; IR (neat) 2955, 2928, 2856, 1462, 1256, 1105, 1080, 962, 837, 777 cm^{-1}; MS (EI) *m/z* (%) 332 (M^+, 2), 276 (27), 275 (100), 245 (16), 201 (34). Anal. Calc. for $C_{21}H_{36}OSi$: C, 75.84; H, 10.91. Found: C, 75.97; H, 11.13%.

4.9.9. (*E*)-1-[3-(Hydroxymethyl)phenyl]-1-octene (**6ai**)

A colorless oil, R_f 0.30 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.32–7.27 (m, 2H), 7.21–7.18 (m, 1H), 6.38 (d, $J = 15.6$ Hz, 1H), 6.26 (dt, $J = 16.0$, 6.8 Hz, 1H), 4.68 (s, 2H), 2.21 (q, $J = 7.2$ Hz, 2H), 1.62 (br s, 1H), 1.51–1.42 (m, 2H), 1.40–1.26 (m, 6H), 0.93–0.87 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 138.3, 131.7, 129.4, 128.7, 125.35, 125.32, 124.4, 65.4, 33.0, 31.7, 29.3, 28.9, 22.6, 14.1; IR (neat) 3329, 2955, 2926, 2855, 1466, 1433, 1020, 962, 775, 733, 696 cm^{-1}; MS (EI) *m/z* (%) 218 (M^+, 36), 134 (42), 132 (16), 131 (16), 129 (24), 128 (12), 118 (14), 117 (100), 115 (22), 105 (10), 91 (20). Anal. Calc. for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.63; H, 10.40%.

4.9.10. (*E*)-1-(2-Methylphenyl)-1-octene (**6aj**)

A colorless oil, R_f 0.71 (hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, $J = 7.2$ Hz, 1H), 7.19–7.10 (m, 3H), 6.57 (d, $J = 15.6$ Hz, 1H), 6.10 (dt, $J = 15.6$, 6.8 Hz, 1H),

2.34 (s, 3H), 2.23 (q, $J = 7.2$ Hz, 2H), 1.54–1.42 (m, 2H), 1.40–1.26 (m, 6H), 0.92–0.88 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 134.8, 132.6, 130.1, 127.5, 126.7, 126.0, 125.4, 33.3, 31.7, 29.4, 28.9, 22.6, 19.8, 14.1; IR (neat) 3020, 2957, 2926, 2855, 1485, 1460, 1377, 962, 745 cm^{-1}; MS (EI) *m*/*z* (%) 202 (M^+, 42), 132 (13), 131 (100), 129 (12), 118 (51), 117 (18), 116 (17), 115 (18), 105 (16), 91 (15). Anal. Calc. for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 88.97; H, 11.18%.

4.9.11. (*E*)-1-(1-Naphthyl)-1-octene (**6ak**)

A colorless oil, R_f 0.50 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, $J = 7.6$ Hz, 1H), 7.84 (d, $J = 7.2$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.58–7.40 (m, 4H), 7.11 (d, $J = 15.2$ Hz, 1H), 6.24 (dt, $J = 16.0$, 7.2 Hz, 1H), 2.33 (q, $J = 7.6$ Hz, 2H), 1.60–1.52 (m, 2H), 1.46–1.32 (m, 6H), 0.94–0.88 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.8, 134.6, 133.6, 131.1, 128.4, 127.1, 126.8, 125.74, 125.65, 125.58, 124.0, 123.5, 33.5, 31.8, 29.4, 29.0, 22.7, 14.1; IR (neat) 3059, 3044, 2955, 2926, 2855, 1591, 1508, 1466, 1394, 964, 775, 727 cm^{-1}; MS (EI) *m*/*z* (%) 238 (M^+, 44), 168 (17), 167 (100), 166 (15), 165 (35), 154 (21), 153 (24), 152 (22), 141 (13). Anal. Calc. for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.61; H, 9.32%.

4.9.12. (*E*)-1-(3-Pyridyl)-1-octene (**6al**)

A colorless oil, R_f 0.35 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (br s, 1H), 8.42 (br d, $J = 3.7$ Hz, 1H), 7.65 (d, $J = 7.9$ Hz, 1H), 7.22 (dd, $J = 7.8$, 4.8 Hz, 1H), 6.38–6.26 (m, 2H), 2.26–2.20 (m, 2H), 1.52–1.43 (m, 2H), 1.40–1.26 (m, 6H), 0.92–0.86 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 147.7, 133.8, 133.5, 132.5, 126.1, 123.4, 33.1, 31.7, 29.1, 28.9, 22.6, 14.1; IR (neat) 3024, 2955, 2926, 2855, 2359, 2341, 1653, 1568, 1466, 1414, 1022, 964, 708 cm^{-1}; MS (EI) *m*/*z* (%) 189 (M^+, 46), 146 (10), 132 (10), 130 (10), 119 (14), 118 (87), 117 (37), 106 (27), 105 (100), 93 (14), 91 (15). Anal. Calc. for $C_{13}H_{19}N$: C, 82.48; H, 10.12. Found: C, 82.20; H, 10.06%.

4.9.13. (*E*)-1-(2-Thienyl)-1-octene (**6am**)

A colorless oil, R_f 0.70 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, $J = 5.2$ Hz, 1H), 6.95–6.91 (m, 1H), 6.86 (d, $J = 3.2$ Hz, 1H), 6.50 (d, $J = 15.6$ Hz, 1H), 6.07 (dt, $J = 15.6$, 6.8 Hz, 1H), 2.17 (q, $J = 7.2$ Hz, 2H), 1.52–1.41 (m, 2H), 1.40–1.24 (m, 6H), 0.94–0.86 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.3, 127.2, 124.1, 123.0, 122.9, 108.2, 32.9, 31.7, 29.2, 28.9, 22.6, 14.1; IR (neat) 2955, 2926, 2855, 1724, 1686, 1676, 1466, 1437, 1420, 1377, 1211, 1042, 953, 853, 723, 692 cm^{-1}; MS (EI) *m*/*z* (%) 194 (M^+, 41), 147 (10), 124 (12), 123 (100), 110 (46), 97 (14), 73 (18); HRMS (EI) Calcd for $C_{12}H_{18}S$: M^+, 194.1129. Found: *m*/*z* 194.1126.

4.9.14. (*E*)-6-(4-Ethoxycarbonylphenyl)-5-hexenenitrile (**6bb**)

A colorless oil, R_f 0.30 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 6.50 (d, $J = 16.0$ Hz, 1H), 6.31–6.22 (m, 1H), 4.36 (q, $J = 7.2$ Hz, 2H), 2.44–2.38 (m, 4H), 1.86 (quint, $J = 7.2$ Hz, 2H), 1.39 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 141.4, 131.2, 130.4, 129.9, 129.1, 125.9, 119.4, 60.9, 31.7, 24.8, 16.5, 14.3; IR (neat) 2984, 2937, 2907, 2243, 1711, 1607, 1458, 1437, 1414, 1366, 1271, 1180, 1126, 1109, 1092, 1024, 968, 955, 768, 750, 694 cm^{-1}; MS (EI) *m*/*z* (%) 244 (M^++1, 14), 243 (M^+, 81), 199 (15), 198 (100), 197 (16), 196 (19), 170 (12), 157 (14), 145 (15), 130 (14), 129 (43), 128 (22), 117 (57), 116 (16), 115 (40); HRMS (EI) Calcd for $C_{15}H_{17}NO_2$: M^+, 243.1259. Found: *m*/*z* 243.1259.

4.9.15. Methyl (*E*)-6-(4-ethoxycarbonylphenyl)-5-hexenoate (**6cb**)

A colorless oil, R_f 0.32 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 8.4$ Hz, 2H), 6.44 (d, $J = 15.8$ Hz, 1H), 6.31 (dt, $J = 15.8$, 6.8 Hz, 1H), 4.37 (q, $J = 7.1$ Hz, 2H), 3.66 (s, 3H), 2.37 (t, $J = 6.8$ Hz, 2H), 2.29 (q, $J = 6.8$ Hz, 2H), 1.84 (quint, $J = 6.8$ Hz, 2H), 1.39 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 166.5, 141.9, 132.4, 130.1, 129.8, 128.8, 125.8, 60.8, 51.5, 33.4, 32.4, 24.3, 14.3; IR (neat) 2982, 2951, 1736, 1717, 1607, 1275, 1178, 1107, 1020, 970, 860, 760 cm^{-1}; HRMS (EI) Calcd for $C_{16}H_{20}O_4$: M^+, 276.1362. Found: *m*/*z* 276.1359.

4.9.16. (*E*)-5-Chloro-1-(4-ethoxycarbonylphenyl)-1-pentene (**6db**)

A colorless oil, R_f 0.25 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, $J = 8.3$ Hz, 2H), 7.39 (d, $J = 8.3$ Hz, 2H), 6.48 (d, $J = 15.9$ Hz, 1H), 6.31 (dt, $J = 15.9$, 6.3 Hz, 1H), 4.37 (q, $J = 7.1$ Hz, 2H), 3.59 (t, $J = 6.3$ Hz, 2H), 2.42 (q, $J = 6.3$ Hz, 2H), 1.97 (quint, $J = 6.3$ Hz, 2H), 1.39 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 141.8, 131.5, 130.5, 129.9, 129.0, 125.8, 60.9, 44.2, 31.8, 30.1, 14.3; IR (neat) 2982, 2959, 2937, 1715, 1607, 1277, 1178, 1107, 1020, 970, 758 cm^{-1}. Anal. Calc. for $C_{14}H_{17}ClO_2$: C, 66.53; H, 6.78. Found: C, 66.61; H, 6.71%.

4.9.17. (*E*)-5-tert-Butyldimethylsiloxy-1-(4-ethoxycarbonylphenyl)-1-pentene (**6eb**)

A colorless oil, R_f 0.23 (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, $J = 8.3$ Hz, 2H), 7.38 (d, $J = 8.3$ Hz, 2H), 6.43 (d, $J = 15.9$ Hz, 1H), 6.31 (dt, $J = 15.9$, 6.3 Hz, 1H), 4.36 (q, $J = 7.1$ Hz, 2H), 3.67 (t, $J = 6.3$ Hz, 2H), 2.31 (q, $J = 7.0$ Hz, 2H), 1.74–1.65 (m, 2H), 1.39 (t, $J = 7.1$ Hz, 3H), 0.91 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 142.3, 133.5, 129.9, 129.4, 128.7, 125.7, 62.4, 60.8, 32.2, 29.5, 26.0, 18.4, 14.4, −5.3; IR (neat) 2955, 2930, 2895, 2856, 1719, 1607, 1275, 1177, 1105, 1020, 968, 837, 775 cm^{-1}; HRMS (CI) Calcd for $C_{20}H_{33}O_3Si$: $[M+H]^+$, 349.2199. Found: *m*/*z* 349.2193.

*4.9.18. (E)-N-[3-(4-Ethoxycarbonylphenyl)-2-propenyl]phthalimide (**6fb**)*

A colorless solid (mp = 124.0–125.0 °C), R_f 0.72 (hexane–ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.3 Hz, 2H), 7.90–7.80 (m, 2H), 7.76–7.66 (m, 2H), 7.40 (d, J = 8.3 Hz, 2H), 6.68 (d, J = 15.9 Hz, 1H), 6.37 (dt, J = 15.9, 6.4 Hz, 1H), 4.48 (d, J = 6.4 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 166.3, 140.6, 134.1, 132.7, 132.1, 129.8, 129.7, 126.4, 125.4, 123.4, 60.9, 39.5, 14.3; IR (KBr) 2968, 1773, 1728, 1703, 1470, 1427, 1396, 1367, 1294, 1265, 1180, 1109, 980, 955, 746, 727, 710, 530 cm^{-1}. Anal. Calc. for $C_{20}H_{17}NO_4$: C, 71.63; H, 5.11. Found: C, 71.58; H, 5.18%.

*4.9.19. (E)-3-(4-Ethoxycarbonylphenyl)-2-propenyl acetate (**6gb**)*

A colorless oil, R_f 0.31 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 6.68 (d, J = 15.9 Hz, 1H), 6.39 (dt, J = 15.9, 6.2 Hz, 1H), 4.75 (d, J = 6.2 Hz, 2H), 4.37 (q, J = 7.1 Hz, 2H), 2.11 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 166.3, 140.5, 132.8, 129.9, 129.8, 126.4, 125.8, 64.7, 61.0, 20.9, 14.3; IR (neat) 2982, 2937, 1742, 1715, 1609, 1366, 1277, 1229, 1178, 1107, 1024, 970, 866, 760, 698 cm^{-1}. Anal. Calc. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.88; H, 6.44%.

*4.9.20. (E)-4-(4-Ethoxycarbonylphenyl)-2-methyl-3-buten-2-ol (**6hb**)*

A colorless solid (mp = 38.0–38.8 °C), R_f 0.29 (hexane–ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 6.64 (d, J = 16.1 Hz, 1H), 6.46 (d, J = 16.1 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.57 (br s, 1H), 1.44 (s, 6H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 141.4, 140.0, 129.9, 129.2, 126.2, 125.6, 71.1, 60.9, 29.9, 14.3; IR (KBr) 3311, 2980, 1712, 1609, 1366, 1281, 1180, 1146, 1111, 1020, 974, 903, 872, 764, 698 cm^{-1}; HRMS (EI) Calcd for $C_{14}H_{18}O_3$: M^+, 234.1256 Found: m/z 234.1248.

*4.9.21. (E)-1-(4-Ethoxycarbonylphenyl)-3-methyl-1,3-butadiene (**6ib**)*

A colorless solid (mp = 43.5–44.5 °C), R_f 0.23 (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 16.1 Hz, 1H), 6.55 (d, J = 16.1 Hz, 1H), 5.19 (s, 1H), 5.15 (s, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.98 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 141.80, 141.77, 134.0, 129.9, 129.1, 127.7, 126.2, 118.9, 60.9, 18.5, 14.3; IR (KBr) 2984, 1705, 1605, 1288, 1263, 1184, 1130, 1109, 1022, 986, 880, 772, 708, 536 cm^{-1}. Anal. Calc. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.48; H, 7.39%.

*4.9.22. (E)-4-Ethoxycarbonylstilbene (**6jb**)*

A colorless solid (mp 106.0–106.5 °C), R_f 0.30 (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 2H), 7.58–7.52 (m, 4H), 7.41–7.36 (m, 2H), 7.32–7.27 (m, 1H), 7.22 (d, J = 16.4 Hz, 1H), 7.13 (d, J = 16.4 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 141.7, 136.7, 131.1, 130.0, 129.2, 128.8, 128.2, 127.6, 126.8, 126.3, 60.9, 14.4; IR (KBr) 2976, 1705, 1607, 1367, 1283, 1180, 1130, 1109, 1024, 976, 770, 696, 527 cm^{-1}; MS (EI) m/z (%) 253 (M^++1, 20), 252 (M^+, 100), 208 (12), 207 (65), 180 (10), 179 (54), 178 (57). Anal. Calc. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 81.18; H, 6.27%.

*4.9.23. (E)-4-(4-Ethoxycarbonylphenyl)-4-octene (**6kb**)*

A colorless oil, R_f 0.40 (hexane–ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.6 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H), 5.76 (t, J = 7.3 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 2.49 (t, J = 7.5 Hz, 2H), 2.19 (q, J = 7.3 Hz, 2H), 1.53–1.42 (m, 2H), 1.41–1.32 (m, 5H), 0.97 (t, J = 7.3 Hz, 3H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 148.0, 139.4, 131.1, 129.5, 128.4, 126.2, 60.8, 31.4, 30.7, 22.9, 21.8, 14.4, 14.0, 13.9; IR (neat) 2959, 2932, 2872, 1720, 1607, 1462, 1408, 1366, 1273, 1180, 1107, 1020, 858, 772, 706 cm^{-1}; MS (EI) m/z (%) 261 (M^++1, 15), 260 (M^+, 79), 231 (16), 217 (44), 215 (31), 190 (21), 189 (15), 187 (51), 173 (30), 159 (16), 157 (13), 146 (13), 145 (100), 143 (17), 131 (35), 130 (15), 129 (46), 128 (32), 127 (10), 117 (63), 116 (11), 115 (31), 91 (19). Anal. Calc. for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.28; H, 9.14%.

*4.9.24. (Z)-4-Ethoxycarbonylstilbene (**6lb**)*

A colorless oil, R_f 0.33 (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.24–7.19 (m, 5H), 6.71 (d, J = 12.4 Hz, 1H), 6.60 (d, J = 12.4 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 142.0, 136.7, 132.1, 109.5, 129.3, 128.9, 128.83, 128.79, 128.3, 127.5, 60.9, 14.3; IR (neat) 2980, 1717, 1607, 1366, 1275, 1178, 1103, 1020, 781, 714, 698 cm^{-1}. Anal. Calc. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.70; H, 6.27%.

*4.9.25. Ethyl 4-vinylbenzoate (**6mb**) [29]*

A colorless oil, R_f 0.30 (hexane–ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 6.75 (dd, J = 17.6, 11.2 Hz, 1H), 5.86 (d, J = 17.2 Hz, 1H), 5.38 (d, J = 10.8 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 1.40 (t, J = 7.2 Hz, 3H).

*4.9.26. 1-(4-Ethoxycarbonylphenyl)propene [(Z):(E) = 94:6] (**6nb**)*

A colorless oil, R_f 0.33 (hexane–ethyl acetate = 20:1). [Spectra of (*Z*)-isomer] ^{1}H NMR (400 MHz, $CDCl_3$) δ

8.01 (dd, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.2$ Hz, 2H), 6.46 (dd, $J = 11.8$, 1.8 Hz, 1H), 5.90 (dq, $J = 11.8$, 7.2 Hz, 1H), 4.38 (q, $J = 7.2$ Hz, 2H), 1.91 (dd, $J = 7.2$, 1.8 Hz, 3H), 1.40 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 142.2, 129.4, 129.1, 129.0, 128.7, 128.3, 60.8, 14.8, 14.3; IR (neat) 2980, 1715, 1609, 1367, 1310, 1277, 1178, 1105, 1020, 866, 773, 733, 721, 700 cm^{-1}; MS (EI) *m/z* (%) 190 (M^+, 50), 162 (12), 146 (13), 145 (100), 117 (20), 115 (25), 91 (10). Anal. Calc. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.90; H, 7.44%.

*4.9.27. 2-(4-Ethoxycarbonylphenyl)propene (**6ob**)*

A colorless oil, R_f 0.40 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, $J = 8.0$ Hz, 2H), 7.52 (d, $J = 8.2$ Hz, 2H), 5.47 (dq, $J = 1.3$, 0.7 Hz, 1H), 5.19 (qd, $J = 1.5$, 1.3 Hz, 1H), 4.38 (q, $J = 7.1$ Hz, 2H), 2.17 (dd, $J = 1.5$, 0.7 Hz, 3H), 1.40 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 145.8, 142.7, 129.8, 129.5, 125.6, 114.7, 61.1, 21.9, 14.6; IR (neat) 2980, 2359, 2341, 1715, 1609, 1367, 1275, 1184, 1123, 1103, 1020, 899, 860, 783, 719 cm^{-1}; MS (EI) *m/z* (%) 190 (M^+, 42), 162 (19), 146 (13), 145 (100), 115 (20); HRMS (FAB+) Calcd for $C_{12}H_{14}O_2$: M^+, 190.0994. Found: *m/z* 190.0993.

*4.9.28. 1-(4-Ethoxycarbonylphenyl)-1-phenylethene (**6pb**)*

A colorless solid (mp 46.7–47.3 °C), R_f 0.33 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, $J = 8.6$ Hz, 2H), 7.41 (d, $J = 8.6$ Hz, 2H), 7.36–7.30 (m, 5H), 5.55 (d, $J = 1.1$ Hz, 1H), 5.54 (d, $J = 1.1$ Hz, 1H), 4.39 (q, $J = 7.1$ Hz, 2H), 1.41 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 149.3, 145.9, 140.8, 129.7, 129.5, 128.3, 128.2, 128.0, 115.8, 60.9, 14.3; IR (KBr) 1717, 1279, 1105, 775, 702 cm^{-1}; MS (EI) *m/z* (%) 253 (M^++1, 18), 252 (M^+, 97), 224 (14), 208 (18), 207 (100), 179 (44), 178 (68), 177 (11), 176 (11). Anal. Calc. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 81.01; H, 6.47%.

*4.9.29. 1-(4-Methoxyphenyl)-1-phenylethene (**6pg**)*

A colorless solid (mp 75.3–76.8 °C), R_f 0.39 (hexane–ethyl acetate = 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.31 (m, 5H), 7.28 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 5.41 (d, $J = 1.4$ Hz, 1H), 5.36 (d, $J = 1.4$ Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 149.7, 142.0, 134.2, 129.6, 128.6, 128.4, 127.9, 113.7, 113.2, 55.5; IR (KBr) 3005, 2951, 2835, 1908, 1811, 1605, 1572, 1508, 1491, 1456, 1441, 1290, 1250, 1180, 1028, 901, 843, 785, 708, 581, 552 cm^{-1}; MS (EI) *m/z* (%) 253 (M^++1, 18), 252 (M^+, 97), 224 (14), 208 (18), 207 (100), 179 (44), 178 (68), 177 (11), 176 (11). Anal. Calc. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.67; H, 6.73%.

*4.9.30. 1-(4-Ethoxycarbonylphenyl)-2-methylpropene (**6qb**)*

A colorless oil, R_f 0.38 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, $J = 8.3$ Hz, 2H), 7.28 (d, $J = 8.3$ Hz, 2H), 6.29 (s, 1H), 4.37 (q, $J = 7.1$ Hz, 2H), 1.93 (s, 3H), 1.88 (s, 3H), 1.39 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 143.3, 137.9, 129.3, 128.5, 127.7, 124.6, 60.8, 27.1, 19.6, 14.3; IR (neat) 2980, 1715, 1607, 1410, 1366, 1275, 1178, 1103, 1020, 878, 760, 706 cm^{-1}; MS (EI) *m/z* (%) 205 (M^++1, 11), 204 (M^+, 78), 160 (14), 159 (100), 131 (32), 116 (12), 115 (19), 91 (16). Anal. Calc. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.24; H, 7.99%.

*4.9.31. (5E,7E)-Tetradeca-5,7-dienenitrile (**8ba**)*

A colorless oil, R_f 0.42 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11–5.94 (m, 2H), 5.63 (dt, $J = 14.6$, 7.0 Hz, 1H), 5.46 (dt, $J = 14.8$, 7.0 Hz, 1H), 2.34 (t, $J = 7.1$ Hz, 2H), 2.22 (q, $J = 7.1$ Hz, 2H), 2.06 (dt, $J = 7.1$, 7.0 Hz, 2H), 1.80–1.71 (m, 2H), 1.45–1.20 (m, 8H), 0.88 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.1, 132.6, 129.6, 128.5, 119.6, 32.6, 31.7, 31.2, 29.2, 28.9, 25.0, 22.6, 16.3, 14.1; IR (neat) 3017, 2957, 2926, 2855, 2247, 1456, 1437, 989, 733 cm^{-1}; MS (EI) *m/z* (%) 206 (M^++1, 10), 205 (M^+, 59), 204 (M^+−1, 13), 177 (37), 176 (34), 162 (13), 148 (36), 135 (16), 134 (100), 121 (29), 120 (60), 107 (15), 106 (16), 95 (15), 94 (26), 93 (52), 91 (25), 83 (21), 82 (10), 81 (67), 80 (45), 79 (39), 77 (22), 67 (45), 55 (15). Anal. Calc. for $C_{14}H_{23}N$: C, 81.89; H, 11.29. Found: C, 82.18; H, 11.56%.

*4.9.32. (5E,7Z)-Tetradeca-5,7-dienenitrile (**8bb**)*

A colorless oil, R_f 0.36 (hexane–ethyl acetate = 7:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 (ddq, $J = 15.1$, 10.9, 1.3 Hz, 1H), 5.94 (t, $J = 10.9$ Hz, 1H), 5.55 (dt, $J = 15.0$, 7.6 Hz, 1H), 5.37 (dt, $J = 10.9$, 7.6 Hz, 1H), 2.35 (t, $J = 7.1$ Hz, 2H), 2.27 (m, 2H), 2.16 (m, 2H), 1.77 (m, 2H), 1.41–1.21(m, 8H), 0.88 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.7, 130.8, 127.84, 127.81, 119.6, 31.7, 31.5, 29.6, 28.9, 27.7, 25.0, 22.6, 16.4, 14.1; IR (neat) 3020, 2957, 2928, 2855, 2247, 1456, 984, 949, 735 cm^{-1}; MS (EI) *m/z* (%) 205 (M^+, 43), 204 (M^+−1, 11), 177 (51), 176 (40), 162 (14), 148 (40), 135 (15), 134 (100), 121 (30), 120 (70), 107 (16), 106 (19), 95 (16), 94 (29), 93 (50), 91 (26), 83 (31), 82 (12), 81 (79), 80 (53), 79 (44), 77 (25), 67 (53), 55 (19), 54 (10). Anal. Calc. for $C_{14}H_{23}N$: C, 81.89; H, 11.29. Found: C, 82.19; H, 11.18%.

*4.10. Gram-scale cross-coupling reaction of **4a** with **5 b***

To a mixture of K_2CO_3 (9.1 g, 66 mmol), $(2\text{-furyl})_3P$ (138 mg, 0.60 mmol), and $PdCl_2$ (54 mg, 0.30 mmol) in DMSO (75 mL) were added **4a** (9.1 g, 33 mmol) and ethyl 4-iodobenzoate (**5 b**, 8.3 g, 30 mmol) sequentially, and the resulting mixture was stirred at 35 °C for 21 h. The mixture was diluted with diethyl ether, washed with water and brine, and dried over anhydrous $MgSO_4$. Concentration in vacuo followed distillation under vacuum (1.0 mmHg) gave cyclic silyl ether **2** (3.1 g, 62%); the residue was further purified by flash chromatography on silica gel (hexane–ethyl acetate = 20:1 as an eluent) to give **6ab** (7.6 g, 97%).

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