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One-Pot Two-fold Unsymmetrical C-Si bond 2,6-Bifunctionalization of Arenes via Sequential [1,4]-Csp^2 to O-Silyl Migration

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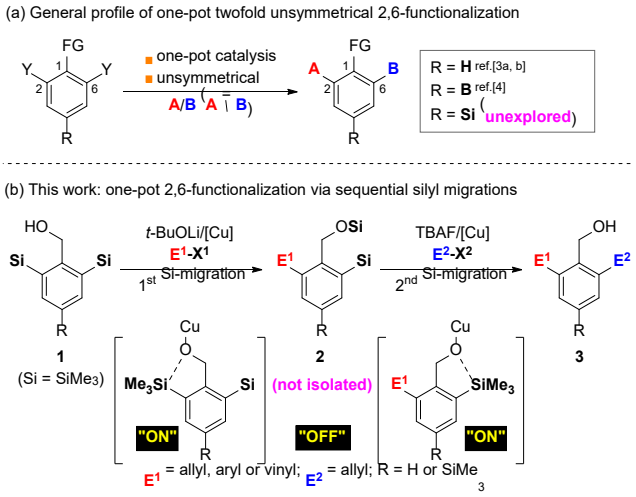
ABSTRACT: Two-fold unsymmetrical C-Si bond bifunctionalization of 2,6-di(trimethylsilyl) benzyl alcohols has been achieved in one pot via sequential [1,4]-Csp^2 to O-silyl migration. The hydroxyl group functions as an "*on-off-on*" switch to control two successive silyl migrations, and 4,7-dimethyl-o-phenanthroline ligand favors cleavage of the endo-cyclic C-Si bond. Diverse Csp^3/Csp^3 or Csp^2/Csp^3 electrophiles can be installed at the 2- and 6-positions. This approach was used to chemoselectively functionalize the three C-Si bonds of 2,4,6-tri(trimethylsilyl) benzyl alcohol, transforming it into isochroman derivatives. The approach even works as a five-component reaction to construct complex symmetric structures.

INTRODUCTION

Two-fold unsymmetrical 2,6-bifunctionalization of 1-substituted arenes provides a useful access to polyfunctionalized aromatic compounds, which are widely applied in organic chemistry, pharmaceuticals and materials. [1] A highly step-efficient reaction in which different groups A and B are added at the 2- and 6-position of arenes in one pot is quite desirable (Scheme 1a), but challenging for the following reasons. (1) The A group introduced in the first C-Y bond functionalization might inhibit subsequent functionalization with the B group. (2) Competitive 2,6-homo-disubstitution[2] with two A groups may be a problem to give the undesired symmetric product. This would lead to a complex mixture containing bi-functionalized chemoisomers (A/A, B/B, A/B), mono-functionalized isomers (A/Y, B/Y), and recovered substrate. (3) Finding one or two compatible catalytic systems that efficiently control the reactivity and selectivity of each functionality is difficult. Given these difficulties, it is no surprise that only a handful of one-pot two-fold unsymmetrical 2,6-bifunctionalizations of arenes have been reported. One involves C-H functionalization to introduce acetyl and pivaloxy groups,[3a, b] another involves 2,6-diboro arenes, in which hydrazone differentiates two symmetric C-B bonds,[4] resulting in a sequential one-pot Suzuki-Miyaura cross-coupling with two different aryl bromides. Another promising substrate is 2,6-disilyl arene, yet we are aware of only separated multi-step functionalization of 2,6-silyl groups as demonstrated by Knochel.[5] To the best of our knowledge, it appears that two-fold unsymmetrical C-Si bond bifunctionalization of 2,6-disilyl arenes in one pot has still remained unexplored.

We have already demonstrated the power of geminal bis(silanes) in organic synthesis by bifunctionalizing the two C-Si bonds.[6] Inspired by these studies, and Smith',[7] Takeda's,[8] our own[9] and others'[10] progress in cross-coupling based on Brook rearrangement involving Csp^2 to O-silyl migration,[11] as well as our recent synthesis of



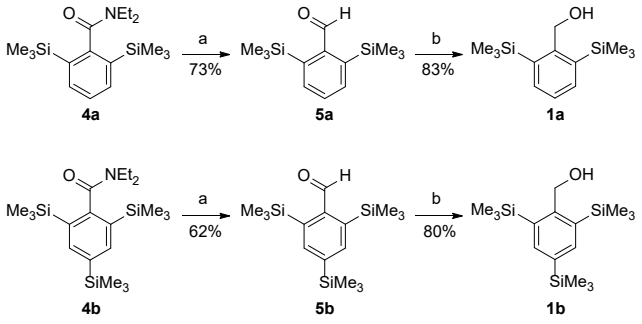
SCHEME 1. General form of two-fold unsymmetrical 2,6-functionalization of arenes in one pot (a); two-fold unsymmetrical C-Si bond 2,6-functionalization of arenes via sequential [1,4]-Csp^2 to O-silyl migrations in one pot (b).

2,6-di(trimethylsilyl) benzaldehyde,[12] we wished to test the scenario in Scheme 1b. In this pathway, the hydroxyl group in **1** acts as an "*on-off-on*" switch to control each step in the sequential [1,4]-Csp^2 to O-silyl migration. Deprotonation under basic conditions turns the hydroxyl group *on,* and the

first silyl migration occurs, in which one of the C-Si bonds is cleaved to facilitate Cu-catalyzed cross-coupling with E^1-X^1. In this process, the hydroxyl group turns *off* by forming the silyl ether **2**. This implies that a second C-Si bond in **2** would remain untouched and no second cross-coupling would occur with the extra E^1-X^1. After complete conversion of **1** to **2**, the hydroxyl group is turned *on* by selective O-Si bond cleavage promoted by TBAF, paving the way for the second silyl migration and cross-coupling with E^2-X^2, giving the two-fold unsymmetrically functionalized product **3**. Here we report the realization of the approach in Scheme 1b.

RESULTS AND DISCUSSION

Syntheses of 1a and 1b The required 2,6-di(trimethylsilyl) benzyl alcohol **1a** was synthesized from the known *N, N*-diethyl benzylamide **4a** (Scheme 2).[13] The approach we developed to reduce steric demanding amides allowed us to transform **4a** into the aldehyde **5a** in73%.[12] The reaction was initiated by activation of amide with EtOTf to form imidate, which was reduced with $LiAlH(OEt)_3$ to give aldehyde by hydrolysis of the resulting hemiaminals. Reduction of aldehyde **5a** with $NaBH_4$ afforded the alcohol **1a** in 83% yield. Similar two-step operation on 2,4,6-tri(trimethylsilyl) benzylamide **4b** gave the corresponding alcohol **1b** in an overall yield of 50%.



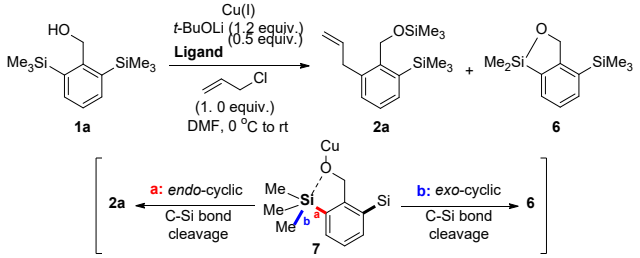
(a) EtOTf, CH_2Cl_2, 45 °C, 4 h, then $LiAlH(OEt)_3$, THF, 0 °C to rt, overnight (73% for **5a**; 62% for **5b**). (b) $NaBH_4$, MeOH, rt, 2 h (83% for **1a**; 80% for **1b**).

SCHEME 2. Syntheses of 1a and 1b.

Sequential cross-coupling of 1a with Csp^3/Csp^3-electrophiles E^1-X^1 and E^2-X^2 Allyl chloride was tested as the electrophile for the first cross-coupling using Takeda's protocol.[8e] The reaction provided mono-allylated silyl ether **2a** in 75% yield, without the undesired further desilylation of O-Si or C-Si bonds (*turning off*). Two silyl groups in **1a** appeared to sterically protect the hydroxyl group from oxidation to the corresponding aldehyde, which has frequently been observed in systems involving thermal degradation of the copper(I).[8e] Cyclic silyl ether **6** was detected as the major by-product: the ratio of products **2a**:**6** was 5.4:1 (Table 1, entry 1). Product **2a** was generated from the *endo*-cyclic Csp^2-Si bond cleavage of **7** (path a), while **6** resulted from *exo*-cyclic Csp^3-Si bond cleavage (path b). *Exo*-cyclic C-Si bond cleavage is very common, and even dominates in Hiyama's[14] and Takeda's[8k] studies using phosphine as ligand. In our case, this pathway should be minimized as much as possible to ensure complete formation of **2a**, because **6** would complicate the second cross-coupling. Unfortunately, further transformation of **6** into **2a** failed with longer reaction time (entry 2). Switching the catalyst from CuI to other copper salts such as CuCl, CuBr or CuCN did not improve the ratio or only led to complex mixtures (entries 3-5).

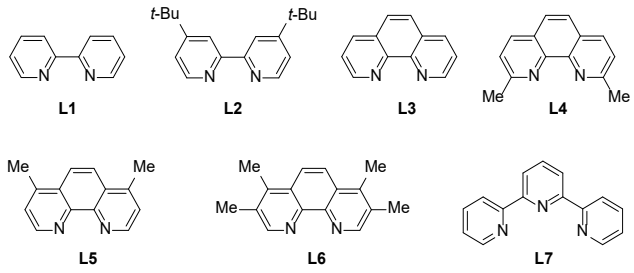
Inspired by the ability of *N, N*-bidentate ligands to facilitate copper-catalyzed aryl or vinyl cross-coupling,[15] we hypothesized that this type of ligand might favor the generation of the desired aryl

TABLE 1. Screening of Reaction Conditions of Cross-coupling with Csp^3-electrophile E^1-X^1[a]



Entry	Cu(I)	Ligand	*t* (h)	**2a**:**4**[b]	**2a** (%)[c]
1	CuI	—	1	5.4:1	75
2	CuI	—	10	N.D.	N.D.
3	CuCl	—	1	N.D.	N.D.
4	CuBr	—	1	3.0:1	62
5	CuCN	—	1	3.6:1	65
6	CuI	**L1**	0.5	7.0:1	78
7	CuI	**L2**	0.5	4.2:1	71
8	CuI	**L3**	0.5	9.0:1	85
9	CuI	**L4**	0.5	4.8:1	72
10	CuI	**L5**	0.5	20:1	93
11	CuI	**L6**	0.5	20:1	91
12	CuI	**L7**	0.5	7.0:1	80

[a]Reaction conditions: Cu(I) (0.05 mmol), *t*-BuOLi (0.12 mmol) in DMF, 0 °C to rt, 10 min; then ligand (0.05 mmol), **1a** (0.1 mmol), allylchloride (0.1 mmol), rt, 30 min. [b]Ratios were determined by ^1H NMR of the crude products. [c]Isolated yields.

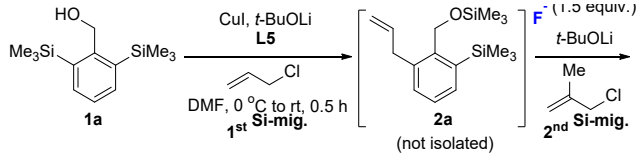


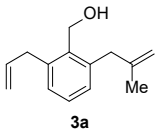
copper species via *endo*-cyclic C-Si bond cleavage. Bipyridine ligands **L1**and **L2** afforded moderate ratios (entries 6 and 7), while more rigid *o*-phenanthroline **L3** significantly improved the ratio to 9:1 (entry 8). Substitution on *o*-phenanthroline greatly affected selectivity. Introducing two methyl groups at the 2- and 9-positions in **L4** lowered the ratio to 4.8:1 (entry 9), probably because the increased steric hindrance weakened the coordination of *o*-phenanthroline with copper. Conversely, the electron-donating effects of the 4,7-dimethyl groups in **L5** appeared to strengthen the coordination with copper, increasing the ratio to 20:1 and giving **2a** in 93% yield (entry 10). Consistent with this idea,

L6, containing two extra dimethyl groups at 3- and 8-positions, led to a similarly high ratio as **L5** (entry 11). Tridentate ligand **L7** was also tested, but less effective than **L5**, affording a ratio of 7:1 (entry 12).

With the optimal conditions for the first cross-coupling in hand, we examined installation of the second Csp^3-electrophile (E^2-X^2) in the same pot. Key for this step is that the O-Si bond in **2** is cleaved selectively over the C-Si bond, thus exposing the alkoxide required for the second silyl migration (*turning on*). Among several fluoride sources tested, KF, CsF and TBAT were unable to remove O-trime

TABLE 2. Screening of Reaction Conditions of Sequential cross-coupling with Csp^3/Csp^3-electrophiles E^1-X^1/E^2-X^2[a]





Entry	F	*t*-BuOLi[b]	3a(%)[c]
1	KF	-	N.D.
2	CsF	-	N.D.
3	TBAT	-	N.D.
4	TBAF	-	41
5	TBAF	2.0 equiv	74

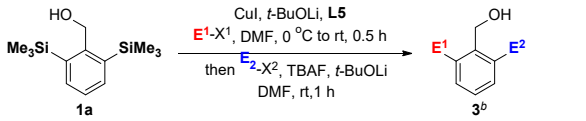
[a]Reaction conditions: **1st Si-migration**: Cu(I) (0.05 mmol), *t*-BuOLi (0.12 mmol) in DMF, 0 °C to rt, 10 min, then **L5** (0.05 mmol), **1a** (0.1 mmol), allylchloride (0.1 mmol), rt, 30 min; **2nd Si-migration**: 2-methyl allylchloride (0.25 mmol), F-source. [b]*t*-BuOLi used in the second cross-coupling. [c]Isolated yields.

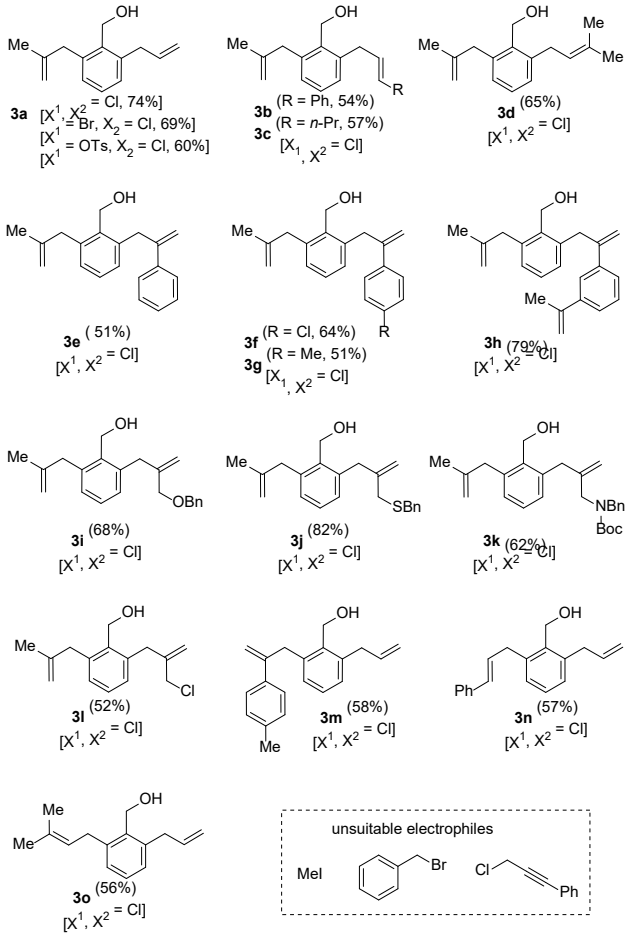
thylsilyl group even at 60 °C (Table 2, entries 1-3). We were delighted to find that TABF functioned effectively for completely selective O-desilylation. However, the resulting alkoxide intermediate only underwent the second silyl migration partially. The desired unsymmetrical two-fold diallylated benzyl alcohol **3a** was obtained in a moderate yield of 41% through the second cross-coupling with 2-methyl allylchloride followed by in situ O-desilylation (entry 4). To solve this problem, another 2.0 equiv. of *t*-BuOLi were added to complete the second silyl migration. The yield of **3a** was improved to 74% yield (entry 5).

The scope of Csp^3/Csp^3-electrophiles E^1-X^1/E^2-X^2 were tested and the results were shown in Table 3. The 2-methyl allylic electrophile was fixed as E^1 firstly, in which Cl, Br and OTs were all compatible leaving groups. The reaction worked well with various E^2-X^2, which were either (*E*)-3-mono-substituted or 3,3′-disubstituted allylchlorides, leading to **3b-d** via addition at the more accessible 1-position. Substituents at the 2-position in E^2-X^2 varied from aryl groups (**3e-h**) to methylene groups substituted with O, S, or N (**3i-k**). The reaction of **1a** with allyl dichloride afforded **3l** in 52% yield. The allylchloride moiety in **3l**, which is sterically more hindered than allyl dichloride, did not act as a competitive electrophile to interfere with the second cross-coupling. Similar to E^2-X^2, 2- or 3-mono-substituted or 3,3′-disubstituted allylchlorides were also suitable for the first cross-coupling, giving **3m-o** in good yields. The approach currently appears only working for allylic electrophiles, as MeI, BnBr or propargyl chloride cannot be cross-coupled with **1a** either as E^1-X^1 or E^2-X^2.

Sequential cross-coupling of 1a with Csp^2/Csp^3-electrophiles Compared with one-pot installation of two Csp^3-electrophiles, sequential cross-coupling of **1a** with Csp^2/Csp^3-electrophiles proved more challenging because of potential incompatibility of reaction conditions. 1-Methyl vinylbromide was initially used to examine the reaction conditions for the first cross-coupling. Typically, strong polar solvents such as DMF[8b] or THF/HMPA [7d] are required to facilitate the silyl migration in Cu/Pd-catalyzed cross-coupling with aryl or vinyl halides. In our case, these solvents indeed promoted silyl

TABLE 3. Scope of Csp^3/Csp^3-electrophiles E^1-X^1 and E^2-X^2[a]

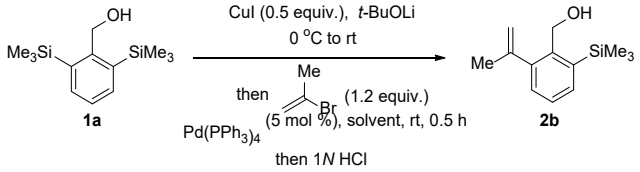




[a]Reaction conditions: **1st Si-migration**: Cu(I) (0.05 mmol), *t*-BuOLi (0.12 mmol) in DMF, 0 °C to rt, 10 min, then **L5** (0.05 mmol), **1a** (0.1 mmol), E^1-X^1 (0.1 mmol), rt, 30 min; **2nd Si-migration**: E^2-X^2 (0.25 mmol), TBAF (0.15 mmol), *t*-BuOLi (0.2 mmol), rt, 1 h. [b]Isolated yields.

migration, but they appeared to interfere with the step of cross-coupling, only providing a complex mixture containing a trace amount of **2b** (Table 4, entries 1 and 2). To our surprise, we found that non-polar toluene, which barely effects C to O silyl migration, functioned efficiently for both silyl migration and cross-coupling, giving **2b** in 43% yield after selective O-desilylation by acidic hydrolysis (entry 3). We speculated that eliminating the steric repulsion between the alkoxide moiety and two silyl groups might drive silyl migration in non-polar toluene. Increasing the loading of *t*-BuOLi from 1.2 equiv. to 2.2 equiv. further favored complete silyl migration to improve the yield of **2b** to 85% (entry 4). Other solvents such as THF, Et_2O or CH_2Cl_2 were less effective, leading to much lower yields (entries 5-7). *o*-Phenanthroline **L5**, which facilitated the cross-coupling of **1a** with Csp^3-electrophiles, did not favor the cross-coupling with Csp^2-electrophile, instead, interfered with the reaction to give a complex mixture (entry 8).

TABLE 4. Screening of Reaction Conditions of Cross-coupling with Csp^2-electrophile E^1-X^1[a]



Entry	*t*-BuOLi (equiv.)	solvent	Ligand	**2b** (%)[b]
1	1.2	DMF	—	N.D.
2	1.2	THF/HMPA	—	N.D.
3	1.2	toluene	—	43%
4	2.2	toluene	—	85%
5	2.2	THF	—	71%
6	2.2	Et_2O	—	34%
7	2.2	CH_2Cl_2	—	31%
8	2.2	toluene	**L5**	N.D.

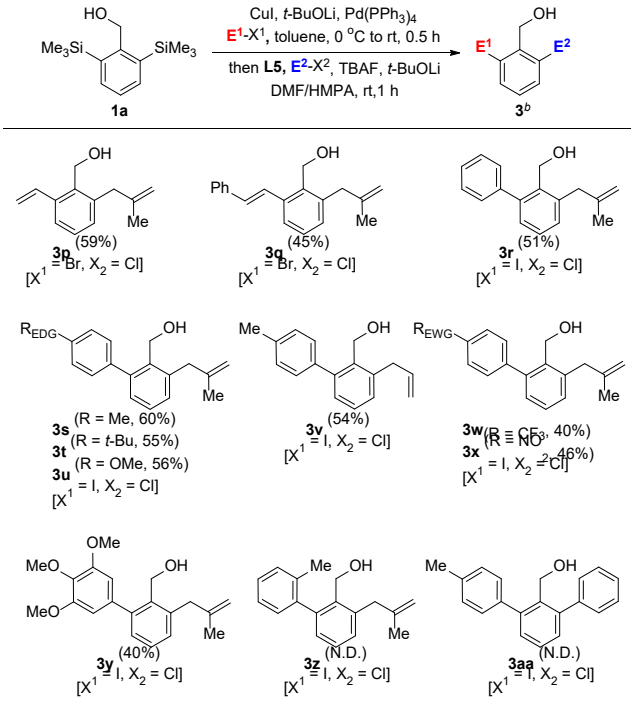
[a]Reaction conditions: Cu(I) (0.05 mmol), *t*-BuOLi, 0 °C to rt, 10 min; then $Pd(PPh_3)_4$ (5 mol %), **1a** (0.1 mmol), 1-methyl vinylbromide (0.12 mmol), rt, 30 min. [b]Isolated yields.

The solvent also has a great impact on the second cross-coupling with Csp^3-electrophile 2-methyl allylchloride in the same pot. Toluene or a co-solvent of toluene/DMF only afforded a complex mixture. Thus, toluene was removed under reduced pressure followed by adding DMF/HMPA (3:1) as the co-solvent for the second cross-coupling.[16] TABF, which is required to turn on the second silyl migration, was added slowly to minimize formation of the *O*-allylated by-product. A range of vinyl bromides and aryl iodides were tolerated to give styrene derivatives **3p** and **3q**[17] and biaryl compounds **3r-w** in generally good yields (Table 5). The electronic nature of the substituents on the phenyl ring in E^1-X^1 showed little impact on the efficiency. But, 2-methyl iodobenzene, which is sterically demanding, cannot be installed in the first cross-coupling to give **3z**. In addition, we have been unable to expand the process to Csp^2/Csp^2-electrophiles to form **3aa**: only protodesilylation occurred at the 6- position under all the conditions we tried. We suspect that steric hindrance during cross-coupling with the second Csp^2-electrophile inhibits the desired reaction.

Sequential cross-coupling of 1b with Csp^3/Csp^3-electrophiles E^1-X^1 and E^2-X^2 The 2,4,6-tri(trimethylsilyl) benzyl alcohol **1b** also served as a good substrate for one-pot cross-coupling with Csp^3/Csp^3-electrophiles to give **3ab-3ad**. Reaction with Csp^2/Csp^3-electrophiles afforded **3ae** and **3af** in higher yields than those obtained from disilylated **1a** (Table 6). Again, TBAF desilylated the O-Si in **2** selectively, without affecting the two other C-Si bonds. Once the alkoxide was exposed, only the C-Si bond at the 6-position was cleaved by the second silyl migration. Thus, the C-Si bond at the 4-position remained in **3** and enabled further functionalization as shown in Scheme 3.

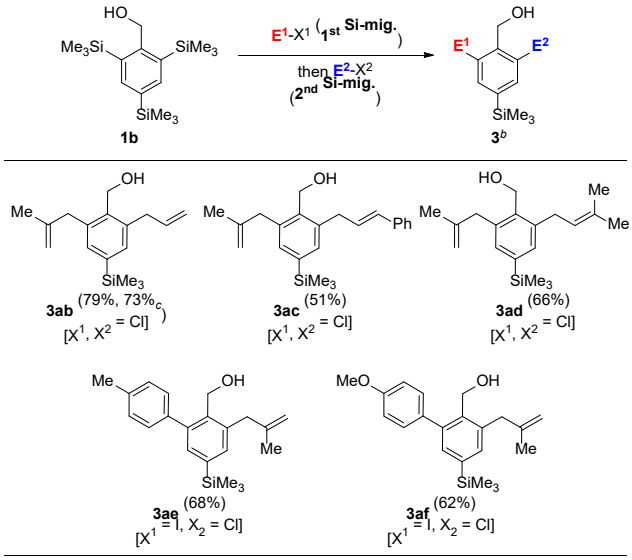
Reaction of **3ae** with 2.5 equiv. of NBS led to cyclization together with bromination of arylsilane into arylbromide, giving the isochroman[18] derivative **8** in 82% yield. The arylbromide moiety was chemoselectively transformed into **9a** by Suzuki cross-coupling with furylboronate, into **9b** by Kumada cross-coupling with aryl magnesium bromide and into **9c** by Sonogashira cross-coupling with terminal alkyne. In this way, three C-Si bonds at 2-, 4- and 6-positions in **1b** were functionalized in a controlled, chemoselective manner.

TABLE 5. Scope of Csp^2/Csp^3-electrophiles E^1-X^1 and E^2-X^2[a]

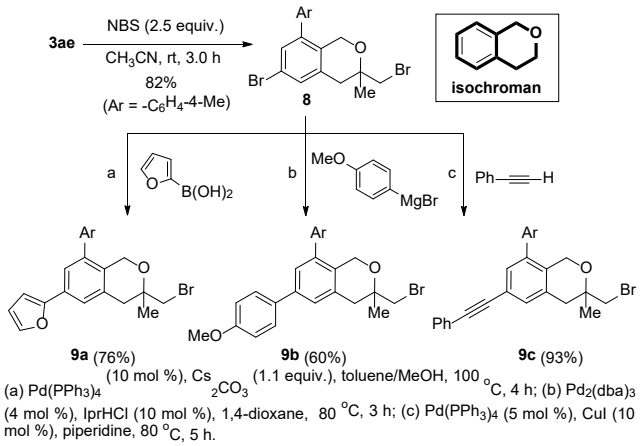


[a]Reaction conditions: **1st Si-migration**: Cu(I) (0.05 mmol), *t*-BuOLi (0.22 mmol) in toluene, 0 °C to rt, 10 min, then $Pd(PPh_3)_4$ (5 mol %), **1a** (0.1 mmol), E^1-X^1 (0.12 mmol), rt, 30 min; **2nd Si-migration**: E^2-X^2 (0.25 mmol), *t*-BuOLi (0.22 mmol), TBAF (0.2 mmol), **L5** (0.05 mmol) in DMF/HMPA (3:1), rt, 1 h. [b]Isolated yields.

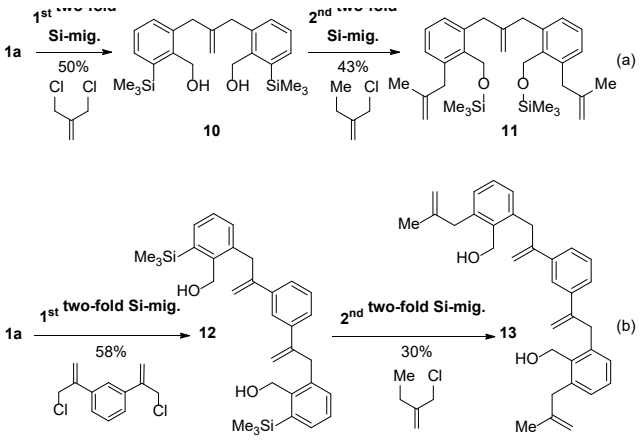
TABLE 6. Reaction of 1b with Csp^3/Csp^3- and Csp^2/Csp^3-electrophiles E^1-X^1 and E^2-X^2[a]



[a]**3ab**-**3ad** were synthesized following the reaction conditions in Table 2; **3ae** and **3af** were synthesized following the conditions in Table 5. [b]Isolated yields. [c]The yield was obtained by on the scale using 0.3 mmol of **1b**.



SCHEME 3. Dibromination of 3ae and its cross-coupling reactions to form 9a-c.



SCHEME 4. Five-component cross-coupling to construct complex symmetric compounds 11 and 13.

Sequential five-component cross-coupling The three-component reaction was not limited to cross-coupling of **1a** with two electrophiles: we were also able to connect allyl dichloride with 2.0 equiv. of **1a** (Scheme 4a). The first two-fold silyl migration generated **10** in 50% yield. The second two-fold silyl migration of **10** initiated cross-coupling with 2.0 equiv. of allyl monochloride, giving **11** in 43% yield. Following the similar operation, using the first electrophile in which two allylchlorides were tethered by a phenyl ring afforded **12** and **13** with high density of aryl and allyl moieties. In this way, we were able to use this two-step sequence to rapidly assemble five components into complex symmetric structures.[19]

CONCLUSION

In summary, we have developed a sequential [1,4]-Csp^2 to O-silyl migration that enables two-fold unsymmetrical 2,6-bifunctionalization of arenes in one pot. The hydroxyl group acts as an "on-off-on" switch to cleave successively two C-Si bonds at the 2- and 6-positions, installing Csp^3/Csp^3 or Csp^2/Csp^3 electrophiles in a well-controlled manner. The approach allows chemoselective functionalization of three C-Si bonds in 2,4,6-tri(trimethylsilyl) benzyl alcohol to give isochroman derivatives. A two-step five-component cross-coupling was developed to construct complex symmetric structures. More applications of this reaction in organic synthesis are under development.

EXPERIMENTAL SECTION

Commercial reagents were used without any purification. All reactions were performed using common anhydrous, inert atmosphere techniques. Reactions were monitored by TLC which was performed on glass-backed silica plates and visualized using UV, $KMnO_4$ stains, $H_3PO_4{\cdot}12MoO_3$/EtOH stains, H_2SO_4 (conc.)/ anisaldehyde/ EtOH stains. Column chromatography was performed using silica gel (200-300 mesh) eluting with EtOAc/petroleum ether. ^1H NMR spectra were recorded at 400 MHz (Varian and Bruker) and 600 MHz (Agilent), ^{13}C NMR spectra were recorded at 100 MHz (Bruker) and 150 MHz (Agilent) using $CDCl_3$ (except where noted) with TMS as standard. Infrared spectra were obtained using KCl plates on a VECTOR22. High-resolution mass spectral analyses performed on Waters Q-TOF. CH_2Cl_2, TMEDA, DMF, Et_2NH and Et_3N were distilled from CaH_2. THF and PhMe were distilled from sodium. The heat source of reactions that require heating is oil bath. All spectral data obtained for new compounds are reported here.

Preparation of allyl chloride: **S1**, **S6**, **S7**, **S8** are known compounds, and **S2**, **S3**, **S4** and **S5** are new compounds. Other electrophiles used in this work are commercially available. Please see Scheme S1 in supporting information for chemical structures of **S1**-**S8** see Scheme 1 in supporting information)

*(3-Chloroprop-1-en-2-yl)benzene (**S1**).* A solution of 2-phenyl-1-propene (1.18 g, 10 mmol), NCS (1.6 g, 12 mmol), $Yb(OTf)_3$ (310 mg, 0.5 mmol) and TMSCl (54 mg, 0.5 mmol) in CH_2Cl_2 (40 mL) and THF (10 mL) was stirred at room temperature for 30 min. The reaction was quenched with sat. aq. NaCl (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The

combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (petroleum ether) to afford **S1** (0.7 g, 46% yield) as a colorless liquid. Please see Scheme S2 in supporting information for the synthesis of **S1**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.42 – 7.27 (m, 3H), 5.56 (s, 1H), 5.45 (s, 1H), 4.46 (s, 2H). The physical and spectral data were consistent with those previously reported.[20]

*1-(3-Chloroprop-1-en-2-yl)-4-methylbenzene (**S2**).* Using the same procedure as that used for **S1**: 1-(3-chloroprop-1-en-2-yl)-4-methylbenzene (0.331g, 2.5 mmol), NCS (0.40 g, 3 mmol), $Yb(OTf)_3$ (77.5 mg, 0.125 mmol), TMSCl (13.5 mg, 0.125 mmol) in CH_2Cl_2 (20 mL) and THF (5 mL) at room temperature for 30 min afforded **S2** (0.21 g, 50% yield) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 5.52 (s, 1H), 5.43 – 5.35 (m, 1H), 4.45 (d, *J* = 0.9 Hz, 2H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.8, 138.1, 134.8, 129.2, 126.0, 115.9, 46.6, 21.1. IR (neat) cm^{-1} 3050, 2961, 2866, 1566, 1513, 1213, 903, 822; HRMS (ESI-TOF), m/z: $(M+Na)^+$ calcd for $C_{10}H_{11}ClNa$ 189.0441; found 189.0442.

*1-Chloro-4-(3-chloroprop-1-en-2-yl)benzene (**S3**).* Using the same procedure as that used for **S1**: 1-chloro-4-(3-chloroprop-1-en-2-yl)benzene (0.381g, 2.5 mmol), NCS (0.40 g, 3 mmol), $Yb(OTf)_3$ (77.5 mg, 0.125 mmol), TMSCl (13.5 mg, 0.125 mmol) in CH_2Cl_2 (20 mL) and THF (5 mL) at room temperature for 30 min afforded **S3** (0.21 g, 45% yield) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 5.55 (s, 1H), 5.47 (s, 1H), 4.44 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.9, 128.7, 128.5, 127.9, 127.5, 117.4, 46.4. IR (neat) cm^{-1}2926, 1625, 1595, 1492, 1451, 1397, 1100, 1012, 912, 832; HRMS (ESI-TOF), m/z: $(M+H)^+$ calcd for $C_9H_9Cl_2$ 187.0076; found 187.0078.

*1-(3-Chloroprop-1-en-2-yl)-3-(prop-1-en-2-yl)benzene (**S4**) AND 1,3-bis(3-chloroprop-1-en-2-yl)benzene (**S5**).* A solution of 1, 3-di(prop-1-en-2-yl)benzene (0.79 g, 5 mmol), NCS (1.6 g, 12 mmol), $Yb(OTf)_3$ (310 mg, 0.25 mmol), TMSCl (54 mg, 0.25 mmol) was stirred in CH_2Cl_2 (40 mL) and THF (10 mL) at room temperature for 3 h. The reaction was quenched with sat. aq. NaCl (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (petroleum ether) to afford **S4** (0.451 g, 47% yield) as a colorless liquid and **S5** (0.227 g, 20% yield) as a colorless liquid. Please see Scheme S3 in supporting information for the syntheses of **S4** and **S5**. **S4:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.50 – 7.30 (m, 3H), 5.59 (s, 1H), 5.49 (s, 1H), 5.40 (s, 1H), 5.13 (s, 1H), 4.50 (s, 2H), 2.19 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.1, 143.1, 141.6, 137.7, 128.4, 125.4, 125.2, 123.4, 116.8, 112.9, 46.6, 21.8. IR (neat) cm^{-1} 3087, 2931, 1803, 1628, 1596, 1574, 1447, 1375, 1259, 1050, 1003, 892, 801; HRMS (ESI-TOF) m/z: $(M+H)^+$ calcd for $C_{12}H_{14}Cl$ 193.0779; found 193.0779. **S5:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 1.8 Hz, 1H), 7.48 – 7.39 (m, 2H), 5.60 (s, 2H), 5.50 (s, 2H), 4.49 (s, 4H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.7, 138.0, 128.6, 126.0, 124.1, 117.2, 46.5. IR (neat) cm^{-1} 2924, 2852, 1834, 1626, 1449, 1259, 1050, 907, 801; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{12}H_{12}Cl_2Na$ 249.0208; found 249.0217.

*(((2-(Chloromethyl)allyl)oxy)methyl)benzene (**S6**).* To a suspension of NaH (120 mg, 5.00 mmol) in THF (5.0 mL) was added benzyl alcohol (0.572 mL, 5.50 mmol) at room temperature. The reaction mixture was stirred for 1 h and then slowly transferred to a solution of 3-chloro-2-(chloromethyl)prop-1-ene (656 mg, 5.25 mmol) in THF at 0 °C. The reaction mixture was stirred for 12 h at room temperature, then quenched with 1*N* HCl and extracted with EtOAc (3 ×10 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 200:1→50:1) to afford **S6** (0.46 g, 47% yield) as a colorless liquid. Please see Scheme S4 in supporting information for the synthesis of **S6.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 5.33 (s, 1H), 5.28 (d, *J* = 1.3 Hz, 1H), 4.54 (s, 2H), 4.15 (d, *J* = 1.0 Hz, 2H), 4.13 (s, 2H). The physical and spectral data were consistent with those previously reported.[21]

*Benzyl(2-(chloromethyl)allyl)sulfane (**S7**).* To a suspension of Cs_2CO_3 (1.295 g, 5.8 mmol) in DMF (15 mL) was added 3-chloro-2-chloromethyl-1-propene (0.50 mL, 4.3 mmol) and benzyl mercaptan (0.55 mL 4.73 mmol). The suspension was heated to 60 °C and stirred for 16 h. The reaction was quenched with H_2O (20 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with H_2O (2 x 10 mL), dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 200:1→100:1) to afford **S7** (0.584 g, 64% yield) as a colorless liquid. Please see Scheme S5 in supporting information for the synthesis of **S7**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 5H), 5.29 – 5.24 (d, *J* = 1.3 Hz, 1H), 5.07 (d, *J* = 1.3 Hz, 1H), 4.21 (d, *J* = 0.9 Hz, 2H), 3.62 (s, 2H), 3.20 (d, *J* = 1.1 Hz, 2H). The physical and spectral data were consistent with those previously reported.[22]

*tert-Butyl benzyl(2-(chloromethyl)allyl)carbamate (**S8**).* To a solution of *tert*-butyl benzylcarbamate (0.5 g, 2.41 mmol) and 3-chloro-2-(chloromethyl) prop-1-ene (0.335 mL, 2.89 mmol) in DMF (2.5 mL) was added NaH (0.145 g, 3.62 mmol). After stirring for 6 h, the reaction was quenched with dropwise addition of water (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with H_2O (2 × 5 mL), dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 200:1→50:1) to afford **S8** (0.403 g, 57% yield) as a colorless liquid. Please see Scheme S6 in supporting information for the synthesis of **S8**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.19 (m, 5H), 5.28 (s, 1H), 5.04 (s, 1H), 4.42 (s, 2H), 4.01 (s, 2H), 3.91 (d, 2H), 1.48 (s, 9H). The physical and spectral data were consistent with those previously reported.[23]

Preparation of 1a (Please see Scheme S7 in supporting information for the synthesis of **1a**.) *N,N-Diethyl-2-(trimethylsilyl)benzamide (**S9**).* To a solution of TMEDA (0.5 mL, 3.3 mmol) and *N*, *N*-diethylbenzamide (0.53 g, 3 mmol) in anhydrous THF (50 mL) was added *s*-BuLi (4.5 mL, 1.0 M in pentane) dropwise at -78 °C under Ar atmosphere. TMSCl (0.5 mL, 3.9 mmol) was added before the reaction was stirring for 1 h at -78 °C. The resulted mixture was allowed to

warm to room temperature with stirring for additional 4 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was prfied by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 200:1→30:1) to afford **S9** (0.6 g, 80% yield) as a white solid. 1H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, *J* = 3.6 Hz, 1H), 7.31 -7.26 (m, 2H), δ 7.17 (d, *J* = 3.6 Hz, 1H), 3.53 (q, *J* = 7.2 Hz, 2H), 3.15 (q, *J* = 7.2 Hz, 2H), 1.26 (q, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H), 0.26 (s, 9 H). The physical and spectral data were consistent with those previously reported.[24]

*N,N-Diethyl-2,6-bis(trimethylsilyl)benzamide (**4a**)*. Using the same procedure as that used for **S9** (0.75 g, 3 mmol), *s*-BuLi (4.5 mL, 1.0 M in pentane), TMEDA (0.5 mL, 3.3 mmol) and TMSCl (0.5 mL, 3.9 mmol) in THF (50 mL) at -78 °C to room temperature for 4 h afforded **4a** (0.89 g, 92% yield) as a colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.24 (m, 1H), 3.57 (q, *J* = 7.2 Hz, 2H), 3.07 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.25 (s, 18H) ^{13}CNMR (150 MHz, $CDCl_3$) δ 172.2, 147.6, 135.8, 135.5, 126.4, 43.2, 38.5, 13.2, 12.8, 0.4. The physical and spectral data were consistent with those previously reported.[12]

*2,6-Bis(trimethylsilyl)benzaldehyde (**5a**).*To a solution of **4a** (0.96 g, 3.0 mmol) in CH_2Cl_2 (20 mL) was added EtOTf (1.07 g, 6.0 mmol). The reaction was stirred at 45 °C for 4 h before removing CH_2Cl_2 and adding THF (10 mL) as solvent. The mixture was cooled to 0 °C and stirred for 20 min. To the resulting mixture was added $LiAlH(OEt)_3$ (18 mL, 1.0 M in THF) dropwise at 0 °C. The reaction was stirred overnight at room temperature before quenching with aq. NaOH (15 mL, 1.0 M) at 0 °C. The mixture was filtered and the white solid was washed with EtOAc (3 × 10 mL). The combined organic layers were then dried over Na_2SO_4, filtered and cocentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 200:1) to afford **5a** (0.55 g, 73% yield) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 0.38 (s, 18H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 193.8, 145.8, 144.1, 136.2, 131.4, 0.7. The physical and spectral data were consistent with those previously reported.[12]

*(2,6-Bis(trimethylsilyl)phenyl)methanol (**1a**).*To a solution of **5a** (1.2 g, 4.8 mmol) in MeOH (15 mL) was added $NaBH_4$ (0.363 g, 9.6 mmol). The reaction was stirred at room temperature for 2 h before quenching with sat. aq. NH_4Cl (10 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 200:1→50:1) to afford **1a** (1.0 g, 83% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.4 Hz, 2H), 7.29 (dd, *J* = 7.4 Hz, 1H), 4.83 (d, *J* = 5.7 Hz, 2H), 1.33 (t, *J* = 5.7 Hz, 1H), 0.38 (s, 18H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.3, 140.1, 136.3, 126.7, 65.3, 1.0; IR (neat) cm^{-1} 3337, 3043, 2952, 2899, 1557, 1245, 1021, 830; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{13}H_{24}OSi_2Na$ 275.1258, found 275.1263; mp: 74.1 -77.5 °C.

Preparation of 1b (Please see Scheme S8 in supporting information for the synthesis of **1b**.) *N,N-Diethyl-4-(trimethylsilyl)benzamide (**S10**).*To a solution of (4-bromophenyl)trimethylsilane (2.06 g, 0.9 mmol) in THF (24 mL) was added dropwise a solution of *n*-BuLi (3.6 mL, 2.5 M in hexanes) at -78 °C under Ar atmosphere. The reaction was stirred at -78 °C for 25 min before transferring via cannula to a solution of diethylcarbamic chloride (3.64 g, 2.7 mmol) in THF (24 mL) at -78 °C. After stirring for 2 h at -78 °C, the mixture was allowed to warm to room temperature overnight. The reaction was quenched with sat. aq. $NaHCO_3$ (20 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 200:1→50:1) to afford **S10** (2.16 g, 96% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.54 (s, 2H), 3.26 (s, 2H), 1.25 (s, 3H), 1.11 (s, 3H), 0.26 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.3, 141.7, 137.5, 133.3, 125.4, 43.2, 39.1, 14.2, 12.9, -1.2. IR (neat) cm^{-1} 2956, 1628, 1545, 1499, 1423, 1286, 1116, 838, 836; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{14}H_{23}NOSiNa$ 272.1441; found 272.1441; mp: 56.9-58.7 °C.

*N,N-Diethyl-2,4-bis(trimethylsilyl)benzamide (**S11**):* Using the same procedure as that used for **S9**. **S10** (0.75 g, 3 mmol), *s*-BuLi (4.5 mL, 1.0 M in pentane), TMEDA (0.5 mL, 3.3 mmol) and TMSCl (0.5 mL, 3.9 mmol) in THF (50 mL) at -78 °C to room temperature for 4 h afforded **S11** (0.59 g, 61% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.60 – 7.42 (m, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 3.56 (q, *J* = 7.1 Hz, 2H), 3.19 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.29 (s, 9H), 0.27 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.4, 143.2, 139.9, 139.8, 136.1, 133.4, 124.6, 43.4, 38.9, 13.8, 12.8, 0.1, -1.1. IR (neat) cm^{-1} 2954, 2897, 1630, 1577, 1530, 1423, 1276, 1260, 1061, 943, 830; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{17}H_{31}NOSi_2Na$ 344.1836; found 344.1841; mp: 37.1-39.7 °C

*N,N-Diethyl-2,4,6-tris(trimethylsilyl)benzamide (**4b**).* Using the same procedure as that used for **S9**. **S11** (0.97 g, 3 mmol), *s*-BuLi (4.5 mL, 1.0 M in pentane), TMEDA (0.5 mL, 3.3 mmol) and TMSCl (0.5 mL, 3.9 mmol) in THF (50 mL) at -78 °C to room temperature for 4 h afforded **4b** (0.8 g, 67% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 1.3 Hz, 1H), 3.66 – 3.46 (m, 2H), 3.25 – 2.96 (m, 2H), 1.33 – 1.18 (m, 3H), 1.18 – 0.87 (m, 3H), 0.27 (s, 27H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.4, 148.2, 140.6, 137.7, 134.4, 43.4, 38.6, 13.3, 12.9, 0.6, -1.0; IR (neat) cm^{-1} 2953, 2897, 1621, 1482, 1406, 1379, 1320, 1246, 1086, 942, 823, 764, 690; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{20}H_{39}NOSi_3Na$: 416.2232, found 416.2229; mp: 100.1-103.9 °C

*2,4,6-Tris(trimethylsilyl)benzaldehyde (**5b**).* Using the same procedure as that used for **5a**. **4b** (0.96 g, 3.0 mmol), EtOTf (1.07 g, 6.0 mmol) in CH_2Cl_2 (20 mL) at 45 °C for 4 h. Then remove CH_2Cl_2, the mixture and $LiAlH(OEt)_3$ (18 mL, 1.0 M in THF) in THF (10 mL) at room temperature overnight afforded **5b** (0.6 g, 62% yield) as a colorless liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 7.91 (s, 2H), 0.38 (s, 18H), 0.31 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.2, 146.2, 144.9, 142.4, 141.2, 0.9, -1.1; IR (neat) cm^{-1} 2954, 2898, 2856, 1694, 1520, 1406, 1247, 854, 831; HRMS (ESI-

TOF) m/z: $(M+Na)^+$ calcd for $C_{16}H_{30}OSi_3Na$ 345.1497, found 345.1501.

*(2,4,6-Tris(trimethylsilyl)phenyl)methanol (**1b**).* Using the same procedure as that used for **1a**. **5b** (1.2 g, 3.7 mmol) and $NaBH_4$ (0.28 g, 7.4 mmol) in MeOH (15 mL) at room temperature for 2 h afforded **1b** (0.96 g, 80% yield) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 2H), 4.81 (d, *J* = 5.6 Hz, 2H), 0.37 (s, 18H), 0.22 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 151.7, 141.2, 138.6, 137.8, 65.2, 1.0, -1.1. IR (neat) cm^{-1} 3393, 2953, 2897, 1528, 1398, 1375, 1309, 1246, 1004, 874, 827. HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{16}H_{32}OSi_3Na$ 347.1653; found 347.1656; mp: 94.5-96.2 °C.

Preparation of Intermediate 2a. *3-Allyl-2-(((trimethylsilyl)oxy)methyl)phenyl)trimethylsilane (**2a**):* To a solution of CuI (10 mg, 0.05 mmol) in DMF (3.0 mL) was added *t*-BuOLi (0.12 mL, 1.0 M in THF) at 0 °C under argon atmosphere. The reaction mixture was stirred at room temperature for 10 min. Then **L5** (0.05 mmol), **1a** (25.2 mg, 0.1 mmol) and 3-chloroprop-1-ene (7 mg, 0.11 mmol) was added successively and kept stirring at room temperature for 0.5 h. The reaction was quenched with 2 mL of saturated NaCl solution, extracted with EtOAc (3 × 5 mL) and washed with H_2O (3 × 2 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 200:1→100:1) to afford **2a** (27.3 mg, 93% yield) as a colorless liquid.^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 4.4 Hz, 1H), 7.31 – 7.21 (d, *J* = 4.4 Hz, 2H), 6.01 (m, 1H), 5.14 – 4.95 (m, 2H), 4.72 (s, 2H), 3.52 (dt, *J* = 6.4, 1.6 Hz, 2H), 0.34 (s, 9H), 0.21 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.9, 140.2, 139.6, 137.8, 133.0, 131.3, 127.6, 115.6, 61.9, 37.0, 1.0, 0.3; IR (neat) cm^{-1} 3059, 2955, 1637, 1429, 1249, 1146, 836, 687, 635; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{16}H_{28}OSi_2Na$ 315.1578; found 315.1571. Because the by-product **6** was unstable on the silica gel column, we were not able to isolate and characterize **6**. The mixed ^1H NMR spetra (Table 1, entry 5) was provided in Supporting Information.

Synthesis of 3a – 3o. *2-Allyl-6-(2-methylallyl)phenyl)methanol (**3a**):* To a solution of CuI (10 mg, 0.05 mmol) in DMF (0.8 mL) was added *t*-BuOLi (0.12 mL, 1.0 M in THF) at 0 °C under Ar atmosphere. The reaction was stirred at room temperature for 10 min. **L5** (10.5 mg, 0.05 mmol), **1a** (25.2 mg, 0.1 mmol) and 3-chloro-2-methylprop-1-ene (9.6 mg, 0.1 mmol) was added successively. The resulted mixture was stirred at room temperature for 0.5 h. Then 3-chloroprop-1-ene (19 mg, 0.25 mmol), TBAF (0.15 mL, 1.0 M in THF) and *t*-BuOLi (0. 2 mL, 1.0 M in THF) was added successively. The resulted mixture was stirred at room temperature for 1 h. The reaction was quenched with sat. aq. NaCl (2 mL), extracted with EtOAc (3 × 5 mL) and washed with H_2O (3 × 3 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 200:1→30:1) to afford **3a** (15 mg, 74% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.5 Hz, 1H), 7.09 (m, 2H), 6.06 (ddt, *J* = 16.5, 10.2, 6.1 Hz, 1H), 5.07 (dd, *J* = 10.1, 1.0 Hz, 1H), 4.97 (dd, *J* = 17.1, 1.4 Hz, 1H), 4.84 (s, 1H), 4.64 (s, 2H), 4.48 (s, 1H), 3.56 (d, *J* = 6.0 Hz, 2H), 3.47 (s, 2H), 1.79 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 147.0, 139.4, 139.0, 138.3, 137.0, 129.2, 128.7, 128.1, 115.6, 111.6, 58.7, 41.6, 37.3, 22.9; IR (neat) cm^{-1} 3318, 3074, 2915, 1641, 1589, 1442, 1276, 996, 892, 838; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{14}H_{18}ONa$ 225.1250; found 225.1252.

*(2-Cinnamyl-6-(2-methylallyl)phenyl)methanol (**3b**):* Using the same procedure as that used for **3a** afforded **3b** (15 mg, 54% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.01 (m, 7H), 7.09 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.51- 6.27 (m, 2H), 4.85 (s, 1H), 4.70 (s, 2H), 4.50 (s, 1H), 3.71 (d, *J* = 5.6 Hz, 2H), 3.47 (s, 2H), 1.79 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 147.1, 139.8, 139.0, 137.3, 137.0, 130.8, 129.8, 129.3, 128.7, 128.4, 128.2, 127.1, 126.0, 111.7, 58.8, 41.7, 36.4, 22.9. IR (neat) cm^{-1} 3329, 2922, 1648, 1446, 1276, 1261,996, 891; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{20}H_{22}ONa$ 301.1563; found 301.1572.

*(E)-(2-(Hex-2-en-1-yl)-6-(2-methylallyl)phenyl)methanol (**3c**):* Using the same procedure as that used for **3a** afforded **3c** (14 mg, 57% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 5.67 – 5.56 (m, 1H), 5.46 – 5.34 (m, 1H), 4.82 (s, 1H), 4.65 (d, *J* = 6.1 Hz, 2H), 4.46 (s, 1H), 3.48 (d, *J* = 6.2 Hz, 2H), 3.45 (s, 2H), 1.96 (m, 2H), 1.77 (s, 3H), 1.35 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.0, 140.5, 138.9, 137.0, 131.7, 129.8, 129.0, 128.5, 128.1, 111.8, 58.7, 41.6, 36.3, 34.6, 22.9, 22.5, 13.6. IR (neat) cm^{-1} 3321, 3070, 2958, 2924, 2856, 1649, 1586, 1444, 1375, 1260, 1174, 996, 970, 890; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{17}H_{24}ONa$ 267.1719; found 267.1724.

*(2-(2-Methylallyl)-6-(3-methylbut-2-en-1-yl)phenyl)methanol (**3d**):* Using the same procedure as that used for **3a** afforded **3d** (15 mg, 65% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 6.8 Hz, 1H), 7.13 – 7.09 (m, 1H), 7.04 (dd, *J* = 7.4, 1.2 Hz, 1H), 5.26 (m, 1H), 4.84 (dd, *J* = 1.9, 1.3 Hz, 1H), 4.65 (s, 2H), 4.50 (d, *J* = 1.0 Hz, 1H), 3.49 (d, *J* = 7.0 Hz, 2H), 3.46 (s, 2H), 1.79 (d, *J* = 1.1 Hz, 3H), 1.76 (d, *J* = 1.2 Hz, 3H), 1.73 (d, *J* = 1.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 147.0 , 141.6 , 138.9 , 136.9, 132.4, 128.8, 128.2, 128.1, 123.8, 111.6, 58.8, 41.6, 32.0, 25.7, 22.9, 17.9. IR (neat) cm^{-1} 3312, 2967, 2919, 2854, 1649, 1587, 1444, 1375, 1276, 1261, 1100, 997, 890. HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{16}H_{22}ONa$ 253.1563; found 253.1573.

*(2-(2-Methylallyl)-6-(2-phenylallyl)phenyl)methanol (**3e**):* Using the same procedure as that used for **3a** afforded **3e** (14 mg, 51% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 2H), 7.38 – 7.27 (m, 3H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.3 Hz, 2H), 5.44 (s, 1H), 4.83 (s, 1H), 4.65 (s, 1H), 4.62 (d, *J* = 5.7 Hz, 2H), 4.46 (s, 1H), 3.95 (s, 2H), 3.47 (s, 2H), 1.78 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ148.3, 147.0, 141.1, 139.0, 138.9, 137.34, 129.4, 129.3, 128.3, 128.1, 127.6, 125.9, 114.0, 111.6, 59.0, 41.6, 38.4, 23.0. IR (neat) cm^{-1} 3333, 3068, 3022, 2917, 2850, 1648, 1592, 1442, 1223, 1079, 994, 892, 838, 803 HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{20}H_{22}ONa$ 301.1563, found 301.1564.

*(2-(2-(4-Chlorophenyl)allyl)-6-(2-methylallyl)phenyl)methanol (**3f**):* Using the same procedure as that used for **3a** afforded **3f** (20 mg, 64% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.32 – 7.25 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.10 (dt, *J* = 7.3, 3.1 Hz, 2H), 5.51 – 5.41 (m, 1H), 4.85 (t, *J* = 1.5 Hz, 1H), 4.72 (q, *J* = 1.5

Hz, 1H), 4.62 (d, *J* = 4.4 Hz, 2H), 4.46 (s, 1H), 3.94 (d, *J* = 1.9 Hz, 2H), 3.48 (s, 2H), 1.80 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.7, 139.1, 138.7, 138.4, 136.9, 134.3, 133.1, 129.2, 128.8, 128.1, 127.8, 126.9, 114.3, 111.3, 58.6, 41.3, 38.0, 22.6. IR (neat) cm^{-1} 3343, 3073, 2920, 2852, 1626, 1492, 1395, 1098, 1010, 895, 834; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{20}H_{21}ClONa$ 335.1173, found 335.1180.

*(2-(2-Methylallyl)-6-(2-(p-tolyl)allyl)phenyl)methanol (**3g**):* Using the same procedure as that used for **3a** afforded **3g** (15 mg, 51% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.25 – 7.06 (m, 5H), 5.43 (d, *J* = 1.6 Hz, 1H), 4.87 – 4.81 (m, 1H), 4.62 (m, 3H), 4.50 – 4.45 (m, 1H), 3.94 (d, *J* = 1.6 Hz, 2H), 3.48 (s, 2H), 2.35 (s, 3H), 1.79 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.2, 147.0, 139.1, 139.0, 138.2, 137.5, 137.4, 129.4, 129.4, 129.0, 128.1, 125.8, 113.3, 111.6, 59.0, 41.6, 38.4, 23.0, 21.1. IR (neat) cm^{-1}3351, 3073, 2921, 2853, 1624, 1442, 1375, 1260, 1091, 995, 891; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{21}H_{24}ONa$ 315.1719; found 315.1721.

*(2-(2-Methylallyl)-6-(2-(3-(prop-1-en-2-yl)phenyl)allyl)phenyl)methanol (**3h**)***:*** Using the same procedure as that used for **3a** afforded **3h** (25 mg, 79% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, *J* = 1.9 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.12 – 7.07 (m, 1H), 5.47 (s, 1H), 5.37 (s, 1H), 5.10 (t, *J* = 1.7 Hz, 1H), 4.85 (s, 1H), 4.70 (t, *J* = 1.6 Hz, 1H), 4.65 (d, *J* = 5.0 Hz, 2H), 4.48 (s, 1H), 3.98 (s, 2H), 3.49 (s, 2H), 2.16 (s, 3H), 1.80 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.2, 146.6, 143.0, 141.0, 140.8, 138.7, 138.6, 137.0, 129.1, 129.0, 127.8, 127.8, 124.7, 124.5, 122.9, 113.8, 112.3, 111.3, 58.7, 41.3, 38.3, 22.6, 21.5. IR (neat) cm^{-1} 3349, 3073, 2921, 1628, 1593, 1441, 1375, 1247, 996, 891, 840; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{23}H_{26}ONa$ 341.1876; found 341.1884.

*(2-(2-((Benzyloxy)methyl)allyl)-6-(2-methylallyl)phenyl)methanol (**3i**):* Using the same procedure as that used for **3a** afforded **3i** (22 mg, 68% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.08 (td, *J* = 7.9, 1.5 Hz, 2H), 5.12 (q, *J* = 1.4 Hz, 1H), 4.82 (d, *J* = 1.9 Hz, 2H), 4.62 (d, *J* = 5.2 Hz, 2H), 4.46 (s, 3H), 3.95 (s, 2H), 3.58(s, 2H), 3.58(s, 2H),1.77 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.6, 146.4, 139.2, 138.3, 137.9, 137.6, 129.3, 129.0, 128.4, 128.0, 127.8, 127.7, 114.3, 111.6, 72.8, 71.8, 58.6, 41.5, 36.8, 23.0. IR (neat) cm^{-1} 3405, 3068, 3028, 2910, 2852, 1648, 1588, 1448, 1373, 1067, 997, 894; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{22}H_{26}O_2Na$ 345.1825; found 345.1831.

*(2-(2-((Benzylthio)methyl)allyl)-6-(2-methylallyl)phenyl)methanol (**3j**):* Using the same procedure as that used for **3a** afforded **3j** (28 mg, 82% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 5H), 7.22 – 7.16 (m, 1H), 7.08 (d, *J* = 7.6 Hz, 2H), 4.95 (d, *J* = 1.3 Hz, 1H), 4.83 (t, *J* = 1.6 Hz, 1H), 4.66 (d, *J* = 1.6 Hz, 1H), 4.64 (m, 4H), 4.46 (d, *J* = 2.2 Hz, 1H), 3.66 (s, 2H), 3.64 (d, *J* = 1.4 Hz, 2H), 3.47 (s, 2H), 3.06 (s, 2H), 1.78 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.8, 145.5, 139.2, 138.4, 138.1, 137.6, 129.4, 129.3, 129.0, 128.5, 128.1, 127.0, 114.7, 111.7, 58.8, 41.5, 37.7, 37.2, 35.4, 23.0. IR (neat) cm^{-1} 3390, 3068, 3026, 2909, 1644, 1590, 1447, 1226, 1174, 1071, 994, 892; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{22}H_{26}OSNa$ 361.1597; found 361.1599.

*tert-Butyl benzyl(2-(2-(hydroxymethyl)-3-(2-methylallyl)benzyl)allyl)carbamate (**3k**):* Using the same procedure as that used for **3a** afforded **3k** (27 mg, 62% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (q, *J* = 8.8, 8.0 Hz, 3H), 7.18 (d, *J* = 8.1 Hz, 3H), 7.05 (m, 2H), 4.92 (m, 1H), 4.81 (s, 1H), 4.71 (m, 1H), 4.58 (s, 2H), 4.42 (m, 2H), 3.76 (s, 2H), 3.44 (m, 4H), 1.79 (s, 3H), 1.43 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.9, 146.5, 145.6, 144.9, 138.0, 137.6, 130.5, 129.4, 128.8, 128.4, 127.9, 127.4, 127.2, 113.4, 111.6, 80.2, 77.2, 58.6, 50.6, 41.4, 37.7, 28.3, 22.9. IR (neat) cm^{-1} 3433, 3068, 2974, 2925, 1691, 1674, 1453, 1246, 1163, 1003, 889, 766; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{27}H_{35}NO_3Na$ 444.2509; found 444.2512.

*(2-(2-(Chloromethyl)allyl)-6-(2-methylallyl)phenyl)methanol (**3l**):* Using the same procedure as that used for **3a** afforded **3l** (13 mg, 52% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 2H), 5.20 (s, 1H), 4.82 (s, 1H), 4.72 (s, 1H), 4.61 (s, 2H), 4.45 (s, 1H), 4.04 (s, 2H), 3.65 (s, 2H), 3.46 (s, 2H), 1.77 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.9, 144.6, 138.3, 136.8, 136.5, 128.7, 128.3, 127.2, 115.2, 110.6, 57.5, 47.0, 40.6, 35.7, 21.9. IR (neat) cm^{-1} 3346, 2923, 1648, 1443, 1276, 1261, 998, 893, 843; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{15}H_{19}ClONa$ 273.1017; found 273.1025.

*(2-Allyl-6-(2-(p-tolyl)allyl)phenyl)methanol (**3m**):* Using the same procedure as that used for **3a** afforded **3m** (16 mg, 58% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.18 (m, 1H), 7.14 (m, 4H), 6.14 – 5.99 (m, 1H), 5.49 – 5.39 (m, 1H), 5.08 (dd, *J* = 10.1, 1.7 Hz, 1H), 4.98 (dd, *J* = 17.1, 1.8 Hz, 1H), 4.67 (d, *J* = 4.1 Hz, 2H), 4.65 – 4.60 (m, 1H), 3.94 (s, 2H), 3.64 – 3.50 (m, 3H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 148.4, 139.4, 139.0, 138.4, 138.1, 137.5, 136.9, 129.3, 129.0, 128.8, 128.3, 125.7, 115.7, 113.3, 58.9, 38.5, 37.4, 37.4, 21.1. IR (neat) cm^{-1} 3339, 3076, 2854, 1636, 1598, 1513, 1464, 1405, 1276, 1176, 995, 905, 823, 750; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{20}H_{22}ONa$ 301.1563; found 301.1566.

*(2-Allyl-6-cinnamylphenyl)methanol (**3n**):* Using the same procedure as that used for **3a** afforded **3n** (15 mg, 57% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.04 (m, 8H), 6.54 – 6.27 (m, 2H), 6.19 – 5.99 (m, 1H), 5.04 (m, 2H), 4.75 (s, 2H), 3.71 (d, *J* = 5.1 Hz, 2H), 3.56 (d, *J* = 6.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 139.7, 139.4, 138.5, 137.3, 136.7, 130.8, 129.9, 128.7, 128.7, 128.5, 128.5, 127.2, 126.1, 115.7, 58.7, 37.5, 36.6. IR (neat) cm^{-1} 3322, 2922, 1638, 1447, 1276, 913, 751; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{19}H_{20}ONa$ 287.1406; found 287.1409.

*(2-Allyl-6-(3-methylbut-2-en-1-yl)phenyl)methanol (**3o**):* Using the same procedure as that used for **3a** afforded **3o** (12 mg, 56% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.5 Hz, 1H), 7.09 (dd, *J* = 12.3, 7.5 Hz, 2H), 6.05 (ddt, *J* = 16.5, 10.2, 6.2 Hz, 1H), 5.26 (t, *J* = 6.9 Hz, 1H), 5.03 (ddd, *J* = 18.5, 13.6, 1.3 Hz, 2H), 3.54 (d, *J* = 6.1 Hz, 2H), 3.48 (d, *J* = 6.9 Hz, 2H), 1.76 (s, 3H), 1.73 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.6, 139.3, 138.5, 136.5, 132.5, 128.4, 128.2, 128.2, 123.9, 115.6, 58.7, 37.5, 32.2, 29.7, 25.7, 17.9; IR (neat) cm^{-1} 3302, 2921, 1637, 1441, 1377, 996, 911; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{15}H_{20}ONa$ 239.1406, found 239.1413.

Preparation of Intermediate 2b. *(2-(Prop-1-en-2-yl)-6-(trimethylsilyl)phenyl)methanol (**2b**):* ^1H NMR (400 MHz,

$CDCl_3$) δ 7.48 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.17 (dd, *J* = 7.6, 1.5 Hz, 1H), 5.26 (dd, *J* = 2.2, 1.5 Hz, 1H), 4.94 (dd, *J* = 2.2, 1.0 Hz, 1H), 4.78 – 4.68 (m, 2H), 2.12 (d, *J* = 0.5 Hz, 3H), 0.38 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 146.5, 144.7, 142.2, 140.6, 134.0, 129.6, 127.2, 115.4, 62.7, 26.0, 0.9; IR (neat) cm^{-1} 3310, 3056, 2923, 1269, 1248, 1008, 852, 798, 617. HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{13}H_{20}OSiNa$ 243.1176, found 243.1178.

Synthesis of 3p – 3y. *(2-(2-Methylallyl)-6-vinylphenyl)methanol (**3p**):* To a solution of CuI (10 mg, 0.05 mmol) in toluene (1.0 mL) was added *t*-BuOLi (0.1 mL, 2.2 M in THF) at 0 °C under Ar atmosphere. The reaction was stirred at room temperature for 10 min. $Pd(PPh_3)_4$ (6 mg, 5 mol %), **1a** (25.2 mg, 0.1 mmol) and bromoethene (0.12 mg, 1.0 M in THF) was added successively. The resulted mixture was stirred at room temperature for 0.5 h. Toluene was removed under reduced pressure before adding DMF (0.6 mL), HMPA (0.2 mL), 3-chloro-2-methylprop-1-ene (22.5 mg, 0.25 mmol) and *t*-BuOLi (0. 1 mL, 2.2 M in THF) successively. TBAF (0.2 mL, 1.0 M in THF) was then added slowly over 10 min. The reaction was stirred at room temperature for 1 h before quenching with sat. aq. NaCl (2 mL), extracting with EtOAc (3 × 5 mL) and washing with H_2O (3 × 3 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 200:1→25:1) to afford **3p** (11 mg, 59% yield) as a colorless viscous liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.30 (m, 1H), 7.28 – 6.97 (m, 3H), 5.68 (d, *J* = 17.3 Hz, 1H), 5.36 (d, *J* = 10.9 Hz, 1H), 4.84 (s, 1H), 4.69 (s, 2H), 4.48 (s, 1H), 3.45 (s, 2H), 1.78 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 146.9, 138.6, 138.5, 135.9, 134.8, 130.4, 128.2, 125.0, 116.9, 111.7, 58.7, 41.6, 22.9. IR (neat) cm^{-1} 3328, 3074, 2968, 2919, 1649, 1581, 1444, 1375, 1291, 1223, 1173, 997, 891, 762; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{13}H_{16}ONa$ 211.1093; found 211.1098.

*(E)-(2-(2-Methylallyl)-6-styrylphenyl)methanol (**3q**):* Using the same procedure as that used for **3p** afforded **3q** (12 mg, 45% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.47 (m, 3H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.31 – 7.18 (m, 2H), 7.16 – 6.95 (m, 3H), 4.86 (s, 1H), 4.77 (s, 2H), 4.51 (d, *J* = 2.2 Hz, 1H), 3.47 (s, 2H), 1.80 (s, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 147.0, 138.7, 138.3, 137.4, 136.2, 131.7, 130.3, 128.6, 128.3, 127.7, 126.7, 126.3, 125.1, 111.8, 58.9, 41.7, 22.9. IR (neat) cm^{-1} 3356, 2924, 2853, 1649, 1446, 1265, 997, 764, 749 HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{19}H_{20}ONa$ 287.1406; found 287.1411; mp: 77.7-79.9 °C

*(3-(2-Methylallyl)-[1,1'-biphenyl]-2-yl)methanol (**3r**):* Using the same procedure as that used for **3p** afforded **3r** (12 mg, 51% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.10 (m, 8H), 4.88 (s, 1H), 4.58 (s, 1H), 4.53 (d, *J* = 3.1 Hz, 2H), 3.55 (s, 2H), 1.82 (s, 3H), 1.71 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.9, 143.5, 141.5, 139.2, 136.2, 130.1, 129.4, 128.8, 128.0, 127.7, 127.0, 112.0, 59.7, 41.6, 22.9. IR (neat) cm^{-1}3355, 2918, 1442, 1277, 1002, 877, 757; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{17}H_{18}ONa$ 261.1250; found 261.1252; mp: 80.4-82.0 °C

*(4'-Methyl-3-(2-methylallyl)-[1,1'-biphenyl]-2-yl)methanol (**3s**):* Using the same procedure as that used for **3p** afforded **3s** (15 mg, 60% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.15 (m, 7H), 4.89 (s, 1H), 4.59 (s, 1H), 4.55 (d, *J* = 4.3 Hz, 2H), 3.56 (s, 2H), 2.41 (s, 3H), 1.83 (s, 3H), 1.70 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.9, 143.5, 139.2, 138.5, 136.7, 136.3, 129.9, 129.2, 128.8, 128.8, 127.7, 112.0, 59.8, 41.6, 22.9, 21.1. IR (neat) cm^{-1} 3335, 2921, 1648, 1586, 1514, 1451, 1261, 1189, 999, 822, 818, 754; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{18}H_{20}ONa$ 275.1406; found 275.1412; mp: 63.9-65.3 °C.

*(4'-(tert-Butyl)-3-(2-methylallyl)-[1,1'-biphenyl]-2-yl)methanol (**3t**):* Using the same procedure as that used for **3p** afforded **3t** (16 mg, 55% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 2H), 4.88 (s, 1H), 4.58 (s, 1H), 4.55 (d, *J* = 5.6 Hz, 2H), 3.55 (s, 2H), 1.82 (s, 3H), 1.74 – 1.70 (t, *J* = 5.6 Hz, 1H), 1.36 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 149.8, 147.0, 143.4, 139.1, 138.4, 136.2, 129.9, 129.0, 128.9, 127.7, 125.0, 111.9, 59.8, 41.5, 34.5, 31.4, 23.0. IR (neat) cm^{-1} 3357, 2960, 1726, 1649, 1585, 1461, 1363, 1270, 1194, 1001, 890, 839, 764, 750; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{21}H_{26}ONa$ 317.1876; found 317.1877; mp: 103.1-104.5 °C.

*(4'-Methoxy-3-(2-methylallyl)-[1,1'-biphenyl]-2-yl)methanol (**3u**):* Using the same procedure as that used for **3p** afforded **3u** (15 mg, 56% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 4.88 (s, 1H), 4.58 (s, 1H), 4.54 (d, *J* = 4.6 Hz, 2H), 3.85 (s, 3H), 3.54 (s, 2H), 1.82 (s, 3H), 1.75 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.8, 147.08, 143.2, 139.2, 136.3, 133.8, 130.5, 129.8, 128.9, 127.7, 113.5, 112.0, 59.8, 55.3, 41.6, 22.9. IR (neat) cm^{-1} 3355, 2924, 1609, 1513, 1461, 1245, 1179, 1035, 1001, 891, 835, 781; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{18}H_{20}O_2Na$ 291.1357; found 291.1356; mp: 49.6-51.9 °C.

*(3-Allyl-4'-methyl-[1,1'-biphenyl]-2-yl)methanol (**3v**):* Using the same procedure as that used for **3p** afforded **3v** (12 mg, 54% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.13 (m, 7H), 6.10 (ddt, *J* = 16.5, 10.3, 6.2 Hz, 1H), 5.08 (m, 2H), 4.58 (d, *J* = 3.7 Hz, 2H), 3.63 (d, *J* = 6.1 Hz, 2H), 2.40 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.5, 139.6, 138.5, 138.4, 136.8, 135.8, 129.3, 129.2, 128.8, 128.7, 127.9, 115.94, 59.69, 37.44, 21.15; IR (neat) cm^{-1} 3322, 2922, 1460, 999, 911, 824, 779, 754; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{17}H_{18}ONa$ 261.1250; found 261.1251; mp: 70.8-72.8 °C.

*(3-(2-Methylallyl)-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)methanol (**3w**):* Using the same procedure as that used for **3p** afforded **3w** (12 mg, 40% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 6.0 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 4.90 (s, 1H), 4.59 (s, 1H), 4.49 (s, 2H), 3.56 (s, 2H), 1.83 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ147.1, 145.1, 142.3, 139.5, 136.1, 130.8, 129.8, 129.5, 128.7, 128.0, 125.0 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 270.2 Hz), 112.1, 59.6, 41.6, 22.9. IR (neat) cm^{-1} 3335, 2919, 1618, 1403, 1325, 1275, 1166, 1125, 1066, 896, 848; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{18}H_{17}F_3ONa$ 329.1124; found 329.1131; mp: 89.9-92.1 °C.

*(3-(2-Methylallyl)-4'-nitro-[1,1'-biphenyl]-2-yl)methanol (**3x**):* Using the same procedure as that used for **3p** afforded **3x** (13 mg, 46% yield) as a colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.19

(d, *J* = 7.4 Hz, 1H), 4.90 (s, 1H), 4.59 (s, 1H), 4.48 (d, *J* = 4.1 Hz, 2H), 3.53 (s, 2H), 1.83 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.2 , 147.1, 147.1, 141.5, 139.7, 135.9, 131.3, 130.4, 128.5, 128.2, 123.2, 112.2, 59.5, 41.6, 22.9; IR (neat) cm^{-1} 3374, 3074, 2917, 2850, 1648, 1597, 1515, 1460, 1445, 1345, 1187, 1002, 857, 755. HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{17}H_{17}NO_3Na$ 306.1101; found 306.1108.

*(3',4',5'-Trimethoxy-3-(2-methylallyl)-[1,1'-biphenyl]-2-yl)methanol (**3y**):* Using the same procedure as that used for **3p** afforded **3y** (13 mg, 40% yield) as a colorless viscous liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.16 (m, 3H), 6.68 (s, 2H), 4.89 (s, 1H), 4.61 (s, 1H), 4.56 (d, *J* = 4.1 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 6H), 3.55 (s, 2H), 1.82 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.7, 147.0, 143.6, 139.3, 137.1, 136.9, 136.2, 130.1, 128.6, 127.8, 112.1, 106.8, 60.9, 59.8, 56.1, 41.7, 22.9. IR (neat) cm^{-1} 3460, 2927, 1648, 1579, 1507, 1463, 1408, 1345, 1174, 893, 754, 667; HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{24}O_4$ $(M+Na)^+$: 351.1567; found 351.1575.

Synthesis of 3ab – 3af. *(2-allyl-6-(2-methylallyl)-4-(trimethylsilyl)phenyl)methanol (**3ab**):* Using the same procedure as that used for **3a** afforded **3ab** (22 mg, 79% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.15 (m, 2H), 6.06 (m, 1H), 5.02 (m, 2H), 4.82 (s, 1H), 4.63 (d, *J* = 5.9 Hz, 2H), 4.45 (s, 1H), 3.55 (d, *J* = 6.0 Hz, 2H), 3.46 (s, 2H), 1.79 (s,3H), 0.24 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 147.4, 140.6, 138.7, 138.6, 138.1, 137.7, 134.5, 133.9, 115.7, 111.7, 59.0, 41.8, 37.6, 23.1, -0.9; IR (neat) cm^{-1} 3393, 2953, 2897, 1528, 1398, 1375, 1309, 1246, 1004, 874, 827, 784; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{17}H_{26}OSiNa$ 297.1645; found 297.1650.

*(2-Cinnamyl-6-(2-methylallyl)-4-(trimethylsilyl)phenyl)methanol (**3ac**):* Using the same procedure as that used for **3a** afforded **3ac** (18 mg, 51% yield) as a colorless liquid. ^1H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.31 – 7.26 (m, 3H), 7.25 – 7.22 (m, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.46 – 6.34 (m, 2H), 4.85 (d, *J* = 1.9 Hz, 1H), 4.70 (s, 2H), 4.49 (s, 1H), 3.72 (d, *J* = 5.8 Hz, 2H), 3.48 (s, 2H), 1.81 (s, 3H), 0.26 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.3, 140.7, 138.8, 138.1, 137.7, 137.4, 134.5, 133.8, 130.6, 130.1, 128.5, 127.1, 126.1, 111.7, 58.9, 41.7, 36.8, 23.0, -1.1. IR (neat) cm^{-1} 3335, 1954, 2923, 2852, 1649, 1446, 1382, 1247, 1205, 1108, 996, 967, 833, 751; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{23}H_{30}OSiNa$ 373.1958; found 373.1964.

*(2-(2-Methylallyl)-6-(3-methylbut-2-en-1-yl)-4-(trimethylsilyl)phenyl)methanol (**3ad**):* Using the same procedure as that used for **3a** afforded **3ad** (20 mg, 66% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 1.4 Hz, 1H), 7.18 (d, *J* = 1.4 Hz, 1H), 5.31 – 5.21 (m, 1H), 4.85 – 4.80 (m, 1H), 4.63 (s, 2H), 4.49 (d, *J* = 1.6 Hz, 1H), 3.47 (d, *J* = 5.9 Hz, 4H), 1.79 (s, 3H), 1.77 (d, *J* = 1.3 Hz, 3H), 1.73 (d, *J* = 1.4 Hz, 3H), 0.25 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.1, 140.6, 140.4, 138.0, 137.5, 134.1, 133.4, 132.2, 124.2, 111.6, 58.9, 41.7, 32.3, 25.7, 23.0, 18.0, -1.1. IR (neat) cm^{-1} 3319, 2956, 2921, 2825, 1649, 1443, 1380, 1247, 1130, 1103, 996, 908, 890, 832, 753; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{19}H_{30}OSiNa$ 325.1958; found 325.1958.

*(4'-Methyl-3-(2-methylallyl)-5-(trimethylsilyl)-[1,1'-biphenyl]-2-yl)methanol (**3ae**):* Using the same procedure as that used for **3p** afforded **3ae** (22 mg, 68% yield) as a colorless viscous liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 4H), 7.25 (s, 1H), 7.23 (s, 1H), 4.88 (d, *J* = 1.8 Hz, 1H), 4.59 (s, 1H), 4.54 (d, *J* = 5.4 Hz, 2H), 3.56 (s, 2H), 2.41 (s, 3H), 1.83 (s, 3H), 0.26 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.2, 142.6, 140.2, 138.7, 138.1, 136.8, 136.7, 135.1, 133.9, 129.3, 128.8, 111.9, 59.8, 41.7, 23.0, 21.1, -1.12. IR (neat) cm^{-1} 3334, 2954, 2924, 1648, 1521, 1444, 1248, 1117, 1000, 888, 857, 834, 753; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{21}H_{28}OSNa$ 347.1802; found 347.1805.

*(4'-Methoxy-3-(2-methylallyl)-5-(trimethylsilyl)-[1,1'-biphenyl]-2-yl)methanol (**3af**):* Using the same procedure as that used for **3p** afforded **3af** (21 mg, 62% yield) as a yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 7.02 – 6.88 (m, 2H), 4.94 – 4.84 (m, 1H), 4.59 (s, 1H), 4.54 (d, *J* = 5.9 Hz, 2H), 3.86 (s, 3H), 3.56 (s, 2H), 1.84 (s, 3H), 1.73 (t, *J* = 6.0 Hz, 1H), 0.27 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.8, 147.3, 142.3, 140.2, 138.1, 136.8, 135.0, 134.0, 133.9, 130.6, 113.5, 111.9, 59.9, 55.3, 41.7, 23.0, -1.1. IR (neat) cm^{-1} 3356, 2924, 2852, 1609, 1453, 1376, 1246, 1287, 1037, 834, 754; HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{21}H_{28}O_2SiNa$ 363.1751; found 363.1759.

Synthesis of 8 and 9a-9c. *6-Bromo-3-(bromomethyl)-3-methyl-8-(p-tolyl)isochromane (**8**):* To a solution of **3ae** (120 mg, 0.37 mmol) in MeCN (3 mL) was added NBS (166 mg, 0.93 mmol). The mixture was stirred at room temperature for 3 h before quenching with sat. aq. NH_4Cl (2 mL) and extracting with EtOAc (3 × 5 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 200:1→100:1) to afford **8** (125 mg, 82% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 4.60 (s, 2H), 3.51 – 3.35 (m, 2H), 3.05 – 2.78 (m, 2H), 2.40 (s, 3H), 1.38 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.0, 137.6, 135.5, 134.7, 130.7, 130.6, 130.5, 129.1, 128.5, 120.3, 71.8, 62.3, 40.1, 36.7, 23.4, 21.2. IR (neat) cm^{-1} 2922, 1578, 1513, 1374, 1290, 1196, 1064, 906, 818. HRMS (ESI-TOF) m/z: $(M+H)^+$ calcd for $C_{18}H_{19}Br_2O$ 408.9797; found 408.9797.

*3-(Bromomethyl)-6-(furan-2-yl)-3-methyl-8-(p-tolyl)isochromane (**9a**):* To a solution of **8** (20.5 mg, 0.05 mmol), furan-2-ylboronic acid (9 mg, 0.075 mmol) in toluene (0.4 mL) and MeOH (0.1 mL) was added $Pd(PPh_3)4$ (6 mg, 10 mol%) and $CsCO_3$ (10 mg, 0.12 mmol) under Ar atmosphere at room temperature. The reaction was refluxed at 100 °C for 4 h. The mixture was concentrated in vacuo. Purification of the crude residue via silica gel flash column chromategraphy (gradient eluent: petroleum ether/EtOAc =200:1→50:1) afforded **9a** (15 mg, 76% yield) as a colorless viscous liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.37 (m, 3H), 7.25 – 7.15 (m, 4H), 6.63 (d, *J* = 3.4 Hz, 1H), 6.47 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.68 (s, 2H), 3.58 – 3.35 (m, 2H), 3.11 – 2.83 (m, 2H), 2.41 (s, 3H), 1.40 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.6, 142.1, 139.5, 137.2, 136.7, 132.9, 130.8, 129.4, 129.1, 128.6, 123.4, 123.1, 111.6, 105.0, 71.9, 62.5, 40.3, 37.1, 23.5, 21.2. IR (neat) cm^{-1} 2953, 2897, 1621, 1482, 1406, 1379, 1320, 1246, 1086, 942, 823, 764, 690. HRMS (ESI-TOF) m/z: $(M+Na)^+$ calcd for $C_{22}H_{21}BrO_2Na$ 419.0617; found 419.0624.

*3-(Bromomethyl)-6-(4-methoxyphenyl)-3-methyl-8-(p-tolyl)isochromane (**9b**):* To a solution of **8** (20.5 mg, 0.05

mmol), (4-methoxyphenyl)magnesium bromide (0.1 mL, 1.0 M in THF) in 1,4-dioxane (0.5 mL) was added Pd_2(dba)3 (2 mg, 4 mol %) and IPrHCl (4 mg, 0.01 mmol) under Ar atmosphere. The reaction was stirred at 80 °C for 3 h before quenching with sat. aq. NH_4Cl (1 mL) and extracting with EtOAc (3 × 3 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 200:1→80:1) to afford **9b** (13 mg, 60% yield) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.7 Hz, 2H), 7.22 (m, 6H), 6.96 (d, *J* = 8.7 Hz, 2H), 4.70 (s, 2H), 3.84 (s, 3H), 3.56 – 3.37 (m, 2H), 3.12 – 2.86 (m, 2H), 2.40 (s, 3H), 1.42 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.2, 139.5, 139.2, 137.1, 137.0, 133.1, 132.9, 130.1, 129.0, 128.7, 128.0, 126.3, 126.0, 114.2, 71.9, 62.5, 55.3, 40.3, 37.2, 23.6, 21.1. IR (neat) cm^{-1} 2924, 1607, 1516, 1374, 1275, 1259, 1177, 822, 764, 749. HRMS (ESI-TOF) m/z: (M+Na)$^+$ calcd for $C_{25}H_{25}BrO_2Na$ 459.0930; found 459.0934.

*3-(Bromomethyl)-3-methyl-6-(phenylethynyl)-8-(p-tolyl)isochromane (**9c**):* To a solution of **8** (20.5 mg, 0.05 mmol), ethynylbenzene (11 μL, 0.1 mmol) in piperidine (0.5 mL) was added Pd(PPh_3)4 (3 mg, 5 mol%) and CuI (1 mg, 10 mol%) under Ar atmosphere at room temperature. The reaction was stirred at 80 °C for 5 h before quenching with sat. aq. NH_4Cl (1 mL) and extracting with EtOAc (3 × 3 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 200:1→100:1) to afford **9c** (20 mg, 93% yield) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 2H), 7.33 (dd, *J* = 5.2, 2.0 Hz, 3H), 7.29 (s, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 4.67 (s, 2H), 3.51 – 3.36 (m, 2H), 3.06 – 2.76 (m, 2H), 2.39 (s, 3H), 1.39 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.3, 137.3, 136.1, 132.8, 132.1, 131.6, 130.9, 130.8, 129.1, 128.6, 128.3, 128.3, 123.2, 121.6, 89.4, 89.0, 71.9, 62.5, 40.2, 36.8, 23.5, 21.2. IR (neat) cm^{-1} 2921, 2850, 1602, 1571, 1275, 1111, 909, 820, 754. HRMS (ESI-TOF) m/z: (M+Na)$^+$ calcd for $C_{26}H_{23}BrONa$ 453.0824; found 453.0830.

Synthesis of 10-13. *((2-Methylenepropane-1,3-diyl)bis(6-(trimethylsilyl)-2,1-phenylene))dimethanol (**10**):* To a solution of CuI (40 mg, 0.2 mmol) in DMF (3.0 mL) was added *t*-BuOLi (0.48 mL, 1.0 M in THF) at 0 °C under Ar atmosphere. The reaction was stirred at room temperature for 10 min. **L5** (42 mg, 0.2 mmol), **1a** (100.8 mg, 0.4 mmol) and 3-chloro-2-methylprop-1-ene (25 mg, 0.2 mmol) was added successively. The resulted mixture was stirred at room temperature for 2 h before quenching with sat. aq. NaCl (3 mL), extracting with EtOAc (3 × 10 mL) and washing with 1*N* HCl (3 × 3 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 200:1→20:1) to afford **10** (41 mg, 50% yield) as a colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 6.9, 1.7 Hz, 2H), 7.29 – 7.19 (m, 4H), 4.66 (s, 4H), 3.57 (s, 4H), 0.35 (s, 18H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.9, 143.9, 140.8, 138.6, 133.4, 132.1, 127.7, 113.4, 62.5, 39.8, 0.9. IR (neat) cm^{-1} 3339, 2953, 1411, 1250, 1005, 838, 761; HRMS (ESI-TOF) m/z: (M+Na)$^+$ calcd for $C_{24}H_{36}O2Si_2Na$ 435.2146; found 435.2150.

*((((2-Methylenepropane-1,3-diyl)bis(6-(2-methylallyl)-2,1-phenylene))bis(methylene))bis(oxy))bis(trimethylsilane) (**11**):* To a solution of CuI (8 mg, 0.04 mmol) in DMF (0.8 mL) was added *t*-BuOLi (0.1 mL, 1.0 M in THF) at 0 °C under Ar atmosphere. The reaction was stirred at room temperature for 10 min. **L5** (9 mg, 0.04 mmol), **10** (17 mg, 0.04 mmol) and 3-chloro-2-methylprop-1-ene (18 mg, 0.2 mmol) was added successively. The resulted mixture was stirred at room temperature for 2 h before quenching with sat. aq. NaCl (2 mL), extracting with EtOAc (3 × 3 mL) and washing with sat. aq. NaCl (3 × 2 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 200:1→80:1) to afford **11** (9 mg, 43% yield) as a colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.5 Hz, 2H), 7.07 – 7.00 (m, 4H), 4.80 (s, 2H), 4.55 (s, 2H), 4.50 (s, 4H), 4.46 (s,2H), 3.47 (s, 4H), 3.43 (s, 4H), 1.76 (d, *J* = 9.8 Hz, 6H), 0.12 (s, 18H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 149.1, 145.6, 139.1, 138.8, 137.1, 129.0, 128.9, 127.9, 113.0, 111.7, 58.2, 41.3, 40.1, 23.0, -0.3; IR (neat) cm^{-1} 2925, 1441, 1250, 1057, 875, 840, 751; HRMS (ESI-TOF) m/z: (M+Na)$^+$ calcd for $C_{32}H_{48}O_2Si_2Na$ 543.3085; found 543.3088.

*((1,3-Phenylenebis(prop-2-ene-2,1-diyl))bis(6-(trimethylsilyl)-2,1-phenylene))dimethanol (**12**):* Using the same procedure as that used for **10** afforded **12** (60 mg, 58% yield) as a colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, *J* = 1.8 Hz, 1H), 7.43 – 7.36 (m, 4H), 7.32 – 7.26 (m, 1H), 7.26 – 7.18 (m, 4H), 5.47 – 5.40 (m, 2H), 4.81 – 4.76 (m, 2H), 4.72 (d, *J* = 3.1 Hz, 4H), 3.98 (s, 4H), 0.34 (s, 18H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.2, 143.7, 141.3, 140.5, 139.14, 133.3, 132.0, 128.5, 127.8, 125.6, 124.0, 114.7, 62.7, 38.3, 1.0. IR (neat) cm^{-1} 3262, 3057, 2952, 1594, 1414, 1250, 1141, 1080, 1008, 838, 802, 762; HRMS (ESI-TOF) m/z: (M+Na)$^+$ calcd for $C_{32}H_{42}O_2Si_2Na$ 537.2616; found 537.2619.

*((1,3-Phenylenebis(prop-2-ene-2,1-diyl))bis(6-(2-methylallyl)-2,1-phenylene))dimethanol (**13**):* Using the same procedure as that used for **11** afforded **13** (7 mg, 30% yield) as a colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 1.9 Hz, 1H), 7.40 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.29 (dd, *J* = 8.4, 7.0 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.09 (dd, *J* = 7.6, 1.5 Hz, 4H), 5.44 (d, *J* = 1.4 Hz, 2H), 4.82 (t, *J* = 1.7 Hz, 2H), 4.71 (d, *J* = 1.5 Hz, 2H), 4.61 (s, 4H), 4.46 (d, *J* = 2.2 Hz, 2H), 3.95 (s, 4H), 3.47 (s, 4H), 1.77 (s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 148.2, 147.0, 141.1, 139.0, 138.9, 137.2, 129.3, 129.2, 128.3, 128.1, 125.3, 123.8, 114.3, 111.6, 58.9, 41.6, 38.4, 22.9. IR (neat) cm^{-1} 3348, 2922, 2853, 1662, 1593, 1450, 1376, 1175, 1088, 999, 892, 892, 765; HRMS (ESI-TOF) m/z: (M+Na)$^+$ calcd for $C_{34}H_{38}O_2Na$ 501.2764; found 501.2763.

ASSOCIATED CONTENT

Reaction schemes for the syntheses of compounds S1-S8 and preparations of compounds 1a and 1b; ^{1} H and ^{13}C NMR spectra for all new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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