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# Regioselective control using a catalyst switch in the reaction of diarylmethyl chlorides with allyltributylstannane

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ABSTRACT

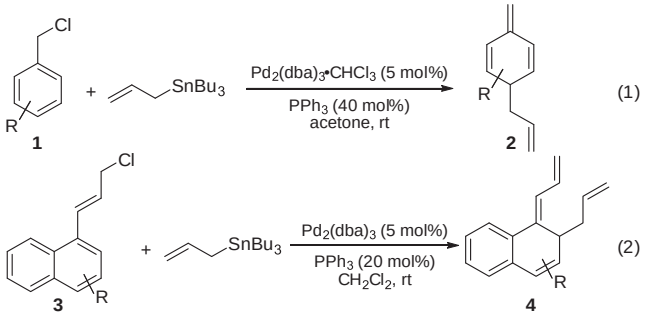
Regioselective control in the reaction of diarylmethyl chlorides **5a** with allyltributyltin is described. The reaction pathway (allylative dearomatization vs cross-coupling) can be easily controlled using different catalysts. When reactions are performed in the presence of $Pd_2(dba)_3$ and $PPh_3$, allylative dearomatization proceeds to provide satisfactory yield of the desired products. However, when $Cy_3P{\cdot}HBF_4$ is employed as a catalyst instead of palladium, a Stille-type cross-coupling reaction takes place exclusively to give excellent yields of the corresponding products.



## 1. Introduction

The palladium-catalyzed Stille cross-coupling reaction has been widely applied as a key step in the synthesis of fine chemicals, bioactive compounds, and natural products since a variety of functional groups can be tolerated in either partner, and the yields of coupled products are often high. In addition, organotin reagents can be readily synthesized, purified, and stored.[1,2] In our previous study, we found that benzyl chlorides **1** react with allytributyltin in the presence of a palladium catalyst to give *para*-allylated dearomatization products **2** (Scheme 1, Eq. 1).[3] Furthermore, we found that the reactions of naphthalene allyl chlorides **3** with allytributyltin in the presence of a palladium catalyst yield *ortho*-allylated products **4** (Scheme 1, Eq. 2).[4] In both cases, the corresponding normal Stille cross-coupling products were not observed at all.

In the course of our continuous research on palladium-catalyzed allylative dearomatization reactions, we examined the reactions of diarylmethyl chlorides **5** in order to extend the scope of substrates for which this type of reaction is applicable. We found that the regioselectivity of the reactions of **5** could be easily controlled by catalyst switch. When reactions of **5** with allyltributyltin were performed in the presence of $Pd_2(dba)_3$ (5 mol %) and $PPh_3$ (20 mol %), the expected dearomatization products **6** were exclusively obtained in moderate to excellent yields. In contrast, when $Cy_3P{\cdot}HBF_4$ (5 mol %) was employed as the catalyst instead of $Pd_2(dba)_3/PPh_3$ (Scheme 2), only the corresponding normal Stille cross-coupling products **7** were obtained in excellent yields from the reactions of the same substrates. The palladium-catalyzed allylative dearomatization reactions of diarylmethyl chlorides **5** with allyltributyltin selectively occurred on the electron-rich and sterically less-hindered benzene ring or on the α-naphthyl group. These regioselectively controllable reactions (allylative dearomatization vs cross-coupling) could be applied for different purposes in organic synthesis.




**Scheme 1.** Dearomatization reactions of benzylic chlorides **1** and naphthalene allyl chlorides **3** with allytributyltin catalyzed by palladium.

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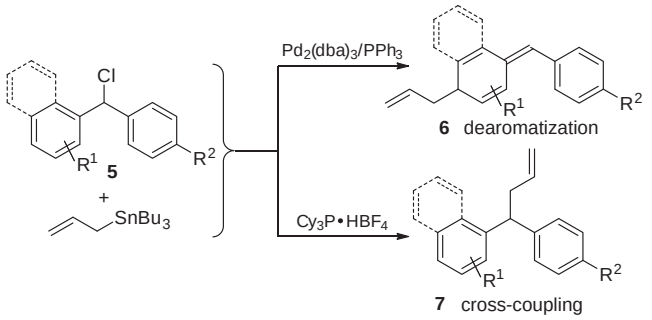



**Scheme 2.** Regioselective control using a catalyst switch in the reaction of diarylmethyl chlorides with allyltributyltin.

## 2. Result and discussion

### 2.1. Palladium-catalyzed allylative dearomatization reaction of 5 with allyltributyltin

Palladium-catalyzed allylative dearomatization reactions of diarylmethyl chlorides **5** with allyltributyltin were performed under the same conditions employed in the allylative dearomatization of **3** with allyltributyltin.[4] Results are summarized in Table 1. Substrates **5** smoothly underwent the desired reaction at room temperature to afford the corresponding dearomatization products in moderate to excellent yields (entries 1–7 and 9), but not for substrate **5h** (entry 8). The allylative dearomatization reactions of **5a** and **5b** occurred on the electron-rich and sterically less-hindered benzene ring to give products **6a** and **6b** in 71% and 70% yields, respectively (entries 1 and 2). The chlorine atom linked to the benzene ring in **5a** did not change, and was maintained in the structure of product **6a**. The reaction of substrate **5c** took place on the naphthalene ring, rather than on the benzene ring, thus providing dearomatization product **6c** in excellent yield (entry 3, 90%). It could be that this regioselectivity is due to the lower resonance energy of the naphthalene ring compared with that of the benzene ring. The reaction of **5d** also occurred on the naphthalene ring to give product **6d** in a good yield, even with an electron-donating group, methyl, linked to the benzene ring (entry 4, 85%).[5] Product **6e** was obtained in a slightly decreased yield from the reaction of **5e** (entry 5, 65%). This may be due to the steric hindrance of the methyl group linked to the naphthalene ring. The double-allylated product **6f** was obtained in 95% yield from the reaction of **5f**, which bears a bromine atom on its naphthalene ring (entry 6). It could be presumed that the product **6f** was generated by intermediate **8**, because we had successfully isolated product **10**,[6] which could transform into the double-allylated product **11**,[3] from the palladium-catalyzed allylative dearomatization reaction of 4-methoxybenzyl chloride (**9**). A similar good yield was obtained from the reaction of **5g**, which has an *ortho*-methyl group on its naphthalene ring, as compared to substrates **5c** and **5d** (entry 7, 83%). After the treatment of reaction of substrate **5h** with allyltributyltin for 36 h, the desired dearomatization product **6h** was obtained in only 6% yield. However, the undesired Stille coupling product **7h** was also isolated as a major product in 40% yield (entry 8). We then examined the reaction of substrate **5i**, which has a β-naphthyl group, and found that its dearomatization reaction proceeded slowly and occurred on the benzene ring, thus producing **6i** as the sole product in 85% yield (entry 9).

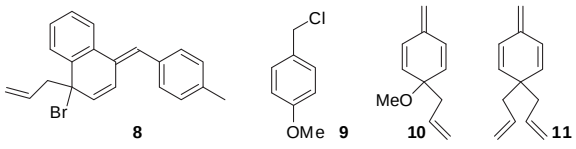
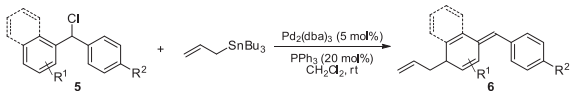
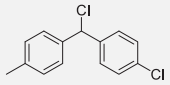
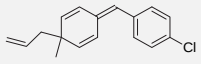
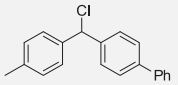
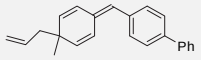
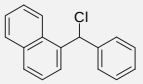
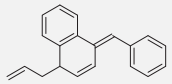
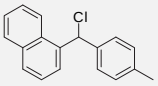
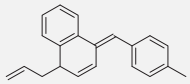
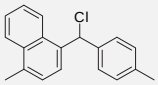
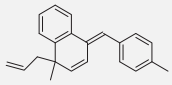
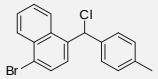
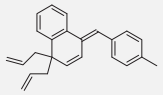
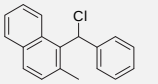
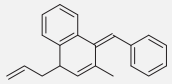
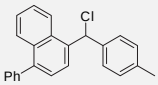
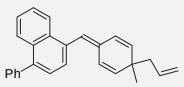
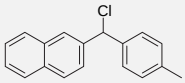
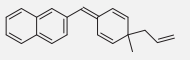



**Table 1**
Palladium-catalyzed dearomatization reaction of diarylmethyl chlorides **5** with allyltributyltin[a]

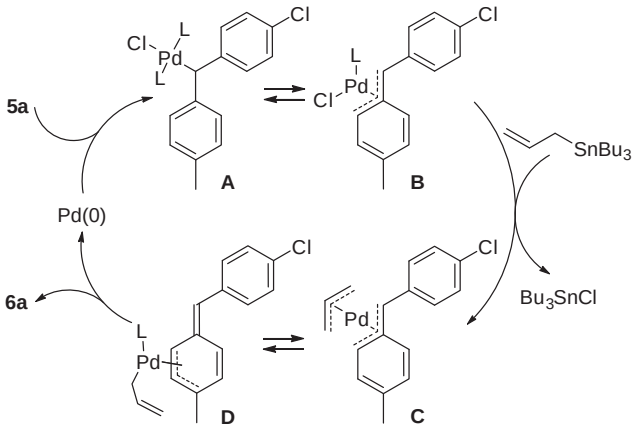



| Entry | Substrate **5** | Time (h) | Product **6** | Yield (%)[b] |
|---|---|---|---|---|
| 1 |  **5a** | 24 |  **6a** | 71 |
| 2 |  **5b** | 36 |  **6b** | 70 |
| 3 |  **5c** | 12 |  **6c** | 90 |
| 4 |  **5d** | 12 |  **6d** | 85 |
| 5 |  **5e** | 24 |  **6e** | 65 |
| 6 |  **5f** | 12 |  **6f** | 95 |
| 7 |  **5g** | 12 |  **6g** | 83 |
| 8 |  **5h** | 36 |  6h | 6[c] |
| 9 |  **5i** | 48 |  **6i** | 85 |

[a] A mixture of diarylmethyl chloride (0.5 mmol), allyltributyltin (0.6 mmol), $Pd_2(dba)_3$ (5 mol %), and $PPh_3$ (20 mol %) in dichloromethane (5 mL) was stirred at room temperature under a nitrogen atmosphere for the period indicated in the table.
[b] Isolated yield.
[c] The Stille coupling product **7h** was obtained as a major product in 40% yield.

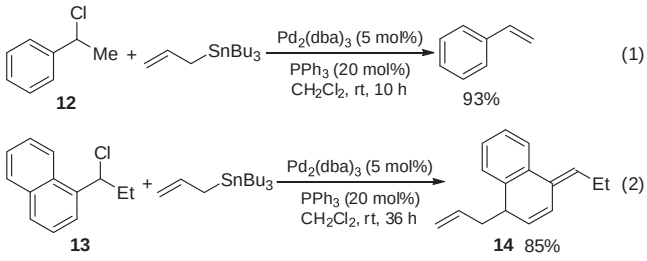
A possible mechanism for the allylative dearomatization reactions of diarylmethyl chlorides is shown in Scheme 3. The oxidative addition of **5a** to a $Pd^0$ species could produce benzylpalladium chloride intermediate **A** and its isomer $\eta^3$-benzylpalladium chloride intermediate **B**, which could then react with allyltributyltin to generate $\eta^3$-allyl-$\eta^3$-benzylpalladium intermediate **C** upon ligand exchange. Isomerization of **C** could occur to give ($\eta^3$-allyl)allylpalladium intermediate **D**, which in turn, could undergo reductive elimination to form the dearomatization product **6a**, and regenerate the $Pd^0$ catalyst. It could be that the coordination of the electron-rich benzene ring in intermediate **A** with palladium, which allowed for the formation of a $\eta^3$-benzylpalladium chloride intermediate, would occur more easily than the coordination with an electron-deficient benzene ring. As such, allylative dearomatization would selectively occur on electron-rich benzene rings.

The success in extending the allylative dearomatization to the diarylmethyl chlorides **5** encouraged us to examine other secondary benzylic chlorides, such as (1-chloroethyl)benzene (**12**) and 1-(1-chloropropyl)naphthalene (**13**). Reaction of **12** gave only a β-hydride elimination product (Scheme 4, Eq. 1, 93% yield).[7]




**Scheme 3.** A possible mechanism for the palladium-catalyzed allylative dearomatization reactions of diarylmethyl chlorides **5**.

However, the substrate **13** could undergo the desired allylative dearomatization smoothly to offer a sole product **14** (Scheme 4), Eq. 2, 85% yield).[5] It was considered that the high reactivity of **13** in the allylative dearomatization is due to the lower resonance energy of naphthalene ring than that of benzene ring. This result indicates that 1-(1-chloroalkyl)naphthalene derivatives may also be utilized in the allylative dearomatization reaction.



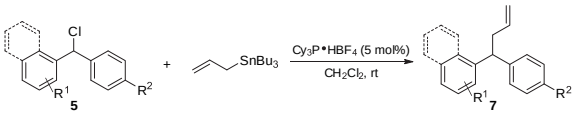

**Scheme 4.** Palladium-catalyzed reactions of (1-chloroethyl)benzene (**12**) and 1-(1-chloropropyl)naphthalene (**13**) with allyltributyltin.

## 2.2. $Cy_3P\cdot HBF_4$-catalyzed cross-coupling reaction of 5 with allyltributyltin

In order to control regioselectivity in the reaction of diarylmethyl chlorides **5** with allyltributyltin and to obtain the corresponding normal Stille cross-coupling product, we examined other palladium catalyst systems, such as those that employ $Pd_2(dba)_3$/P(OPh)$_3$, $Pd_2(dba)_3$/$PCy_3$, and $Pd_2(dba)_3$/dppe. However, we failed to control regioselectivity in the reaction of diarylmethyl chlorides **5** with allyltributyltin using a palladium catalyst. After further study, we found that $BF_3\cdot\cdot OEt_2$[8] and $Cy_3P\cdot HBF_4$[9] could be utilized as Lewis acid catalysts to achieve excellent yields of the desired cross-coupling reaction. As it is not easy to handle $BF_3\cdot OEt_2$ solutions in small scale, the air-stable $Cy_3P\cdot HBF_4$ solid was used as the catalyst in the reactions of various diarylmethyl chlorides **5** with allyltributyltin, the results of which are shown in Table 2. Substrates **5a**–**i** exhibited high reactivities in the $Cy_3P\cdot HBF_4$-catalyzed cross-coupling reactions to give the corresponding products in excellent yields within 2.5 h. An electron-donating group or electron-withdrawing group linked to the aromatic ring did not exert any influence on the $Cy_3P\cdot HBF_4$-catalyzed cross-coupling reaction. Substrates **5a** and **5b**, both of which possess two benzene rings in each molecule, quickly underwent cross-coupling reactions to give the products **7a** and **7b** in 92% and 96% yields (entries 1 and 2), respectively. Reactions of substrates **5c**–**i**, which include a naphthalene ring and a benzene ring in each molecule, also proceeded quickly to offer products **7c**–**i** in 89–98% yields (entries 3–9). It is worthy to note that the chlorine and bromine atoms linked to the aromatic ring did not change and were maintained in the structures of the products under this cross-coupling reaction conditions (entries 1 and 6). Interestingly, substrate **5h**, which had been found to be problematic in the palladium-catalyzed allylative dearomatization reaction, was found to be an effective partner in the $Cy_3P\cdot HBF_4$-catalyzed cross-coupling reaction (entry 8).

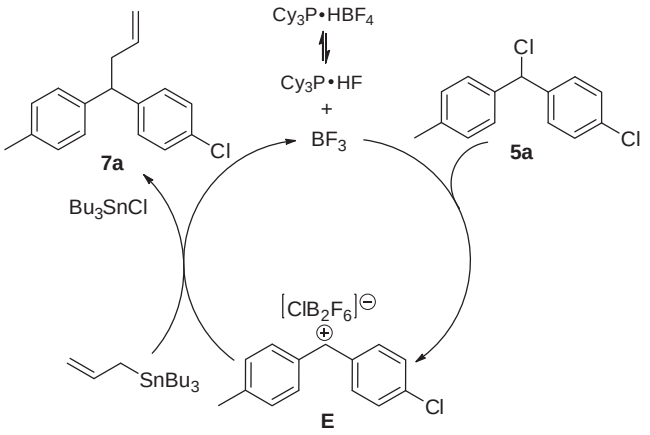
A possible mechanism for the $Cy_3P\cdot HBF_4$-catalyzed cross-coupling reaction of diarylmethyl chlorides **5** with allyltributyltin is shown in Scheme 5. The reaction of **5a** with $BF_3$, which was generated in situ from $Cy_3P\cdot HBF_4$, could produce the cationic

**Table 2**
$Cy_3P\cdot HBF_4$-catalyzed cross-coupling reaction of diarylmethyl chlorides **5** with allyltributyltin[a]




| Entry | Substrate **5** | Time (h) | Product **7** | Yield[b] (%) |
|---|---|---|---|---|
| 1 | **5a** | 2 | **7a** | 92 |
| 2 | **5b** | 2.5 | **7b** | 96 |
| 3 | **5c** | 1.5 | **7c** | 95 |
| 4 | **5d** | 1.5 | **7d** | 98 |
| 5 | **5e** | 1.5 | **7e** | 97 |
| 6 | **5f** | 1.5 | **7f** | 93 |
| 7 | **5g** | 2.5 | **7g** | 89 |
| 8 | **5h** | 2 | **7h** | 90 |
| 9 | **5i** | 1.5 | **7i** | 95 |

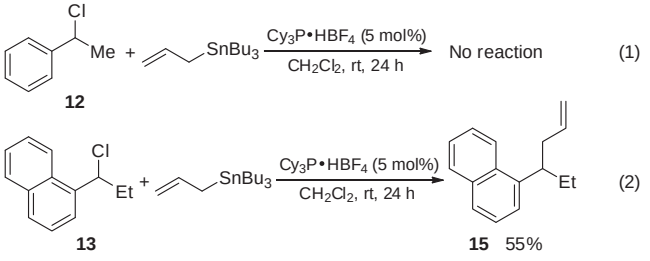
[a] A mixture of diarylmethyl chloride (0.5 mmol), allyltributyltin (0.6 mmol), and $Cy_3P\cdot HBF_4$ (5 mol %) in dichloromethane (5 mL) was stirred at room temperature under a nitrogen atmosphere for the period indicated in the table.
[b] Isolated yield.




**Scheme 5.** A possible mechanism for the $Cy_3P{\cdot}HBF_4$-catalyzed cross-coupling reactions of diarylmethyl chlorides **5** with allyltributyltin.

intermediate **E**.[10] The reaction of **E** with allyltributyltin could give the cross-coupling product **7a** along with the by-product tributylchlorostannane, and regenerate $BF_3$.

We then investigated the reactivities of secondary benzylic chlorides **12** and **13** under the same reaction conditions as employed in the cross-coupling reactions of **5a** with allyltributyltin. It was found that **12** resulted in no reaction (Scheme 6, Eq. 1), and **13** exhibited low reactivity to give product **15** with a 55% yield after the treatment of the reaction mixture for 24 h (Scheme 6, Eq. 2).




**Scheme 6.** $Cy_3P{\cdot}HBF_4$-catalyzed reactions of (1-chloroethyl)benzene (**12**) and 1-(1-chloropropyl)naphthalene (**13**) with allyltributyltin.

## 3. Conclusion

In conclusion, we have studied regioselective control in the reaction of diarylmethyl chlorides with allyltributyltin using a catalyst switch. The reaction pathway (allylative dearomatization vs cross-coupling) can be easily controlled by different catalysts. When the reactions were performed in the presence of $Pd_2(dba)_3$ and $PPh_3$, allylative dearomatization proceeded to provide satisfactory yields of the desired products. This palladium-catalyzed allylative dearomatization reaction of diarylmethyl chlorides often occurred on the electron-rich benzene ring or the sterically less-hindered naphthalene ring. However, when $Cy_3P{\cdot}HBF_4$ was employed as the catalyst instead of palladium, a Stille-type cross-coupling reaction took place exclusively giving excellent yields of the corresponding products.

## 4. Experimental

### 4.1. General procedure

$^1H$ and $^{13}C$ NMR spectra were recorded in a $CDCl_3$ solution on a Varian Inova-400 spectrometer (400 MHz for $^1H$ and 100 MHz for $^{13}C$). The chemical shifts are reported in parts per million downfield ($\delta$) from $Me_4Si$. IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on a Q-TOF mass spectrometer (Micromass, England) equipped with a Z-spray ionization source. TLC was carried out on $SiO_2$ (silica gel 60 $F_{254}$, Merck), and the spots were located with UV light, iodoplatinate reagent, or 1% aqueous $KMnO_4$. Flash chromatography was also carried out on either $SiO_2$ (silica gel 60, 200–300 mesh) or basic $Al_2O_3$ ($Al_2O_3$ 90, 100–200 mesh).

### 4.2. Representative procedure for the palladium-catalyzed dearomatization reaction of 5a with allyltributyltin

Diarylmethyl chloride **5a** (125.5 mg, 0.5 mmol) and allyltributyltin (198.6 mg, 0.6 mmol) were added to a mixture of $Pd_2(dba)_3$ (22.9 mg, 0.025 mmol) and $PPh_3$ (26.2 mg, 0.1 mmol) in dichloromethane (3 mL) at room temperature. The mixture was stirred under a $N_2$ atmosphere and the reaction progress was monitored by TLC. After all the allyltributyltin had been consumed, the solvent was removed under reduced pressure. The product was filtered through a short basic alumina column with pentane to remove the palladium residue and then purified with also a basic alumina column using pentane as the eluent. The dearomatization product **6a** was obtained as a colorless liquid in 71% yield (91.2 mg).

*4.2.1. 1-((4-Allyl-4-methylcyclohexa-2,5-dienylidene)methyl)-4-chlorobenzene (**6a**).* Colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.27 (dd, $J$=8.8, 8.8 Hz, 2H), 7.25 (dd, $J$=8.8, 8.8 Hz, 2H), 6.70 (d, $J$=10.0 Hz, 1H), 6.22 (dd, $J$=1.2, 10.0 Hz, 1H), 6.16 (s, 1H), 5.79–5.67 (m, 3H), 5.03–4.99 (m, 2H), 2.18 (d, $J$=7.2 Hz, 2H), 1.13 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 139.9, 137.2, 135.8, 134.6, 132.1, 131.8, 130.2, 128.3, 128.1, 124.8, 121.4, 117.2, 46.9, 40.1, 27.9; IR (neat) 3021, 2965, 2921, 1655, 1638, 1488, 1455, 1091, 1012, 915, 865, 797, 670 $cm^{-1}$; HRMS (EI) calcd for $C_{17}H_{17}Cl$: 256.1019 $[M]^+$; found: 256.1030.

*4.2.2. 1-((4-Allyl-4-methylcyclohexa-2,5-dienylidene)methyl)-4-phenylbenzene (**6b**).* Colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.60 (d, $J$=8.0 Hz, 2H), 7.56 (d, $J$=8.0 Hz, 2H), 7.45–7.39 (m, 4H), 7.33 (dd, $J$=7.2, 7.2 Hz, 1H), 6.84 (dd, $J$=0.8, 10.0 Hz, 1H), 6.27–6.24 (m, 2H), 5.79–5.67 (m, 3H), 5.03–4.99 (m, 2H), 2.19 (d, $J$=7.6 Hz, 2H), 1.14 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 140.7, 139.5, 139.2, 136.8, 136.5, 134.7, 131.5, 129.4, 138.8, 128.4, 127.2, 126.9, 126.8, 125.8, 121.8, 117.1, 47.0, 40.0, 28.0; IR (neat) 3024, 2956, 2921, 1655, 1638, 1485, 1454, 1119, 994, 870, 754, 698 $cm^{-1}$; HRMS (EI) calcd for $C_{23}H_{22}$: 298.1722 $[M]^+$; found: 298.1724.

*4.2.3. (E)-1-Allyl-4-benzylidene-1,4-dihydronaphthalene (**6c**).* Colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.86–7.84 (m, 1H), 7.42–7.35 (m, 4H), 7.29–7.23 (m, 4H), 7.14 (s, 1H), 6.95 (d, $J$=10.0 Hz, 1H), 6.12 (dd, $J$=4.8, 10.0 Hz, 1H), 5.80–5.70 (m, 1H), 5.02–4.89 (m, 2H), 3.69–3.66 (m, 1H), 2.57–2.40 (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 138.4, 137.7, 135.4, 133.8, 132.2, 131.3, 129.4, 128.4, 128.2, 127.2, 126.7, 126.3, 124.8, 122.76, 122.73, 116.9, 43.0, 40.8; IR (neat) 3385, 3073, 2976, 2908, 1638, 1597, 1492, 1452, 1204, 994, 915, 756, 698 $cm^{-1}$; HRMS (EI) calcd for $C_{20}H_{18}$: 258.1409 $[M]^+$; found: 258.1411.

*4.2.4. (E)-1-Allyl-4-(4-methylbenzylidene)-1,4-dihydronaphthal-ene (**6d**).* Colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.85–7.83 (m, 1H), 7.31 (d, $J$=7.6 Hz, 2H), 7.28–7.26 (m, 3H), 7.18 (d, $J$=7.6 Hz, 2H), 7.11 (s, 1H), 6.95 (d, $J$=10.4 Hz, 1H), 6.10 (dd, $J$=4.8, 10.0 Hz, 1H), 5.80–5.72 (m, 1H), 5.02–4.98 (m, 2H), 3.69–3.65 (m, 1H), 2.54–2.39 (m, 2H), 2.37 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 138.4, 136.6, 135.6, 134.9, 134.1, 132.0, 130.9, 129.5, 129.1, 128.6, 127.2, 126.5, 125.1, 122.9, 122.8, 117.1, 43.3, 41.0, 21.4; IR (neat) 3021, 2918, 1638, 1508, 1480, 1457, 1263, 1019, 911, 748, 694 $cm^{-1}$; HRMS (EI) calcd for $C_{21}H_{20}$: 272.1565 $[M]^+$; found: 272.1567.

*4.2.5. (E)-1-Allyl-1-methyl-4-(4-methylbenzylidene)-1,4-dihydronaphthalene (**6e**).* Colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.90 (dd, $J$=1.6, 8.0 Hz, 1H), 7.44 (dd, $J$=1.6, 7.6 Hz, 1H), 7.35–7.32 (m,

2H), 7.31 (dd, *J*=1.6, 4.0 Hz, 1H), 7.28–7.26 (m, 1H), 7.21 (d, *J*=8.0 Hz, 2H), 7.16 (s, 1H), 6.95 (d, *J*=10.4 Hz, 1H), 5.81 (dd, *J*=1.6, 10.4 Hz, 1H), 5.61–5.51 (m, 1H), 4.97–4.91 (m, 2H), 2.65–2.60 (m, 1H), 2.43–2.37 (m, 4H), 1.46 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 142.1, 137.6, 136.4, 134.8, 133.1, 130.6, 129.4, 128.9, 127.4, 126.5, 126.1, 123.0, 122.8, 122.5, 117.1, 48.8, 40.4, 29.8, 21.2; IR (neat) 3026, 2972, 1639, 1509, 1448, 1374, 1264, 1108, 914, 754 cm$^{-1}$; HRMS (EI) calcd for $C_{22}H_{22}$: 286.1722 $[M]^+$; found: 286.1731.

*4.2.6. (E)-1,1-Diallyl-4-(4-methylbenzylidene)-1,4-dihydronaph-thalene (**6f**).* Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.86 (dd, *J*=1.2, 7.6 Hz, 1H), 7.38 (dd, *J*=1.6, 8.0 Hz, 1H), 7.31–7.24 (m, 4H), 7.17 (d, *J*=8.0 Hz, 2H), 7.12 (s, 1H), 6.98 (d, *J*=10.4 Hz, 1H), 5.72 (dd, *J*=1.6, 10.4 Hz, 1H), 5.55–5.44 (m, 2H), 4.94–4.86 (m, 4H), 2.86–2.63 (m, 2H), 2.43–2.37 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 140.1, 136.6, 135.9, 135.0, 134.6, 134.3, 130.8, 129.6, 129.0, 127.5, 126.8, 126.3, 124.7, 123.1, 122.7, 117.4, 47.5, 44.6, 21.4; IR (neat) 3073, 2919, 1639, 1509, 1443, 1109, 992, 913, 752 cm$^{-1}$; HRMS (EI) calcd for $C_{21}H_{19}$: 271.1487 $[M\text{-}C_3H_5]^+$; found: 271.1485.

*4.2.7. (E)-4-Allyl-1-benzylidene-2-methyl-1,4-dihydronaphthal-ene (**6g**).* Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.30–7.28 (m, 3H), 7.24–7.10 (m, 5H), 6.86 (dd, *J*=7.2, 7.2 Hz, 1H), 6.68 (s, 1H), 5.96 (d, *J*=4.0 Hz, 1H), 5.88–5.77 (m, 1H), 5.01–4.98 (m, 2H), 3.49–3.48 (m, 1H), 2.49–2.38 (m, 2H), 2.11 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 140.8, 138.7, 136.0, 135.8, 135.7, 133.8, 129.5, 129.1, 128.3, 127.9, 126.8, 126.7, 124.8, 122.7, 116.8, 42.9, 42.2, 19.8; IR (neat) 3073, 2920, 1639, 1610, 1480, 1443, 1366, 998, 858, 750 cm$^{-1}$; HRMS (EI) calcd for $C_{21}H_{20}$: 272.1571 $[M]^+$; found: 272.1565.

*4.2.8. 1-((4-Allyl-4-methylcyclohexa-2,5-dienylidene)methyl)-4-phenylnaphthalene (**6h**).* Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.08 (d, *J*=8.0 Hz, 1H), 7.92 (d, *J*=8.4 Hz, 1H), 7.51–7.47 (m, 6H), 7.44–7.38 (m, 3H), 6.75 (s, 1H), 6.60 (dd, *J*=0.8, 10.0 Hz, 1H), 6.44 (dd, *J*=1.6, 9.6 Hz, 1H), 5.79–5.70 (m, 3H), 5.05–5.00 (m, 2H), 2.21 (d, *J*=8.2 Hz, 2H), 1.16 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 140.8, 139.5, 138.9, 137.0, 134.7, 133.8, 132.9, 132.4, 131.7, 130.1, 128.2, 128.0, 127.2, 126.7, 126.5, 126.3, 125.8, 125.7, 125.4, 123.9, 122.4, 117.1, 47.0, 40.1, 28.0; IR (neat) 3018, 2920, 1636, 1508, 1380, 1072, 994, 913, 772 cm$^{-1}$; HRMS (EI) calcd for $C_{27}H_{24}$: 348.1878 $[M]^+$; found: 348.1877.

*4.2.9. 2-((4-Allyl-4-methylcyclohexa-2,5-dienylidene)methyl)naphthalene (**6i**).* $\delta$ 7.81–7.76 (m, 4H), 7.46–7.42 (m, 3H), 6.88 (dd, *J*=0.8, 10.0 Hz, 1H), 6.38 (s, 1H), 6.30 (dd, *J*=1.2, 9.6 Hz, 1H), 5.80–5.70 (m, 3H), 5.04–5.00 (m, 2H), 2.20 (d, *J*=9.6 Hz, 2H), 1.16 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 139.6, 136.9, 135.0, 134.7, 133.4, 132.2, 131.7, 128.4, 127.9, 127.6, 127.4, 126.3, 126.1, 125.7, 121.8, 117.1, 47.0, 40.1, 28.0; IR (neat) 3054, 2964, 1653, 1605, 1503, 1276, 1120, 1018, 899, 799 cm$^{-1}$; HRMS (EI) calcd for $C_{21}H_{20}$: 272.1565 $[M]^+$; found: 272.1563.

*4.2.10. (E)-1-Allyl-4-propylidene-1,4-dihydronaphthalene (**14**).* Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.67–7.65 (m, 1H), 7.22–7.18 (m, 3H), 6.70 (d, *J*=10.0 Hz, 1H), 6.10 (dd, *J*=11.6, 11.6 Hz, 1H), 6.01–5.97 (m, 1H), 5.78–5.68 (m, 1H), 4.99–4.96 (m, 2H), 3.61–3.60 (m, 1H), 2.51–2.45 (m, 1H), 2.40–2.30 (m, 3H), 1.09 (t, *J*=7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 137.3, 135.6, 133.8, 130.1, 129.1, 128.3, 126.5, 126.2, 126.1, 123.4, 122.3, 116.7, 43.1, 40.5, 20.9, 14.3; IR (neat) 3073, 2971, 2934, 1639, 1516, 1450, 912, 751 cm$^{-1}$; HRMS (EI) calcd for $C_{16}H_{18}$: 210.1409 $[M]^+$; found: 210.1410.

### 4.3. Representative procedure for the $Cy_3P\cdot HBF_4$-catalyzed Stille-type cross-coupling reaction of 5a with allyltributyltin

Diarylmethyl chloride **5a** (125.5 mg, 0.5 mmol) and allyltributyltin (198.6 mg, 0.6 mmol) were added to a solution of $Cy_3P\cdot HBF_4$ (9.2 mg, 0.025 mmol) in dichloromethane (3 mL) at room temperature. The mixture was stirred under a $N_2$ atmosphere and the reaction progress was monitored by TLC. After all the allyltributyltin had been consumed, the solvent was removed under reduced pressure. The product was purified with a silica column using pentane as the eluent, giving the Stille-type cross-coupling product **7a** in 92% yield (118.1 mg) as a colorless liquid.

*4.3.1. 1-Chloro-4-(1-p-tolylbut-3-enyl)benzene (**7a**)[11].* Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.22 (d, *J*=8.4 Hz, 2H), 7.14 (d, *J*=8.4 Hz, 2H), 7.09–7.08 (m, 4H), 5.73–5.63 (m, 1H), 5.03–4.93 (m, 2H), 3.94 (t, *J*=8.0 Hz, 1H), 2.78–2.73 (m, 2H), 2.29 (s, 3H).

*4.3.2. 1-Phenyl-4-(1-p-tolylbut-3-enyl)benzene (**7b**).* Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.55 (d, *J*=7.6 Hz, 2H), 7.49 (d, *J*=8.4 Hz, 2H), 7.40 (dd, *J*=7.6, 7.6 Hz, 2H), 7.32–7.28 (m, 3H), 7.16 (d, *J*=8.0 Hz, 2H), 7.10 (d, *J*=8.0 Hz, 2H), 5.80–5.70 (m, 1H), 5.08–4.95 (m, 2H), 4.01 (t, *J*=8.0 Hz, 1H), 2.83 (dd, *J*=7.2, 7.2 Hz, 2H), 2.30 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 143.9, 141.4, 140.9, 139.0, 136.9, 135.7, 129.2, 128.7, 128.2, 127.8, 127.1, 127.06, 127.02, 116.3, 50.5, 40.0, 21.0; IR (neat) 2922, 1639, 1512, 1486, 913, 744 cm$^{-1}$; HRMS (EI) calcd for $C_{23}H_{22}$: 298.1722 $[M]^+$; found: 298.1718.

*4.3.3. 1-(1-Phenylbut-3-enyl)naphthalene (**7c**).* Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.10–8.08 (m, 1H), 7.82–7.80 (m, 1H), 7.73–7.70 (m, 1H), 7.46–7.38 (m, 4H), 7.27–7.19 (m, 4H), 7.13 (dd, *J*=6.8, 6.8 Hz, 1H), 5.85–5.75 (m, 1H), 5.08–4.95 (m, 2H), 4.81 (t, *J*=7.6 Hz, 1H), 3.00–2.85 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.5, 139.9, 137.1, 134.2, 132.0, 129.0, 128.5, 128.3, 127.2, 126.3, 126.1, 125.5, 124.8, 123.8, 116.5. 46.5, 40.7; IR (neat) 3060, 2927, 1639, 1509, 1450, 912, 777, 699 cm$^{-1}$; HRMS (EI) calcd for $C_{20}H_{18}$: 258.1409 $[M]^+$; found: 258.1402.

*4.3.4. 1-(1-p-Tolylbut-3-enyl)naphthalene (**7d**).* Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.11–8.09 (m, 1H), 7.82–7.80 (m, 1H), 7.46–7.41 (m, 4H), 7.16 (d, *J*=8.0 Hz, 2H), 7.05 (d, *J*=8.0 Hz, 2H), 5.86–5.76 (m, 1H), 5.09–4.95 (m, 2H), 4.79 (t, *J*=7.6 Hz, 1H), 2.98–2.84 (m, 2H), 2.27 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.5, 140.2, 137.2, 135.7, 134.2, 132.0, 129.2, 129.0, 128.2, 127.1, 126.1, 125.5, 125.4, 124.7, 123.9, 116.4, 46.1, 40.7, 21.1; IR (neat) 3047, 2920, 1639, 1510, 1442, 912, 779 cm$^{-1}$; HRMS (EI) calcd for $C_{21}H_{20}$: 272.1565 $[M]^+$; found: 272.1564.

*4.3.5. 1-Methyl-4-(1-p-tolylbut-3-enyl)naphthalene (**7e**).* Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.12–8.10 (m, 1H), 7.99–7.97 (m, 1H), 7.48–7.41 (m, 2H), 7.35 (d, *J*=7.2 Hz, 1H), 7.30 (d, *J*=7.2 Hz, 1H), 7.15 (d, *J*=8.0 Hz, 2H), 7.04 (d, *J*=8.0 Hz, 2H), 5.86–5.76 (m, 1H), 5.08–4.94 (m, 2H), 4.76 (t, *J*=7.6 Hz, 1H), 2.97–2.82 (m, 2H), 2.66 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$141.6, 138.1, 137.2, 135.5, 133.1, 132.8, 131.9, 129.0, 127.9, 126.1, 126.5, 125.5, 125.1, 124.8, 124.2, 116.1, 45.8, 40.6, 20.9, 19.5; IR (neat) 3073, 2921, 1638, 1512, 1388, 911, 755 cm$^{-1}$; HRMS (EI) calcd for $C_{22}H_{22}$: 286.1722 $[M]^+$; found: 286.1729.

*4.3.6. 1-Bromo-4-(1-p-tolylbut-3-enyl)naphthalene (**7f**).* Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.25 (dd, *J*=1.2, 9.6 Hz, 1H), 8.09 (d, *J*=8.0 Hz, 1H), 7.75 (d, *J*=8.0 Hz, 1H), 7.52–7.44 (m, 2H), 7.29 (d, *J*=8.0 Hz, 1H), 7.11 (d, *J*=8.4 Hz, 2H), 7.04 (d, *J*=8.0 Hz, 2H), 5.82–5.72 (m, 1H), 5.07–4.95 (m, 2H), 4.74 (t, *J*=8.0 Hz, 1H), 2.92–2.83 (m, 2H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.5, 140.2, 137.2, 135.7, 134.2, 132.0, 129.2, 129.0, 128.2, 127.1, 126.1, 125.5, 125.4, 124.7, 123.9, 116.4, 46.1, 40.7, 21.1; IR (neat) 3074, 2920, 1639, 1510, 1377, 912, 755 cm$^{-1}$; HRMS (EI) calcd for $C_{21}H_{19}Br$: 350.0670 $[M]^+$; found: 350.0668.

*4.3.7. 2-Methyl-1-(1-phenylbut-3-enyl)naphthalene (**7g**).* Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.75 (d, *J*=8.0 Hz, 2H), 7.64 (d, *J*=8.0 Hz, 1H), 7.31–7.13 (m, 8H), 5.69–5.58 (m, 1H), 5.01–4.97 (m, 2H), 4.84 (d, *J*=10.4 Hz, 1H), 3.33–3.26 (m, 1H), 3.06–3.03 (m, 1H),

2.49 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.5, 137.4, 137.1, 134.7, 133.6, 129.68, 129.64, 128.9, 128.4, 127.27, 127.23, 125.8, 125.35, 125.32, 124.4, 116.0, 43.6, 37.0, 22.0; IR (neat) 3052, 2921, 1639, 1509, 1446, 912, 808 $cm^{-1}$; HRMS (EI) calcd for $C_{21}H_{20}$: 272.1565 $[M]^+$; found: 272.1560.

*4.3.8. 1-Phenyl-4-(1-p-tolylbut-3-enyl)naphthalene (**7h**).* Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.90 (dd, $J$=1.2, 8.4 Hz, 1H), 7.35–7.14 (m, 12H), 7.03 (d, $J$=6.0 Hz, 1H), 7.01 (d, $J$=6.0 Hz, 1H), 5.81 (dd, $J$=1.6, 10.4 Hz, 1H), 5.62–5.52 (m, 1H), 5.01–4.90 (m, 2H), 3.14–3.09 (m, 1H), 3.00–2.95 (m, 1H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 147.6, 141.5, 136.6, 136.2, 134.7, 134.3, 133.1, 130.2, 129.5, 129.2, 128.9, 128.2, 127.6, 127.5, 126.17, 126.15, 123.5, 122.8, 122.0, 117.6, 48.7, 45.2, 21.2; IR (neat) 3022, 2918, 1637, 1508, 1443, 912, 752 $cm^{-1}$; HRMS (EI) calcd for $C_{27}H_{24}$: 348.1878 $[M]^+$; found: 348.1876.

*4.3.9. 2-(1-p-Tolylbut-3-enyl)naphthalene (**7i**).* Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.79–7.75 (m, 2H), 7.72 (d, $J$=8.4 Hz, 1H), 7.69 (s, 1H), 7.46–7.38 (m, 2H), 7.32 (dd, $J$=1.6, 8.4 Hz, 1H), 7.16 (d, $J$=8.0 Hz, 2H), 7.08 (d, $J$=8.0 Hz, 2H), 5.81–5.70 (m, 1H), 5.07–4.93 (m, 2H), 4.14 (t, $J$=8.0 Hz, 1H), 2.96–2.84 (m, 2H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 142.1, 141.3, 136.9, 135.7, 135.5, 133.5, 132.1, 129.1, 128.0, 127.9, 127.7, 127.5, 126.8, 125.9, 125.3, 116.3, 50.8, 39.8, 21.0; IR (neat) 3052, 2922, 1638, 1509, 1411, 1083, 911, 813, 745 $cm^{-1}$; HRMS (EI) calcd for $C_{21}H_{20}$: 272.1565 $[M]^+$; found: 272.1576.

*4.3.10. 1-(Hex-5-en-3-yl)naphthalene (**15**).* Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.11 (d, $J$=8.0 Hz, 1H), 7.82 (d, $J$=7.6 Hz, 1H), 7.68 (d, $J$=8.0 Hz, 1H), 7.48–7.40 (m, 3H), 7.33 (d, $J$=7.2 Hz, 1H), 5.74–5.64 (m, 1H), 4.98 (d, $J$=16.8 Hz, 1H), 4.89 (d, $J$=10.0 Hz, 1H), 3.51–3.48 (m, 1H), 2.50 (dd, $J$=7.2, 7.2 Hz, 2H), 1.90–1.72 (m, 2H), 0.80 (t, $J$=7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.3, 137.2, 134.1, 132.5, 129.1, 126.4, 125.7, 125.6, 125.3, 123.4, 116.0, 40.3, 28.2, 12.0; IR (neat) 3071, 2961, 2930, 1639, 1509, 1396, 994, 911, 776 $cm^{-1}$; HRMS (EI) calcd for $C_{16}H_{18}$: 210.1409 $[M]^+$; found: 210.1413.

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## Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.06.019. These data include MOL files and InChIKeys of the most important compounds described in this article.

## References and notes

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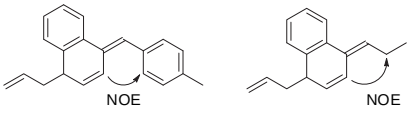


**6d** **14**

6. 3-Allyl-3-methoxy-6-methylenecyclohexa-1,4-diene (**10**): colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.46 (d, $J$=8.4 Hz, 2H), 5.74–5.63 (m, 3H), 5.09 (s, 2H), 5.05–5.01 (m, 2H), 3.07 (s, 3H), 2.38 (d, $J$=7.2 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 136.9, 133.0, 131.6, 130.4, 117.7, 117.3, 74.9, 51.5, 45.9; IR (neat) 3068, 2917, 1638, 1511, 1433, 1245, 1027, 912, 743, 695 $cm^{-1}$; HRMS (EI) calcd for $C_8H_9O$: 121.0653 $[M-C_3H_3]+$; found: 121.0655.
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