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A vesicular self-assembled amphiphilic palladium NNC-pincer complex-catalyzed allylic arylation of allyl acetates with sodium tetraarylborates in water

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The authors would like to dedicate this article to Professor Jiro Tsuji for his peerless contribution to the broad discipline of organic chemistry

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ABSTRACT

The allylic arylation of various allyl acetates with sodium tetraarylborates proceeded in water in the presence of a vesicular self-assembled amphiphilic palladium NNC-pincer complex to give the corresponding arylated products in high yield, whereas the same complex as an amorphous powder did not promote the reaction efficiently. The formation of a vesicular structure was therefore shown to be essential for efficient promotion of the reaction.

1. Introduction

The development of supramolecular catalyst systems as enzyme-inspired systems for the efficient catalysis of various reactions has received considerable attention from many chemists.[1] In this context, nanosized self-assembled architecture-based catalytic systems, such as bilayer vesicles, have been investigated.[2] Several research groups have reported that amphiphilic polymers and low-molecular weight amphiphiles containing a catalytically active site can self-assemble to form catalytically active self-assembled nanoarchitectures (micelles, vesicles, nanotubes, etc.) that can be used to induce organic reactions in water.[3] We recently reported that vesicular self-assembled amphiphilic pincer palladium complexes can catalyze organic transformations in water.[4,5] For example, amphiphilic palladium NNC-pincer complexes **1a** and **1b** self-assembled in water to form the vesicles $\mathbf{1a}_{vscl}$ and $\mathbf{1b}_{vscl}$, respectively (Fig. 1). Vesicles $\mathbf{1b}_{vscl}$ efficiently catalyzed a copper-free Sonogashira coupling reaction in water, whereas the amorphous complex $\mathbf{1b}_{amps}$ did not significantly promote the reaction.[5] We also showed that the formation of vesicles was necessary for the efficient promotion of the reactions in water. The effect of the formation of vesicular structures is explained as follows (Fig. 2). The organic substrates spontaneously concentrate within the hydrophobic region of the membranes of vesicles as a result of hydrophobic interactions. Subsequently, the substrates approach the catalytic center and the organic transformation takes place rapidly as a result of the presence of high concentrations of the substrates near the catalytic center.

The allylic substitution reaction known as the Tsuji–Trost reaction is an important transformation in the synthesis of natural compounds and pharmaceuticals.[6] In an attempt to demonstrate the scope and utility of our concept (Fig. 2), we decided to apply vesicular catalysts to the allylic arylation of allyl acetates with sodium tetraarylborates in water.[7] Here, we report the application of self-

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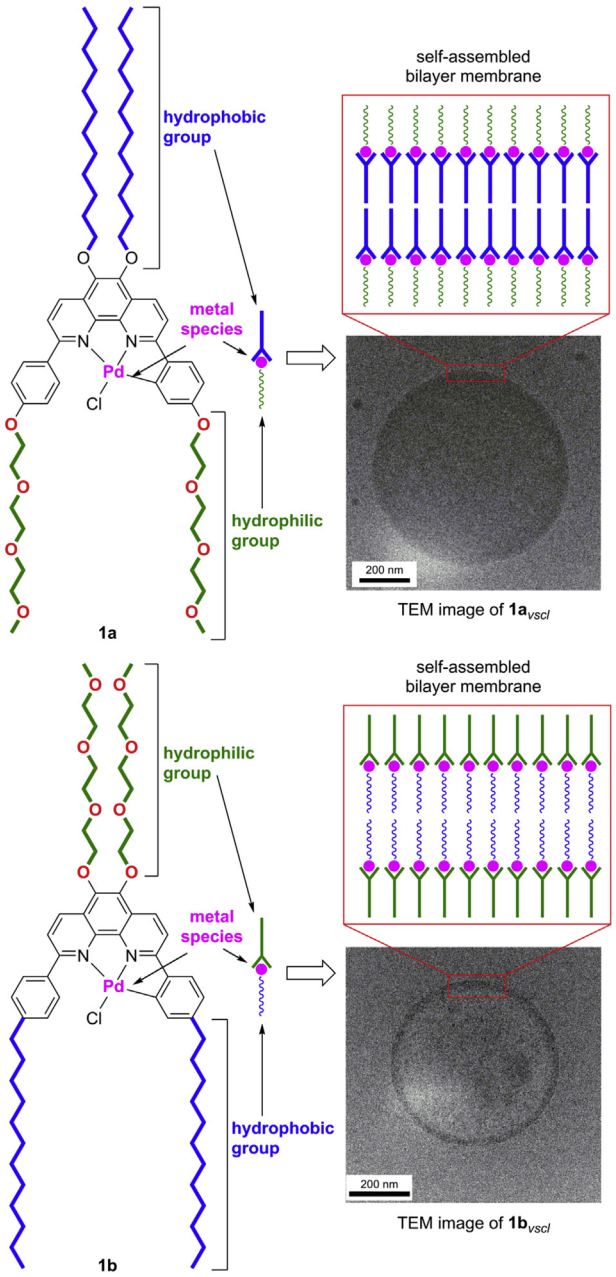


Fig. 1. Self-assembly of amphiphilic pincer Pd complexes **1a** and **1b**.

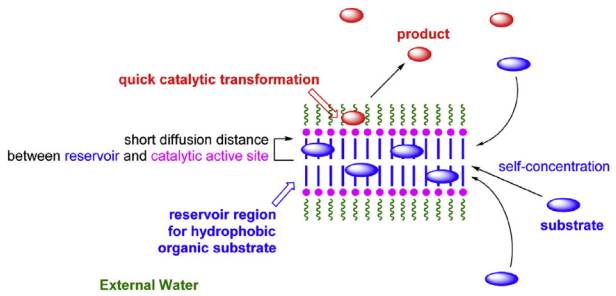


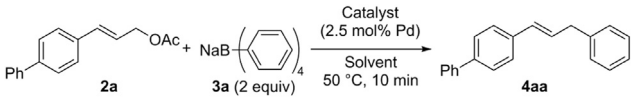
Fig. 2. Schematic image of the concept of catalysis within the membranes of vesicles.

assembled vesicles (**1a**$_{vscl}$ and **1b**$_{vscl}$) of amphiphilic palladium NNC-pincer complexes **1a** and **1b** as catalysts in the allylic arylation of allyl acetates with sodium tetraarylborates in water. The formation of a vesicular structure is essential for the promotion of this reaction.

2. Results and discussion

We examined the reaction of (2*E*)-3-biphenyl-4-ylprop-2-en-1-yl acetate (**2a**) with sodium tetraphenylborate (**3a**) in the presence of amorphous pincer palladium complexes **1a**$_{amps}$ and **1b**$_{amps}$ and their self-assembled vesicular nanocomposites **1a**$_{vscl}$ and **1b**$_{vscl}$ as catalysts (Table 1). When the reaction was performed with amorphous amphiphilic palladium pincer complex **1a**$_{amps}$ in water at 50 °C for 10 min, only an 8% yield of the desired arylated product **4aa** was obtained (entry 1). In contrast, the reaction proceeded smoothly in the presence of the self-assembled vesicular **1a**$_{vscl}$, where the potentially reactive Pd–Cl site faced the hydrophilic outer region, as shown in the schematic images of the bilayer membrane of **1a**$_{vscl}$ [Fig. 1 (top) and Fig. 2], to give 4-[(1*E*)-3-phenylprop-1-en-1-yl]biphenyl (**4aa**) in 59% yield (entry 2). These results show that the formation of vesicles of complex **1a** significantly accelerates the allylic arylation reaction in water. The reaction with the amorphous complex **1b**$_{amps}$ and the corresponding vesicles **1b**$_{vscl}$ gave **4aa** in 9 and 16% yield, respectively (entries 3 and 4). The formation of a vesicular structure by the self-assembly of **1b** therefore resulted in only a slight promotion of the allylic arylation reaction in water. These results suggested that the position of the hydrophilic and hydrophobic groups on the pincer backbone is critical for efficient promotion of this allylic arylation reaction. When the reaction was carried out in various organic solvents, such as 1,2-dichloroethane (DCE), toluene, acetonitrile, methanol, or *N*,*N*-dimethylformamide (DMF), the yield of the desired arylated product **4aa** was 14% or less, even when the vesicular composite **1a**$_{vscl}$ was used as the catalyst (entries 5–16). These results indicated that vesicular **1a**$_{vscl}$ disassembled or dissolved in organic solvents to give the catalytically less active monomeric **1a**. Therefore, the formation of a vesicular architecture was confirmed to be essential for the efficient promotion of the allylic arylation.

Table 1
Effects of catalysts and solvents in the allylic arylation of (2*E*)-3-biphenyl-4-ylprop-2-en-1-yl acetate (**2a**) with sodium tetraphenylborate (**3a**)[a]



Entry	Catalyst	Solvent	Yield[b] (%)
1	**1a**$_{amps}$	H_2O	8
2	**1a**$_{vscl}$	H_2O	59
3	**1b**$_{amps}$	H_2O	9
4	**1b**$_{vscl}$	H_2O	16
5	**1a**$_{amps}$	DCE	3
6	**1a**$_{vscl}$	DCE	8
7	**1a**$_{amps}$	Toluene	0
8	**1a**$_{vscl}$	Toluene	10
9	**1a**$_{amps}$	THF	13
10	**1a**$_{vscl}$	THF	14
11	**1a**$_{amps}$	MeCN	0
12	**1a**$_{vscl}$	MeCN	14
13	**1a**$_{amps}$	MeOH	14
14	**1a**$_{vscl}$	MeOH	14
15	**1a**$_{amps}$	DMF	0
16	**1a**$_{vscl}$	DMF	10

[a] *Reaction conditions*: **2a** (0.034 mmol), **3a** (0.068 mmol), catalyst (8.5×10^{-4} mmol), solvent (1.0 mL), 50 °C, 10 min.
[b] Isolated yield.

Next, we investigated the acceleration effects produced by the formation of the vesicular structure in the allylic arylation of various allyl acetates with sodium tetraarylborates in water (Table 2). For all the substrates, the formation of a vesicular structure accelerated the reaction in water. The allylic arylation reaction of cinnamyl acetate (**2b**) with sodium tetraphenylborate (**3a**) in the presence of amorphous complex **1a**$_{amps}$ gave 1,1′-(1*E*)-prop-1-ene-

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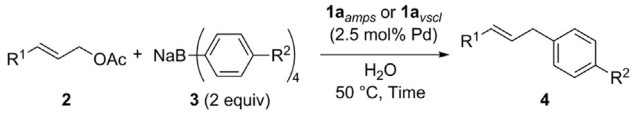
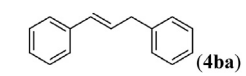
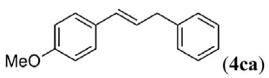
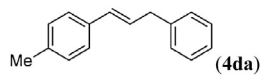
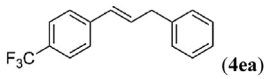
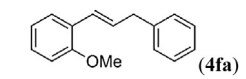
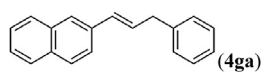
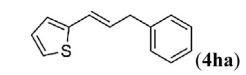
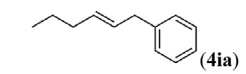
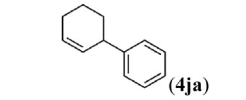
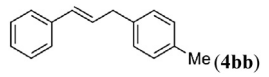
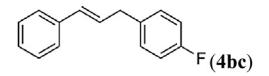
Table 2
Scope of the allylic arylation of allyl acetates with sodium tetraarylborates[a]



Entry	Catalyst	Product	Time	Yield[b] (%)
1	**1a**$_{amps}$	 **(4ba)**	1 h	9
2	**1a**$_{vscl}$		1 h	82
3	**1a**$_{amps}$	 **(4ca)**	1 h	5
4	**1a**$_{vscl}$		1 h	76
5	**1a**$_{amps}$	 **(4da)**	1 h	16
6	**1a**$_{vscl}$		1 h	68
7	**1a**$_{amps}$	 **(4ea)**	1 h	39
8	**1a**$_{vscl}$		1 h	70
9	**1a**$_{amps}$	 **(4fa)**	0.5 h	29
10	**1a**$_{vscl}$		0.5 h	86
11	**1a**$_{amps}$	 **(4ga)**	10 min	11
12	**1a**$_{vscl}$		10 min	66
13	**1a**$_{amps}$	 **(4ha)**	1 h	9
14	**1a**$_{vscl}$		1 h	46
15	**1a**$_{amps}$	 **(4ia)**	4 h	11
16	**1a**$_{vscl}$		4 h	44
17	**1a**$_{amps}$	 **(4ja)**	24 h	9
18	**1a**$_{vscl}$		24 h	41
19	**1a**$_{amps}$	 **(4bb)**	0.5 h	23
20	**1a**$_{vscl}$		0.5 h	68
21	**1a**$_{amps}$	 **(4bc)**	8 h	37
22	**1a**$_{vscl}$		8 h	78

[a] *Reaction conditions*: **2a** (0.034 mmol), **3a** (0.068 mmol), catalyst (8.5×10^{-4} mmol), H_2O (1.0 mL), 50 °C.
[b] Isolated yield.

1,3-diyldibenzene (**4ba**) in only 9% yield (entry 1). In contrast, the reaction with vesicular **1a**$_{vscl}$ gave the desired arylated product **4ba** in 82% yield (entry 2). This acceleration effect resulting from the formation of a vesicular structure was also observed in the reaction of sodium tetraphenylborate (**3a**) with cinnamyl acetates **2c**–**2e**, bearing electron-donating or electron-withdrawing substituents (entries 3–8). When the sterically hindered 2-methoxycinnamyl acetate (**2f**) was subjected to the allylic arylation, the reaction in the presence of catalyst **1a**$_{vscl}$ gave 1-methoxy-2-[(1*E*)-3-phenylprop-1-en-1-yl]benzene (**4fa**) in 86% yield (entry 10), whereas catalyst **1a**$_{amps}$ gave a 29% yield of **4fa** (entry 9). Vesicles **1a**$_{vscl}$ also catalyzed the reaction of naphthyl- and thienyl-substituted acetates **2g** and **2h** to give the corresponding arylated products **4ga** and **4ha** in 66 and 46% yield, respectively (entries 12 and 14). However, the amorphous complex **1a**$_{amps}$ did not promote the reaction efficiently (entries 11 and 13). We also examined the reaction of less-reactive aliphatic alk-2-enyl acetates with sodium tetraphenylborate (**3a**). The reactions of hex-2-en-1-yl acetate (**2i**) and cyclohex-2-en-1-yl acetate (**2j**) with **3a** in the presence of **1a**$_{amps}$ proceeded in water to give the corresponding arylated products **4ia** and **4ja** in 11 and 9% yield, respectively (entries 15 and 17). On the other hand, when vesicular **1a**$_{vscl}$ was used as the catalyst, the desired products **4ia** and **4ja** were obtained in 44 and 41% yield, respectively (entries 16 and 18). A similar acceleration effect resulting from the formation of the vesicular structure was also observed in the reaction of cinnamyl acetate (**2b**) with sodium tetraarylborates **3b** and **3c** (entries 19–22).

3. Conclusions

In summary, vesicles **1a**$_{vscl}$ showed a superior catalytic activity to that of the amorphous complex **1a**$_{amps}$ in the allylic arylation reaction of allyl acetates with sodium tetraarylborates in water. The formation of a vesicular structure is essential for efficient promotion of this reaction. On the other hand, when vesicles **1b**$_{vscl}$ and amorphous complex **1b**$_{amps}$ were used as catalysts, the formation of vesicles **1b**$_{vscl}$ did not significantly improve the catalytic activity for the reaction. The directions of the hydrophilic chains and the hydrophobic chains attached to the phenanthroline backbone influence the catalytic activity. Other catalytic applications of the vesicular catalysts **1a**$_{vscl}$ and **1b**$_{vscl}$ are currently under investigation in our laboratory.

4. Experimental section

4.1. General information

Commercially available chemicals (purchased from Sigma–Aldrich, TCI, Kanto Chemical, Wako Pure Chemical Industries, Nacalai Tesque, or Merck) were used without further purification unless otherwise noted. Silica gel was purchased from Kanto Chemical (Silica gel 60N; spherical neutral) or Yamazen Corp. (Hi-Flash™ Column Silica gel). TLC plates were purchased from Merck (TLC Silica gel 60 F_{254}). NMR spectra were recorded on a JEOL JNM ECS-400 spectrometer (396 MHz for ^{1}H, 100 MHz for ^{13}C). ^{1}H NMR chemical shifts are reported in δ (ppm) relative to tetramethylsilane as internal standard; ^{13}C NMR chemical shifts are relative to $CDCl_3$ as internal standard (δ=77.0). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C. GC/MS analyses were performed with an Agilent 6890 GC/5973N MS Detector. Elemental analyses were performed on a J-Science Lab Micro Corder JM10. Melting points were determined by using a Yanaco MP-J3 micro melting point apparatus and are uncorrected. IR spectra were obtained by using a JASCO FT/IR-460plus spectrometer in the ATR mode. Pure water was obtained from a Millipore Milli-Q Academic A10 purification unit. (2*E*)-3-Biphenyl-4-ylprop-2-en-1-yl acetate (**2a**),[8] (2*E*)-

3-(4-methoxyphenyl)prop-2-en-1-yl acetate (**2c**),[8] (2*E*)-3-(4-methylphenyl)prop-2-en-1-yl acetate (**2d**),[8] (2*E*)-3-[4-(trifluoromethyl)phenyl]prop-2-en-1-yl acetate (**2e**),[8] (2*E*)-3-(2-methoxyphenyl)prop-2-en-1-yl acetate (**2f**),[8] (2*E*)-3-(2-naphthyl) prop-2-en-1-yl acetate (**2g**),[9] (2*E*)-3-(2-thienyl)prop-2-en-1-yl acetate (**2h**),[8] cyclohex-2-en-1-yl acetate (**2j**),[10] sodium tetrakis(4-methylphenyl)borate (**3b**),[11] and sodium tetrakis(4-fluorophenyl) borate (**3c**)[11] were prepared by the reported methods.

4.2. Preparation of 1a$_{vscl}$

A chloroform solution of **1a** (0.1 mL, 10 mg/mL) was charged in a 4 mL vial equipped with a screw cap. After evaporation of the chloroform, a thin film of **1a** was formed on the inner glass surface of the vial. Then, 1 mL of Millipore water was added to the vial followed by heating the resulting mixture at 80 °C for 12 h without stirring. After standing at 25 °C for overnight, the resulting mixture was sonicated for 10 min to generate a yellow suspension of vesicles **1a**$_{vscl}$.

4.3. Preparation of 1b$_{vscl}$

A chloroform solution of **1b** (0.1 mL, 10 mg/mL) was charged in a 4 mL vial equipped with a screw cap. After evaporation of the chloroform, a thin film of **1b** was formed on the inner glass surface of the vial. Then, 1 mL of Millipore water was added to the vial followed by heating the resulting mixture at 60 °C for 4 h without stirring. After standing at 25 °C for overnight, the resulting mixture was sonicated for 10 min to generate a yellow suspension of vesicles **1b**$_{vscl}$.

4.4. Allylic arylation in water; typical procedure

A vial equipped with a screw cap was charged with a suspension of **1a**$_{vscl}$ (1.0 mg, 8.5×10^{-4} mmol), $NaBPh_4$ (**3a**) (23.3 mg, 0.068 mmol), and (2*E*)-3-biphenyl-4-ylprop-2-en-1-yl acetate (**2a**) (8.6 mg, 0.034 mmol) in H_2O (1 mL). The mixture was agitated by shaking at 50 °C for 10 min then allowed to cool to 25 °C. The cooled mixture was extracted with *t*-BuOMe (4×1.0 mL), and the organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography (silica gel, hexane) to give 4-[(1*E*)-3-phenylprop-1-en-1-yl]biphenyl (**4aa**; 5.4 mg, 0.020 mmol, 59%) as a white solid.

*4.4.1. 4-[(1E)-3-Phenylprop-1-en-1-yl]biphenyl (**4aa**).* White solid; mp 90–91 °C; ^{1}H NMR (396 MHz, $CDCl_3$) δ 7.60–7.52 (m, 4H, ArH), 7.45–7.41 (m, 4H, ArH), 7.35–7.31 (m, 2H, ArH), 7.27–7.21 (m, 4H, ArH), 6.50 (d, *J*=15.6 Hz, 1H, −C**H**=CHCH$_2$−), 6.41 (dt, *J*=15.6, 6.5 Hz, 1H, −CH=C**H**CH$_2$−), 3.58 (d, *J*=6.5 Hz, 2H, −CH=CHC**H**$_2$−); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 140.1, 139.8, 136.5, 130.6, 129.4, 128.7, 128.7, 128.5, 127.2 (2C), 126.9, 126.5, 126.2, 39.4; IR (ATR): 1600, 1487, 966, 836, 754, 700, 685, 588 cm^{-1}; EIMS *m*/*z* 270 [M$^+$]; Anal. Calcd for $C_{21}H_{18}$: C, 93.29: H, 6.71%. Found: C, 93.24: H, 6.71%.

*4.4.2. 1,1′-(1E)-Prop-1-ene-1,3-diyldibenzene (**4ba**).* [CAS: 3412-44-0].[7d] ^{1}H NMR (396 MHz, $CDCl_3$) δ 7.37–7.18 (m, 10H, ArH), 6.46 (d, *J*=15.8 Hz, 1H, −C**H**=CHCH$_2$−), 6.36 (dt, *J*=15.8, 6.7 Hz, 1H, −CH=C**H**CH$_2$−), 3.55 (d, *J*=6.7 Hz, 2H, −CH=CHC**H**$_2$−); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 137.5, 131.1, 129.3, 128.7, 128.5 (2C), 127.2, 126.2, 126.2, 39.4; EIMS *m*/*z* 194 [M$^+$].

*4.4.3. 1-Methoxy-4-[(1E)-3-phenylprop-1-en-1-yl]benzene (**4ca**).* [CAS: 35856-81-6].[7d] ^{1}H NMR (396 MHz, $CDCl_3$) δ 7.33–7.20 (m, 7H, ArH), 6.83 (d, *J*=8.7 Hz, 2H, ArH), 6.40 (d, *J*=15.7 Hz, 1H, −C**H**=CHCH$_2$−), 6.22 (dt, *J*=15.7, 6.8 Hz, 1H, −CH=C**H**CH$_2$−), 3.80 (s, 3H, −OCH$_3$), 3.53 (d, *J*=6.8 Hz, 2H, −CH=CHC**H**$_2$−); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 140.4, 130.4, 130.3, 128.6, 128.4, 127.2, 127.0, 126.1, 113.9, 55.3, 39.3; EIMS *m*/*z* 224 [M$^+$].

*4.4.4. 1-Methyl-4-[(1E)-3-phenylprop-1-en-1-yl]benzene (**4da**).* [CAS: 134539-87-0].[7d] ^{1}H NMR (396 MHz, $CDCl_3$) δ 7.35–7.19 (m, 7H, ArH), 7.10 (d, *J*=8.3 Hz, 2H, ArH), 6.43 (d, *J*=15.4 Hz, 1H, −C**H**=CHCH$_2$−), 6.30 (dt, *J*=15.4, 7.0 Hz, 1H, −CH=C**H**CH$_2$−), 3.54 (d, *J*=7.0 Hz, 2H, −CH=CHC**H**$_2$−), 2.31 (s, 3H, CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 136.8, 134.7, 130.9, 129.2, 128.7, 128.4, 128.1, 126.1, 126.0, 39.3, 21.2; EIMS *m*/*z* 208 [M$^+$].

*4.4.5. 1-[(1E)-3-Phenylprop-1-en-1-yl]-4-(trifluoromethyl)-benzene (**4ea**).* [CAS: 62056-35-3].[12] ^{1}H NMR (396 MHz, $CDCl_3$) δ 7.53 (d, *J*=8.0 Hz, 2H, ArH), 7.43 (d, *J*=8.0 Hz, 2H, ArH), 7.35–7.23 (m, 5H, ArH), 6.48–6.46 (m, 2H, −C**H**=C**H**CH$_2$−), 3.57 (d, *J*=3.7 Hz, 2H, −CH=CHC**H**$_2$−); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 139.6, 132.1, 129.8, 128.9 (q, *J*=32.4 Hz), 128.7, 128.6, 126.4, 126.3, 125.5 (q, *J*=3.8 Hz), 124.3 (q, *J*=271.8 Hz), 39.4; EIMS *m*/*z* 262 [M$^+$].

*4.4.6. 1-Methoxy-2-[(1E)-3-phenylprop-1-en-1-yl]benzene (**4fa**).* [CAS: 1246889-00-6].[13] ^{1}H NMR (396 MHz, $CDCl_3$) d 7.6 0 (d, *J*=7.5 Hz, 1H, ArH), 7.46–7.41 (m, 2H, ArH), 7.37–7.16 (m, 4H, ArH), 6.92–6.85 (m, 2H, ArH), 6.82 (d, *J*=15.8 Hz, 1H, −C**H**=CHCH$_2$−), 6.42 (dt, *J*=15.8, 7.1 Hz, 1H, −CH=C**H**CH$_2$−), 3.85 (s, 3H, −OCH$_3$), 3.57 (d, *J*=7.1 Hz, 2H, −CH=CHC**H**$_2$−); ^{13}C NMR (100 MHz, $CDCl_3$) d 156.4, 140.5, 129.7, 128.6, 128.4, 128.1, 126.5, 126.4, 126.0, 125.7, 120.5, 110.7, 55.3, 39.8; EIMS *m*/*z* 224 [M$^+$].

*4.4.7. 2-[(1E)-3-Phenylprop-1-en-1-yl]naphthalene (**4ga**).* [CAS: 5751-32-6].[14] ^{1}H NMR (396 MHz, $CDCl_3$) δ 7.79–7.74 (m, 3H, ArH), 7.70 (s, 1H, ArH), 7.58 (dd, *J*=8.3, 1.8 Hz, 1H, ArH), 7.46–7.39 (m, 2H, ArH), 7.29–7.22 (m, 5H, ArH), 6.62 (d, *J*=15.7 Hz, 1H, −C**H**=CHCH$_2$−), 6.49 (dt, *J*=15.7, 6.9 Hz, 1H, −CH=C**H**CH$_2$−), 3.61 (d, *J*=6.9 Hz, 2H, −CH=CHC**H**$_2$−); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 134.9, 133.6, 132.7, 131.1, 129.6, 128.7, 128.5, 128.1, 127.8, 127.6, 126.2, 126.1, 125.7, 125.5, 123.5, 39.4; EIMS *m*/*z* 244 [M$^+$].

*4.4.8. 2-[(1E)-3-Phenylprop-1-en-1-yl]thiophene (**4ha**).* [CAS: 1403462-93-0].[15] ^{1}H NMR (396 MHz, $CDCl_3$) δ 7.33–7.30 (m, 2H, ArH), 7.26–7.21 (m, 3H, ArH), 7.10 (d, *J*=4.8 Hz, 1H, thiophene 5-H), 6.93 (dd, *J*=4.8, 3.2 Hz, 1H, thiophene 4-H), 6.89 (d, *J*=3.2 Hz, 1H, thiophene 3-H), 6.56 (d, *J*=15.6 Hz, 1H, −C**H**=CHCH$_2$−), 6.21 (dt, *J*=15.6, 6.7 Hz, 1H, −CH=C**H**CH$_2$−), 3.51 (d, *J*=6.7 Hz, 2H, −CH=CHC**H**$_2$−); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 139.8, 129.1, 128.7, 128.5, 127.2, 126.2, 124.8, 124.2, 123.5, 39.1; EIMS *m*/*z* 200 [M$^+$].

*4.4.9. (2E)-Hex-2-en-1-ylbenzene (**4ia**).* [CAS: 78633-31-5].[7d] ^{1}H NMR (396 MHz, $CDCl_3$) δ 7.31–7.27 (m, 2H, ArH), 7.20–7.18 (m, 3H, ArH), 5.57 (dt, *J*=15.0, 5.9 Hz, 1H, −CH=C**H**CH$_2$Ph), 5.50 (dt, *J*=15.4, 5.9 Hz, 1H, −C**H**=CHCH$_2$Ph), 3.33 (d, *J*=5.9 Hz, 2H, −CH=CHC**H**$_2$Ph), 2.00 (q, *J*=6.7 Hz, 2H, −C**H**$_2$CH=CHCH$_2$Ph), 1.40 (sext, *J*=7.4 Hz, 2H, −C**H**$_2$CH$_2$CH=CHCH$_2$Ph), 0.90 (t, *J*=7.4 Hz, 3H, −CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 131.9, 128.9, 128.4, 128.3, 125.8, 39.1, 34.6, 22.6, 13.7; EIMS *m*/*z* 160 [M$^+$].

*4.4.10. 1-(Cyclohex-2-enyl)benzene (**4ja**).* [CAS: 15232-96-9].[7d] ^{1}H NMR (396 MHz, $CDCl_3$) δ 7.32–7.28 (m, 2H, ArH), 7.23–7.18 (m, 3H, ArH), 5.91–5.88 (m, 1H, −CH=C**H**−CHPh−), 5.73–5.70 (m, 1H, −C**H**=CH−CHPh−), 3.43–3.38 (m, 1H, −CH=CH−C**H**Ph−), 2.11–1.98 (m, 3H, −(CH$_2$)$_3$−CHPh−), 1.77–1.72 (m, 1H, −(CH$_2$)$_3$−CHPh−), 1.67–1.51 (m, 2H, −(CH$_2$)$_3$−CHPh−); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 130.1, 128.3, 128.2, 127.7, 125.9, 41.8, 32.6, 25.0, 21.2; EIMS *m*/*z* 158 [M$^+$].

*4.4.11. 1-Methyl-4-[(2E)-3-phenylprop-2-en-1-yl]benzene (**4bb**).* [CAS: 134539-86-9].[7d] ^{1}H NMR (396 MHz, $CDCl_3$) δ 7.35 (d,

J=7.5 Hz, 2H, ArH), 7.29 (d, *J*=7.5 Hz, 2H, ArH), 7.21–7.18 (m, 1H, ArH), 7.15–7.10 (m, 4H, ArH), 6.45 (d, *J*=15.6 Hz, 1H, −C**H**=CHCH$_2$−), 6.34 (dt, *J*=15.6, 6.7 Hz, 1H, −CH=C**H**CH$_2$−), 3.51 (d, *J*=6.7 Hz, 2H, −CH=CHC**H**$_2$−), 2.33 (s, 3H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.5, 137.0, 135.6, 130.8, 129.5, 129.1, 128.52, 128.45, 127.0, 126.1, 38.9, 21.0; EIMS *m*/*z* 208 [M$^+$].

*4.4.12. 1-Fluoro-4-[(2E)-3-phenylprop-2-en-1-yl]benzene (**4bc**).* [CAS: 485844-19-7].[7d] ^{1}H NMR (396 MHz, CDCl$_3$) δ 7.37–7.18 (m, 7H, ArH), 6.99 (t, *J*=8.1 Hz, 2H, ArH), 6.44 (d, *J*=15.0 Hz, 1H, −C**H**=CHCH$_2$−), 6.32 (dt, *J*=15.0, 6.6 Hz, 1H, −CH=C**H**CH$_2$−), 3.52 (d, *J*=6.6 Hz, 2H, −CH=CHC**H**$_2$−); ^{13}C NMR (100 MHz, CDCl$_3$) δ 161.5 (d, *J*=243.3 Hz), 137.3, 135.7 (d, *J*=3.9 Hz), 131.2, 130.0 (d, *J*=7.7 Hz), 128.9, 128.5, 127.2, 126.1, 115.2 (d, *J*=21.0 Hz), 38.43; EIMS *m*/*z* 212 [M$^+$].

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Supplementary data

Supplementary data (Copies of ^{1}H and ^{13}C NMR spectra of arylated products. This material is available via the internet at www.sciencedirect.com.) related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.04.108.

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