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Note

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Palladium-catalyzed sp^2–sp^3 coupling of chloromethylarenes with allytrimethoxysilane: Synthesis of allyl arenes

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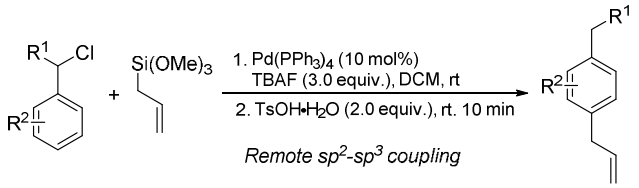
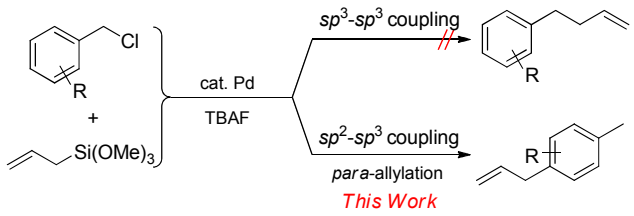


ABSTRACT: Palladium-catalyzed remote sp^2–sp^3 coupling reaction of chloromethylarenes with allyltrimethoxysilane is described in this work. The allylation reaction regioselectively occurred on the *para*-positions of 1-(chloromethyl)naphthalenes and benzyl chlorides to form new C(sp^2)–C(sp^3) bonds. The reaction proceeds smoothly under mild conditions to produce allyl arenes in moderate to excellent yields.

The transition metal-catalyzed cross-coupling reaction between organometallic reagents and organic halides or pseudo-halides containing a C–X bond (X = I, Br, Cl, OTf, OTs, etc.) is one of the most important carbon–carbon bond-forming methods in the organic synthesis.[1] Over the past decades, many kinds of organometallic reagents, such as organomagnesiums,[2] organozincs,[3] organostannanes,[4] organosilanes,[5] organoboranes,[6] and organobismuths,[7] have been developed and applied for this purpose. Among organometallic reagents utilized, organosilanes have attracted considerable attention because of their commercial availability, relatively low toxicity, and high tolerance to functional groups. New carbon–carbon bonds could be successfully constructed through the palladium-catalyzed cross-coupling between organosilanes and organic halides as well as pseudo-halides, namely the Hiyamacoupling, with different coupling patterns, including *sp*–*sp* (between ethynylsilanes and ethynyl halides),[8] *sp*–sp^2 (between ethynylsilanes and alkenyl halides),[9] sp^2–sp^2 (between alkenylsilanes and aryl halides or alkenyl halides),[10] sp^2–sp^3 (between allylsilanes and aryl halides),[11] and sp^3–sp^3 (between allylsilanes and allyl acetates)[12] coupling. Although the palladium-catalyzed cross-coupling reactions of allylsilanes with aryl halides and allyl acetates have been widely applied for allylic functionalization of organic molecules, the cross-coupling reaction of allylsilanes with chloromethylarenes in the presence of palladium catalyst, to the best of our knowledge, has not yet been reported so far. Recently, the palladium nanoparticle-catalyzed Hiyama coupling of benzyl halides with aryltrialkoxysilanes was reported by Sarkar and co-workers; the diarylmethanes were obtained in good to

excellent yields.[13] Our research on palladium catalysis showed that the palladium-catalyzed sp^3–sp^3 coupling between allylsilanes and chloromethylarenes did not occur at all; instead, a remote sp^2–sp^3 coupling reaction unexpectedly took place to produce *para*-allylated products (Scheme 1).[14] The results are reported in this work.

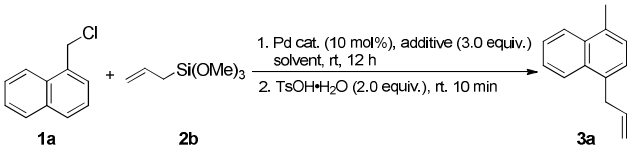
Scheme 1. Palladium-catalyzed remote cross-coupling reaction of chloromethylarenes with allysilanes.



In the initial study, the cross-coupling reactions of 1-(chloromethyl)naphthalene (**1a**) with different allylsilane reagents including allyltrimethylsilane (**2a**), allyltrimethoxysilane (**2b**), and allyltriethoxysilane (**2c**) were performed in the presence of $PdCl_2(PPh_3)_2$ as precatalyst and tetrabutylammonium fluoride (TBAF) as fluoride ion source in tetrahydrofuran (THF) at room temperature for 12 h followed by the treatment under acidic condition to investigate the reactivity of allylsilane reagents. The results obtained indicated that the reactivity of **2b** higher than that of others. Therefore, the cross-coupling reaction of **1a** with **2b** was selected to optimize the reaction conditions, and the results are summarized in Table 1. The palladium catalyst was first screened using

dichloromethane (DCM) as solvent and TBAF as fluoride ion source at room temperature. The desired *para*-allylated product **3a** was isolated in the range of 26% to 76% yield when the Pd(II) precatalysts [$PdCl_2(PPh_3)_2$, $PdCl_2(OAc)_2$, $Pd(acac)_2$, and $PdCl_2$] were examined in the absence or presence of PPh_3 (entries 1–4). The yield of **3a** could not be improved by using $Pd_2(dba)_3$ as a precatalyst in the presence of PPh_3 (entry 5, 68%). To our delight, an excellent yield of **3a** was achieved when $Pd(PPh_3)_4$ was employed as the catalyst (entry 6, 92%). The solvent was subsquently screened using $Pd(PPh_3)_4$ as catalyst and TBAF as fluoride ion source. Among the examined solvents, DCM proved to be the best solvent (entry 6 vs. entries 7–9). A fluoride ion-containing additive is usually necessary in the Hiyama reaction to activate organosilane reagents. Therefore, the additive was finally screened by using the frequently used fluoride ion sources, including TBAF,[15] CsF,[16] AgF,[17] and KF/18-crown-6.[18] No reaction or low yield (13%) was observed when CsF, AgF, and KF/18-crown-6 were examined (entries 10–12); TBAF was selected as the fluoride source because it provided the highest yield of **3a**. It was found that the yield of **3a** decreased along with the decrease of $Pd(PPh_3)_4$ or TBAF loading (entries 13 and 14). No reaction was observed in the absence of TBAF (entry 15). Therefore, the subsequent cross-coupling reactions of various chloromethylarenes with allyltrimethoxysilane were conducted in the presence of $Pd(PPh_3)_4$ (10 mol%) and TBAF (3.0 equiv.) in DCM solvent at room temperature.

Table 1. Reaction Condition Screening[a]



1a **2b** **3a**

entry	catalyst	solvent	additive	yield (%)
1	$PdCl_2(PPh_3)_2$	DCM	TBAF	76
2	$Pd(OAc)_2/PPh_3$	DCM	TBAF	53
3	$Pd(acac)_2/PPh_3$	DCM	TBAF	37
4	$PdCl_2/PPh_3$	DCM	TBAF	26
5	$Pd_2(dba)_3/PPh_3$	DCM	TBAF	68
6	$Pd(PPh_3)_4$	DCM	TBAF	92
7	$Pd(PPh_3)_4$	THF	TBAF	41
8	$Pd(PPh_3)_4$	acetone	TBAF	39
9	$Pd(PPh_3)_4$	hexane	TBAF	NR[b]
10	$Pd(PPh_3)_4$	DCM	CsF	NR[b]
11	$Pd(PPh_3)_4$	DCM	AgF	NR[b]
12	$Pd(PPh_3)_4$	DCM	KF/18-crown-6	13
13	$Pd(PPh_3)_4$	DCM	TBAF	58[c]
14	$Pd(PPh_3)_4$	DCM	TBAF	61[d]
15	$Pd(PPh_3)_4$	DCM	none	NR[b]

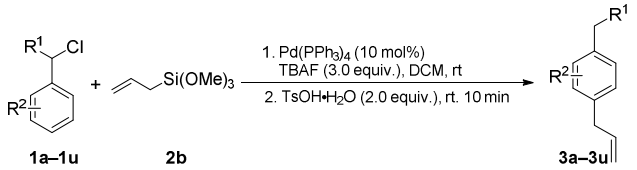
[a]Reaction conditions: **1a** (0.2 mmol), **2b** (0.4 mmol), catalyst (10 mol%), additive (0.6 mmol), solvent (3 mL), then $TsOH \cdot H_2O$ (0.4 mmol). [b]**1a** was recovered. [c] $Pd(PPh_3)_4$ (5 mol%). [d]TBAF (0.4 mmol).

The cross-coupling reactions of chloromethylarenes **1a**–**1r** with allylsilane reagent **2b** were conducted under optimized conditions. The results are summarized in Table 2. Reactions of 1-(chloromethyl)naphthalene substrates **1a**–**1e** proceeded smoothly to produce the *para*-allylated products **3a**–**3e** in moderate to excellent yields (entries 1–5, 60%–92%). Interestingly, the reactions of substrates **1c**, **1d**, and **1e** took place on the naphthalene ring, rather than on the benzene ring. It could be that this regioselectivity is due to the lower resonance energy of the naphthalene ring compared with that of the benzene ring (entries 3–5). The benzyl chloride substrates were then examined under the

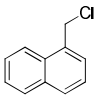
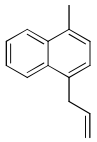
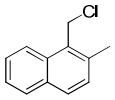
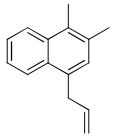
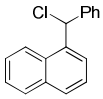
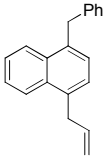
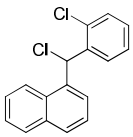
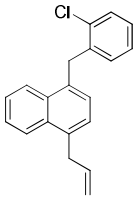
optimized conditions. Allyl benzene derivatives **3f**–**3j** were obtained in range of 65% to 92% yields from the reactions of *ortho*-substituted benzyl chloride substrates **1f**–**1j** (entries 6–10). These results suggested that the electron property and steric hindrance of *ortho*-substituent did not exert significant influence on reactivity. Halogen atoms (F, Cl, and Br) linked to the benzene rings of substrates were notably maintained in the structures of products **3d**, **3e**, **3g**, and **3h**, suggesting that further manipulation may produce a more useful compounds.[19] The substrates *meta*-methyl benzyl chloride (**1k**), *meta*-phenyl benzyl chloride (**1l**), and *meta*-allyl benzyl chloride (**1m**) underwent the expected allylation reaction also smoothly to produce the *para*-allylated benzene derivatives **3k**–**3m** in satisfactory to good yields (entries 11–13, 72%–88%). The product **3m** having two adjacent allyl groups could be converted to 6-methyl-1,4-dihydronaphthalene via ruthenium-catalyzed metathesis reaction.[20] The reactivities of benzyl chloride substrates **1n**–**1p** having two methyl groups linked on benzene rings were subsequently investigated. The *para*-allylated benzene derivatives **3n**–**3p** were obtained in also satisfactory to good yields (entries 14–16, 73%–83%). The allylated product **3q** was obtained in 80% yield when the reaction mixture of 1-(chloromethyl)-2-methoxybenzene (**1q**) with a strong electron-donating group (OMe) and **2b** was treated for a prolonged time under the optimal reaction conditions (entry 17). The desired products **3r** and **3s** were also obtained in satisfactory yields (72% and 70%, respectively) when the benzyl chloride substrates **1r** and **1s** bearing a strong electron-withdrawing group (CN or COOMe) on *ortho*-position (entries 18 and 19). A

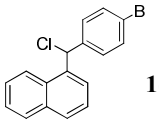
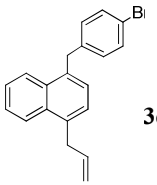
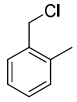
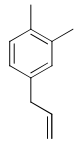
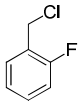
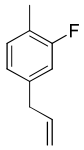
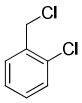
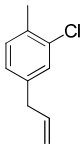
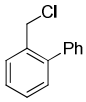
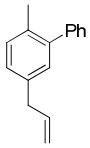
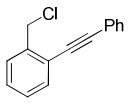
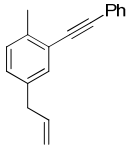
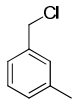
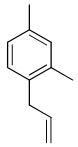
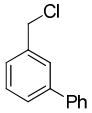
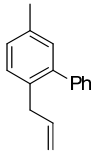
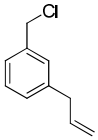
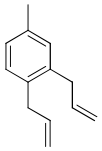
moderate yield of **3t** was observed when the substrate (chloromethylene)dibenzene (**1t**) was employed in this type of coupling reaction (entry 20, 60%). The substrate 9-(chloromethyl)anthracene (**1u**) was finally examined, and the expected product 9-allyl-10-methylanthracene (**3u**) was obtained in 65% yield (entry 21). All the new products **3** were identified through their NMR and HRMS data as well as IR spectra.

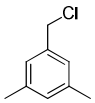
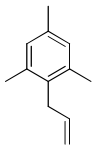
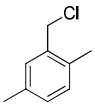
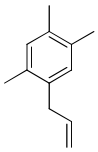
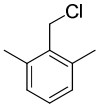
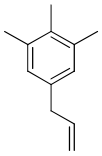
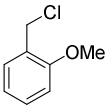
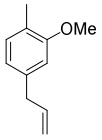
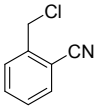
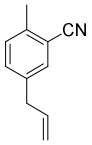
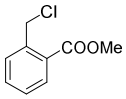
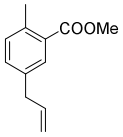
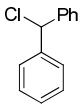
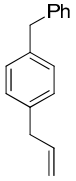
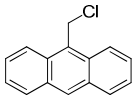
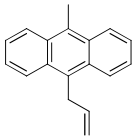
Table 2. Palladium-catalyzed regioselective allylation reaction between benzyl chlorides and allytrimethoxysilane[a]



1a–1u **2b** **3a–3u**

Entry	Substrate **1**	Time (h)	Product **3**	Yield (%)
1	 **1a**	12	 **3a**	92
2	 **1b**	12	 **3b**	78
3	 **1c**	14	 **3c**	85
4	 **1d**	14	 **3d**	69

5		**1e**	14		**3e**	60
6		**1f**	18		**3f**	79
7		**1g**	18		**3g**	76
8		**1h**	18		**3h**	82
9		**1i**	12		**3i**	92
10		**1j**	18		**3j**	65
11		**1k**	18		**3k**	72
12		**1l**	12		**3l**	77
13		**1m**	18		**3m**	88

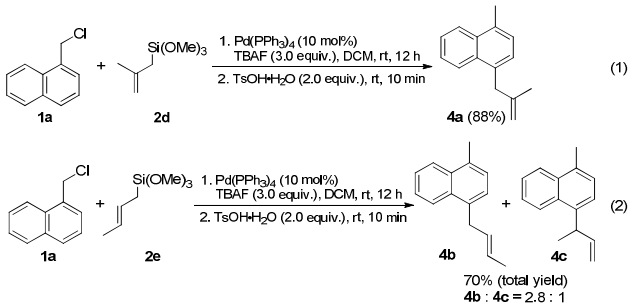
14		**1n**	18		**3n**	73
15		**1o**	18		**3o**	77
16		**1p**	18		**3p**	83
17		**1q**	24		**3q**	80
18		**1r**	12		**3r**	72
19		**1s**	12		**3s**	70
20		**1t**	18		**3t**	62
21		**1u**	20		**3u**	65

[a]Reaction conditions: **1** (0.2 mmol), **2b** (0.4 mmol), $Pd(PPh_3)_4$ (10 mol%), TBAF (0.6 mmol) in DCM (3 mL), then $TsOH \cdot H_2O$ (0.4 mmol).

Then, **1a** was used as an electrophile to determine the scope of allylsilanes under the optimized reaction conditions. The results are shown in Scheme 2. The reaction of **1a**

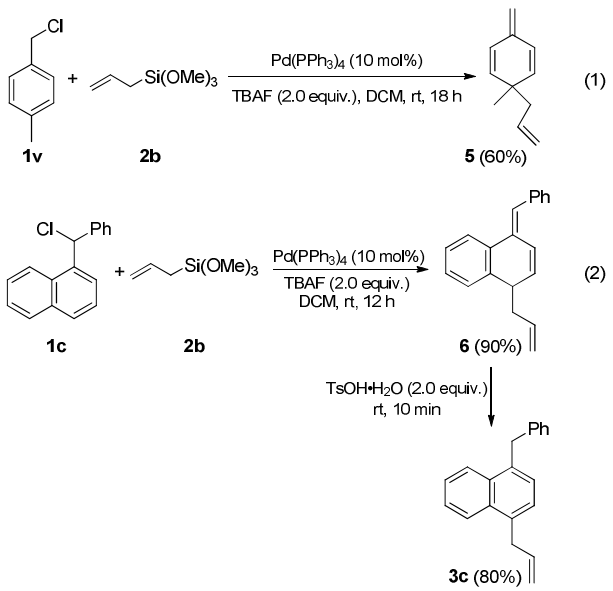
with (2-methylallyl)trimethoxysilane (**2d**) proceeded smoothly to produce the desired product **4a** in 88% yield (eq. 1). A 2.8/1 mixture of **4b** and **4c** was obtained in 70% total yield when the crotyltrimethoxysilane (**2e**) was examined (eq. 2). These results indicated that a substituted allylsilane reagent can also be employed in this type of allylation reaction.

Scheme 2. Palladium-catalyzed regioselective allylation reaction between 1-(chloromethyl)naphthalene and substituted allyltrimethoxysilanes



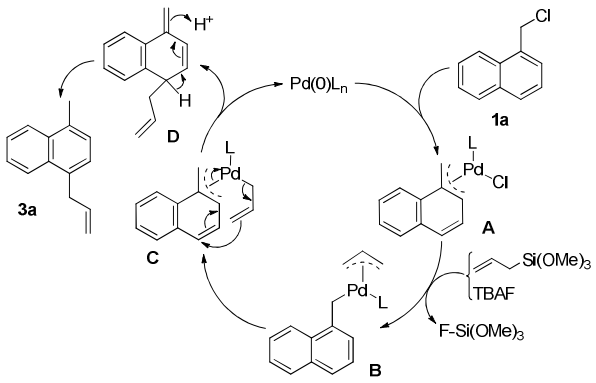
Control experiments were conducted to gain insights into the mechanism of this type of allylation reaction (Scheme 3). Methyl group as a blocking group was placed in the *para* position of the benzyl chloride. The reaction was also exclusively occurred at the *para*-position to produce the dearomatization product **5** in 60% yield (eq. 1). Dearomatization product **6** was successfully separated in 90% yield from the reaction of **1c** with **2b** in the absence of acid; the product **6** was subsequently transformed to more stable rearomatized product **3c** by acid treatment process (eq. 2).

Scheme 3. Control experiments.



On the basis of our experimental outcomes and previous report,[21] a plausible mechanism for the remote sp^2–sp^3 coupling reaction is shown in Scheme 4.[21] The oxidative addition of **1a** to a Pd(0) species would produce the η^3-allylpalladium chloride intermediate **A**, which would undergo transmetalation with allyltrimethoxysilane in the presence of TBAF to generate the intermediate **B**. Isomerization of intermediate **B** would occur to produce intermediate **C**. Reductive elimination of intermediate **C** through coupling of the C-3 terminus of the η^1-allyl ligand with the C-4 of the η^3-benzyl ligand would occur to produce the allylative dearomatization intermediate **D** and regenerating a Pd(0) species. Finally, re-aromatization reaction of intermediate **D** would occur under acidic conditions to produce *para*-allylated naphthalene derivative **3a**.

Scheme 4. A proposed mechanism.



In summary, we have developed a new method for obtaining allyl aromatic compounds using chloromethylarenes and allylsilanes as coupling partners. The palladium-catalyzed remote sp^2–sp^3 coupling reaction proceeded smoothly under mild conditions to exclusively produce *para*-allylated aromatic compounds. This work represents a significant expansion in the scope of the Hiyama reaction.

EXPERIMENTAL SECTION

General Information.

All reactions were carried out under a nitrogen atmosphere unless otherwise noted. Solvents were purified by standard techniques without special instructions. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Inova-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C) or a Bruker Avance II-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C) or Bruker Avance III-500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C); $CDCl_3$ and TMS were used as a solvent and an internal standard, respectively. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants J are

given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on a GC-TOF mass spectrometry. 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 carried out on SiO_2 (silica gel 60, 200-300 mesh). All the starting materials were commercially available and used without further purification.

Representative procedure for sp^2–sp^3 coupling of chloromethylarenes with allytrimethoxysilane

1-(Chloromethyl)naphthalene (**1a**, 35.3 mg, 0.2 mmol), allyltrimethoxysilane (**2b**, 64.9 mg, 0.4 mmol), and TBAF (1.0 M in THF; 0.6 mL, 0.6 mmol) were added into a solution of $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol) in dry dichloromethane (3.0 mL). After the reaction mixture was stirred under N_2 atmosphere at room temperature for 12 h, $TsOH•H_2O$ (76.1 mg, 0.4 mmol) was added and the mixture was stirred for 10 min to obtain a pure *para*-allylated benzene derivative. The solvent was removed under a reduced pressure. The residue obtained was purified via silica gel chromatography (eluent: petroleum ether), obtaining 92% yield (33.5 mg) of 1-allyl-4-methylnaphthalene (**3a**) in the form of a colorless oil.

1-Allyl-4-methylnaphthalene **(3a)**: colorless oil (33.5 mg, 92% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04–7.98 (m, 2H), 4.49 (ddd, J = 8.4, 7.2, 4.4 Hz, 2H), 7.22 (dd, J = 9.6, 7.2 Hz, 2H), 6.13–6.06 (m, 1H), 5.09–5.05 (m, 2H), 3.79 (d, J = 6.0 Hz, 2H), 2.65 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 137.4, 134.4, 133.1, 133.0, 132.1, 126.5, 125.5, 124.9, 124.7, 116.1, 37.4, 19.5; IR (neat) 3072, 3033, 2976, 1637, 1597, 1423, 912, 828, 750 cm^{-1}; HRMS (EI, m/z) calcd for $C_{14}H_{14}$: 182.1096 [M]$^+$; found: 182.1104.

4-Allyl-1,2-dimethylnaphthalene **(3b)**: colorless oil (30.6 mg, 78% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 (dd, J = 22.0, 8.4 Hz, 2H), 7.47–7.42 (m, 2H), 7.15 (s, 1H), 6.13–6.06 (m, 1H), 5.10–5.06 (m, 2H), 3.77 (d, J = 6.4 Hz, 2H), 2.56 (s, 3H), 2.44 (s, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 141.4, 139.0, 137.9, 137.7, 129.1, 128.8, 126.6, 126.2, 115.8, 41.7, 40.0, 18.6; IR (neat) 3073, 2975, 2864, 1638, 1514, 1382, 993, 911, 753 cm^{-1}; HRMS (EI, m/z) calcd for $C_{15}H_{16}$: 196.1252 $[M]^+$; found: 196.1256.

1-Allyl-4-benzylnaphthalene **(3c)**: colorless oil (43.9 mg, 85% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (dd, J = 17.6, 8.0 Hz, 2H), 7.54–7.46 (m, 2H), 7.33–7.20 (m, 7H), 6.20–6.13 (m, 1H), 5.17–5.13(m, 2H), 4.47 (s, 2H), 3.87 (d, J = 6.4 Hz, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 140.9, 137.2, 135.5, 135.2, 132.6, 128.9, 128.6, 127.3, 126.2, 125.8, 125.6, 125.1, 124.9, 116.3, 39.3, 37.5; IR (neat) 3078, 3020, 2976, 2853, 1638, 1497, 913, 755, 689 cm^{-1}; HRMS (EI, m/z) calcd for $C_{20}H_{18}$: 258.1409 $[M]^+$; found: 258.1414.

1-Allyl-4-(2'-chlorobenzyl)naphthalene **(3d)**: colorless oil (40.3 mg, 69% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.49–7.39 (m, 3H), 7.25 (d, J = 8.8 Hz, 1H), 7.14–7.10 (m, 2H), 7.02 (ddd, J = 8.8, 7.6, 1.2 Hz, 1H), 6.84 (dd, J = 7.6, 1.2 Hz, 1H), 6.16–6.06 (m, 1H), 5.12–5.07 (m, 2H), 4.48 (s, 2H), 3.82 (d, J = 6.0 Hz, 2H); ^{13}C{^{1}H}NMR (100 MHz, CDCl3) δ 138.3, 137.1, 135.3, 134.2, 133.9, 132.5, 130.7, 129.4, 127.6, 127.1, 126.8, 126.1, 125.8, 125.6, 124.8, 116.2, 37.4, 36.4; IR (neat) 3075, 3005, 2975, 1595, 1486, 1071, 914, 750 cm^{-1}; HRMS (EI, m/z) calcd for $C_{20}H_{17}Cl$: 292.1019 $[M]^+$; found: 292.1017.

1-Allyl-4-(4'-bromobenzyl)naphthalene **(3e)**: colorless oil (40.3 mg, 60% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.45 (ddd, J = 21.2, 14.8, 7.2 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 7.2 Hz, 1H), 7.19 (d, J = 7.2 Hz, 1H), 7.02 (d, J = 8.4 Hz, 2H), 6.15–6.05 (m, 1H), 5.12–5.07 (m, 2H), 4.34 (s, 2H), 3.82 (d, J = 6.0 Hz, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 139.8, 137.0, 135.4, 134.7, 131.5, 130.4, 127.3, 126.0, 125.8, 125.6, 124.8, 124.8, 119.9, 116.3, 38.6, 37.4; IR (neat) 3073, 3008, 2975, 1594, 1472, 1443, 1040, 914, 749 cm^{-1}; HRMS (EI, m/z) calcd for $C_{20}H_{17}Br$: 336.0514 $[M]^+$; found: 336.0518.

4-Allyl-1,2-dimethylbenzene **(3f)**: colorless oil (23.1 mg, 79% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.06 (d, J = 7.6 Hz, 1H), 6.97 (s, 1H), 6.93 (d, J = 7.6 Hz, 1H), 5.99–5.91 (m, 1H), 5.10–5.03 (m, 2H), 3.32 (d, J = 6.8 Hz, 2H), 2.24 (s, 3H), 2.23 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 137.9, 137.5, 136.6, 134.2, 130.0, 129.7, 126.0, 115.5,

39.9, 19.8, 19.4; IR (neat) 2916, 2849, 1735, 1658, 1576, 1468, 1384, 1132 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{14}$: 146.1096 $[M]^+$; found: 146.1090.

4-Allyl-2-fluoro-1-methylbenzene **(3g)**: colorless oil (22.8 mg, 76% yield). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.10–7.06 (m, 1H), 6.86–6.82 (m, 2H), 5.98–5.88 (m, 1H), 5.10–5.06 (m, 2H), 3.33 (d, J = 6.4 Hz, 2H), 2.23 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 161.3 (d, J = 242.9 Hz), 139.7 (d, J = 7.2 Hz), 136.9, 131.2 (d, J = 5.4 Hz), 123.9 (d, J = 3.2 Hz), 122.3 (d, J = 17.2 Hz), 116.1, 115.0 (d, J = 21.8 Hz), 39.6 (d, J = 1.5 Hz), 14.2 (d, J = 3.5 Hz); IR (neat) 3080, 3026, 2926, 1578, 1508, 1422, 1253, 1116, 996, 816 cm^{-1}; HRMS (EI, m/z) calcd for $C_{10}H_{11}F$: 150.0845 $[M]^+$; found: 150.0843.

4-Allyl-2-chloro-1-methylbenzene **(3h)**: colorless oil (27.2 mg, 82% yield). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.20–7.13 (m, 2H), 6.99 (dd, J = 7.6, 1.2 Hz, 1H), 6.00–5.89 (m, 1H), 5.12–5.08 (m, 2H), 3.34 (d, J = 6.4 Hz, 2H), 2.36 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 139.4, 137.0, 134.0, 131.0, 129.2, 127.0, 116.3, 39.5, 19.7; IR (neat) 3077,2978, 2923,1639, 1493, 1437, 1051,916, 815cm^{-1}; HRMS (EI, m/z) calcd for $C_{10}H_{11}Cl$: 166.0549 $[M]^+$; found: 166.0557.

4-Aallyl-2-phenyl-1-methylbenzene **(3i)**: colorless oil (38.3 mg, 92% yield). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.42–7.39 (m, 2H), 7.35–7.31 (m, 3H), 7.20 (d, J = 7.6 Hz, 1H), 7.10–7.07 (m, 2H), 6.02–5.95 (m, 1H), 5.12–5.04 (m, 2H), 3.39 (d, J = 6.4 Hz , 2H), 2.24 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 142.0, 141.9, 137.5, 134.6, 133.0, 130.4, 130.0, 129.2, 128.0, 127.4, 126.7, 115.8, 39.8, 20.0; IR (neat) 3056, 2923, 2854, 1638, 1486, 1441, 913, 701 cm^{-1}; HRMS (EI, m/z) calcd for $C_{16}H_{16}$: 208.1252 $[M]^+$; found: 208.1258.

4-Allyl-1-methyl-2-(phenylethynyl)benzene **(3j)**: colorless oil (30.2 mg, 65% yield). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.53–7.51 (m, 2H), 7.33–7.30 (m, 4H), 7.14 (d, J = 7.6 Hz, 1H), 7.04 (dd, J = 8.0 , 1.6 Hz, 1H), 5.98–5.89 (m, 1H), 5.10–5.05 (m, 2H), 3.33 (d, J = 7.2 Hz, 2H), 2.47 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 138.0, 137.5, 137.4, 132.1, 131.7, 129.7, 128.9, 128.5, 128.3, 123.8, 123.2, 116.1, 93.3, 88.7, 39.7, 20.4; IR (neat) 3423, 3073, 2976, 1638, 1597, 1494, 914, 754 cm^{-1}; HRMS (EI, m/z) calcd for $C_{18}H_{16}$: 232.1252 $[M]^+$; found: 232.1247.

4-Allyl-1,3-dimethylbenzene **(3k)**[22]: Colorless oil (21.0 mg, 72% yield). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.02 (d, J = 7.2 Hz, 1H), 6.96–6.94 (m, 2H), 5.98–5.88 (m, 1H), 5.04–4.96 (m, 2H), 3.32 (d, J = 6.0 Hz, 2H), 2.28 (s, 3H), 2.25 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz,

$CDCl_3$) δ 136.9, 136.2, 135.8, 135.1, 131.0, 129.1, 126.7, 115.4, 37.4, 20.9, 19.3.

4-Allyl-3-phenyl-1-methylbenzene **(3l)**: colorless oil (32.1 mg, 77% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40–7.36 (m, 2H), 7.34–7.29 (m, 3H), 7.18 (d, J = 8.0 Hz, 1H), 7.12 (dd, J = 8.0, 1.6 Hz, 1H), 7.07 (s, 1H), 5.90–5.83 (m, 1H), 5.00–4.88 (m, 2H), 4.29 (d, J = 6.4 Hz, 2H), 2.35 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 141.8, 141.7, 138.0, 135.6, 134.2, 130.8, 129.7, 129.2, 128.2, 128.0, 126.8, 115.5, 37.1, 21.0; IR (neat) 3058, 2919, 2837, 1637, 1487, 912, 823, 701 cm^{-1}; HRMS (EI, m/z) calcd for $C_{16}H_{16}$: 208.1252 $[M]^+$; found: 208.1250.

1,2-Diallyl-4-methylbenzene **(3m)**: colorless oil (30.3 mg, 88% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.05–6.97 (m, 3H), 6.00–5.90 (m, 2H), 5.09–4.96 (m, 4H), 3.36–3.34 (m, 4H), 3.00 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 137.8, 137.4, 137.2, 135.9, 134.9, 130.3, 129.5, 127.2, 115.6, 115.5, 37.1, 36.7, 21.0; IR (neat) 3003, 2955, 2923, 2853, 1637, 1457, 911, 823 cm^{-1}; HRMS (EI, m/z) calcd for $C_{13}H_{16}$: 172.1252 $[M]^+$; found: 172.1254.

2-Allyl-1,3,5-trimethylbenzene **(3n)**[23]: colorless oil (23.4 mg, 73% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.91 (s, 1H), 6.90 (s, 1H), 5.96–5.87 (m, 1H), 5.04–4.96 (m, 2H), 3.30 (d, J = 6.4 Hz, 2H), 2.22 (s, 3H), 2.20 (s, 6H).

3-Allyl-2,4,5-trimethylbenzene **(3o)**[24]: colorless oil (24.6 mg, 77% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.87 (s, 2H), 5.94–5.88 (m, 1H), 5.02–4.87 (m, 2H), 3.39 (d, J = 5.6 Hz, 2H), 2.32 (s, 3H), 2.31 (s, 3H), 2.29 (s, 3H).

5-Allyl-1,2,3-trimethylbenzene **(3p)**: colorless oil (26.5 mg, 83% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.84 (s, 2H), 5.99–5.89 (m, 1H), 5.10–5.02 (m, 2H), 3.28 (d, J = 6.8 Hz, 2H), 2.25 (s, 6H), 2.13 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 138.0, 136.9, 136.5, 132.7, 127.8, 115.4, 39.9, 20.6, 15.0; IR (neat) 3077, 2924, 2853, 1639, 1485, 1460, 1377, 993, 911, 858 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{16}$: 160.1252 $[M]^+$; found: 160.1256.

4-Allyl-2-methoxy-1-methylbenzene **(3q)**: colorless oil (26.0 mg, 80% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.05 (d, J = 7.5 Hz, 1H), 6.69 (d, J = 7.5 Hz, 1H), 6.66 (s, 1H), 6.01–5.93 (m, 1H), 5.11–5.05 (m, 2H), 3.82 (s, 3H), 3.36 (d, J = 7.0 Hz, 2H), 2.18 (s, 3H); ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) δ 157.7, 138.9, 137.7, 130.5, 124.2, 120.3, 115.6, 110.4, 55.2, 40.3, 15.8; IR (neat) 3077, 3001, 2923, 2834, 1638, 1613, 1584, 1509, 1465, 1414, 1255, 1133, 1043, 995, 913, 813, 747 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{14}O$: 162.1045 $[M]^+$; found: 162.1043.

5-Allyl-2-methylbenzonitrile **(3r)**: colorless oil (22.6 mg, 72% yield). ^{1}H NMR ($CDCl_3$,

400 MHz) δ 7.42 (d, J = 1.6 Hz, 1H), 7.30 (dd, J = 8.0, 1.6 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 5.96–5.86 (m, 1H), 5.14–5.06 (m, 2H), 3.37 (d, J = 6.8 Hz, 2H), 2.51 (s, 3H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$) δ 139.6, 138.3, 136.1, 133.1, 132.4, 130.3, 118.3, 116.9, 112.7, 39.1, 20.0; IR (neat) 3079, 2920, 2226, 1639, 1418, 1436, 1384, 1288, 995, 918, 829, 766, 478 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{11}N$: 157.0891 $[M]^+$; found: 157.0891.

Methyl 5-allyl-2-methylbenzoate **(3s)**: colorless oil (26.6 mg, 70% yield). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.73 (d, J = 1.6 Hz, 1H), 7.22 (dd, J = 7.6, 1.6 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 6.00–5.90 (m, 1H), 5.10–5.06 (m, 2H), 3.88 (s, 3H), 3.38 (d, J = 6.8 Hz, 2H), 2.56 (s, 3H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$) δ 168.2, 137.9, 137.5, 137.0, 132.3, 131.8, 130.6, 129.5, 116.1, 51.8, 39.5, 21.3; IR (neat) 3079, 2978, 2951, 2929, 2848, 2226, 1724, 1499, 1435, 1298, 1260, 1197, 1082, 994, 916, 785 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{14}O_2$: 190.0994 $[M]^+$; found: 190.0990.

1-Allyl-4-benzylbenzene **(3t)**: colorless oil (25.8 mg, 62% yield). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.26–7.24 (m, 2H), 7.18–7.16 (m, 2H), 7.10 (m, 3H), 5.99–5.89 (m, 1H), 5.08–5.02 (m, 2H), 3.94 (s, 2H), 3.34 (d, J = 6.4 Hz, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 137.5, 133.6, 133.0, 130.9, 129.8, 125.5, 124.6, 124.5, 124.5, 116.1, 37.4, 20.9; IR (neat) 3082, 3025, 2977, 2849, 1638, 1511, 1494, 913, 697cm^{-1}; HRMS (EI, m/z) calcd for $C_{16}H_{16}$: 208.1252 $[M]^+$; found: 208.1256.

9-Allyl-10-methylanthracene **(3u)**: green solid (30.2 mg, 65% yield), mp 98.3–99.2 ºC. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.39–8.36 (m, 2H), 8.32–8.28 (m, 2H), 7.57–7.53 (m, 4H), 6.31–6.21 (m, 1H), 5.13–4.97 (m, 2H), 4.40 (dd, J = 4.0, 2.0 Hz, 2H), 3.14 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 136.7, 130.1, 129.8, 125.5, 125.2, 125.1, 124.8, 116.0, 32.1, 14.3; IR (KBr) 3073, 2975, 2869, 1637, 1443, 917, 745 cm^{-1}; HRMS (EI, m/z) calcd for $C_{18}H_{16}$: 232.1252 $[M]^+$; found: 232.1254.

1-Methyl-4-(2-methylallyl)naphthalene **(4a)**: colorless oil (34.5 mg, 88% yield). ^1H NMR ($CDCl_3$, 500 MHz) δ 8.03–8.00 (m, 2H), 7.51–7.46 (m, 2H), 7.24–7.21 (m, 2H), 4.84 (s, 1H), 4.62 (s, 1H), 3.75 (s, 2H), 2.67 (s, 3H), 1.77 (s, 3H); $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$) δ 144.9, 133.9, 133.0, 132.5, 126.9, 126.3, 125.34, 125.30, 124.9, 124.7, 112.1, 41.6, 22.8, 19.5; IR (neat) 3071, 2968, 3035, 2930, 1650, 1597, 1515, 1443, 1393, 1022, 889, 817, 797, 749 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{16}$: 196.1252 $[M]^+$; found: 196.1254.

(E)-1-(But-2-en-1-yl)-4-methylnaphthalene **(4b)** and 1-(but-3-en-2-yl)-4-methylnaphthalene (**4c**): colorless oil (27.5 mg, 70% yield). ^1H NMR ($CDCl_3$, 500 MHz) δ for **4b** 8.05–7.24 (m, 6H), 5.68–5.59 (m, 2H), 3.81 (d, J = 5.5 Hz,

2H), 2.67 (s, 3H), 1.80 (d, J = 6.0 Hz, 3H); for **4c** 8.16–7.24 (m, 6H), 6.18–6.12 (m, 1H), 5.13–5.09 (m, 2H), 4.29–4.26 (m, 1H), 2.67 (s, 3H), 1.50 (d, J = 7.0 Hz, 3H).

3-Allyl-3-methyl-6-methylenecyclohexa-1,4-diene (**5**)[14b]: colorless oil (17.5 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 (d, J = 9.6 Hz, 2H), 5.62–5.74 (m, 3H), 4.97–5.01 (m, 2H), 4.81 (s, 2H), 2.14 (d, J = 7.2 Hz, 2H), 1.10 (s, 3H).

(E)-1-Allyl-4-benzylidene-1,4-dihydronaphthalene (**6**)[14a]: colorless oil (46.5 mg, 90% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ for 7.85–7.83 (m, 1H), 7.41–7.34 (m, 4H), 7.28–7.24 (m, 4H), 7.14 (s, 1H), 6.95 (d, J = 10.0 Hz, 1H), 6.13–6.08 (m, 1H), 5.80–5.70 (m, 1H), 5.02–4.98 (m, 2H), 3.69–3.65 (m, 1H), 2.56–2.40 (m, 2H).

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SUPPORTING INFORMATION

Copies of ^{1}H and ^{13}C{^{1}H}NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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