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Propargylic and Allenic Carbocycle Synthesis through Palladium-Catalyzed Dearomatization Reaction

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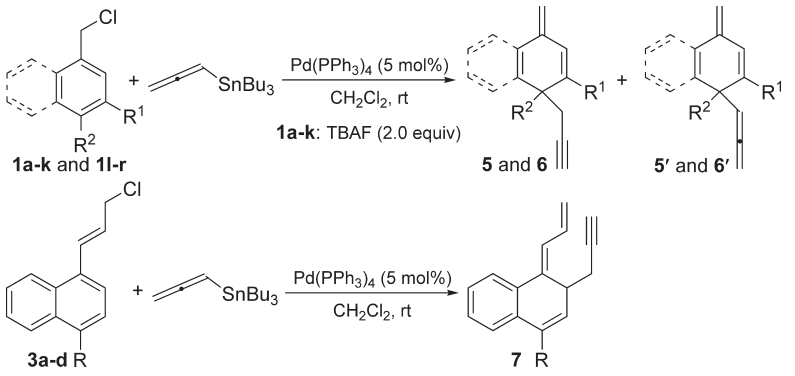

The dearomatization reaction of benzylic chlorides (**1a**−**k**), chloromethylnaphthalenes (**1l**−**r**), and naphthalene allyl chlorides (**3a**−**d**) with allenyltributyltin proceeded smoothly in the presence of $Pd(PPh_3)_4$ catalyst at room temperature to give the corresponding propargylated and/or allenylated dearomatization products (**5**, **5′**; **6**, **6′**; and **7**, respectively) in high to fair yields. The reaction of **1a**−**k** proceeded smoothly in the presence of TBAF, whereas it was not necessary to use TBAF as an additive in the reactions of **1l**−**k** and **3a**−**d**. These reactions provided a new and efficient method for the synthesis of propargylic and allenic carbocycles.

Introduction

Development of efficient methods for the synthesis of alicyclic compounds has attracted considerable attention because the aliphatic carbocycle moieties frequently appear in the molecules of natural products and bioactive compounds. Among the methods developed, the dearomatization reaction of arenes has become a simple and useful tool for the preparation of alicyclic compounds since the aromatic compounds are stable and widely available. Over the past four decades, many types of dearomatization reaction, including oxidation,[1] reduction,[2] photocycloaddition,[3] [2,3]-σ-rearrangement,[4]

(1) For oxidation of phenol and its derivatives, see: (a) Stang, P. J.; Zhdankin, V. V. *Chem. Rev*. **1996**, *96*, 1123–1178. (b) Lebrasseur, N.; Fan, G. J.; Oxoby, M.; Looney, M. A.; Quideau, S. *Tetrahedron* **2005**, *61*, 1551–1562. (c) Carreño, M. C.; González-López, M.; Urbano, A. *Angew. Chem*. **2006**, *118*, 2803−2807; *Angew. Chem., Int. Ed*. **2006**, *45*, 2737−2741. (d) Pitsinos, E. N.; Cruz, A. *Org. Lett*. **2005**, *7*, 2245–2248. (e) Stephane, Q.; Laurent, P.; Aurelie, O.; Julien, G. *Molecules* **2005**, *10*, 201–216. (f) Mejorado, L. H.; Hoarau, C.; Pettus, T. R. R. *Org. Lett*. **2004**, *6*, 1535–1538. (g) Van De Water, R. W.; Hoarau, C.; Pettus, T. R. R. *Tetrahedron Lett*. **2003**, *44*, 5109–5133. (h) Mandal, S.; Macikenas, D.; Protasiewicz, J. D.; Sayre, M. L. *J. Org. Chem*. **2000**, *65*, 4804–4809. (i) Swenton, J. S.; Carpenter, K.; Chen, Y.; Kerns, M. L.; Morrow, G. W. *J. Org. Chem*. **1993**, *58*, 3308–3316. . See also ref 1h. For microbial oxidation, see: (j) Bui, V.; Hansen, T. V.; Stenstrøm, Y.; Ribbons, D. W.; Hudlicky, T. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1669–1672. (k) Boyd, D. R.; Sharma, N. D.; Bowers, N. I.; Duffy, J.; Harrison, J. S.; Dalton, H. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1345–1350. (l) Boyd, D. R.; Sharma, N. D.; Barr, S. A.; Dalton, H.; Chima, J.; Whited, G.; Seemayer, R. *J. Am. Chem. Soc*. **1994**, *116*, 1147–1148.

(2) For catalytic hydrogenation, see: (a) Heller, E.; Lautenschlager, W.; Holzgrabe, U. *Tetrahedron Lett*. **2005**, *46*, 1247–1249. (b) Donohoe, T. J.; Garg, R.; Stevenson, C. A. *Tetrahedron: Asymmetry* **1996**, *7*, 317–344. For Birch reduction, see: (c) Birch, A. J. *Pure Appl. Chem*. **1996**, *68*, 553–556.

(3) (a) For a review, see: Cornelisse, J. *Chem. Rev*. **1993**, *93*, 615–669. (b) Kohmoto, S.; Masu H.; Tatsuno, C.; Kishikawa, K.; Yamamoto, M.; Yamaguchi, K. *J. Chem. Soc., Perkin Trans. 1*, **2000**, 4464−4468 and references therein. (c) Yokoyama, A.; Mizuno, K. *Org. Lett*. **2000**, *2*, 3457−3459 and references therein.

(4) For nitrogen−ylide rearrangement, see: (a) Shirai, N.; Watanabe, Y.; Sato, Y. *J. Org. Chem*. **1990**, *55*, 2767−2770 and references therein. For sulfur−ylide rearrangement, see: (b) McComas, C. C.; Van Vranken, D. L. *Tetrahedron Lett*. **2003**, *44*, 8203−8205 and references therein. (c) Burdon, M. G. *J. Am. Chem. Soc*. **1967**, *89*, 4725–4735. (d) Hauser, C. R.; Kantor, S. W.; Brasen, W. R. *J. Am. Chem. Soc*. **1953**, *75*, 2660–2663. For Still−Wittig rearrangement, see: (e) Monje, P.; Grana, P.; Paleo, M. R.; Sardina, F. J. *Org. Lett*. **2006**, *8*, 951–954. (f) Caruana, P. A.; Frontier, A. J. *Tetrahedron* **2004**, *60*, 10921–10926.

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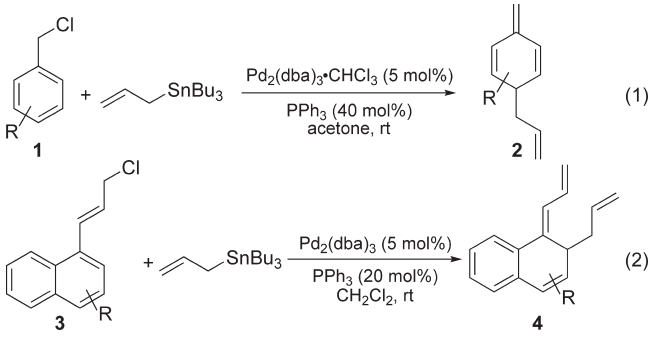
SCHEME 1. Allylative Dearomatization Reactions of Benzylic Chlorides 1 and Naphthalene Allyl Chlorides 3 with Allyltributyltin Catalyzed by Pd



electrophilic addition,[5] nucleophilic addition,[6] and other reactions,[7] have been developed for breaking up the conjugated π-system. The complexation of the aromatic system to transition metals leads to activation of arenes and thus facilitates the electrophilic addition of [M(η^2-arene)] (M = Os, Re, Mo, and W) complexes and the nucleophilic addition of [M(η^6-arene)] (M = Cr, Mn, and Ru) complexes.

In our previous study, we found benzylic chlorides **1** reacted with allytributyltin in the presence of palladium catalyst to give *para* allylated dearomatization products **2** (Scheme 1, eq 1).[8] Furthermore, we found the reaction of naphthalene allyl chlorides **3** with allytributyltin in the presence of palladium catalyst furnished *ortho* allylated products **4** (Scheme 1, eq 2).[9] In the two cases the corresponding Stille cross-coupling products were not observed at all.

In this paper, we report that the reaction of benzylic chlorides **1a**−**k** and chloromethylnaphthalenes **1l**−**r** with allenyltributyltin gave the propargylic and allenic dearomatization products **5**, **5′**and **6**, **6′** (Scheme 2, eqs 3 and 4). However, the reaction of naphthalene allyl chlorides **3a**−**d** with allenyltributyltin offered only propargylic dearomatization products **7** (Scheme 2, eq 5).

SCHEME 2. Palladium-Catalyzed Dearomatization Reactions of Benzylic Chlorides 1a−k, Chloromethylnaphthalenes 1l−r, and Naphthalene Allyl Chlorides 3a−d with Allenyltributyltin

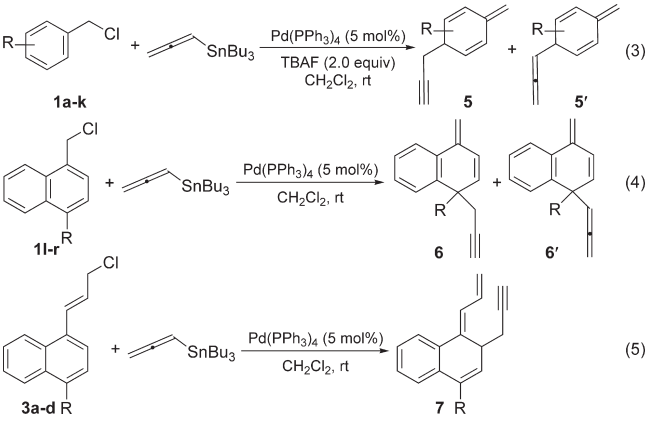
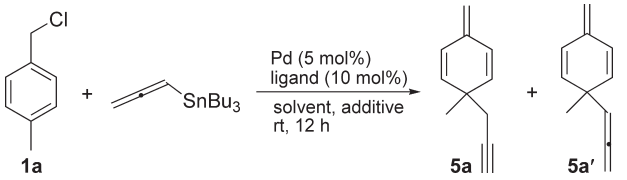


TABLE 1. Optimization of Pd-Catalyzed Dearomatization Reaction of 1a with Allenyltributyltin[a]



entry	Pd source/ligand/solvent/additive	yield [%][b,c]
1	$Pd_2(dba)_3/PPh_3$/acetone/none	11 (86/14)
2	$Pd(acac)_2/PPh_3$/acetone/nones	16 (80/20)
3	$Pd(OAc)_2/PPh_3$/acetone/none	17 (50/50)
4	$PdCl_2(CH_3CN)_2/PPh_3$/acetone/none	NR[d]
5	$Pd(PPh_3)_4$/none/acetone/none	35 (76/24)
6	$Pd(PPh_3)_4$/none/CH_3CN/none	24 (93/7)
7	$Pd(PPh_3)_4$/none/CH_2Cl_2/none	36 (86/14)
8	$Pd(PPh_3)_4$/none/THF/none	7 (46/54)
9	$Pd(PPh_3)_4$/none/ethyl ether/none	NR[d]
10	$Pd(PPh_3)_4$/none/CH_2Cl_2/KF	66 (45/55)
11	$Pd(PPh_3)_4$/none/CH_2Cl_2/TBAF	82 (98/2)
12	$Pd(PPh_3)_4$/none/CH_2Cl_2/DIPEA	23 (75/25)

[a]Reaction conditions: 0.5 mmol of **1a**, 0.6 mmol of allenyltributyltion, 5 mol % Pd, 10 mol % ligand, and 2.0 equiv of additive in 5 mL of solvent under nitrogen atmosphere at room temperature for 12 h. [b]The yield was determined by ^{1}H NMR using 4-bromobenzaldehyde as an internal standard. [c]The ratio of **5a** to **5a′** is indicated in parentheses. [d]NR: no reaction.

Results and Discussion

In our initial studies, we chosen the reaction of 4-methyl benzylic chloride (**1a**) with allenyltributyltin as a model reaction to screen the reaction conditions, and the results are shown in Table 1. When the reaction of **1a** with allenyltributyltin was carried out under similar conditions as employed in the allylative dearomatization of **1a** with allyltributyltin,[8] a 86/14 mixture of **5a** and **5a′** was obtained in only 11% yield (entry 1). The use of $Pd(acac)_2$, $Pd(OAc)_2$, and $PdCl_2(CH_3CN)_2$ as Pd source, instead of $Pd_2(dba)_3$, did not give the desired products in high yields (entries 2−4). Slightly increased yield was obtained when the reaction was performed in the presence of $Pd(PPh_3)_4$ as a catalyst in

(5) For reviews, see: (a) Keane, J. M.; Harman, W. D. *Organometallics* **2005**, *24*, 1786–1798. (b) Harman, W. D. *Coord. Chem. Rev.* **2004**, *248*, 853–866. (c) Pape, A. R.; Kaliappan, K. P.; Kündig, E. P. *Chem. Rev.* **2000**, *100*, 2917–2940. See also: (d) Delafuente, D. A.; Myers, W. H.; Sabat, M.; Harman, W. D. *Organometallics* **2005**, *24*, 1876–1885.

(6) Arenes were activated by electron-withdrawing groups; see: (a) Ramallal, A. M.; Fernández, I.; Ortiz, F. L.; González, J. *Chem.—Eur. J.* **2005**, *11*, 3022−3031 and references therein. (b) Wang, Z.; Xi, Z. *Synlett* **2006**, 1275–1277. (c) Clayden, J.; Knowles, F. E.; Baldwin, L. R. *J. Am. Chem. Soc.* **2005**, *127*, 2412–2413. (d) Clayden, J.; Turnbull, R.; Helliwell, M.; Pinto, I. *Chem. Commun.* **2004**, 2430–2431. (e) Clayden, J.; Tumbull, R.; Pinto, I. *Org. Lett.* **2004**, *6*, 609–611. (f) Clayden, J.; Kenworthy, M. N.; Helliwell, M. *Org. Lett.* **2003**, *5*, 831–834. (g) Barluenga, J.; Nandy, S. K.; Laxmi, Y. R. S.; Suárez, J. R.; Merino, I.; Flórez, J.; García-Granda, S.; Montejo-Bernardo, J. *Chem.—Eur. J.* **2003**, *9*, 5725–5736. Arenes were activated by complexation to transition metals; see: (h) Zhou, L.; Wu, L. Z.; Zhang, L. P.; Tung, C. H. *Organometallics* **2006**, *25*, 1707–1711. (i) Kündig, E. P.; Bellido, A.; Kaliappan, K. P.; Pape, A. R.; Radix, S. *Org. Biomol. Chem.* **2006**, *4*, 342–351. (j) Pigge, F. C.; Coniglio, J. J.; Dalvi, R. *J. Am. Chem. Soc.* **2006**, *128*, 3498–3499. (k) Pigge, F. C.; Coniglio, J. J.; Rath, N. P. *Org. Lett.* **2003**, *5*, 2011–2014. . See also ref 6c.

(7) For organolanthanide-induced dearomatization, see: (a) Liu, R.; Zhang, C.; Zhu, Z.; Luo, J.; Zhou, X.; Weng, L. *Chem.—Eur. J.* **2006**, *12*, 6940–6952. For radical addition, see: (b) Crich, D.; Sannigrahi, M. *Tetrahedron* **2002**, *58*, 3319–3322. (c) Boivin, J.; Yousfi, M.; Zard, S. Z. *Tetrahedron Lett.* **1997**, *38*, 5985–5988. For a dearomatization involving naphthylborate anions, see: (d) Negishi, E.; Merrill, R. E. *J. Chem. Soc., Chem. Commun.* **1974**, 860–861.

(8) Bao, M.; Nakamura, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **2001**, *123*, 759–760.

(9) Lu, S.; Xu, Z.; Bao, M.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 4366–4369.

acetone, CH_3CN, or CH_2Cl_2 (entries 5−7, 35%, 24%, and 36%, respectively). However, the yield was decreased to 7% and 0%, when the solvent was changed to tetrahydrofuran (THF) or diethyl ether (entries 8 and 9). It was thought that the lower yields of the desired products **5a** and **5a′** would be due to lower reactivity of allenyltributyltin. It has been described that fluoride additives could be employed to activate organotin reagents.[10] Indeed, the reaction yield was dramatically increased when potassium fluoride (KF) or tetrabutylammonium fluoride (TBAF) was added in the reaction mixture (entries 10 and 11, 66% and 82%, respectively). However, the use of *N*,*N*-diisopropylethylamine (DIPEA)[11] as an additive did not improve the yield (entry 13, 23%). Under the above conditions examined, **5a** was usually obtained as a major product. The highest ratio of **5a** to **5a′** was 98/2, as shown in entry 11. Therefore, in the subsequent studies, the reactions of benzylic chlorides **1a**−**k** with allenyltributyltin were performed in the presence of $Pd(PPh_3)_4$ as a catalyst using TBAF as an additive in CH_2Cl_2.

The reactions of various benzylic chlorides **1a**−**k** with allenyltributyltin were performed under optimized conditions, and the results are summarized in Table 2. After the reaction of **1a** was completed, only the major product **5a** could be isolated in 71% yield (entry 1). Although the formation of **5a′** was detected by ^{1}H NMR analysis of a product mixture in entry 11, Table 1, **5a′** was not isolated; it was considered that the formation of **5a′** was too small. Products **5b** and **5b′** were obtained in total 67% yield with a ratio of 75/25 from the reaction of **1b** (entry 2). The substrates **1c** and **1d** having one or two methoxy groups on aromatic ring also smoothly underwent the dearoamtization reaction to offer the propargylic compounds **5c** and **5d** in 82% and 78% yield, respectively (entries 3 and 4). The reaction of 4-chlorobenzyl chloride (**1e**) gave product **5e** bearing two propargyl groups on the *para* position of the exocyclic methylene group in 92% yield (entry 5). It was considered that the product **5e** would be formed through the second propargylation of the intermediate **8**, which was given by the first propargylation, as ordinarily observed. However, the substrate **1f** possessing two chlorine atoms on the aromatic ring could not undergo the dearomatization reaction (entry 6); perhaps this is due to the fact that the electron-deficient benzene ring of **1f** could not generate a stable π-benzylpalladium chloride intermediate.[8] A similar result was observed when 4-formylbenzyl chloride (**1g**) was treated with allenyltributyltin (entry 7). Interestingly, an excellent yield was obtained when the formyl group of **1g** was protected by ethylene glycol (entry 8, 92%). A lower yield was obtained from the reaction of 4-*tert*-butylbenzyl chloride (**1i**) with allenyltributyltin even under the prolonged reaction time (48 h); perhaps this is due to the steric hindrance of a *tert*-butyl group at the reaction site. Reaction of substrate **1j** having two benzene rings occurred selectively on the electron-richer benzene ring to give propargylic and allenic products **5j** and **5j′** in total 63% yield with a ratio of 62/28 (entry 10). The propargylic and allenic products **5k** and **5k′** were obtained in total 48% yield with a ratio of 83/17 from the reaction of substrate **1k**, which has a structure similar to **1j**. The desired reaction occurred selectively on the sterically less hindered benzene ring (entry 11).

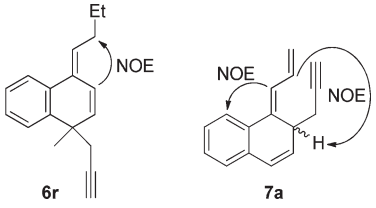
We then examined the reactions of chloromethylnaphthalene derivatives **1l**−**r** with allenyltributyltin to expand the scope of this type dearomatization reaction, and the results are shown in Table 3. Comparison of the result of entry 1 (85% yield with a ratio of 20/80) with that of entry 2 (89% yield with a ratio of 18/82) leads to a conclusion that the reaction of chloromethyl naphthalene **1l** did not need TBAF to activate allenyltributyltin. Therefore, in the following examples, we carried out the reactions of **1m**−**r** in the absence of TBAF. Only allenic product **6m′** could be isolated in 89% yield from the reaction of **1m** (entry 3). When a mixture of substrate **1n**, bearing a hydroxymethyl group on the *para* position of the chloromethyl group, and allenyltributyltin was treated as usual for 12 h, the expected product was not obtained and the starting materials were decomposed (entry 4). As expected, when the hydroxymethyl group of **1n** was protected by *tert*-butyldimethylsilyl group (TBS), the desired reaction proceeded to give propargylic and allenic products **6o** and **6o′** in total 94% yield with a ratio of 39/61 (entry 5). We then examined deprotection reaction of the product **6o** by using TBAF as a deprotection reagent, and the desired product **9** was obtained in 76% yield (Scheme 3). However, under the same deprotection reaction conditions, **6o′** underwent polymerization reaction. The reaction of substrate **1p** bearing a phenyl group on the *para* position of the chloromethyl group gave a propargylic product **6p** as a sole isolated product in 65% yield (entry 6). Allenyl group could be introduced into 9-(chloromethyl)anthracene (**1q**) to offer allenic product **6q′** in an excellent yield (entry 7, 96%). Finally, we examined the reaction of substrate **1r**, which had an ester as a leaving group (OCOR) and a hydrogen atom beta to the OCOR group, and found that this reaction proceeded more slowly than those of **1l**−**q** to provide propargylic product **6r** in 71% yield,[12] without the formation of any β-hydride elimination product (entry 8).[13]

A plausible mechanism for the dearomatization reactions of benzylic chlorides and chloromethylnaphthalenes is shown in Scheme 4. The oxidative addition of **1** to a Pd^0

(10) Fluoride additives have been utilized to activate organotin reagents. See: (a) Mee, S. P. H.; Lee, V.; Baldwin, J. E. *Chem.—Eur. J.* **2005**, *11*, 3294−3308 and references therein. TBAF was also employed as an additive to activate organosilane reagents. See: (b) Fernandes, R. A.; Yamamoto, Y. *J. Org. Chem.* **2004**, *69*, 735–738. (c) Nakamura, K.; Nakamura, H.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 2614–2615.

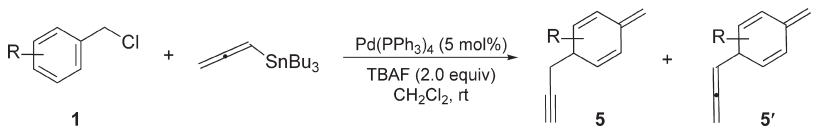
(11) It has been reported that organotin reagents could be activated by intramolecular coordination of nitrogen atom to Sn(IV). See: (a) Vedejs, E.; Haight, A. R.; Moss, W. O. *J. Am. Chem. Soc.* **1992**, *114*, 6556–6558. (b) Brown, J. M.; Pearson, M.; Jastrzebski, J. T. B. H.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1992**, 1440–1441. (c) Jensen, M. S.; Yang, C.; Hsiao, Y.; Rivera, N.; Wells, K. M.; Chung, J. Y. L.; Yasuda, N.; Hughes, D. L.; Reider, P. J. *Org. Lett.* **2000**, *2*, 1081–1084. (d) Sebahar, H. L.; Yoshida, K.; Hegedus, L. S. *J. Org. Chem.* **2002**, *67*, 3788–3795.

(12) The connection and configuration of products **6r** and **7a** were obtained from ^{1}H−^{1}H COSY and NOESY spectrum.

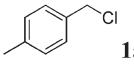
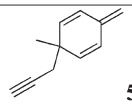
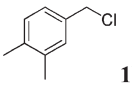
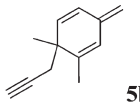
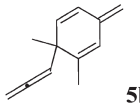
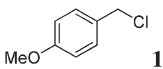
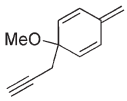
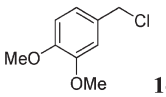
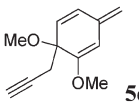
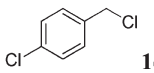
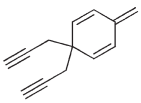
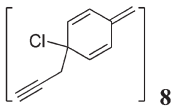
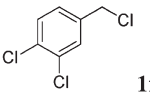
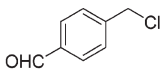
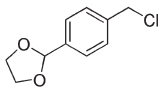
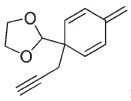
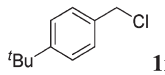
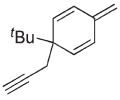
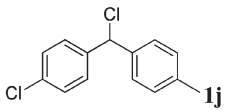
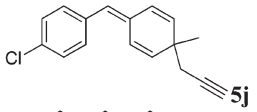
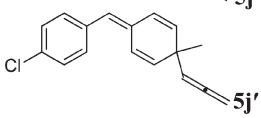
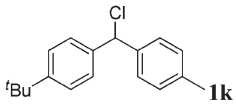
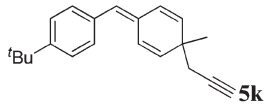
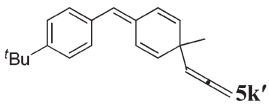


(13) In the Stille cross-coupling reaction of C(sp3)-X electrophiles, the β hydride elimination often gave alkenes in preference to coupling products; see: (a) Cárdenas, D. J. *Angew. Chem.* **2003**, *115*, 398−401; *Angew. Chem., Int. Ed.* **2003**, *42*, 384−387. (b) Luh, T. Y.; Leung, M. k.; Wong, K. T. *Chem. Rev.* **2000**, *100*, 3187–3204.

TABLE 2. Dearomatization Reaction of Benzylic Chlorides 1a−k with Allenyltributyltin[a]

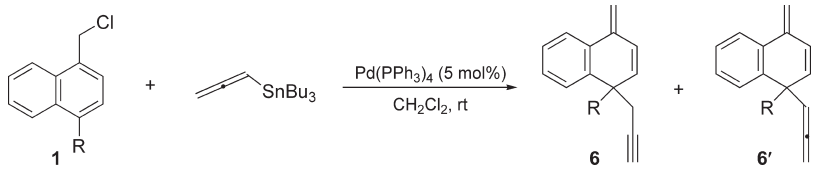


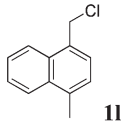
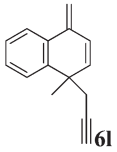
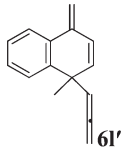
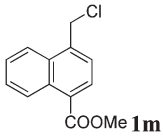
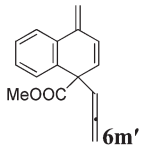
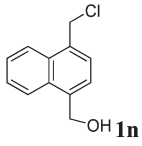
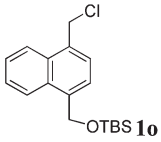
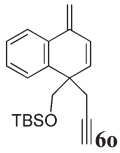
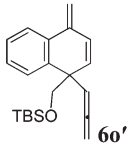
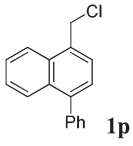
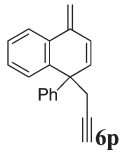
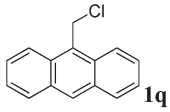
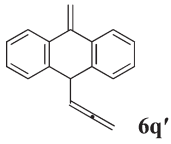
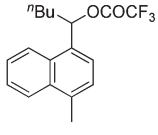
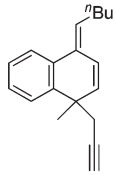
1 5 5′

entry	substrate	time (h)	product	yield [%][b]
1	 **1a**	12	 **5a**	71
2	 **1b**	6	 **5b**  **5b′**	67 (75/25)
3	 **1c**	12	 **5c**	82
4	 **1d**	10	 **5d**	78
5	 **1e**	3	 **5e**  **8**	92
6	 **1f**	24		NR[c]
7	 **1g**	24		NR[c]
8	 **1h**	8	 **5h**	92
9	 **1i**	48	 **5i**	25
10	 **1j**	12	 **5j**  **5j′**	63 (62/38)
11	 **1k**	72	 **5k**  **5k′**	48 (83/17)

[a]A mixture of benzylic chloride (0.5 mmol), allenyltributyltion (0.6 mmol), $Pd(PPh_3)_4$ (5 mol %), and TBAF (1.0 mmol) in dichloromethane (5 mL) was stirred at room temperature under nitrogen atmosphere for the period indicated in the table. [b]The ratio of **5** to **5′** is indicated in parentheses. [c]NR: no reaction. The starting material, benzylic chloride, was recovered, and the allenyltributyltin was decomposed.

TABLE 3. Dearomatization Reaction of Chloromethylnaphthalene Derivatives 1l−1s with Allenyltributyltin[a]



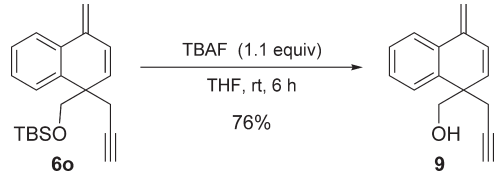
entry	substrate	time(h)	product	yield [%][b]
1	 **1l**	5	 **6l**  **6l′**	85 (20/80)[c]
2	**1l**	6	**6l**	**6l′**	89 (18/82)
3	 **1m**	4	 **6m′**	89
4	 **1n**	12		0
5	 **1o**	24	 **6o**  **6o′**	94 (39/61)
6	 **1p**	24	 **6p**	65
7	 **1q**	12	 **6q′**	96
8	 **1r**	48	 **6r**	71

[a]A mixture of chloromethylnaphthalene (0.5 mmol), allenyltributyltion (0.6 mmol), and $Pd(PPh_3)_4$ (5 mol %) in dichloromethane (5 mL) was stirred at room temperature under nitrogen atmosphere for the period indicated in the table. [b]The ratio of **6** to **6′** is indicated in parentheses. [c]One millimole of TBAF was used as an additive.

species would produce the η^3-allylpalladium chloride intermediate **A**, which would react with allenyltributylstannane to generate a η^3-allyl-η^3-propargylpalladium intermediate **B** upon ligand exchange. The isomerization of **B** would occur to give (η^3-allyl)allenylpalladium intermediate **C** and/or (η^3-allyl)propargylpalladium intermediate **D**, which could undergo reductive elimination to form the dearomatization products **5**, **6** and **5′**, **6′**, respectively, and regenerate Pd^0 catalyst.[14]

We finally investigated the reactions of naphthalene allyl chlorides **3a**−**d** with allenyltributyltin, and the results are summarized in Table 4. Similar to the chloromethyl

SCHEME 3. Deprotection Reaction of Propargylic Product 6o



naphthalene derivatives **1l**−**r**, naphthalene allyl chlorides **3a**−**d** also exhibited high reactivities in the dearomatization reaction. All of the reactions of **3a**−**d** with allenyltributyltin proceeded smoothly in the absence of TBAF activator to provide propargylic products in satisfactory yields. For example, the reaction of substrate **3a** completed within 4 h to give propargylic product **7a** in 93% yield (entry 1).[12] The reaction of substrate **3b** bearing a bromine atom in the *para* position of the chloroallyl group gave the desired product **7b** in 75% yield. A bromine atom remained on the product **7b**, suggesting that further manipulation may produce a useful compound. The substrate **3c** bearing a methyl group, an electron-donating group, underwent the dearomatization, but the reaction progress was slightly slow compared to the reactions of **3a** and **3b**, and the product **7c** was obtained in a good yield (entry 3, 84%). Obviously, the substrate **3d** exhibited a reactivity lower than that of substrates **3a**−**c**. Product **7d** was obtained in 62% yield after 24 h (entry 4).

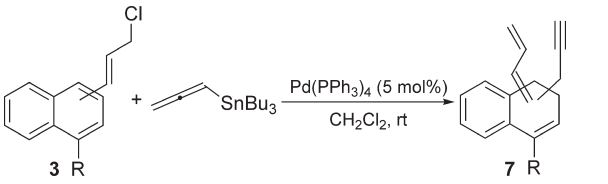
A plausible mechanism for the dearomatization reaction of naphthalene allyl chlorides is shown in Scheme 5. Naphthalene allyl chloride **3a** reacts with Pd^0 to produce the η^3-allylpalladium chloride intermediate **D**, which would react with allenyltributylstannane to generate a η^3-allyl-η^3-propargylpalladium intermediate **E** upon ligand exchange. The isomerization of **E** would give η^3-allyl-η^1-allenylpalladium intermediate **F**, which could undergo reductive elimination to form the dearomatization product **7a** and regenerate Pd^0 catalyst.[14]

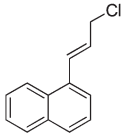
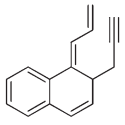
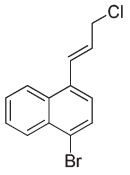
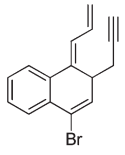
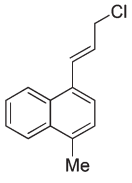
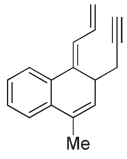
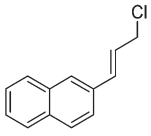
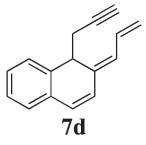
Conclusions

In conclusion, we have expanded the scope of palladium-catalyzed allylative dearomatization reaction to the propargylative and allenylative dearomatization of benzylic chlorides, chloromethyl naphthalenes, and naphthalene allyl chlorides by using allenyltributyltin as a reaction partner, instead of allyltributyltin. The reactivity of benzylic chlorides with allenyltributyltin was different from those of benzylic chlorides with allyltributytin previously reported; the former needed an activator (TBAF) to promote the reaction, producing the propargylic isomer as the major product. However, chloromethyl naphthalenes and naphthalene allyl chlorides could react with allenyltributyltin in the absence of TBAF, which might be due to higher reactivities of them than benzylic chlorides. All of the reactions of chloromethylnaphthalene derivatives, except for the reactions of **1p** and **1r**, afforded allenic derivatives as major products or as a sole isolated product. In the reactions of naphthalene allyl chlorides, propargylic products were isolated exclusively, and the reason why the allenic products could not be formed is not clear at present. We believe that these reactions reported herein provided a new and efficient method for the synthesis of propargylic and allenic carbocycles.

(14) This proposed mechanism is primarily based on the analogy of the allylative dearomatization (see ref 8). After our allylative deaaromatization paper appeared in 2001, Ariafared and Lin reported DFT studies on the mechanism of the allylative dearomatization, and the computational result suggested that an alternative mechanism would be more appropriate than our originally proposed mechanism (see: Ariafard, A.; Lin, Z. *J. Am. Chem. Soc.* **2006**, *128*, 13010–13016.); σ-allyl-hapto-3-exo-benzyl palladium is a key intermediate, in which a 1,3-allyl migration from palladium to the C-4 position of the six-membered ring takes place to lead to the dearomatization product. We believe this is a plausible and interesting mechanism. We are not sure whether a similar 1,3-rearrangement easily takes place in the case of the allenyl-system. It is an interesting point whether such 1,3-rearrangement takes place equally or more easily in the σ-allenyl than in the σ-allyl palladium intermediate. Accordingly, there is possibility that a mechanism proposed by Ariafared and Lin may be operative in the present case.

TABLE 4. Dearomatization Reaction of Naphthalene Allyl Chlorides 3a−d with Allenyltributyltin[a]



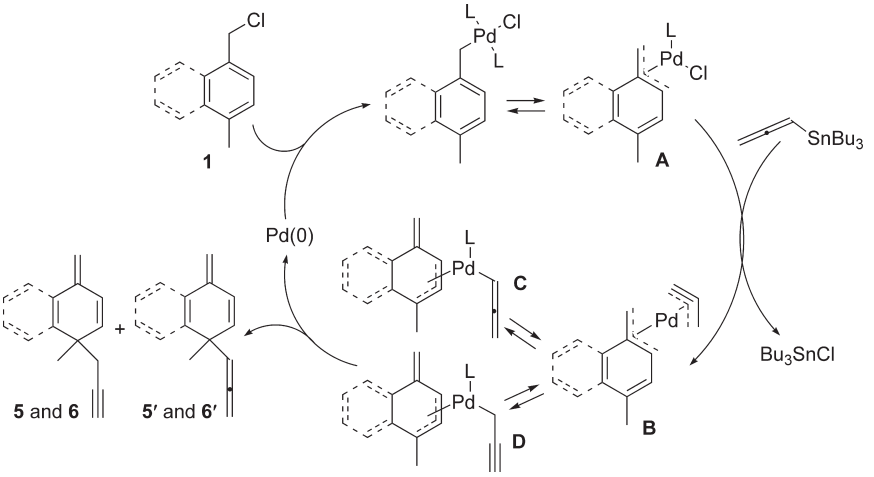
entry	substrate	time (h)	product	yield (%)
1	 **3a**	4	 **7a**	93
2	 **3b**	3	 **7b**	75
3	 **3c**	10	 **7c**	84
4	 **3d**	24	 **7d**	62

[a]A mixture of naphthalene allyl chloride (0.5 mmol), allenyltributyltion (0.6 mmol), and $Pd(PPh_3)_4$ (5 mol %) in dichloromethane (5 mL) was stirred at room temperature under nitrogen atmosphere for the period indicated in the table.

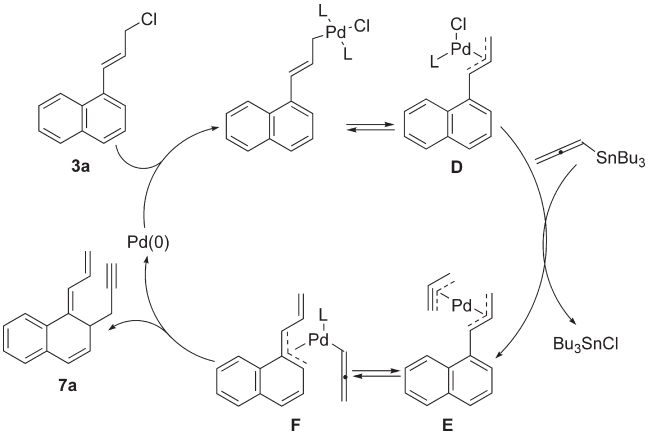
Experimental Section

Representative Procedure for the Palladium-Catalyzed Dearomatization Reaction of 1a−k with Allenyltributyltin. To a mixture of $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol) and TBAF (261.5 mg, 1.0 mmol) in dichloromethane (3 mL) at room temperature were added benzylic chloride **1a** (70.0 mmg, 0.5 mmol) and allenyltributyltin (197.5 mg, 0.6 mmol), and then the mixture was stirred under a N_2 atmosphere. The reaction progress was monitored by TLC. After the allenyltributyltin was consumed,

SCHEME 4. Proposed Mechanism for the Dearomatization Reaction of Benzylic Chlorides with Allenylributyltin



SCHEME 5. Proposed Mechanism for the Dearomatization Reaction of Naphthalene Allyl Chlorides with Allenylributyltin



the solvent was removed under a reduced pressure. The product was filtered through a short basic alumina column with pentane to remove palladium residue and then was purified with a basic alumina column using pentane as eluent, giving propargylic product **5a** in 71% yield (51.1 mg) as a colorless liquid.

3-Methyl-6-methylene-3-(prop-2-ynyl)cyclohexa-1,4-diene (5a). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 (d, J = 10.0 Hz, 2H), 5.76 (d, J = 10.0 Hz, 2H), 4.87 (s, 2H), 2.25 (d, J = 2.4 Hz, 2H), 2.03 (t, J = 2.4 Hz, 1H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 135.9, 126.5, 112.5, 80.5, 70.5, 38.4, 32.2, 27.0; IR (neat) 3295, 2924, 2044, 2025, 1652, 1506, 1456, 1280, 1083, 838, 636 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{12}$: 144.0939 $[M]^+$; found: 144.0946.

3-Methyl-6-methylene-3-(propa-1,2-dienyl)cyclohexa-1,4-diene (5a′). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (d, J = 8.0 Hz, 2H), 5.69 (d, J = 8.0 Hz, 2H), 5.09 (t, J = 8.0 Hz, 1H), 4.68 (s, 2H), 4.81 (d, J = 8.0 Hz, 2H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 137.3, 136.1, 125.3, 112.4, 98.1, 77.6, 38.8, 27.7; IR (neat) 2965, 1950, 1663, 1584, 1384, 1061, 870, 657 cm^{-1}; HRMS (EI) calcd for $C_{10}H_9$: 129.0704 $[M - CH_3]^+$; found: 129.0708.

1,6-Dimethyl-3-methylene-6-(prop-2-ynyl)cyclohexa-1,4-diene (5b). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.23 (d, J = 12.0 Hz, 1H), 6.06 (s, 1H), 5.74 (d, J = 12.0 Hz, 1H), 4.76 (d, J = 8.0 Hz, 2H), 2.36 (d, J = 8.0 Hz, 2H), 1.97 (s, 1H), 1.82 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 138.5, 136.7, 126.3, 125.3, 110.5, 81.1, 70.1, 41.3, 30.2, 25.8, 18.5; IR (neat) 3295, 2968, 2928, 1694, 1669, 1586, 1382, 798, 657 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{14}$: 158.1096 $[M]^+$; found: 158.1101.

1,6-Dimethyl-3-methylene-6-(propa-1,2-dienyl)cyclohexa-1,4-diene (5b′). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (d, J = 9.6 Hz, 1H), 6.00 (s, 1H), 5.62 (d, J = 9.6 Hz, 1H), 5.05 (t, J = 6.4 Hz, 1H), 4.82 (d, J = 6.4 Hz, 2H), 4.74 (d, J = 8.8 Hz, 2H), 1.80 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 142.0, 138.4, 137.3, 124.9, 124.0, 110.2, 97.4, 77.4, 41.6, 24.8, 18.9; IR (neat) 2967, 2925, 1951, 1667, 1586, 1375, 876, 796, 652 cm^{-1}; HRMS (EI) calcd for C_9H_{11}: 119.0861 $[M - C_3H_3]^+$; found: 119.0863.

3-Methoxy-6-methylene-3-(prop-2-ynyl)cyclohexa-1,4-diene (5c). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (d, J = 9.6 Hz, 2H), 5.75 (d, J = 9.6 Hz, 2H), 5.15 (s, 2H), 3.09 (s, 3H), 2.51 (d, J = 2.4 Hz, 2H), 2.02 (d, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 131.1, 130.2, 118.2, 79.6, 73.8, 70.5, 51.9, 31.9; IR (neat) 3298, 2933, 2121, 1940, 1729, 1587, 1245, 1089, 1065, 685 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{12}O$: 160.0888 $[M]^+$; found: 160.0882.

1,6-Dimethoxy-3-methylene-6-(prop-2-ynyl)cyclohexa-1,4-diene (5d). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.6 Hz, 1H), 6.89 (d, J = 7.6 Hz, 1H), 6.85 (s, 1H), 4.44 (s, 2H), 3.84 (s, 3H), 3.55 (d, J = 2.8 Hz, 2H), 3.38 (s, 3H), 2.16 (t, J = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 138.4, 128.8, 124.1, 119.9, 109.4, 82.1, 74.8, 70.4, 58.2, 55.5, 19.2; IR (neat) 3292, 2923, 2119,1940, 1719, 1586, 1463, 1262, 1192, 1154, 817, 639 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{14}O_2$: 190.0994 $[M]^+$; found: 190.0999.

6-Methylene-3,3-di(prop-2-ynyl)cyclohexa-1,4-diene (5e). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (d, J = 10.0 Hz, 2H), 5.84 (d, J = 1.0 Hz, 2H), 4.93 (s, 2H), 2.45 (d, J = 2.8 Hz, 4H), 2.05 (t, J = 2.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 133.1, 128.3, 114.0, 80.2, 71.2, 41.1, 29.7; IR (neat) 3296, 2923, 2117, 1586, 1428, 1384, 945, 803, 636 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{12}$: 168.0939 $[M]^+$; found: 168.0941.

2-(4-Methylene-1-(prop-2-ynyl)cyclohexa-2,5-dienyl)-1,3-dioxolane (5h). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 (d, J = 10.0 Hz, 2H), 5.80 (d, J = 10.0 Hz, 2H), 4.95 (s, 2H), 4.90 (s, 1H), 3.97−3.85 (bm, 4H), 2.46 (d, J = 2.8 Hz, 2H), 1.97 (t, J = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 129.75, 129.72, 114.3, 106.4, 80.3, 70.4, 65.5, 46.4, 26.0; IR (neat) 3399, 3291, 1665, 1383, 1145, 1079, 1051, 945, 809, 690 cm^{-1}; HRMS (EI) calcd for $C_{10}H_9$: 129.0704 $[M - C_3H_5O_2]^+$; found: 129.0707.

3-*tert*-Butyl-6-methylene-3-(prop-2-ynyl)cyclohexa-1,4-diene (5i). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (d, J = 10.0 Hz, 2H), 5.77 (d, J = 10.0 Hz, 2H), 4.87 (s, 2H), 2.42 (d, J = 2.8 Hz, 2H), 1.89 (t, J = 2.8 Hz, 1H), 0.92 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 132.9, 129.1, 112.7, 82.4, 69.9, 48.2, 37.8, 26.1, 25.8; IR (neat) 3308, 2967, 1664, 1584, 1367, 1193, 871, 629 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{18}$: 186.1409 $[M]^+$; found: 186.1417.

1-Chloro-4-((4-methyl-4-(prop-2-ynyl)cyclohexa-2,5-dienylidene)methyl)benzene (5j). Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30−7.24 (m, 4H), 6.72 (d, J = 10.4 Hz, 1H), 6.26 (dd, J = 1.6, 9.2 Hz, 1H), 6.22 (s, 1H), 5.90 (d, J = 10.0 Hz,1H), 5.82 (dd, J = 1.6, 9.2 Hz, 1H), 2.30 (d, J = 2.8 Hz, 2H), 2.04 (t, J = 2.8 Hz, 1H), 1.25(s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.3, 135.7, 135.6, 132.4, 131.4, 130.2, 128.47, 128.72, 125.6, 121.8, 80.7, 70.6, 39.1, 32.2, 27.0; IR (neat) 3302, 2922, 1658, 1488, 1273,1013, 866, 796, 661 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{12}Cl$: 215.0628; $[M - C_3H_3]^+$; found: 215.0635.

1-Chloro-4-((4-methyl-4-(propa-1,2-dienyl)cyclohexa-2,5-dienylidene)methyl)benzene (5j′). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.23 (m, 4H), 6.68 (d, J = 10.0, 1H), 6.22−6.20 (m, 2H), 5.83 (d, J = 10.0, 1H), 5.75 (d, J = 10.0, 1H), 5.12 (t, J = 6.4, 1H), 4.83 (d, J = 6.4, 2H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 138.5, 135.9, 135.7, 132.4, 131.2, 130.2, 128.4, 127.4, 125.6, 120.6, 97.8, 77.4, 39.5, 27.7; IR (neat) 2921, 1950, 1488, 1089, 1012, 847, 796, 657 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{15}Cl$: 254.0862 $[M]^+$; found: 254.0869.

1-*tert*-Butyl-4-((4-methyl-4-(prop-2-ynyl)cyclohexa-2,5-dienylidene)methyl)benzene (5k). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.34 (m, 2H), 7.28−7.25 (m, 2H), 6.82 (d, J = 10.4, 1H), 6.28−6.25 (m, 2H), 5.86−5.83 (m, 1H), 5.79−5.76 (m, 1H), 2.29 (d, J = 2.8, 2H), 2.03 (t, J = 2.8, 1H), 1.32 (s, 9H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 137.3, 134.8, 134.3, 130.5, 128.8, 128.7, 127.1, 125.1, 122.3, 80.9, 70.5, 38.9, 34.5, 32.4, 31.3, 27.1; IR (neat) 3304, 3023, 2962, 1653, 1507, 1363, 1268, 1123, 796, 661 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{24}$: 276.1878 $[M]^+$; found: 276.1880

1-*tert*-Butyl-4-((4-methyl-4-(propa-1,2-dienyl)cyclohexa-2,5-dienylidene)methyl)benzene (5k′). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.33 (m, 2H), 7.28−7.25 (m, 2H), 6.78 (d, J = 10.0, 1H), 6.25 (s, 1H), 6.22 (d, J = 10.0, 1H), 5.77 (d, J = 10.0, 1H), 5.70 (d, J = 10.0, 1H), 5.12 (t, J = 8.4, 1H), 4.81 (d, J = 8.4, 2H), 1.32 (s, 9H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 149.7, 137.5, 135.0, 134.3, 130.3, 128.7, 127.7, 127.0, 125.1, 121.2, 98.1, 77.6, 39.4, 34.5, 31.3, 27.8; IR (neat) 2962, 1950, 1362, 1268, 906, 845, 796 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{24}$: 276.1878, found: 276.1885.

Representative Procedure for the Palladium-Catalyzed Dearomatization Reaction of 1l−r and 3a−d with Allenyltributyltin. To a solution of $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol) in dichloromethane (3 mL) at room temperature were added chloromethylnaphthalene **1l** (95.3, 0.5 mmol) and allenyltributyltin (197.5 mg, 0.6 mmol), and then the mixture was stirred under a N_2 atmosphere. The reaction progress was monitored by TLC. After the allenyltributyltin consumed, the solvent was removed under a reduced pressure. The product was filtered through a short basic alumina column with hexane to remove palladium residue and then was purified with a basic alumina column using hexane as eluent, giving propargylic and allenic products **6l** and **6l′** in 17% (16.4 mg) and 68% yield (66.7 mg), respectively.

1-Methyl-4-methylene-1-(prop-2-ynyl)-1,4-dihydronaphthalene (6l). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−7.76 (m, 1H), 7.43−7.40 (m, 1H), 7.33−7.29 (m, 1H), 7.26−7.22 (m, 1H), 6.44 (d, J = 10.0 Hz, 1H), 5.90 (d, J = 10.0 Hz, 1H), 5.68 (s, 1H), 5.05 (s, 1H), 2.55 (t, J = 2.4 Hz, 2H), 1.93 (t, J = 2.4 Hz, 1H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 137.4, 134.9, 131.2, 128.1, 127.5, 126.4, 126.3, 123.3, 109.6, 81.3, 70.3, 39.6, 34.2, 28.7; IR (neat) 3294, 2967, 1590, 1481, 776, 755, 638 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{14}$: 194.1096 $[M]^+$; found: 194.1098.

1-Methyl-4-methylene-1-(propa-1,2-dienyl)-1,4-dihydronaphthalene (6l′). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76−7.74 (m, 1H), 7.42−7.39 (m, 1H), 7.31−7.27 (m, 1H), 7.24−7.20 (m, 1H), 6.36 (d, J = 10.0 Hz, 1H), 5.74 (d, J = 10.0 Hz, 1H), 5.68 (s, 1H), 5.30 (t, J = 6.8 Hz, 1H), 5.04 (s, 1H), 4.91−4.87 (m, 2H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 141.8, 137.2, 135.4, 130.4, 128.14, 128.12, 126.4, 126.3, 123.1. 109.5, 99.7, 78.0, 40.4, 29.4; IR (neat) 2925, 1952, 1695, 1590, 1455, 870, 775, 755 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{14}$: 194.1096 $[M]^+$; found: 194.1100.

Methyl 4-Methylene-1-(propa-1,2-dienyl)-1,4-dihydronaphthalene-1-carboxylate (6m′). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79−7.77 (m, 1H), 7.42−7.39 (m, 1H), 7.30−7.27 (m, 2H), 6.55 (d, J = 10.0 Hz, 1H), 5.91 (d, J = 8.0 Hz, 1H), 5.86 (d, J = 6.8 Hz, 1H), 5.77 (s, 1H), 5.16 (s, 1H), 4.82−4.71 (m, 2H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7, 173.1, 136.3, 134.9, 130.7, 128.9, 128.7, 128.3, 127.6. 127.3, 123.5, 111.7, 96.4, 78.8, 53.1, 52.4; IR (neat) 3063, 2950, 1956, 1731, 1592, 1482, 1229, 772 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{14}O_2$: 238.0994 $[M]^+$; found: 238.1002.

***tert*-Butyldimethyl((4-methylene-1-(prop-2-ynyl)-1,4-dihydronaphthalen-1-yl)methoxy)silane (6o).** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 7.2 Hz, 1H), 7.35−7.29 (m, 2H), 6.60 (d, J = 10.0 Hz, 1H), 6.01 (d, J = 10.0 Hz, 1H), 5.74 (s, 1H), 5.11 (s, 1H), 3.71−3.65 (m, 2H), 2.90−2.70 (bm, 2H), 1.90 (s, 1H), 0.90 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 137.6, 132.1, 131.4, 129.6, 127.6, 127.0, 126.7, 123.2, 109.8, 81.5, 70.1, 70.0, 45.3, 27.7, 25.8, 18.2, −5.5, −5.6; IR (neat) 3310, 2953, 1471, 1388, 1254, 1100, 776 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{28}OSi$: 324.1909 $[M]^+$; found: 324.1906.

***tert*-Butyldimethyl((4-methylene-1-(propa-1,2-dienyl)-1,4-dihydronaphthalen-1-yl)methoxy)-silane (6o′).** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.29−7.21 (m, 2H), 6.48 (d, J = 10.0 Hz, 1H), 5.87 (d, J = 10.0 Hz, 1H), 5.67 (s, 1H), 5.51 (t, J = 6.4 Hz, 1H), 5.04 (s, 1H), 4.82−4.74 (m, 2H), 3.73−3.66 (m, 2H), 0.78 (s, 9H), −0.09 (s, 3H), −0.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 138.3, 137.5, 131.9, 131.8, 128.4, 128.3, 127.6, 126.5, 122.9. 109.5, 95.7, 77.3, 71.1, 46.3, 25.7, 18.1, −5.5, −5.6; IR (neat) 2953, 1593, 1471, 1387, 1255, 1104, 839, 775 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{28}OSi$: 324.1909 $[M]^+$; found: 324.1898.

4-Methylene-1-phenyl-1-(prop-2-ynyl)-1,4-dihydronaphthalene (6p). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.6 Hz, 1H), 7.30−7.25 (m, 4H), 721−7.12 (bm, 3H), 6.96 (d, J = 8.0 Hz, 1H), 6.56 (d, J = 9.6 Hz, 1H), 5.96 (d, J = 10.0 Hz, 1H), 5.77 (s, 1H), 5.15 (s, 1H), 3.16−2.95 (bm, 2H), 1.90 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 140.8, 137.1, 134.0, 131.2, 129.0, 128.3, 128.2, 127.6. 127.5, 126.5, 126.4, 123.1, 110.4, 80.0, 71.2, 48.3, 31.5; IR (neat) 3291, 2924, 1591, 1493, 1035, 910, 753, 698 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{16}$: 256.1252 $[M]^+$; found: 256.1253.

10-Methylene-9-(propa-1,2-dienyl)-9,10-dihydroanthracene (6q′). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.68 (m, 2H), 7.39−7.37 (m, 2H), 7.32−7.26 (m, 4H), 5.68 (s, 2H), 5.20 (dt, J = 5.6, 6.8 Hz, 1H), 4.69 (dd, J = 2.0, 6.8 Hz, 2H), 4.65 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 141.4, 137.3, 135.2, 128.0, 127.9, 127.0, 124.5, 110.0. 95.6, 76.6, 46.0; IR (neat) 3060, 2922, 1952, 1478, 1032, 892, 779 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{11}$: 191.0861 $[M - C_3H_3]^+$; found: 191.0867.

(*E*)-1-Methyl-4-pentylidene-1-(prop-2-ynyl)-1,4-dihydronaphthalene (6r). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 726−7.19 (m, 2H), 6.71 (d, J = 10.4 Hz, 1H), 6.16 (t, J = 7.6 Hz, 1H), 5.92 (d, J = 10.0 Hz, 1H), 2.52 (d, J = 1.6 Hz, 2H), 2.34 (dt, J = 6.8, 6.8 Hz, 2H), 1.94 (t, J = 2.4 Hz, 1H), 1.51−1.34 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 134.4, 132.9, 129.1, 126.9, 126.3, 126.1, 125.7, 122.3, 122.1, 81.3, 70.2, 39.2, 34.1, 31.9, 28.5, 27.4, 22.4, 14.0; IR (neat) 3307, 2956, 2116,

1480, 1370, 1044, 753 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{22}$: 250.1722 $[M]^+$; found: 250.1729.

(*E*)-1-Allylidene-2-(prop-2-ynyl)-1,2-dihydronaphthalene (7a). Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55−7.52 (m, 1H), 7.21−7.19 (m, 2H), 7.04−7.02 (m, 1H), 6.88−6.79 (bm, 1H), 6.61 (d, J = 11.2 Hz, 1H), 6.50 (d, J = 5.6 Hz, 1H), 6.21−6.18 (m, 1H), 5.42−5.38 (m, 1H), 5.29−5.27 (m, 1H), 3.83−3.77 (m, 1H), 2.34−2.21 (m, 2H), 1.96 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 133.1, 132.5, 132.0, 130.1, 128.5, 128.1, 127.8, 127.3. 126.8, 124.2, 119.4, 81.9, 69.9, 36.1, 25.1; IR (neat) 3296, 3031, 2923, 1616, 1480, 1453, 906, 757 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{14}$: 206.1096 $[M]^+$; found: 206.1101.

(*E*)-1-Allylidene-4-bromo-2-(prop-2-ynyl)-1,2-dihydronaphthalene (7b). Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.32−7.25 (m, 2H), 6.84−6.75 (bm, 1H), 6.61−6.57 (m, 2H), 5.43 (d, J = 16.4 Hz, 1H), 5.32 (d, J = 10.0 Hz, 1H), 3.83 (dd, J = 7.2, 7.2 Hz, 1H), 2.38−2.20 (m, 2H), 1.97 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 134.2, 131.9, 131.8, 131.2, 129.8, 129.2, 128.5, 127.4, 124.6, 121.8, 120.6, 81.3, 70.7, 38.7, 24.5; IR (neat) 3296, 3028, 1620, 1319, 985, 830, 758, 640 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{13}Br$: 284.0201 $[M]^+$; found: 284.0206.

(*E*)-1-Allylidene-4-methyl-2-(prop-2-ynyl)-1,2-dihydronaphthalene (7c). Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.2 Hz, 1H), 7.27−7.22 (m, 3H), 6.90−6.80 (m, 1H), 6.56 (d, J = 11.2 Hz, 1H), 6.02 (d, J = 6.0 Hz, 1H), 5.38 (d, J = 16.4 Hz, 1H), 5.26 (d, J = 10.0 Hz, 1H), 3.78−3.71 (m, 1H), 2.30−2.16 (bm, 2H), 2.08 (s, 3H), 1.94 (t, J = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 134.0, 133.6, 132.2, 131.6, 128.3, 128.2, 127.6, 127.1, 124.6, 123.5, 119.2, 82.3, 70.7, 36.1, 24.9, 19.5; IR (neat) 3297, 2970, 2116, 1620, 1479, 1378, 984, 758, 633 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{16}$: 220.1252 $[M]^+$; found: 220.1261.

(*E*)-2-Allylidene-1-(prop-2-ynyl)-1,2-dihydronaphthalene (7d). Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 7.2 Hz, 1H), 7.21−7.15 (m, 2H), 7.10 (d, J = 7.2 Hz, 1H), 6.87−6.78 (m, 1H), 6.41 (d, J = 9.6 Hz, 1H), 6.23 (d, J = 9.6 Hz, 1H), 6.18 (d, J = 11.2 Hz, 1H), 5.33 (d, J = 16.8 Hz, 1H), 5.25 (d, J = 10.0 Hz, 1H), 4.17 (t, J = 7.2 Hz, 1H), 2.43 (dd, J = 2.8, 7.2 Hz, 2H), 1.99 (t, J = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 137.0, 132.8, 132.3, 131.1, 129.3, 128.7, 127.4, 127.2, 127.1, 127.0, 119.3, 82.3, 71.3, 40.1, 29.2; IR (neat) 3299, 3024, 1805, 1616, 1486, 1294, 903, 794, 749 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{14}$: 206.1096 $[M]^+$; found: 206.1099.

Procedure for the Deprotection of 6o. To a solution of **6o** (45.0 mg, 0.14 mmol) in THF (3.0 mL) at 0 °C was added TBAF (39.2 mg, 0.15 mmol). After the mixture was stirred for 5 h, the solvent was removed under reduced pressure, and the residue was purified by basic alumina column chromatography (eluent: hexane/ethyl acetate = 5/1) to give **9** in 76% yield (22.1 mg).

(4-Methylene-1-(prop-2-ynyl)-1,4-dihydronaphthalen-1-yl)-methanol (9). Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.37−7.27 (m, 2H), 6.65 (d, J = 10.0 Hz, 1H), 5.95 (d, J = 10.0 Hz, 1H), 5.74 (s, 1H), 5.11 (s, 1H), 3.87−3.71 (bm, 2H), 2.74−2.60 (bm, 2H), 1.95 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 137.0, 132.9, 131.2, 130.9, 128.5, 127.3, 126.2, 123.9, 111.0, 80.6, 71.0, 70.3, 45.8, 28.6; IR (neat) 3292, 2925, 2117, 1720, 1591, 1481, 1457, 1429, 1281, 1055, 878, 778, 757, 639 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{14}O$: 210.1045 $[M]^+$; found: 210.1045.

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Supporting Information Available: Experimental procedures, characterization data for all new compounds, and NMR spectra for the corresponding products. This material is available free of charge via the Internet at http://pubs.acs.org.