ChemPubSoc Europe

DOI: 10.1002/ejoc.201901481

EurJOC European Journal of Organic Chemistry

Full Paper

Fused Aromatic Compounds

Rhodium(I)-Catalyzed Arylative Annulation of β-Alkynyl Ketones for Preparation of Fused Aromatics

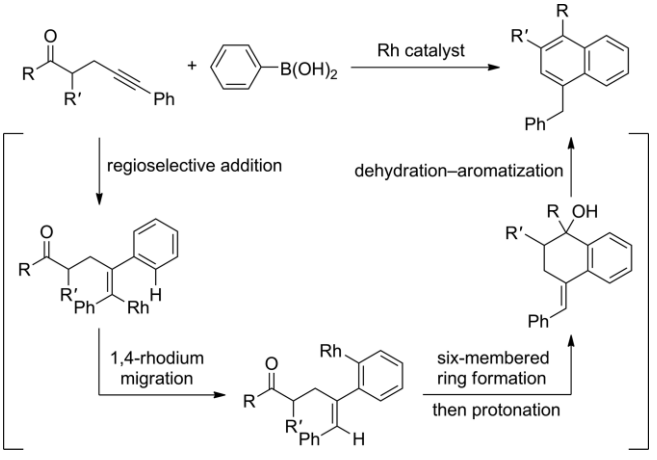
Takanori Matsuda,*[a] Takashi Izutsu,[a] and Masaru Hashimoto[a]

Abstract: Rhodium(I)-catalyzed addition of arylboronic acids to β-(arylethynyl) ketones proceeds through 1,4-rhodium migration to afford 4-(arylmethylene)tetralin-1-ols, which upon treatment with triflic anhydride furnish (arylmethyl)naphthalenes through sequential dehydration–aromatization. Fused aromatic compounds with three to five rings have been prepared using the arylative annulation strategy.

Introduction

Rhodium(I)-catalyzed addition of arylboron compounds is a useful C–C bond-forming reaction with broad substrate scope and reasonable functional group tolerance, with remarkable progress achieved in this area over the past two decades.[1] Rhodium-, iridium-, and cobalt-catalyzed arylative annulations of alkynyl ketones with arylboron compounds are efficient methods for synthesis of four- to seven-membered cyclic alcohols and ketones.[2–4] The substrate scope of β-alkynyl ketones employed thus far in the rhodium(I)-catalyzed arylative annulation reactions is limited to the use of α,α-disubstituted substrates,[3] and β-alkynyl ketones bearing at least one hydrogen at the α position have not been examined as substrates for this reaction.[5,6] Continuing our interest in the synthesis of aromatic compounds by annulation–aromatization sequences,[7] we examined the possibility of transforming the annulation products of rhodium(I)-catalyzed arylation of the β-alkynyl ketones to fused aromatic compounds.

For such an annulation–dehydration–aromatization sequence forming a benzene structure to be feasible, the formation of a six-membered ring via annulation of β-alkynyl ketones is necessary (Scheme 1). In this regard, the addition of an arylrhodium(I) species to the alkyne moiety of a β-alkynyl ketone followed by 1,4-rhodium migration[8,9] would generate a nucleophilic arylrhodium(I) species requisite for the six-membered ring formation. To circumvent the regioselectivity issues of the arylrhodation to the alkyne, we chose to use the arylethynyl group, which would direct the addition to the desired regioselectivity.[10] The resulting six-membered cyclic alcohols through arylative annulation are amenable to sequential dehydration–aromatization, thus affording fused aromatics. We report herein, rhodium(I)-catalyzed arylative annulation of β-alkynyl ketones which furnish fused aromatic compounds with three to five rings.



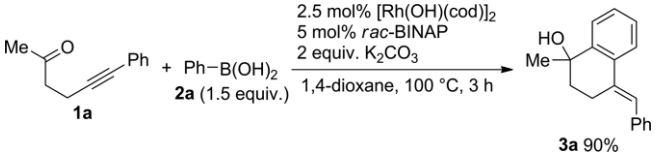
Scheme 1. Postulated arylative annulation of β-alkynyl ketones involving 1,4-rhodium migration.

Results and Discussion

We began the methodology development with 6-phenyl-5-hexyn-2-one (**1a**) as the substrate, which was allowed to react with phenylboronic acid (**2a**, 1.5 equiv.) in the presence of $[Rh(OH)(cod)]_2$ (2.5 mol-%, 5 mol-% Rh) and *rac*-BINAP (5 mol-%) in 1,4-dioxane at 100 °C for 3 h. The expected arylative annulation involving 1,4-rhodium migration occurred to afford tetralin alcohol **3a** in 90 % yield (Scheme 2). We had previously reported that silica gel is effective for inducing dehydration–aromatization of similar substrates,[7a] and we attempted this approach by addition of silica gel to the reaction mixture containing **3a** after annulation, followed by heating the reaction mixture at the same temperature. However, no reaction occurred under these conditions, and **3a** was recovered in 77 % yield. The use of molecular sieves 4Å or Na_2SO_4 was also ineffective for the conversion.

[a] *Department of Applied Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan*
E-mail: mtd@rs.tus.ac.jp
http://www.rs.tus.ac.jp/mtd

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejoc.201901481.

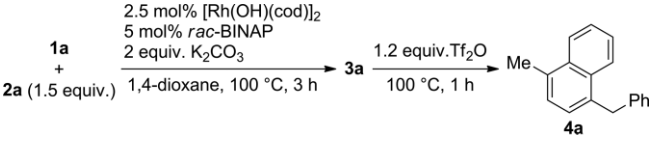


Scheme 2. Rhodium(I)-catalyzed reaction of 6-phenyl-5-hexyn-2-one (**1a**) with phenylboronic acid (**2a**).

To our delight, the addition of triflic anhydride (1.2 equiv.) to the same reaction mixture after annulation, followed by additional heating (1 h) resulted in clean conversion to the desired 1-benzyl-4-methylnaphthalene (**4a**),[11] which was isolated in 84 % yield (Table 1, Entry 1). With the initial conditions in hand, we carried out a series of reactions to optimize the reaction conditions. While increasing the ligand loading to 10 mol-% of *rac*-BINAP delivered **4a** in excellent yield (Entry 2), the reaction efficiency was largely reduced in the absence of the ligand (Entry 3).[12] The use of 1,2-bis(diphenylphosphino)benzene (DPPBZ) as the ligand instead of *rac*-BINAP furnished **4a** in a slightly lower 78 % yield. However, no reaction was observed when 1,2-bis(diphenylphosphino)ethane (DPPE) was employed as the ligand. Next, we evaluated the use of other solvents such as toluene, chlorobenzene, and diglyme, and found them compatible with the reaction (Entries 5–7). While the absence of K_2CO_3 allowed the reaction of **1a** with **2a** to **4a** in 83 % yield (Entry 8), further studies revealed that the presence of the base is crucial for obtaining reproducible results for all substrates.

Having optimized and established the protocol for annulation–dehydration–aromatization sequence, we examined the scope of this transformation (Table 2). We evaluated a variety of arylboronic acids **2b**–**l** for the rhodium(I)-catalyzed arylative annulation of β-alkynyl ketone **1a**. The reactions furnished the

Table 1. Rhodium(I)-catalyzed arylative annulation/dehydration of **1a** with **2a**.

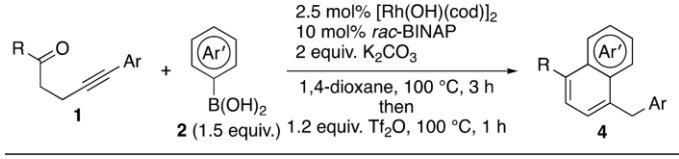


Entry	Deviation from standard conditions	Yield[a] [%]
1	standard conditions	84
2	10 mol-% *rac*-BINAP instead of 5 mol-%	86
3	no *rac*-BINAP	54
4	DPPBZ instead of *rac*-BINAP	78
5	toluene, 110 °C	64
6	chlorobenzene, 100 °C	75
7	diglyme, 160 °C	74
8	without K_2CO_3	83

[a] Isolated yield.

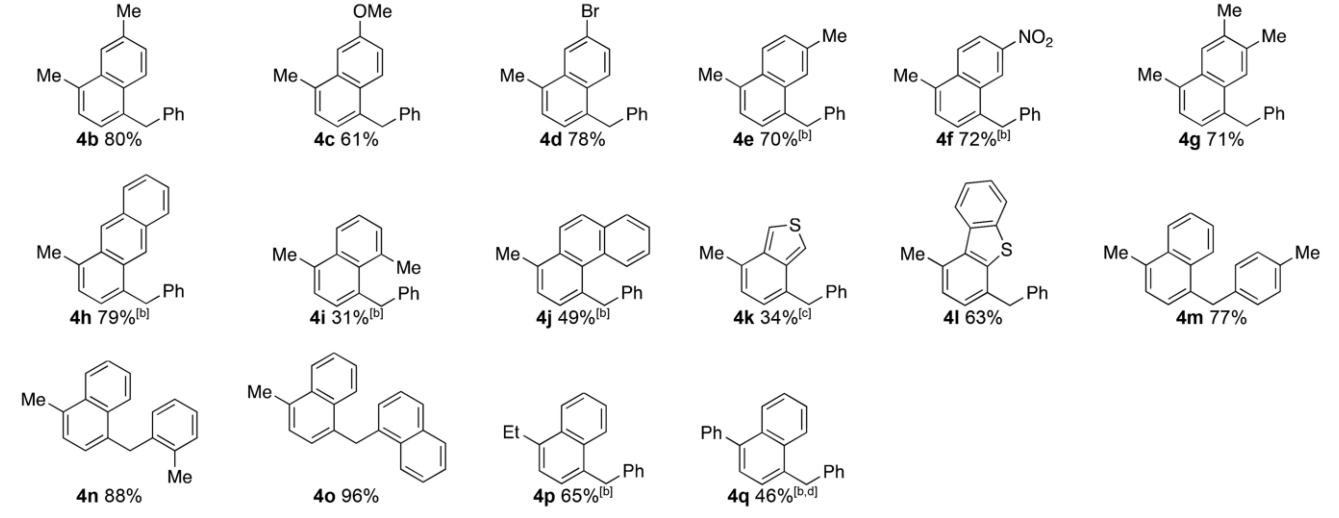
tricyclic products, anthracene, phenanthrene, and benzo-fused thiophenes, as well as naphthalenes. The annulation of **1a** with phenylboronic acids bearing para substituents (**2b**–**d**) provided the corresponding 1,4,6-trisubstituted naphthalenes **4b**–**d** in 61–80 % yields. In the reactions using 3-methylphenyl-, 3-nitrophenyl-, 3,4-dimethylphenyl-, and 2-naphthylboronic acids (**2e**–**h**), the 1,4-rhodium migration occurred regioselectively at the less sterically hindered site on the aromatic ring and furnished the products (**4e**–**h**) in 70–79 % yields. The use of 2-methylphenyl- and 1-naphthylboronic acids (**2i** and **2j**) afforded the products in low yields of **4** likely due to the steric hindrance of the boronic acids.[13,14] Thiophenes **2k** and **2l** were tolerated, leading to the products **4k** and **4l**, respectively.[15] In the reaction using **2k**, benzo[*c*]thiophene **4k** was obtained through the selective migration of rhodium to the 4 position of the thio-

Table 2. Arylative annulation of β-alkynyl ketones **1** with arylboronic acids **2**.[a]



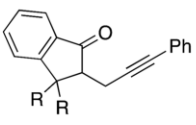
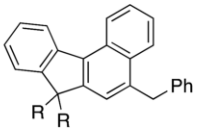
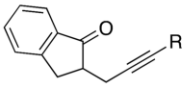
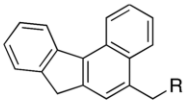
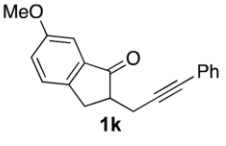
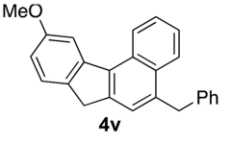
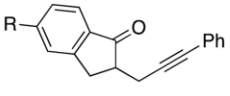
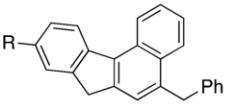
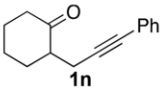
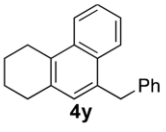
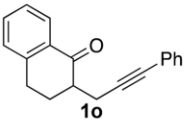
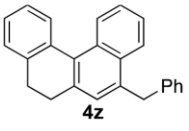
1a: R = Me, Ar = Ph
1b: R = Me, Ar = 4-MeC_6H_4
1c: R = Me, Ar = 2-MeC_6H_4
1d: R = Me, Ar = 1-naphthyl
1e: R = Et, Ar = Ph
1f: R = Ar = Ph

2a: Ph; **2b:** 4-MeC_6H_4; **2c:** 4-$MeOC_6H_4$; **2d:** 4-BrC_6H_4; **2e:** 3-MeC_6H_4; **2f:** 3-$(O_2N)C_6H_4$; **2g:** 3,4-$Me_2C_6H_3$; **2h:** 2-naphthyl; **2i:** 2-MeC_6H_4; **2j:** 1-naphthyl; **2k:** 3-thienyl; **2l:** benzo[*b*]thiophen-2-yl



phene ring. The attempted reaction with (*E*)-styrylboronic acid was unsuccessful, giving a complex mixture of products. Other 6-aryl-5-hexyn-2-ones **1b**–**d** also underwent the arylative annulation to generate the corresponding substituted naphthalene products **4m**–**o**, respectively. Particularly, the 2-methylphenyl and 1-naphthyl derivatives delivered the products in high yields, which could be attributed to the increased regioselectivity of the initial phenylrhodium(I) addition across C–C triple bond of **1** due to the presence of sterically demanding aryl substituents. Furthermore, 7-phenyl-6-heptyn-3-one (**1e**) and 1,5-diphenyl-4-pentyn-1-one (**1f**) were viable coupling partners for the arylative annulation and produced 1-benzyl-4-ethylnaphthalene (**4p**) and 1-benzyl-4-phenylnaphthalene (**4q**), respectively.[16]

Table 3. Arylative annulation of α-(arylpropargyl) cyclic ketones with **2a**.[a]

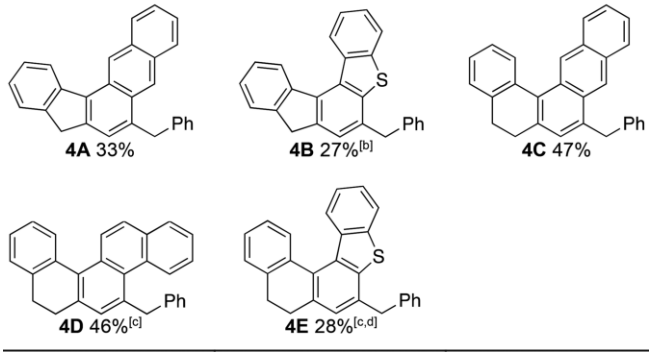
Entry	β-Alkynyl ketone **1**	Product **4**	Yield[b] [%]
1[c]	 **1g** (R = H)	 **4r**	69
2	**1h** (R = Me)	**4s**	62
3	 **1i** (R = 4-MeC$_6$H$_4$)	 **4t**	80
4	**1j** (R = 2-MeC$_6$H$_4$)	**4u**	91
5[d]	 **1k**	 **4v**	63
6	 **1l** (R = OMe)	 **4w**	67
7	**1m** (R = Br)	**4x**	75
8	 **1n**	 **4y**	79
9[c]	 **1o**	 **4z**	73

[a] Alkynyl ketone **1**, arylboronic acid **2** (1.5 equiv.), $[Rh(OH)(cod)]_2$ (5.0 mol-% Rh), *rac*-BINAP (10 mol-%), and K_2CO_3 (2 equiv.) were reacted at 100 °C in 1,4-dioxane (0.10 M). After 3 h, Tf_2O (1.2 equiv.) was added, and the mixture was heated further for 1 h. [b] Isolated yield. [c] 5.0 mol-% *rac*-BINAP was used. [d] 73 % yield in diglyme at 160 °C.

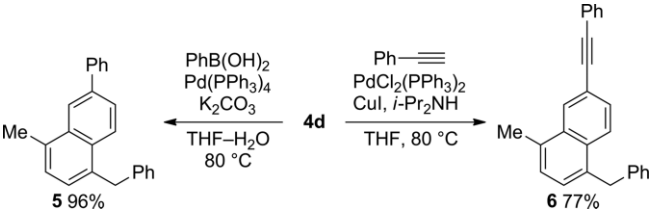
We then studied the reactions of various α-(arylpropargyl) cyclic ketones **1g**–**o** in reaction with phenylboronic acid (**2a**), which afforded the corresponding fused naphthalenes (Table 3). The reaction of 2-(3-phenylpropargyl)-1-indanone derivatives **1g**–**m** furnished the corresponding tetracyclic products **4r**–**x**, respectively, with the benzo[*c*]fluorene core (entries 1–7). Additionally, the six-membered ring ketones, cyclohexanone **1n**, and 1-tertalone **1o** underwent the arylative annulation with **2a** to afford tetrahydrophenanthrene **4y**, and dihydrobenzo[*c*]phenanthrene **4z**, respectively (entries 8 and 9).

Having prepared a variety of bicyclic, tricyclic, and tetracyclic ring systems using the developed methodology, we sought to extend the arylative annulation to the synthesis of pentacyclic products (Table 4). Arylative annulation of 1-indanone **1g** with 2-naphthylboronic acid (**2g**) and benzo[*b*]thiophen-2-ylboronic acid (**2l**) produced indeno[1,2-*a*]anthracene **4A** in 33 % and benzo[*b*]fluoreno[4,3-*d*]thiophene **4B** in 27 % yields, respectively. Dihydrobenzo[*a*]tetraphene **4C** and dihydrobenzo[*c*]chrysene **4D** were prepared from the reaction of 1-tetralone **1o** with **2h** and **2j**, respectively. Similarly, the reaction between **1o** and **2l** afforded dihydrobenzo[*b*]phenanthro[4,3-*d*]thiophene **4E**, showcasing the efficiency of the methodology for rapid synthesis of fused aromatics.

Table 4. Synthesis of pentacyclic products.[a]



We studied the derivatization of the prepared 1-benzyl-6-bromo-4-methylnaphthalene (**4d**) using cross-coupling reactions (Scheme 3). Suzuki–Miyaura coupling of **4d** with phenylboronic acid (**2a**) afforded 1-benzyl-4-methyl-6-phenylnaphthalene (**5**) in 96 % yield. Sonogashira coupling of **4d** with phenylacetylene provided 1-benzyl-4-methyl-6-(phenylethynyl)-naphthalene (**6**) in 77 % yield.



Scheme 3. Product derivatizations.

Conclusion

In summary, we developed a rhodium(I)-catalyzed arylative annulation of β-(arylethynyl) ketones that proceeds through 1,4-rhodium migration. The resulting tetralin alcohols undergo dehydration–aromatization upon treatment with Tf_2O, providing access to a variety of fused aromatic compounds, up to pentacyclic systems bearing a variety of substituents.

Experimental Section

General Procedure for the Rhodium(I)-Catalyzed Arylative Annulation of β-Alkynyl Ketones 1 with Arylboronic Acids 2: A Schlenk tube containing a magnetic stirring bar was charged with arylboronic acid **2** (0.150 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.5 μmol), and *rac*-BINAP (3.1 mg, 5.0 μmol or 6.2 mg, 10 μmol) under nitrogen atmosphere. The solvent 1,4-dioxane (1.0 mL) and β-alkynyl ketone **1** (0.100 mmol) were added through the septum using a syringe, and the mixture was stirred at 100 °C. After 3 h, Tf_2O (0.120 mmol) was added to the reaction mixture, and the mixture was heated further for 1 h at 100 °C. After cooling to room temperature, the reaction mixture was filtered through a plug of Florisil® eluting with hexane/AcOEt (2:1). The filtrate was concentrated, and the residue was purified by preparative thin-layer chromatography (TLC) to furnish the naphthalene **4**.

1-Benzyl-4-methylnaphthalene (4a): The general procedure was followed using **1a** (17.2 mg, 0.100 mmol), **2a** (18.3 mg, 0.150 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol), *rac*-BINAP (6.2 mg, 10 μmol), K_2CO_3 (27.7 mg, 0.200 mmol), 1,4-dioxane (1.0 mL), and Tf_2O (33.8 mg, 0.120 mmol). Purification by preparative TLC (hexane/AcOEt = 10:1) yielded **4a** (19.9 mg, 0.086 mmol, 86 %) as an orange oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.07–8.00 (m, 2H), 7.55–7.45 (m, 2H), 7.31–7.25 (m, 3H), 7.24–7.18 (m, 4H), 4.45 (s, 2H), 2.71 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 140.9, 134.7, 133.2, 133.0, 132.1, 128.7, 128.4, 127.1, 126.3, 125.9, 125.6, 125.4, 124.8, 124.7, 39.0, 19.5; HRMS (ESI): *m/z* calcd. for $C_{18}H_{16}+Na^+$: 255.1144 [*M* + Na]$^+$, found 255.1145.

(*E*)-4-Benzylidene-1-methyltetralin-1-ol (3a): The title compound was obtained as a pale yellow oil in 90 % yield when the reaction was performed without treatment with Tf_2O. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.70–7.64 (m, 2H), 7.41–7.37 (m, 4H), 7.36–7.25 (m, 3H), 7.06 (s, 1H), 3.04–2.97 (m, 1H), 2.85–2.77 (m, 1H), 2.02 (ddd, *J* = 12.9, 6.6, 4.9 Hz, 1H), 1.94 (ddd, *J* = 13.0, 10.3, 5.0 Hz, 1H), 1.83 (s, 1H), 1.56 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.3, 137.8, 135.2, 136.4, 129.3, 128.2, 128.1, 127.6, 126.7, 125.3, 124.8, 124.3, 70.8, 39.2, 29.4, 25.3; IR (neat): $\tilde{\nu}$ = 3347, 1597, 1492, 1444 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{18}H_{18}O+Na^+$: 273.1250 [*M* + Na]$^+$, found 273.1249.

5-Benzylbenzo[*c*]fluorene (4r): The general procedure was followed using **1g** (24.6 mg, 0.100 mmol), **2a** (18.3 mg, 0.150 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol), *rac*-BINAP (3.1 mg, 5.0 μmol), K_2CO_3 (27.6 mg, 0.200 mmol), 1,4-dioxane (1.0 mL), and Tf_2O (33.9 mg, 0.120 mmol). Purification by preparative TLC (hexane/AcOEt = 10:1) yielded **4r** (21.1 mg, 0.069 mmol, 69 %) as a brown solid. M.p. 140–142 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.84 (d, *J* = 9.0 Hz, 1H), 8.41 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 9.0 Hz, 1H), 7.68–7.62 (m, 2H), 7.55–7.48 (m, 3H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.33–7.20 (m, 5H), 4.55 (s, 2H), 3.99 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.1, 142.8, 142.0, 140.7, 136.1, 135.2, 131.9, 130.1, 128.8, 128.5, 126.9, 126.1, 126.08, 125.5, 125.4, 125.1, 125.0, 124.8, 124.3, 122.7, 39.5, 37.8; HRMS (ESI): *m/z* calcd. for $C_{24}H_{18}+Na^+$: 329.1301 [*M* + Na]$^+$, found 329.1296.

(*E*)-5-Benzylidene-5,6,6a,7-tetrahydro-11b*H*-benzo[*c*]fluoren-11b-ol (3r): The title compound was obtained as a yellow oil in 68 % yield when the reaction was performed without treatment with Tf_2O. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.91 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.66–7.61 (m, 2H), 7.43–7.33 (m, 5H), 7.32–7.15 (m, 5H), 7.14 (s, 1H), 3.02 (dd, *J* = 15.5, 7.0 Hz, 1H), 2.97 (ddd, *J* = 13.7, 4.8, 1.5 Hz, 1H), 2.91–2.81 (m, 2H), 2.66 (dd, *J* = 15.8, 7.3 Hz, 1H), 2.38 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.2, 142.0, 138.6, 137.8, 135.5, 129.3, 128.4, 128.3, 128.2, 127.8, 126.8, 126.7, 126.4, 125.2, 124.7, 124.1, 81.1, 49.4, 34.5, 28.1; IR (neat): $\tilde{\nu}$ = 3331, 1473, 1443 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{24}H_{20}O+Na^+$: 347.1406 [*M* + Na]$^+$, found 347.1402.

6-Benzyl-8*H*-indeno[1,2-*a*]anthracene (4A): The general procedure was followed using **1g** (49.3 mg, 0.200 mmol), **2h** (51.6 mg, 0.300 mmol), $[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μmol), *rac*-BINAP (12.5 mg, 20.1 μmol), K_2CO_3 (55.3 mg, 0.400 mmol), 1,4-dioxane (2.0 mL), and Tf_2O (67.9 mg, 0.241 mmol). Purification by preparative TLC ($CHCl_3$/hexane = 2:1) yielded **4A** (43.0 mg, 0.121 mmol, 60 %) as an orange solid. M.p. 143–148 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 9.35 (s, 1H), 8.68 (s, 1H), 8.58 (d, *J* = 7.5 Hz, 1H), 8.15 (d, *J* = 9.0 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.59–7.45 (m, 4H), 7.40–7.20 (m, 6H), 4.66 (s, 2H), 4.00 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.1, 143.1, 141.8, 140.5, 136.4, 134.7, 131.6, 130.75, 130.71, 128.9, 128.7, 128.5, 128.2, 126.9, 126.2, 125.8, 125.40, 125.36, 124.7, 124.6, 124.3, 122.8, 122.5, 39.8, 38.2; HRMS (ESI): *m/z* calcd. for $C_{28}H_{20}+Na^+$: 379.1457 [*M* + Na]$^+$, found 379.1458.

1-Benzyl-4-methyl-6-phenylnaphthalene (5): An oven-dried Schlenk tube containing a magnetic stirring bar was charged with **4d** (31.2 mg, 0.100 mmol), $PhB(OH)_2$ (24.4 mg, 0.200 mmol), $Pd(PPh_3)_4$ (5.8 mg, 5.0 μmol), and K_2CO_3 (34.6 mg, 0.250 mmol). THF (2.5 mL) and H_2O (125 μL) were added successively through the septum with a syringe, and the mixture was stirred at 80 °C. After 9 h, the reaction mixture was passed through a plug of Florisil® eluting with hexane/AcOEt (4:1). The filtrate was concentrated, and the residue was purified by preparative TLC (hexane/AcOEt = 10:1 × 2, then hexane) to afford **5** (29.8 mg, 0.097 mmol, 96 %) as a pale yellow solid. M.p. 84–87 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.25–8.23 (m, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.77–7.73 (m, 3H), 7.55–7.49 (m, 2H), 7.44–7.37 (m, 1H), 7.35–7.29 (m, 3H), 7.28–7.21 (m, 4H), 4.48 (s, 2H), 2.78 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.4, 140.9, 138.0, 134.6, 133.4, 133.3, 131.3, 128.8, 128.7, 128.4, 127.5, 127.3, 127.2, 126.8, 126.0, 125.4, 125.2, 122.8, 39.0, 19.6; HRMS (ESI) calcd. for $C_{24}H_{20}+Na^+$: 331.1457 [*M* + Na]$^+$, found 331.1460.

1-Benzyl-4-methyl-6-(phenylethynyl)naphthalene (6): An oven-dried Schlenk tube containing a magnetic stirring bar was charged with **4d** (31.2 mg, 0.100 mmol), phenylacetylene (12.7 mg, 0.124 mmol), $PdCl_2(PPh_3)_2$ (2.8 mg, 4.0 μmol), and CuI (0.4 mg, 2.1 μmol). $(iPr)_2NH$ (0.50 mL), THF (1.0 mL) were added successively through the septum via a syringe, and the mixture was stirred at 80 °C. After 6 h, the reaction mixture was passed through a plug of Florisil® eluting with hexane/AcOEt (4:1). The filtrate was concentrated, and the residue was purified by preparative TLC (hexane/AcOEt = 10:1, then hexane × 2) to afford **6** (25.6 mg, 0.077 mmol, 77 %) as a pale yellow solid. M.p. 97–99 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.27 (s, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.64–7.55 (m, 3H), 7.42–7.34 (m, 3H), 7.33–7.27 (m, 3H), 7.25–7.19 (m, 4H), 4.44 (s, 2H), 2.73 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 140.6, 134.7, 133.2, 132.8, 131.65, 131.61, 128.6, 128.5, 128.44, 128.36, 128.3, 128.1, 127.9, 127.0, 126.1, 125.0, 123.3, 120.0, 90.0, 89.6, 38.9, 19.4; HRMS (ESI): *m/z* calcd. for $C_{26}H_{20}+Na^+$: 355.1457 [*M* + Na]$^+$, found 3355.1452.

Acknowledgments

This work was supported by JSPS, Japan (Grant-in-Aid for Scientific Research (C) No. 16K05783).

Keywords: Annulation · Homogeneous catalysis · Hydrocarbons · Polycycles · Rhodium

[1] a) K. Fagnou, M. Lautens, *Chem. Rev.* **2003**, *103*, 169–196; b) T. Hayashi, K. Yamasaki, *Chem. Rev.* **2003**, *103*, 2829–2844; c) T. Miura, M. Murakami, *Chem. Commun.* **2007**, 217–224; d) S. W. Youn, *Eur. J. Org. Chem.* **2009**, *2009*, 2597–2605; e) H. J. Edwards, J. D. Hargrave, S. D. Penrose, C. G. Frost, *Chem. Soc. Rev.* **2010**, *39*, 2093–2105; f) P. Tian, H.-Q. Dong, G.-Q. Lin, *ACS Catal.* **2012**, *2*, 95–119; g) M. M. Heravi, M. Dehghani, V. Zadsirjan, *Tetrahedron: Asymmetry* **2016**, *27*, 513–588; h) A. Claraz, F. Serpier, S. Darses, *ACS Catal.* **2017**, *7*, 3410–3413.

[2] a) R. Shintani, K. Okamoto, Y. Otomaru, K. Ueyama, T. Hayashi, *J. Am. Chem. Soc.* **2005**, *127*, 54–55; b) T. Miura, M. Shimada, M. Murakami, *Synlett* **2005**, 667–669; c) T. Matsuda, M. Makino, M. Murakami, *Angew. Chem. Int. Ed.* **2005**, *44*, 4608–4611; *Angew. Chem.* **2005**, *117*, 4684–4687; d) Y. Li, M.-H. Xu, *Org. Lett.* **2014**, *16*, 2712–2715.

[3] a) T. Miura, M. Shimada, M. Murakami, *Tetrahedron* **2007**, *63*, 6131–6140; b) B. M. Partridge, J. Solana González, H. W. Lam, *Angew. Chem. Int. Ed.* **2014**, *53*, 6523–6527; *Angew. Chem.* **2014**, *126*, 6641–6645; c) T. Johnson, K.-L. Choo, M. Lautens, *Chem. Eur. J.* **2014**, *20*, 14194–14197; d) J. Yan, N. Yoshikai, *ACS Catal.* **2016**, *6*, 3738–3742.

[4] For the arylative annulation of β-alkynyl esters, see: a) T. Miura, T. Sasaki, H. Nakazawa, M. Murakami, *J. Am. Chem. Soc.* **2005**, *127*, 1390–1391; b) L. O'Brien, S. N. Karad, W. Lewis, H. W. Lam, *Chem. Commun.* **2019**, *55*, 11366–11369. For the reaction of β-alkynyl aldimines, see: c) K. Choi, J. M. Joo, C. Lee, *Tetrahedron* **2015**, *71*, 5910–5917.

[5] Lam reported arylative annulation of a β-enynyl ketone, stating that the geminal substituents at the α-position improve the yields of products. B. M. Partridge, M. Callingham, W. Lewis, H. W. Lam, *Angew. Chem. Int. Ed.* **2017**, *56*, 7227–7232; *Angew. Chem.* **2017**, *129*, 7333–7338.

[6] For a review on the synthesis of naphthalene derivatives from *o*-alkynylphenyl ketones and aldehydes, see: L. Chen, K. Chen, S. Zhu, *Chem* **2018**, *4*, 1208–1262.

[7] a) T. Matsuda, N. Miura, *Org. Biomol. Chem.* **2013**, *11*, 3424–3427; b) T. Matsuda, T. Matsumoto, *Org. Biomol. Chem.* **2016**, *14*, 5023–5027. See also c) T. Matsuda, I. Yuihara, K. Kondo, *Org. Biomol. Chem.* **2016**, *14*, 7024–7027.

[8] For reviews, see: a) S. Ma, Z. Gu, *Angew. Chem. Int. Ed.* **2005**, *44*, 7512–7517; *Angew. Chem.* **2005**, *117*, 7680–7685; b) F. Shi, R. C. Larock, *Top. Curr. Chem.* **2010**, *292*, 123–164.

[9] For recent examples of 1,4-migration of rhodium(I), see: a) T. Matsuda, S. Watanuki, *Org. Biomol. Chem.* **2015**, *13*, 702–705; b) A. Masarwa, M. Weber, R. Sarpong, *J. Am. Chem. Soc.* **2015**, *137*, 6327–6334; c) T. Sawano, M. Hashizume, S. Nishimoto, K. Ou, T. Nishimura, *Org. Lett.* **2015**, *17*, 2630–2633; d) E. A. B. Kantchev, F. Zhou, S. R. Pangestu, M. B. Sullivan, H. Su, *Eur. J. Org. Chem.* **2015**, *2015*, 7114–7121; e) J. Ming, T. Hayashi, *Org. Lett.* **2016**, *18*, 6452–6455; f) M. Callingham, B. M. Partridge, W. Lewis, H. W. Lam, *Angew. Chem. Int. Ed.* **2017**, *56*, 16352–16356; *Angew. Chem.* **2017**, *129*, 16570–16574; g) J. Ming, Q. Shi, T. Hayashi, *Chem. Sci.* **2018**, *9*, 7700–7704; h) J.-X. Wang, Y.-X. Tan, W.-W. Liao, P. Tian, G.-Q. Lin, Q. Zhao, *Synlett* **2018**, *29*, 1223–1228; i) S.-S. Zhang, T.-J. Hu, M.-Y. Li, Y.-K. Song, X.-D. Yang, C.-G. Feng, G.-Q. Lin, *Angew. Chem. Int. Ed.* **2019**, *58*, 3387–3391; *Angew. Chem.* **2019**, *131*, 3425–3429; j) N. Liu, J. Yao, L. Yan, T. Lu, Z. Tian, X. Dou, *ACS Catal.* **2019**, *9*, 6857–6863.

[10] a) T. Hayashi, K. Inoue, N. Taniguchi, M. Ogasawara, *J. Am. Chem. Soc.* **2001**, *123*, 9918–9919; b) T. Miura, M. Murakami, *Org. Lett.* **2005**, *7*, 3339–3341; c) R. Shintani, K. Okamoto, T. Hayashi, *Chem. Lett.* **2005**, *34*, 1294–1295; d) T. Matsuda, M. Makino, M. Murakami, *Chem. Lett.* **2005**, *34*, 1416–1417; e) Y. Harada, J. Nakanishi, H. Fujihara, M. Tobisu, Y. Fukumoto, N. Chatani, *J. Am. Chem. Soc.* **2007**, *129*, 5766–5771; f) M. Miyamoto, Y. Harada, M. Tobisu, N. Chatani, *Org. Lett.* **2008**, *10*, 2975–2978; g) T. Morimoto, K. Yamasaki, A. Hirano, K. Tsutsumi, N. Kagawa, K. Kakiuchi, Y. Harada, Y. Fukumoto, N. Chatani, T. Nishioka, *Org. Lett.* **2009**, *11*, 1777–1780; h) M. Tobisu, M. Onoe, Y. Kita, N. Chatani, *J. Am. Chem. Soc.* **2009**, *131*, 7506–7507; i) R. Shintani, S. Isobe, M. Takeda, T. Hayashi, *Angew. Chem. Int. Ed.* **2010**, *49*, 3795–3798; *Angew. Chem.* **2010**, *122*, 3883–3886.

[11] For the use of Tf_2O in a dehydration–aromatization, see: W. Yang, J. Wang, Z. Wei, Q. Zhang, X. Xu, *J. Org. Chem.* **2016**, *81*, 1675–1680.

[12] It was determined later that the use of 10 mol-% of the ligand affords superior activity in majority of other reactions examined in Table 2, Table 3, and Table 4.

[13] Alkynyl ketone **1a** was completely consumed during the reaction. The low yields of **4i** and **4j** might be attributed to a side reaction.

[14] The reaction of **1a** with 9-phenanthreneboronic acid afforded the corresponding annulation product 1-benzyl-4-methyltriphenylene in yields below 10 %.

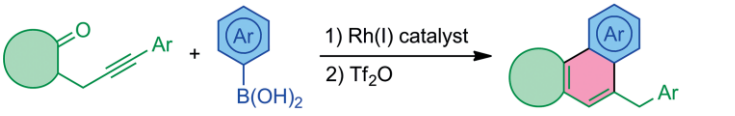
[15] In the case with **2k**, 26 % of alkynyl ketone **1a** was recovered.

[16] When 5-phenylpent-4-ynal was treated with **2a**, 4-benzylidene-1-tetralone was obtained in 20 % yield through β-hydride elimination of the corresponding rhodium(I) tetralin-1-olate.

Received: October 8, 2019

Fused Aromatic Compounds

Annulation–Dehydration–Aromatization



31 examples, up to 96% yield

Rhodium(I)-catalyzed arylative annulation of β-(phenylethynyl) ketones with arylboronic acids affords 4-(arylmethylene)tetralin-1-ols, treatment of which with Tf_2O resulted in a dehydration–aromatization sequence, giving rise to (arylmethyl)naphthalenes. Aromatic compounds with as many as five cycles can be prepared using this method.

DOI: 10.1002/ejoc.201901481