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Rhodium-catalyzed arylative cyclization of alkynyl malonates by 1,4-rhodium(I) migration†

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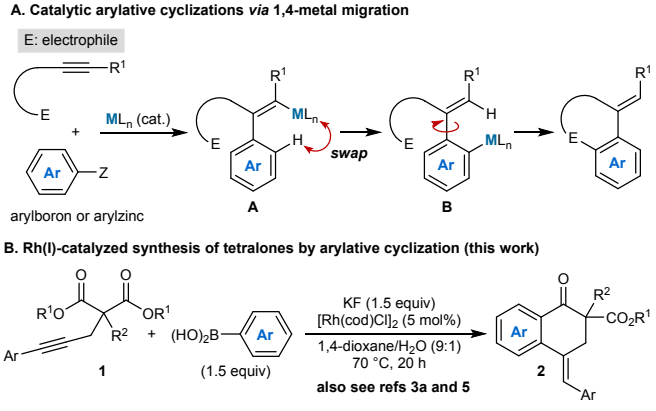
The synthesis of functionalized 1-tetralones by the rhodium(I)-catalyzed reaction of alkynyl malonates with arylboronic acids is described. These arylative cyclizations proceed *via* an alkenyl-to-aryl 1,4-Rh(I) migration as a key step. Preliminary results of an enantioselective variant of these reactions are also presented.

Domino reactions that consist of a metal-catalyzed addition of an aryl nucleophile to an alkyne, followed by an intramolecular nucleophilic addition of the resulting alkenylmetal species onto a tethered electrophile, are versatile transformations for the preparation of hetero- and carbocyclic products.[1] A variation of these arylative cyclizations involves the 1,4-migration of the metal[2] from the initially formed alkenylmetal species **A** onto an aryl site, followed by cyclization of the resulting arylmetal species **B** onto the electrophile (Scheme 1A). This through-space transmission of reactivity further increases the synthetic capabilities of arylative cyclizations, and to date, reactions based upon alkenyl-to-aryl 1,4-migrations of rhodium,[3] iridium,[4] and cobalt[5] have been described.[6,7,8,9,10,11] The use of esters as the electrophiles in these reactions leads to the formation of aromatic ketones. In this context, the Murakami[3a] and Yoshikai[5] groups have shown that alkyne-tethered esters react with arylboron and arylzinc reagents in arylative cyclizations under rhodium and cobalt catalysis, respectively. However, only symmetrical alkynes were employed in these studies.[3a,5] Although this feature eliminates the challenge of controlling regioselectivity in the initial arylmetalation, it does limit synthetic utility. Here, we describe the rhodium-catalyzed reaction of arylboronic acids with alkynyl malonates **1**, in which the alkyne is unsymmetrically substituted (Scheme 1B). These arylative cyclizations produce 1-tetralones containing an all-carbon quaternary stereocenter at C2, a structural motif that appears in several natural products such as (±)-nidemone,[12] aspewentin B,[13] and diomuscinone[14] (Figure 1). Preliminary results of an enantioselective variant are also described.



Scheme 1 Catalytic arylative cyclizations *via* 1,4-metal migration

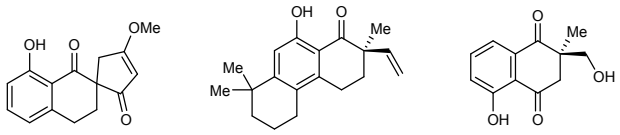


Fig 1 Natural products containing a 1-tetralone with an all-carbon quaternary stereocenter at C2

It is known that carbometalation of alkynes substituted with one alkyl and one aryl group are often highly regioselective.[15] Accordingly, bis(2,2,2-trifluoroethyl)malonate **1a**, which contains such an alkyne, was selected for our initial experiments in the hope that a highly regioselective synthesis of 1-tetralones by arylative cyclization could be achieved. First, a mixture of **1a** and PhB(OH)$_2$ (1.5 equiv) was heated at 70 °C for 20 h in the presence of 5 mol% of [Rh(cod)Cl]$_2$ and various bases (1.5 equiv) (Table 1).[16] We were pleased to observe that arylative cyclization was successful and the best results were obtained using KF as the base in 1,4-dioxane/H$_2$O (9:1) as the solvent, which gave 1-tetralone **2aa** in 75% yield as determined by ^{1}H NMR analysis of the crude mixture using 1,4-dimethoxybenzene as an internal standard (entry 1). This experiment also gave alkyne hydroarylation product **3ab** in 14% yield. Changing the quantity of H$_2$O in the reaction medium by using anhydrous

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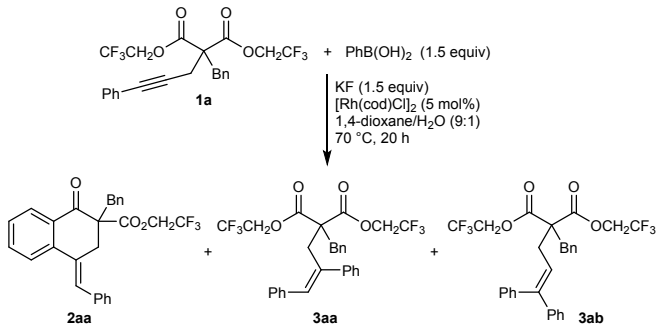
† Electronic Supplementary Information (ESI) available: Experimental procedures, full spectroscopic data for new compounds, and crystallographic data for **2ea.** CCDC 1938497. See DOI: 10.1039/x0xx00000x

Table 1 Evaluation of reaction conditions[a]



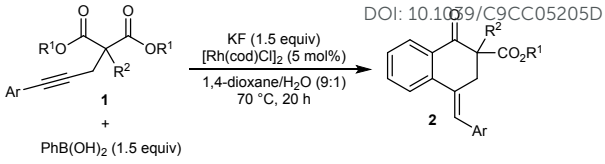
Entry	Deviation from standard conditions	Yield of **2aa** (%)[b]	Yield of **3aa** (%)[b]	Yield of **3ab** (%)[b]
1	None	75	–	14
2	1,4-Dioxane as solvent	42	19	14
3	In 1,4-dioxane/H_2O (4:1)	54	5	9
4	Toluene as solvent	28	28	14
5	Xylenes as solvent	33	42	14
6	Et_3N instead of KF	47	19	14
7	Cs_2CO_3 instead of KF	56	–	9

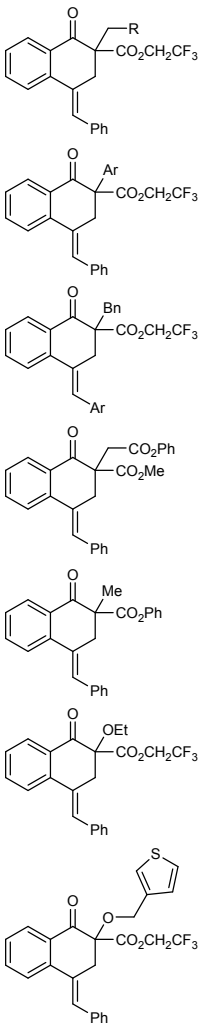
[a] Reactions were conducted with 0.05 mmol of **1a**. [b] Determined by ^1H NMR analysis of the crude reactions using 1,4-dimethoxybenzene as an internal standard.

1,4-dioxane or 1,4-dioxane/H_2O (4:1) gave lower yields of **2aa** along with significant quantities of alkyne hydroarylation products **3aa** and **3ab** (entries 2 and 3). Other solvents such as toluene (entry 4) and xylenes (entry 5) also gave inferior results. Other bases such as Et_3N (entry 6) and Cs_2CO_3 (entry 7) are also effective but the yields of **2aa** are appreciably lower compared with using KF (entry 1). The conditions shown in entry 1 were therefore selected for use in further experiments.

The scope of this reaction with respect to the alkynyl malonate was then examined in reactions with $PhB(OH)_2$, which gave 1-tetralones **2aa**–**2qa** in 33–74% yield (Table 2). In some cases (**2ha** and **2pa**), it proved beneficial to increase the loading of $[Rh(cod)Cl]_2$ to 10 mol% and the quantity of $PhB(OH)_2$ to 2.0 equivalents. The reaction producing **2aa** also gave a 1:1.25 mixture of inseparable alkyne hydroarylation products **3aa** and **3ab** (see Table 1 for the structures), respectively, in 19% combined yield. Alkyne hydroarylation products corresponding to **3aa** and **3ab** were not isolated in subsequent experiments using other substrates. The reaction is tolerant of a wide range of carbon-linked substituents at the 2-position of the substrate, including benzyl (**2aa** and **2ja**–**2ma**), methyl (**2ba** and **2oa**), 2-thienylmethyl (**2ca**), 2-oxo-2-phenylethyl (**2da**), 2-oxo-2-phenoxyethyl (**2ea**[17] and **2na**), phenyl (**2fa**), 2-methoxyphenyl (**2ga**), 2-naphthyl (**2ha**), and 3-thienyl (**2ia**) groups. Heteroatom substituents at the 2-position are also accommodated, such as ethoxy (**2pa**) and 3-thienylmethoxy (**2qa**) groups. The alkynyl substituent can be changed from a phenyl group (**2aa**–**2ia** and **2na**–**2qa**) to 4-methoxyphenyl (**2ja**), 3-methylphenyl (**2ka**), 1-naphthyl (**2la**), and 2-thienyl (**2ma**) groups. A substrate with a methyl-substituted alkyne did undergo arylative cyclization in low yield but the product **2ra** contained unidentified, inseparable impurities.[18] In addition, a substrate containing a terminal alkyne gave only a complex mixture of unidentified products. Pleasingly, the reaction is not limited to bis(2,2,2-trifluoroethyl) malonates;

Table 2 Scope with respect to the alkynyl malonate[a]





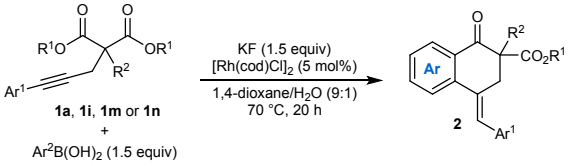
2aa	R = Ph	67%[b]
2ba	R = H	58%
2ca	R = 2-thienyl	50%
2da	R = COPh	36%[c]
2ea	R = CO_2Ph	55%
2fa	Ar = Ph	62%
2ga	Ar = 2-$MeOC_6H_4$	54%
2ha	Ar = 2-naphthyl	56%[d]
2ia	Ar = 3-thienyl	57%
2ja	Ar = 4-$MeOC_6H_4$	64%
2ka	Ar = 3-MeC_6H_4	74%
2la	Ar = 1-naphthyl	68%
2ma	Ar = 2-thienyl	66%
2na		72%
2oa		55%
2pa		36%[d]
2qa		33%[c]

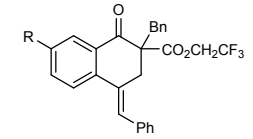
[a] Reactions were conducted with 0.30 mmol of **1a**–**1q** in 3 mL of 1,4-dioxane/H_2O (9:1). Yields are of isolated products. [b] This experiment also gave a 1:1.25 inseparable mixture of **3aa** and **3ab**, respectively, in 19% combined yield. [c] The reaction time was 24 h. [d] Conducted using 10 mol% of $[Rh(cod)Cl]_2$ and 2.0 equiv of $PhB(OH)_2$.

substrates containing dimethyl or diphenyl malonates gave 1-tetralones **2na** and **2oa** in 55% and 72% yield, respectively.

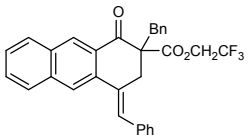
Table 3 presents the results of the reactions of representative substrates **1a**, **1i**, **1m**, and **1n** with various arylboronic acids, which gave 1-tetralones **2ab**–**2nj** in 45–79% yield. The arylboronic acid scope includes a range of *para*- (**2ab**, **2ac**, **2nh**, and **2ni**), *meta*- (**2mg**), and disubstituted phenylboronic acids (**2ie** and **2mf**) containing methyl (**2ab**), halide (**2ac**, **2mf**, and **2ni**), carboethoxy (**2mg**), or alkoxy groups (**2ge** and **2nh**). 2-Naphthylboronic acid (**2ad**) is also tolerated. In the case of 2-naphthylboronic acid and 3-ethoxycarbonylphenylboronic acid, 1,4-Rh(I) migration occurred to the sterically more accessible position (**2ad** and **2mg**, respectively). 3-Thienylboronic acid also reacted successfully with **1a**; however,

Table 3 Scope with respect to the boronic acid[a]

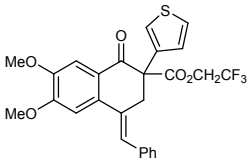




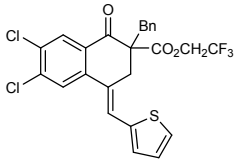
2ab R = Me 79%
2ac R = F 68%



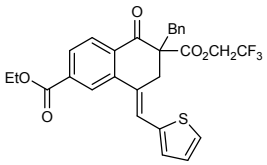
2ad 56%



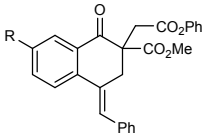
2ie 50%



2mf 51%

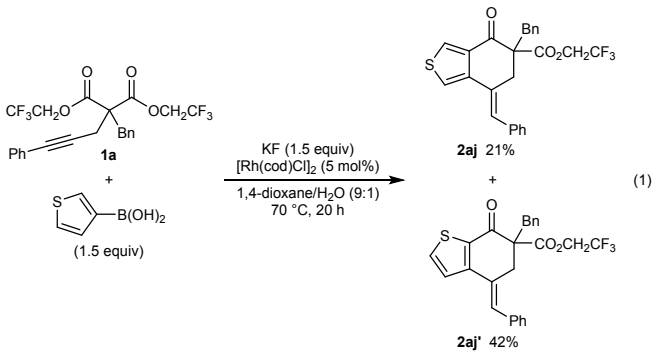


2mg 56%



2nh R = OMe 51%
2ni R = Cl 45%

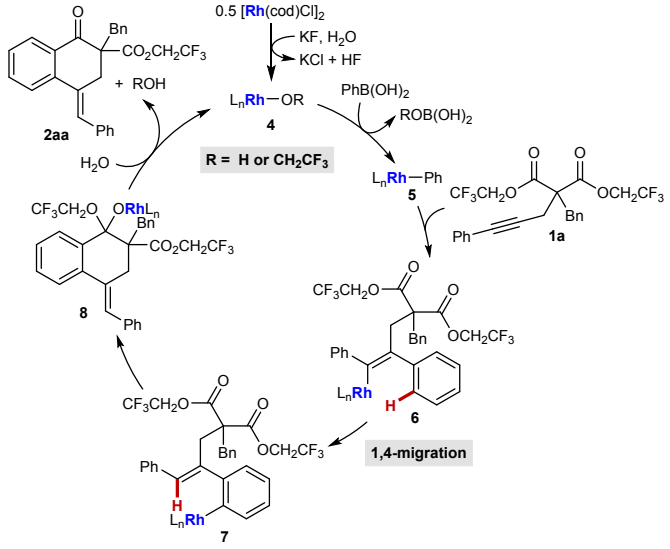
[a] Reactions were conducted with 0.30 mmol of **1a**, **1g**, **1m** or **1n** in 3 mL of 1,4-dioxane/H_2O (9:1). Yields are of isolated products.



(1)

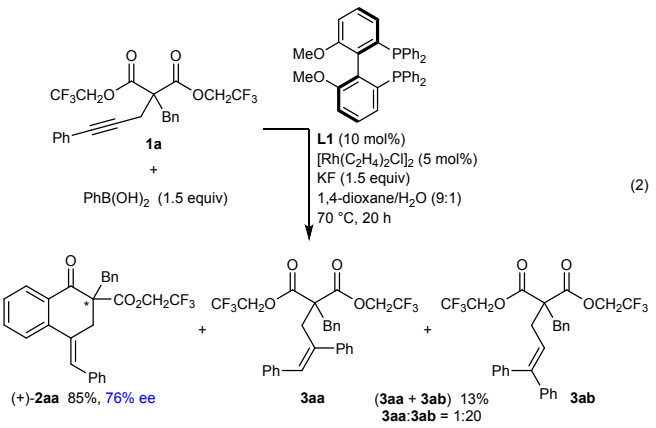
two products **2aj** and **2aj'** were obtained in 21% and 42% yield, respectively, resulting from 1,4-Rh(I) migration to different sites of the thiophene prior to cyclization (eqn (1)).

A possible catalytic cycle for these reactions is depicted in Scheme 2, using substrate **1a** and $PhB(OH)_2$ as example reaction partners. Heating a mixture of $[Rh(cod)Cl]_2$, KF, and H_2O may generate rhodium hydroxide **4** (R = H), which can undergo transmetalation with $PhB(OH)_2$ to give arylrhodium species **5**. Phenylrhodation of the alkyne of **1a** gives alkenylrhodium species **6**, which then undergoes alkenyl-to-aryl 1,4-Rh(I) migration to give arylrhodium species **7**. Cyclization of **7** by 1,2-addition onto one of the esters produces rhodium alkoxide **8**, which collapses to release the product **2aa** and regenerate the active rhodium complex **4** (which could have a either a trifluoroethoxide or hydroxide counterion).



Scheme 2 Possible catalytic cycle

Finally, preliminary efforts at developing an enantioselective variant of this reaction were conducted. After some experimentation,[19] heating **1a** with $PhB(OH)_2$ (1.5 equiv) in the presence of $[Rh(C_2H_4)_2Cl]_2$ (5 mol%), (*R*)-MeO-BIHEP (**L1**, 10 mol%), and KF (1.5 equiv) in 1,4-dioxane/H_2O (9:1) at 70 °C gave (+)-**2aa** in 85% yield and 76% ee, along with an inseparable mixture of **3aa** and **3ab** in 13% yield (eqn (2)).



(2)

In summary, we have developed the rhodium(I)-catalyzed reaction of alkynyl malonates with arylboronic acids to give diverse 1-tetralones. A key step in these arylative cyclizations is an alkenyl-to-aryl 1,4-Rh(I) migration. Use of a chiral bisphosphine-ligated rhodium complex as the precatalyst gives promising enantioselectivity (76% ee). Our investigations into development of

new domino reactions involving 1,4-metal migration are ongoing and will be reported in due course.[20]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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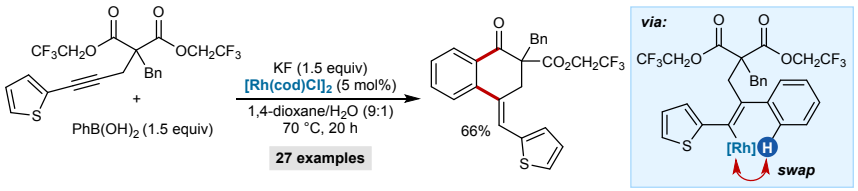
18 See the Supplementary Information for further details.

19 For further details about the evaluation of chiral ligands in these reactions, see the Supplementary Information.

20 The research data associated with this publication can be found at DOI: 10.17639/nott.7008



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The synthesis of functionalized 1-tetralones by the rhodium(I)-catalyzed reaction of alkynyl malonates with arylboronic acids is described.