Communication

Catalytic, Directed C–C Bond Functionalization of Styrenes

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Catalytic, Directed C–C Bond Functionalization of Styrenes

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Supporting Information Placeholder

ABSTRACT: A method for catalytic conversion of C(aryl)–C(alkenyl) bonds in styrene derivatives to new C–C bonds is developed. In the presence of a rhodium catalyst, the alkenyl groups of styrenes bearing a pyrazolyl directing group were efficiently converted to other carbon substituents upon reacting with various alkenes including styrenes, aliphatic alkenes, and allyl alcohols. It is also indicated that the C–C bond cleavage proceeded via a hydrometalation/β-carbon elimination pathway.

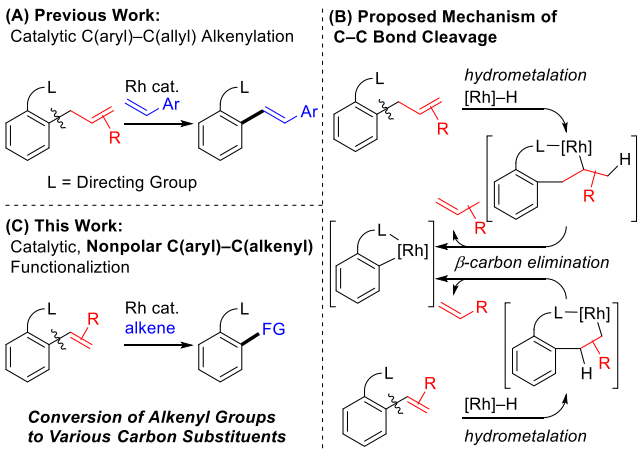
Transition-metal-catalyzed bond formation via cleavage of unstrained C–C single bonds has attracted increasing attention because such strategies would provide unconventional methods to synthesize complex organic molecules.[1] There have been a large number of reports on unstrained C–C bond functionalization, but types of cleavable C–C bonds are still limited. Namely, C–C bonds adjacent to polar groups such as cyano, carbonyl, imino and hydroxy groups have been frequently targeted as the cleavage sites.[1] In contrast, catalytic functionalization via cleavage of nonpolar C–C bonds is relatively unexplored.[2-5]

Recently, we reported a rhodium-catalyzed alkenylation of allylbenzenes via chelation-assisted C–C bond cleavage (Scheme 1A).[4] The preliminary mechanistic study suggested that the C–C bond was cleaved via hydrometalation of alkene moieties followed by chelation-assisted β-carbon elimination.[6] We then envisioned that the hydrometalation/β-carbon elimination strategy would also be applicable to conversion of more challenging bonds such as C(aryl)–C(alkenyl) bonds of styrenes, and the metalacyclic intermediate formed after the C–C bond cleavage would be applicable to various C–C bond forming reactions (Scheme 1B). To date, reported methods for catalytic conversion of nonpolar C(aryl)–C(alkenyl) bonds have been limited to a few examples[5] such as Youn's palladium-catalyzed arylation of alkenes using 2-alkenylphenyl β-keto esters via aromatization-driven β-carbon elimination.[5a]

In this communication, we report a rhodium-catalyzed reaction to convert C(aryl)–C(alkenyl) bonds in styrene derivatives to new C–C bonds (Scheme 1C). In the presence of a Cp*Rh(III) catalyst, alkenyl groups in styrene derivatives bearing a directing group were efficiently substituted with carbon substituents by the reactions with various alkenes.

First, we examined the reaction of isopropenylbenzene derivatives bearing a directing group (Table 1).[7] When an isopropenylbenzene derivative having a 1-pyrazolyl directing group (**1a**) was reacted with styrene (**2a**) in the presence of $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (**3a**) under EtOH refluxing conditions for 3 h, conversion of the isopropenyl group to a β-styryl group proceeded to afford the alkenylation product **4aa** in 94% isolated yield (entry 1). The reaction of a substrate bearing a 2-pyridyl directing group (**5**) under the same reaction conditions gave the corresponding product **6** in 22% NMR yield (entry 2), but increase of the catalyst loading to 4 mol % and extension of the reaction time to 24 h improved the NMR yield to 85% (entry 3).

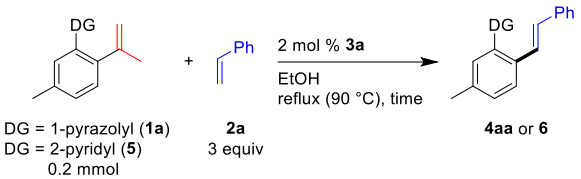
Scheme 1. Catalytic C–C Bond Cleavage of Aromatic Compounds Bearing Alkenes



Substrate scope was then examined for the pyrazolyl-directed dealkenylative alkenylation (Table 2). First, the reactions using styrenes possessing various *para*-substituents were investigated. The alkenylation of **1a** with styrene derivatives having electron-donating groups (Me, ^{t}Bu, OMe) offered the corresponding products **4ab**-**4ad** in 88-97% isolated yields. The reaction with a styrene bearing an electron-withdrawing CF_3 group also gave **4ae** in 95% yield. Halogeno groups (F, Cl, Br) were tolerated under the reaction conditions, and excellent yields of the alkenylation products **4af**-**4ah** were achieved. The alkenylation with 2-methylstyrene also proceeded to give **4ai** in 96% yield.[8] The reactions of substrates bearing a substituent (Me, Cl) at the position ortho to the pyrazolyl group provided the corresponding alkenylation products **4ba** and **4ca** in 90 and 77% yields, respectively. Even when substrates possessing a sterically-less congested hydrogen at the position ortho to the pyrazolyl group were used for the reaction, the ortho

isopropenyl group was selectively converted to β-styryl group.[9] For example, the reaction of arylpyrazole **1d** (R^1 = H), as well as para-substituted substrates **1e** (R^1 = Me) and **1f** (R^1 = Cl) with **2a** provided only monoalkenylation product **4da**, **4ea**, and **4fa** in high yields. In metal-catalyzed directed C–H functionalization, the use of *meta*-methoxy substituted arenes is often challenging, because regioselective reaction at an ortho position over the other is difficult to achieve.[10] In this alkenylation, the isopropenyl group of **1g** was converted into the β-styryl group to give **4ga** in 87% yield.[11,12] The pyrazolyl directing group of **4ga** could be transformed into an amino group using the method developed by our group (eq 1).[4]

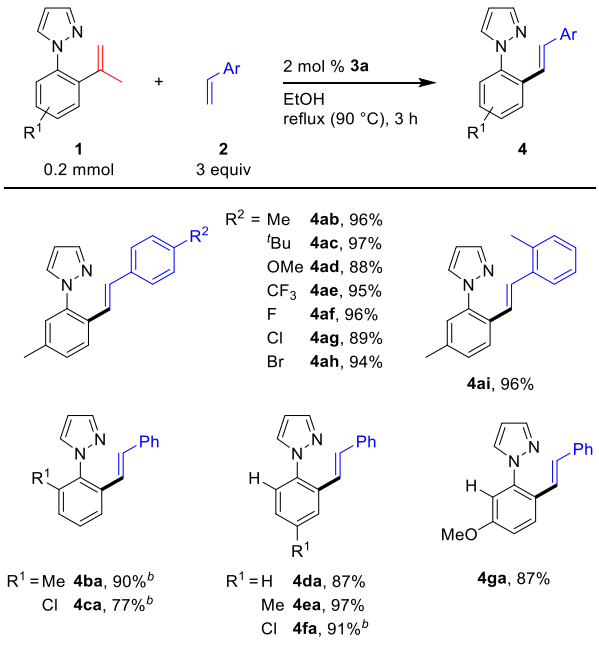
Table 1. Dealkenylative Styrylation[a]



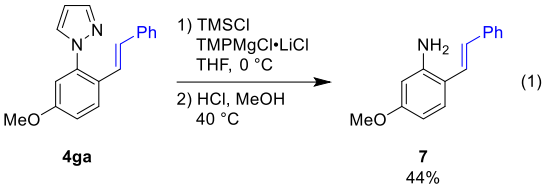
entry	substrate	time	product	yield
1	**1a**	3 h	**4aa**	94%[b] (94%)[c]
2	**5**	3 h	**6**	22%[d]
3[e]	**5**	24 h	**6**	85%[d]

[a]Reaction conditions: **1a** or **5** (0.2 mmol), **2a** (0.6 mmol), **3a** (4 μ mol), EtOH (1.6 mL), reflux. [b]Yield was determined by ^{1}H NMR using 9*H*-fluorene as an internal standard. [c]The isolated yield is shown in parentheses. [d]Yield was determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [e]Performed with 8 μmol (4 mol %) of **3a**.

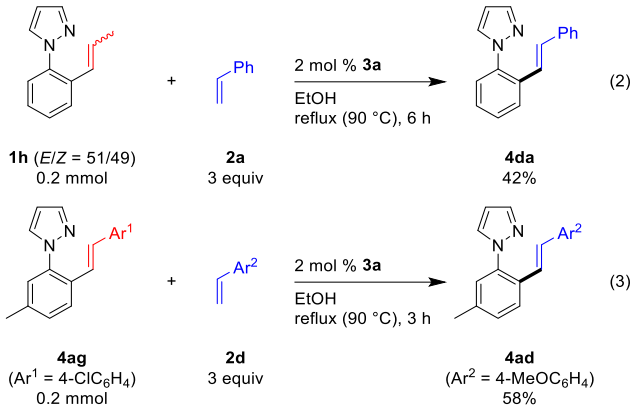
Table 2. Dealkenylative Alkenylation with Styrene Derivatives 2[a]



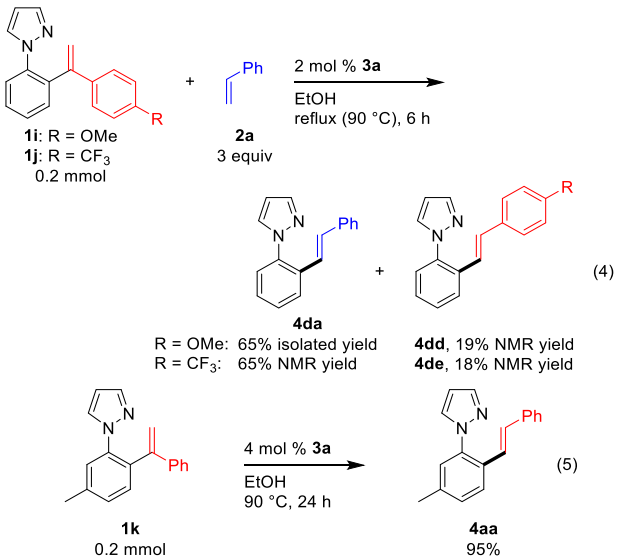
[a]Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), **3a** (4 μmol), EtOH (1.6 mL), reflux, 3 h. Isolated yields are shown. [b]Performed for 5 h.



The dealkenylative alkenylation was also examined using substrates bearing other alkenyl groups. The reaction of an arylpyrazole possessing 1-propenyl group (**1h**) with **2a** for 6 h afforded **4da** in 42% yield (eq 2). A stilbene derivative **4ag** also reacted with 4-methoxystyrene (**2d**) to give **4ad** in 58% yield (eq 3).

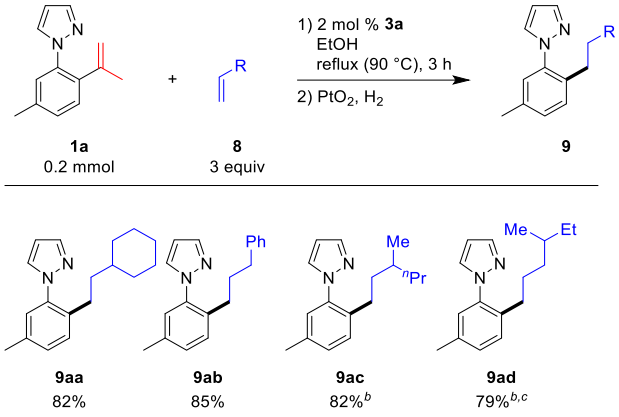


Interestingly, when the alkenylation of a substrate having 1-(4-methoxyphenyl)vinyl group (**1i**) with **2a** was performed, **4da** was isolated in 65% yield along with 19% NMR yield of **4dd**, which was formed via alkenylation with cleaved 4-methoxystyrene instead of **2a** (eq 4). A similar result was obtained in the case of the reaction of **1j**. The formation of the β-styrylation products derived from **1i** and **1j** motivated us to examine 1,2-migration of an aryl group of the arylpyrazolyl moiety in the absence of a coupling partner. In fact, while increasing the catalyst loading to 4 mol % and extension of the reaction time to 24 h were needed, the migration of the arylpyrazolyl moiety of **1k** proceeded to give **4aa** in 95% yield (eq 5).



Unactivated aliphatic alkenes were also applicable to the coupling with **1a** in the dealkenylative functionalization, but the products were formed as a mixture of double bond isomers. Therefore, after the coupling reaction, the products were hydrogenated using PtO_2 as a catalyst to the corresponding alkylation product **9** for isolation (Table 3). The reaction with vinylcyclohexane (**8a**) followed by hydrogenation afforded the 2-cyclohexylethylation product **9aa** in 82% yield. Allylbenzene (**8b**) also reacted with **1a** smoothly, and alkylation product **9ab** was isolated in 85% yield. The reactions with alkenes **8c** and **8d** provided the alkylation products **9ac** and **9ad** in good yields after the hydrogenation, although the use of 6 equiv of the alkene was necessary to achieve full conversion of **1a**, due to low boiling points of the alkenes.

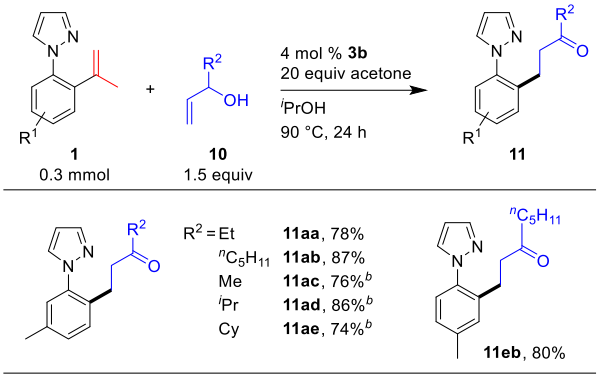
Table 3. Dealkenlative Alkenylation of 1a with Aliphatic Alkenes 8[a]



[a]Reaction conditions: **1a** (0.2 mmol), **8** (0.6 mmol), **3a** (4 μmol), EtOH (1.6 mL), reflux, 3 h. Isolated yields are shown. [b]Performed with 1.2 mmol of **8**. [c]Performed for 5 h.

Allyl alcohols were also found to serve as an efficient coupling partner for the dealkenylative functionalization (Table 4).[13] When a reaction of **1a** with allyl alcohol **10a** was performed in the presence of $[Cp^*Rh(CH_3CN)_3][PF_6]_2$ (**3b**) in acetone/^{i}PrOH for 24 h, substitution of the isopropenyl group with a β-acylalkyl group proceeded to give **11aa** in 78% yield.[14] A variety of allyl alcohols bearing *n*-pentyl (**10b**), methyl (**10c**), isopropyl (**10d**), and cyclohexyl (**10e**) groups were applicable to the reaction, and the corresponding β-acylalkylation products **11ab**-**11ae** were isolated in 74-87% yields. The reaction of substrate **1e** with **10b** again provided monoalkylation product **11eb** in 80% yield.

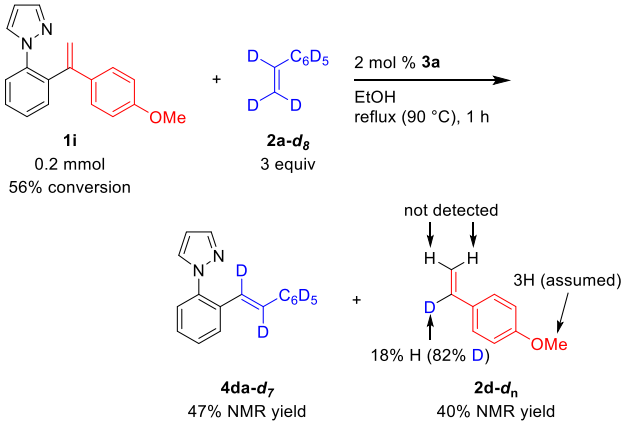
Table 4. Dealkenlative Functionalization of 1 with Allyl Alcohols 10[a]



[a]Reaction conditions: **1** (0.3 mmol), **10** (0.45 mmol), **3b** (12 μmol), acetone (6 mmol), ^{i}PrOH (0.3 mL), 90 °C, 24 h. Isolated yields are shown. [b]Performed for 48 h.

In order to gain insights into the mechanism of the dealkenylative functionalization, the reaction of **1i** with styrene-d_8 (**2a-*d*$_8$**) was examined (Scheme 2). The reaction was stopped after 1 h, and **4da-*d*$_7$** and deuterium incorporated **2d** (**2d-*d*$_n$**) were obtained in 47 and 40% NMR yields respectively. Deuterium was partially introduced (82% D) at the α-position of **2d**. Based on this result, a catalytic cycle is proposed for the dealkenylative alkenylation as shown in Figure 1.[15] Hydrometalation of the alkene moiety in **1** by an in situ-generated rhodium hydride species (**A**→**B**→**C**), followed by chelation-assisted β-carbon elimination gives rhodacyclic intermediate **D** (**C**→**D**). Regioselective 2,1-insertion of styrene into the Rh–C bond and subsequent β-hydride elimination provide product **4** with regenerating the rhodium hydride species **A** (**D**→**E**→**F**→**A**).

Scheme 2. Dealkenylative Alkenylation of 1i with 2a-*d*$_8$



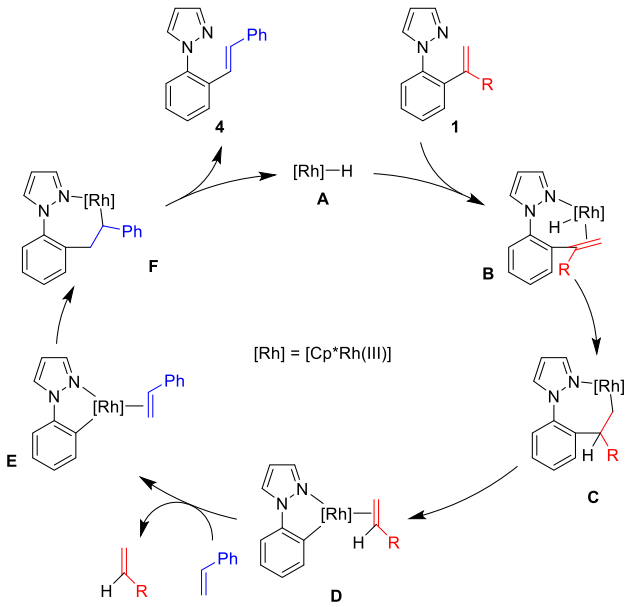


Figure 1. A proposed mechanism of the dealkenylative alkenylation with styrene (**2a**).

In summary, we developed a novel, catalytic functionalization of styrene derivatives via C–C bond cleavage. A variety of alkenes including styrenes, unactivated aliphatic alkenes, and allyl alcohols were applicable to the dealkenylative functionalization as coupling partners under the simple catalyst system. This is the first example for conversion of the alkenyl groups in styrene derivatives to various carbon functional groups. We also revealed that the C–C bond was cleaved via hydrometalation followed by β-carbon elimination, and we believe that this strategy can lead to development of new catalytic, more challenging C–C bond functionalization reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Full experimental details and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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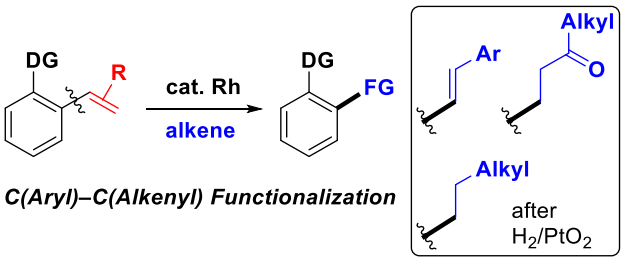
(11) A trace amount of the C–H alkenylation product of **1g** was observed.

(12) When a reaction of 1-(3-methoxyphenyl)-1*H*-pyrazole with **2a** was performed under the conditions developed by Satoh and Miura (ref 9), a mixture of 2- and 6-monoalkenylation products along with the dialkenylation product were formed.

(13) Examples of Cp*Rh(III)-catalyzed C–H functionalization with allyl alcohols, see: (a) Huang, L.; Wang, Q.; Qi, J.; Wu, X.; Huang, K.; Jiang, H. Rh(III)-Catalyzed *ortho*-Oxidative Alkylation of Unactivated Arenes with Allylic Alcohols. *Chem. Sci.* **2013**, *4*, 2665-2669. (b) Shi, Z.; Boultadakis-Arapinis, M.; Glorius, F. Rh(III)-Catalyzed Dehydrogenative Alkylation of (Hetero)arenes with Allylic Alcohols, Allowing Aldol Condensation to Indenes. *Chem. Commun.* **2013**, *49*, 6489-6491.

(14) A manuscript on details of the C–C bond functionalization with allyl alcohols is in preparation.

(15) See the Supporting Information for details of the deuterium labelling experiments.



C(Aryl)–C(Alkenyl) Functionalization