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Ruthenium-Catalyzed Monoalkenylation of Aromatic Ketones by Cleavage of Carbon–Heteroatom Bonds with Unconventional Chemoselectivity**

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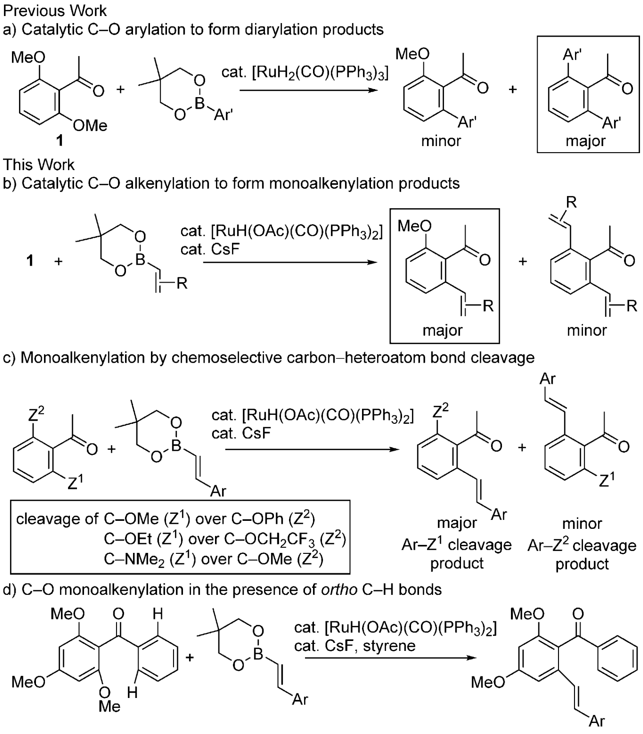
Abstract: *Ruthenium-catalyzed selective monoalkenylation of ortho C–O or C–N bonds of aromatic ketones was achieved. The reaction allowed the direct comparison of the relative reactivities of the cleavage of different carbon-heteroatom bonds, thus suggesting an unconventional chemoselectivity, where smaller, more-electron-donating groups are more easily cleaved. Selective monofunctionalization of C–O bonds in the presence of ortho C–H bonds was also achieved.*

Transition-metal-catalyzed carbon–carbon bond-formation by selective cleavage of unreactive bonds has been extensively investigated because it allows transformations with unconventional chemoselectivity.[1,2] Our group has reported ruthenium-catalyzed functionalizations of aromatic ketones with organoboronates through the cleavage of carbon–hydrogen and carbon–heteroatom bonds by oxidative addition.[3–8] In these reactions, simple carbonyl groups, which are useful for further transformations, effectively function as directing groups by forming a chelate and selectively convert the unreactive bonds at the *ortho*-positions of the aryl ring into carbon–carbon bonds. In many cases, however, selective monofunctionalization is difficult for substrates bearing more than one *ortho* carbon–hydrogen or carbon–oxygen bond.[9] For example, the reaction of 2′,6′-dimethoxyacetophenone (**1**) with arylboronates in the presence of a catalytic amount of $[RuH_2(CO)(PPh_3)_3]$ gave the diarylation products as major products, and it is indicated that the second C–O bond cleavage is faster than the dissociation of the monoarylation product from the catalyst (Scheme 1 a).[5a]



Scheme 1. Ruthenium-catalyzed C–O functionalization of aromatic ketones possessing multiple *ortho* C–O bonds.

Herein we report that selective monoalkenylation of *ortho* carbon–heteroatom bonds of aromatic ketones was achieved for the ruthenium-catalyzed reaction with alkenylboronates (Scheme 1 b). This work allowed direct comparison of the relative ease of the cleavage of different carbon–heteroatom bonds, and it is suggested that smaller, more-electron-donating groups are more easily cleaved (Scheme 1 c), a phenomenon which is unconventional for reactions proceeding by oxidative addition to transition metals. Selective monofunctionalization of C–O bonds in the presence of *ortho* C–H bonds is also found to be possible for benzophenone derivatives (Scheme 1 d).

First, we examined the ruthenium-catalyzed C–O alkenylation[5a,11] of **1** with the styrylboronate **2a** (Table 1). When the reaction of **1** was performed with 2 equivalents of **2a** in the presence of 4 mol % of $[RuH_2(CO)(PPh_3)_3]$ at 140 °C in *p*-xylene for 8 hours, alkenylation of the C–O bond proceeded to give the monoalkenylation product **3a** in 57 % yield (NMR) along with 6 % yield (NMR) of dialkenylation product **4a** (entry 1). The observed selectivity toward the monoalkenylation is in contrast with the C–O arylation of **1**,[5a] which mainly affords diarylation products (Scheme 1 a). Our group reported that the reaction of 2′-methoxyacetophenone, which has both *ortho* C–H and C–O bonds, with alkenylboronates in the presence of a catalytic amount of $[RuH_2(CO)(PPh_3)_3]$ provides the C–H alkenylation product selectively, and C–O alkenylation was not observed.[4c] In this

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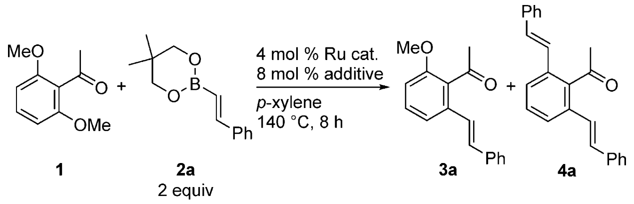
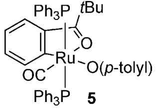
Table 1: Ruthenium-catalyzed monoselective C–O alkenylation of the acetophenone derivative **1** with **2a**.[a]

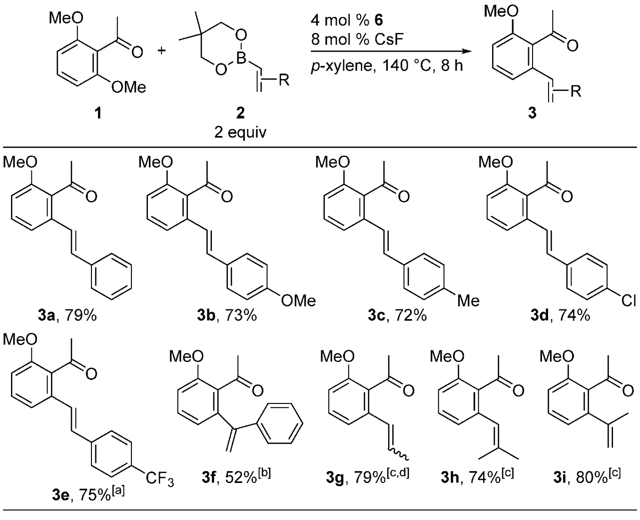


Entry	Ru cat.	Additive	Conv. [%][b]	Yield [%][b] 3a	Yield [%][b] 4a
1	$[RuH_2(CO)(PPh_3)_3]$	–	63	57	6
2	 **5**	–	85	80	5
3	$[RuCl(TMS)(CO)(PPh_3)_2]$	–	36	35	1
4	$[RuH(OAc)(CO)(PPh_3)_2]$ (**6**)	–	72	69	3
5	$[RuH_2(CO)(PPh_3)_3]$	CsF	61	55	5
6	**5**	CsF	63	58	3
7	$[RuCl(TMS)(CO)(PPh_3)_2]$	CsF	82	76	6
8	**6**	CsF	90	83	7
9	**6**	Cs_2CO_3	87	80	6
10	**6**	K_2CO_3	88	81	5

[a] Reaction conditions: **1** (0.5 mmol), **2a** (1.0 mmol), Ru cat. (0.02 mmol), additive (0.04 mmol), p-xylene (0.5 mL), 140 °C, 8 h. [b] Determined by ^{1}H NMR analysis. TMS = trimethylsilyl.

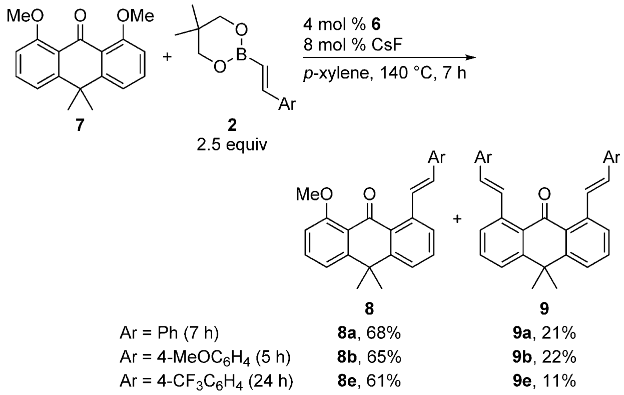
case, coordination of the alkenyl group from the C–H alkenylation product is thought to disrupt the interaction of the C–O bond with the metal center. In the alkenylation of **1** with **2a**, therefore, similar coordination of the alkenyl group in **3a** may prevent the second C–O bond cleavage (Table 1). Screening of the catalyst was then examined. The reaction with the catalyst **5**, which is effective in the C–H-selective alkenylation of 2′-methoxyacetophenone, gave **3a** in 80% yield (entry 2). In search of more convenient catalysts, the reaction with other carbonyl ruthenium(II) complexes having two triphenylphosphines ligands[12] was examined, and the use of $[RuCl(TMS)(CO)(PPh_3)_2]$ and $[RuH(OAc)(CO)(PPh_3)_2]$ (**6**) was found to give **3a** in 35 and 69% yields, respectively (entries 3 and 4). Additives were then investigated for the C–O monoalkenylation, and addition of CsF was found to be effective for some catalysts.[4e] While the use of CsF as an additive did not improve the product yield (entries 5 and 6), increase of the yield was observed for the reaction in the presence of $[RuCl(TMS)(CO)(PPh_3)_2]$ and **6** (entries 7 and 8). Particularly the highest yield of 83% was obtained for the reaction using **6** and CsF (entry 8). Other additives such as Cs_2CO_3 and K_2CO_3 also gave **3a** in high yields but did not exceed the yield achieved with CsF.

The C–O monoalkenylation products formed using various alkenylboronates can be isolated in high yields (Scheme 2). In addition to **3a**, β-styrylboronates having electron-donating groups such as methoxy and methyl groups, and electron-withdrawing groups such as chloro and trifluoromethyl groups were reacted with **1** to afford the corresponding monoalkenylation products **3b–e** in yields of 72–75%. The reaction with α-styrylboronate required a longer reaction time but provided the monoalkenylation product **3f** in 52% yield. The reaction with alkyl-substituted alkenylboronates gave high yields of the monoalkenylation products **3g–i** when styrene was used as an additive.[13]



Scheme 2. Ruthenium-catalyzed monoselective C–O alkenylation of **1** with alkenylboronates (**2**). Reaction conditions: **1** (0.5 mmol), **2** (1.0 mmol), **6** (0.02 mmol), CsF (0.04 mmol), p-xylene (0.5 mL), 140 °C, 8 h. Yields of the isolated products are shown. [a] Performed for 24 h. [b] Performed for 40 h. [c] Styrene (2 equiv) was used as an additive. [d] $E/Z = 91{:}9$.

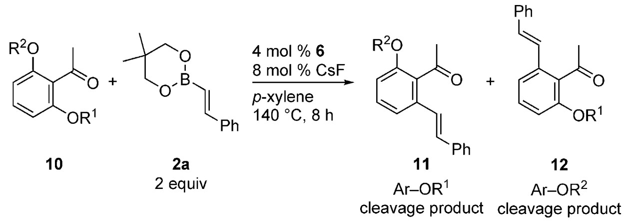
The ruthenium-catalyzed alkenylation was also conducted with the anthrone derivative **7**, which possesses an *ortho* C–O bond on each of the two aromatic rings (Scheme 3). The reaction with **2a** proceeded to give the monoalkenylation product **8a** in 68% yield upon isolation.[14,15] Similarly, the reaction with the methoxy-substituted styrylboronate **2b** afforded **8b** in 65% yield within 5 hours. Higher product selectivity was observed for the reaction with the alkenylboronate **2e** to provide **8e** and the dialkenylation product **9e** in 61 and 11% yields, respectively.



Scheme 3. Ruthenium-catalyzed monoselective C–O alkenylation of the anthrone derivative **7** with the alkenylboronates **2**.

The high selectivity of the C–O alkenylation to give monoalkenylation products allows direct comparison of the

Table 2: Ruthenium-catalyzed chemoselective C–O alkenylation of the acetophenone derivatives **10** with **2a**.[a]



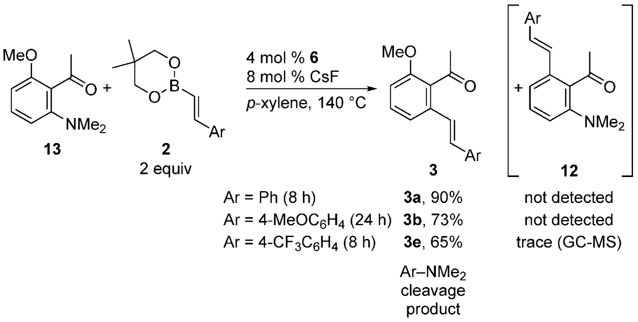
Entry	**10**	R^{1}O	R^{2}O	Conv. [%]	Yield [%]	
					11	**12**
1	**10a**	MeO	PhO	72[b]	55[b] (**11a**)	7[b] (**12a**)
2[c]	**10a**	MeO	PhO	85[b]	71[b] (**11a**)	8[b] (**12a**)
3[c]	**10b**	MeO	4-$CF_3C_6H_4O$	79[b]	59[b] (**11b**)	8[b] (**12a**)
4[c]	**10c**	MeO	4-MeC_6H_4O	84[b]	70[b] (**11c**)	9[b] (**12a**)
5[c]	**10d**	MeO	4-$MeOC_6H_4O$	82[b]	66[b] (**11d**)	11[b] (**12a**)
6	**10e**	MeO	EtO	82[d]	50[e] (**11e**)	27[e] (**12a**)
7	**10f**	MeO	*i*PrO	73[d]	68[e] (**11f**)	5[e] (**12a**)
8[f]	**10f**	MeO	*i*PrO	84[d]	80[e] (**11f**)	4[e] (**12a**)
9	**10g**	MeO	CF_3CH_2O	77[d]	61[e] (**11g**)	4[e] (**12a**)
10	**10h**	EtO	CF_3CH_2O	62[d]	45[e] (**11g**)	13[e] (**12b**)

[a] Reaction conditions: **10** (0.5 mmol), **2a** (1.0 mmol), **6** (0.02 mmol), CsF (0.04 mmol), *p*-xylene (0.5 mL), 140 °C, 8 h. [b] Determined by ^{1}H NMR analysis. [c] Used 3 equiv of **2a**, 6 mol% of **6**, and 12 mol% of CsF. [d] Determined based on the amount of **10** recovered by isolation. [e] Yield of isolated product. [f] Performed for 24 h.

relative reactivity of the unreactive C–O bonds in this reaction. The reaction of several acetophenone derivatives possessing two different oxygen functional groups (**10**) at the *ortho* positions were examined (Table 2). First, acetophenone with methoxy and phenoxy groups (**10a**) were employed as substrates for the reaction under the standard reaction conditions (entry 1). Although phenoxide is less basic and generally considered as a better leaving group than methoxide, the ruthenium-catalyzed reaction gave the monoalkenylation product formed by Ar–OMe bond cleavage (**11a**), which still has a phenoxy group, as a major product. The yield of **11a** was improved to 71% by increasing the amounts of **6**, CsF, and **2a** to 6 mol%, 12 mol%, and 3 equivalents, respectively (entry 2). The reaction of 2′-methoxyacetophenones possessing various aryloxy groups with *para* substituents (**10b–d**) also delivered the alkenylation products **11b–d** (resulting from Ar–OMe bond cleavage) as major products in 59–70% yields (entries 3–5). The C–O alkenylation was then examined with acetophenones having two different alkoxy groups. The reaction of an acetophenone derivative having both methoxy and ethoxy groups (**10e**) proceeded to give the alkenylation products, for both Ar–OMe and Ar–OEt bond cleavage, in 50 and 27% yields, respectively (entry 6). In this case, the larger size of ethoxy group relative to the methoxy group appears to become an important factor in determining the product selectivity, because methoxide and ethoxide have similar basicity. Higher product selectivity toward Ar–OMe bond cleavage was observed for the reaction with a substrate having both methoxy and isopropoxy groups (**10f**) to give **11f** in 68% yield (entry 7). The yield of **11f** was improved to 80% by performing the reaction for 24 hours (entry 8). To investigate the reactivity of substrates with two different alkoxy leaving groups having different basicities, the reaction was conducted with an acetophenone having methoxy and 2,2,2-trifluoroethoxy groups (**10g**), and the major product was the monoalkenylation product formed by cleaving the more-electron-donating methoxy group (**11g**; entry 9). The reaction of a substrate with ethoxy and 2,2,2-trifluoroethoxy groups, which have similar steric bulk but different electron-donating ability, also gave the alkenylation product arising from Ar–OEt bond cleavage as the major product (entry 10).

The results of the C–O alkenylation with acetophenone derivatives having two different oxygen functional groups suggest that smaller, more-electron-donating groups are more easily cleaved in this reaction. The lower reactivity of the bonds with better leaving groups is not commonly observed for bond-cleavage reactions by oxidative addition. The reason for the observed trend is unclear, but it can be explained by considering that smaller, more-electron-donating groups coordinate to the metal center more easily to increase the chances of being cleaved by oxidative addition, as observed for our previously reported aromatic C–N bond cleavage by a ruthenium center.[6c]

The alkenylation of an acetophenone derivative, possessing both a methoxy and dimethylamino group (**13**), with **2a** proceeded to give the monoalkenylation product **3a** in 90% yield upon isolation (Scheme 4). The result essentially showed that completely selective cleavage of the more-electron-donating dimethyamino group over the methoxy group occurred in this reaction.[6a,12] The selective C–N alkenylation was also observed for the reaction with the alkenylboronates **2b** and **2e** to give **3b** (73%) and **3e** (65%), respectively.

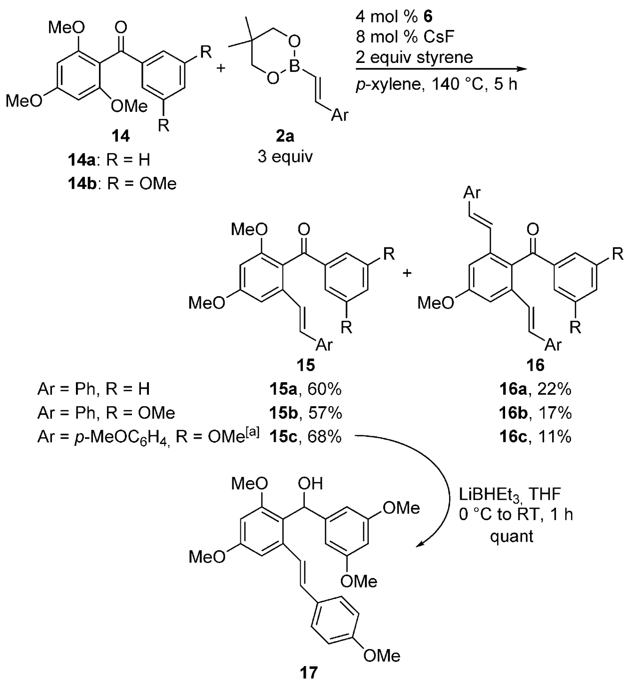


Scheme 4. Selective ruthenium-catalyzed C–N alkenylation in the presence of an *ortho* C–O bond.

Another important feature of the C–O monoalkenylation is that it may allow the selective conversion of one C–O bond in highly oxygenated aromatic compounds without damaging other C–O bonds, and even C–H bonds at positions *ortho* to carbonyl groups. Therefore, the reaction may be applied for the synthesis of polyoxygenated aromatic compounds, which are found in the structures of many naturally occurring molecules.

The C–O monoalkenylation was examined with 2,4,6-trimethoxybenzophenenone derivatives (**14**; see Scheme 5), which can be readily prepared in high yields from 1,3,5-

trimethoxybenzene and benzoyl chloride derivatives. The reaction of 2,4,6-trimethoxybenzophenenone (**14a**), which has two C–O bonds and two C–H bonds at positions *ortho* to the carbonyl group, with **2a** in the presence of **6**, CsF, and styrene gave the corresponding C–O monoalkenylation product **15a** in 60% yield along with 22% of the C–O dialkenylation product **16a** (Scheme 5).[16] The reaction of the pentamethoxybenzophenone **14b** also provided **15b** in 57% yield. The use of the methoxy-substituted styrylboronate **2b** for the reaction with **14b** gave **15c** in 68% yield. This alkenylated benzophenone derivative (**15c**) as well as its reduction product **17**, which was quantitatively obtained by the reduction of **15c** with $LiBHEt_3$, have been used as common intermediates in Snyder's synthesis of various resveratrol-based natural products.[17]



Scheme 5. Selective ruthenium-catalyzed C–O alkenylation in the presence of *ortho* C–H bonds. [a] The reaction was performed in styrene/*p*-xylene (1.2:1) at 130 °C for 4 h. THF = tetrahydrofuran.

In summary, we described the selective ruthenium-catalyzed monoalkenylation of either *ortho* C–O or C–N bonds of aromatic ketones. A novel catalyst system consisting of **6** and CsF was identified as for this reaction and various alkenyl groups were introduced to the aromatic rings. The reaction enabled the direct comparison of the relative reactivities of different carbon–heteroatom bonds, and it was suggested that smaller, more-electron-donating groups are more easily cleaved, a phenomenon which is unconventional for reactions proceeding by oxidative addition. Exceedingly chemoselective C–N alkenylation in the presence of an *ortho* C–O bond was also observed. Selective monofunctionalization of C–O bonds can also be achieved in the presence of *ortho* C–H bonds. Studies on the synthetic applications of the selective monoalkenylation of carbon–heteroatom bonds are underway.

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[11] Higher reactivity of C–N bonds than C–O bonds in the ruthenium-catalyzed reactions has been indicated in Ref. [8c].

[12] This C–O alkenylation is considered to proceed by coordination of the carbonyl oxygen atom of the substrate to the ruthenium, oxidative addition of the C–O bond, transmetalation, and reductive elimination, which is a similar mechanism to the previsouly reported C–O arylation. In the alkenylation, the product may coordinate to the ruthenium through both the carbonyl oxygen atom and the introduced alkene moiety, after the reductive elimination. The strong binding of the product may inhibit the coordination of the incoming substrate, and the lowering of the equivalents of PPh_3 ligands from three to two may be effective for creating an open coordination site for the substrate.

[13] The role of the styrene additive is unclear at this point, but this additive may be effective in stabilizing the low-valent catalytically active species to prevent the catalyst decomposition.

[14] When the reaction of **7** with 4 equivalents of **2a** was performed for 36 h, the dialkenylation product **9a** was obtained in 99% yield.

[15] The lower monoselectivity for the reaction of **7** can be attributed to the difference in the lone pairs of the carbonyl oxygen atom used for the C–O bond cleavage. In the cleavage of the second C–O bond in **7**, the lone pair of the carbonyl oxygen atom used to bind to the metal is different from the one used for the second C–O bond cleavage and is further from the introduced alkene moiety, and thus may be less effective in disturbing the interaction of the second C–O bond with the metal center.

[16] To examine the tolerance of C–Br bonds, 2-bromophenyl 2,4,6-trimethoxyphenyl ketone was used instead of **14a** for the reaction but did not give any C–O alkenylation product.

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