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Access to Substituted Propenoic Acids via Rh(III)-Catalyzed C−H Allylation of (Hetero)Arenes with Methyleneoxetanones

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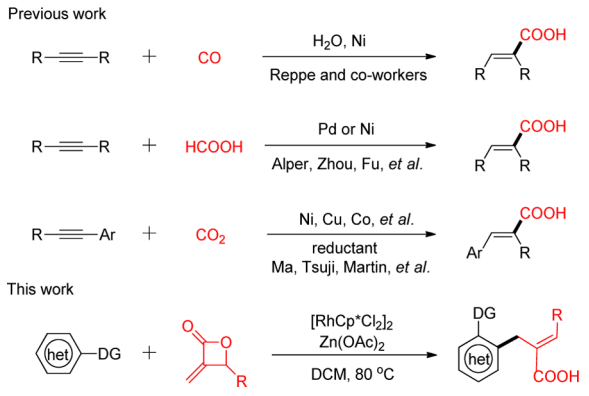
Supporting Information

ABSTRACT: An efficient synthesis of disubstituted acrylic acids has been realized via Rh(III)-catalyzed C−H activation of (hetero)arenes and coupling with four-membered methyleneoxetanones under redox-neutral conditions. In most cases, the reactions are silver-free, and the products are exclusively *E*-selective with a broad substrate scope. The transformation proceeds via ortho C−H activation followed by selective olefin insertion and *β*-oxygen elimination.

Acrylic acids represent a privileged building block and have been widely applied in the construction of functional molecules such as organic polymers, plastics, and pharmaceuticals.[1] Consequently, a large number of methods have been established to access acrylic acids. For example, Reppe, Alper, and others[2] realized catalytic hydrocarboxylation of alkynes with CO, HCOOH, and CO_2 as a C1 source (Scheme 1). However,

Scheme 1. Synthesis of Substituted Acrylic Acids



these methods often suffer from high pressure, a stoichiometric amount of organometallic reagent or metal reductant, and poor functional group tolerance with the employment of sensitive reagents. Thus, the development of an efficient strategy to access acrylic acids remains highly attractive.

Over the past decades, transition-metal-catalyzed C−H bond functionalization has been recognized as a powerful strategy for efficient transformation of (hetero)arenes.[3] In particular, C−H allylation of arenes has been extensively explored because allyl moieties can be readily manipulated to access a wide variety of versatile functional groups.[4] In this regard, a large array of C−H allylation systems have been developed by Glorius,[5] Ackermann,[6] Cramer,[7] Ellman,[8] Kanai,[9] Ma,[10] Li,[11] Loh and others.[12]

Despite these achievements, the allylating reagents are mostly limited to allyl alcohol derivatives and strained or reactive rings such as vinyl oxiranes, cyclopropanes, vinyl-dioxolanones, and vinyl benzoxazinanones.[3o,11] While three-, five-, and six-membered rings have been applied as coupling partners in C−H activation,[13] four-membered rings are rarely employed in high-valent metal-catalyzed C−H activation systems apart from Zeng's Rh(III)-catalyzed oxidative coupling using cycloalkanols.[13k] We reasoned that four-membered rings such as methyleneoxetanone, which first prepared by Howell,[14a] were activated by ring strain as well as by the ester group, which may serve as an efficient substrate for allylation (Scheme 1). However, challenges remain in the following aspects: (i) four membered rings are less strained and less reactive than a three-membered one, which may lead to competitive decomposition; (ii) insertion into the C═C bond might be terminated by undesired protonolysis or reductive elimination without ring scission;[14b] and (iii) the coupling system can be complicated by stereoisomers of the olefin product with possible decarboxylation. We now report Rh(III)-catalyzed C−H activation of (hetero)arenes and coupling with methyleneoxetanones, leading to efficient access to *α*,*β*-unsaturated carboxylic acids with >20:1 *E*-selectivity.

We embarked on our studies with exploration of the reaction parameters in the coupling of *N*-(2-pyrimidinyl)-indole (**1a**) with 3-methylene-4-phenethyloxetan-2-one (**2a**, Table 1). With $[RhCp^*Cl_2]_2/AgSbF_6$ as a catalyst, the product **3aa** was isolated in 21% yield as a single stereoisomer (entry 1), and the *E*-configuration was established by X-ray crystallography. The yield was improved to 59% when $Zn(OAc)_2$ was further added (entry 2). A brief screening of the solvent revealed that DCM was optimal (entries 3,4), and increasing the amount of $AgSbF_6$ resulted in a diminished yield (entry 5). It was found that the silver additive had a significant effect on the efficiency (entries 6−

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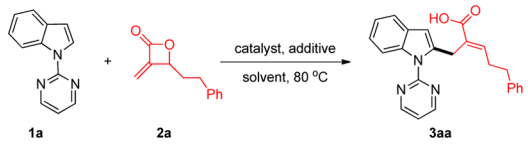
Table 1. Screening of the Reaction Conditions[a]



entry	cat. (mol %)	additive (mol %)	solvent	yield[b]
1	$[RhCp^*Cl_2]_2$ (4)	$AgSbF_6$ (16)	DCE	21
2	$[RhCp^*Cl_2]_2$ (4)	$AgSbF_6$ (16), $Zn(OAc)_2$ (30)	DCE	59
3	$[RhCp^*Cl_2]_2$ (4)	$AgSbF_6$ (16), $Zn(OAc)_2$ (30)	DME	42
4	$[RhCp^*Cl_2]_2$ (4)	$AgSbF_6$ (16), $Zn(OAc)_2$ (30)	DCM	73
5	$[RhCp^*Cl_2]_2$ (4)	$AgSbF_6$ (30), $Zn(OAc)_2$ (30)	DCM	59
6	$[RhCp^*Cl_2]_2$ (4)	$AgNTf_2$ (16), $Zn(OAc)_2$ (30)	DCM	30
7	$[RhCp^*Cl_2]_2$ (4)	$AgBF_4$ (16), $Zn(OAc)_2$ (30)	DCM	49
8	$[RhCp^*Cl_2]_2$ (4)	AgOTf (16), $Zn(OAc)_2$ (30)	DCM	55
9	$[RhCp^*Cl_2]_2$ (4)	$AgNO_3$ (16), $Zn(OAc)_2$ (30)	DCM	75
10	$[RhCp^*Cl_2]_2$ (4)	Ag_2SO_4 (8), $Zn(OAc)_2$ (30)	DCM	97
11[c]	$[RhCp^*Cl_2]_2$ (4)	$Zn(OAc)_2$ (30)	DCM	94
12	$[RhCp^*Cl_2]_2$ (2)	$Zn(OAc)_2$ (30)	DCM	66
13	$[RhCp^*Cl_2]_2$ (3)	$Zn(OAc)_2$ (30)	DCM	85
14[d]	$[RhCp^*Cl_2]_2$ (4)	$Zn(OAc)_2$ (30)	DCM	0
15	$[CoCp^*(CO)I_2]$ (10)	$Zn(OAc)_2$ (30)	DCM	trace
16	$[Ru(p\text{-cymene})Cl_2]_2$ (4)	$Zn(OAc)_2$ (30)	DCM	38

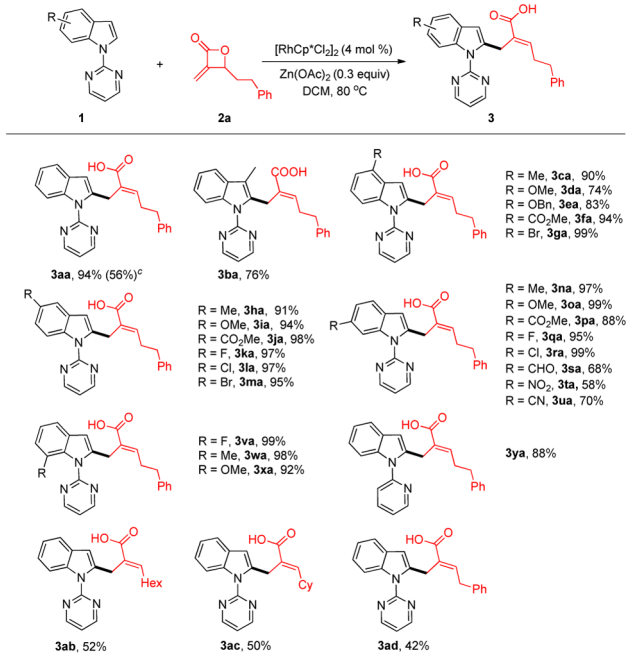
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.30 mmol), $[RhCp^*Cl_2]_2$ (4 mol %), additive, solvent (2 mL), 80 °C under N_2 for 16 h. [b]Isolated yield. [c]**2a** (0.24 mmol) was used. [d]3-Hydroxy-2-methylene-5-phenylpentanoic acid was employed as a substrate.

10). While a combination of $Ag_2SO_4/Zn(OAc)_2$ as additives delivered an excellent yield (entry 10), a comparable yield was also realized when the silver salt was omitted (entry 11). Control experiments revealed that both $[RhCp^*Cl_2]_2$ and $Zn(OAc)_2$ were necessary and **2a** could not be replaced by the corresponding allylic alcohol precursor (entry 14). Switching the catalyst to $[CoCp^*(CO)I_2]$ or $[Ru(p\text{-cymeme})Cl_2]_2$ all afforded inferior results (entries 15, 16).

We next evaluated the scope of the indole substrate under the optimal conditions (Scheme 2). *N*-Pyrimidylindoles bearing various electron-donating and -withdrawing and halogen substituents at different positions all coupled smoothly with **2a** in 58−99% yields (**3aa**−**3xa**). Of note, useful functional groups such as −CHO (**3sa**), $-NO_2$ (**3ta**), and −CN (**3ua**) were well tolerated, affording the corresponding products in 58−70% yields. A 3-methylindole also coupled in high yield (**3ba**), indicative of tolerance of the steric effect. Moreover, the pyrimidyl directing group (DG) could be extended to a pyridyl group in high yield (**3ya**). The scope of the methyleneoxetanone substrate was next briefly explored. The substituent at the 4-position of 3-methylene-4-oxetan-2-one was successfully extended to a benzyl, long-chain primary alkyl, and cyclohexyl group (**3ab**−**3ad**). In all cases, the products were isolated in acceptable yield and in excellent *E* selectivity. Extension of the substrate to 4-benzhydryl-substututed methyleneoxetanone, however, met with failure, likely due to the steric effect.

To better define the scope of the arene, other representative classes of arenes have been examined (Scheme 3). It was found that, under modified conditions (Conditions B), 2-phenylpyridine and 1-phenyl-1*H*-pyrazole efficiently coupled with 3-methylene-4-phenethyloxetan-2-one in moderate to good yields (**5a**, **5b**). *N*-Substituted pyridine and various substituted isoquinolones are also viable arene substrates, and the carboxylic acids products (**5c**−**5i**) were obtained in moderate to excellent yields. Unfortunately, *N*-pyrimidyl benzimidazole and *N*-pyrimidyl carbazole failed to give any reactivity.

Scheme 2. Coupling of *N*-Substituted Indoles[a,b]



[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), $[RhCp^*Cl_2]_2$ (4 mol %), $Zn(OAc)_2$ (0.3 equiv), DCM (2 mL), 80 °C under N_2 for 16 h. [b]Isolated yields. [c]Reaction was performed with 5 mmol of **1a** at 1.5 mol % catalyst loading.

To demonstrate the synthetic applications, gram-scale synthesis of product **3aa** was performed and was isolated in 56% yield under a reduced catalyst loading (1.5 mol %, Scheme 2). Besides, a series of derivatization reactions have been carried out (Scheme 4). Rh(III)-catalyzed oxidative C(7)-H olefination of **3aa** using methyl acylate afforded product **6** in 57% yield.[15a] To take advantage of the electrophilicity of the carboxylic acid

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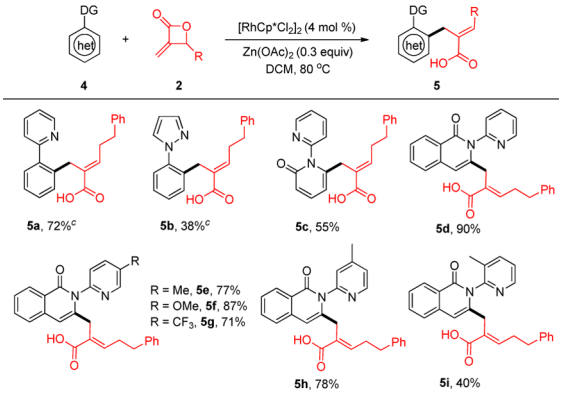
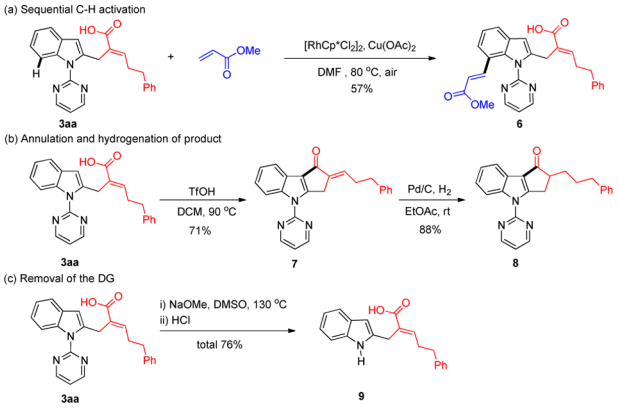
Scheme 3. Scope of Other Arene Substrates[a,b]



[a]Reaction conditions: arene **4** (0.2 mmol), **2** (0.24 mmol), $[RhCp^*Cl_2]_2$ (4 mol %), $Zn(OAc)_2$ (0.3 equiv), DCM (2 mL), 80 °C under N_2 for 16 h. [b]Isolated yields. [c]Conditions B: **4** (0.2 mmol), **2** (0.24 mmol), $[RhCp^*Cl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), PivOH (1.0 equiv), DCE (2 mL), 80 °C under N_2 for 16 h.

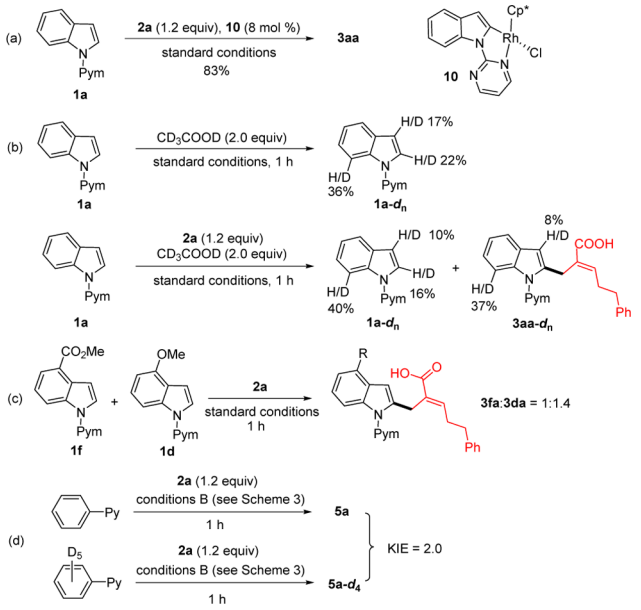
Scheme 4. Diversification of the Products



moiety in the product, **3aa** was treated with TfOH, which led to an intramolecular Friedel–Crafts acylation product **7** in 71% yield.[15b] Hydrogenation of enone **7** then afforded tricyclic product **8** in good yield.[15c] Finally, removal of the N-directing group of **3aa** gave NH indole **9** in good yield.[15d]

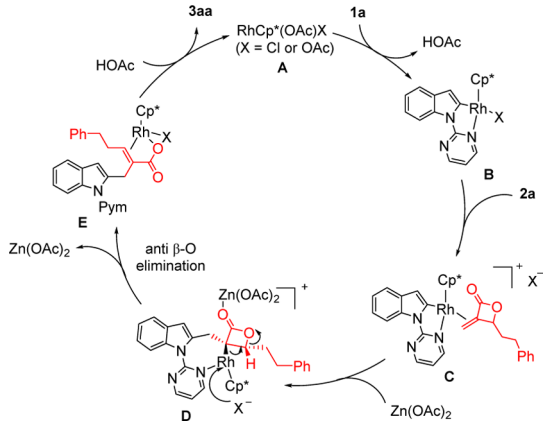
We next performed preliminary mechanistic studies to briefly explore this catalytic system (Scheme 5). Rhodacyclic complex **10** was synthesized as a catalyst precursor for the coupling of **1a** and **2a** under the same conditions, from which **3aa** was isolated in 83% yield (Scheme 5a). This suggested that the reaction likely occurred via a C–H activation pathway. To explore the reversibility of the C–H bond cleavage, H/D exchange experiments have been performed between **1a** and CD_3COOD in the absence or presence of a coupling partner **2a** (Scheme 5b). In both cases, H/D exchange at the 2-, 3-, and 7-positions have been observed, indicating that only the C(2)–H activation is constructive and it is reversible. A competitive experiment was next performed using an equimolar mixture of **1d** and **1f** that differs in electronic effects. The ^1H NMR analysis revealed that a more electron-rich indole was kinetically favored (**3fa**:**3da** = 1:1.4, Scheme 5c). A kinetic isotope effect of 2.0 was then obtained from two side-by-side reactions using **3a** and **3a**-d_5 in the coupling with **2a** at a low conversion (Scheme 5d), indicating that the C–H cleavage was probably involved in the turnover-limiting step.

Scheme 5. Mechanistic Studies



Based on the mechanistic studies and literature precedents, a plausible mechanism is proposed (Scheme 6). Starting from an

Scheme 6. Proposed Mechanism



active $[RhCp^*(OAc)X]$ (X = OAc or Cl) species (**A**), cyclometalation of **1a** produces a rhodacyclic intermediate **B**. Subsequent coordination of **2a** gives a cationic Rh(III) olefin intermediate **C**, which is followed by selective migratory insertion of the Rh–C bond into the olefin to generate a tertiary alkyl intermediate **D**. Subsequent anti β-oxygen elimination[11c,16] is facilitated by relief of the ring strain to provide intermediate **E**. Protonolysis of **E** furnishes the final product and regenerates the active rhodium(III) species for the next catalytic cycle. At this stage, it is also possible that the migratory insertion into the olefin occurs in different stereochemistry, followed by syn-coplanar elimination of the oxygen (see Supporting Information).

In conclusion, we have developed a Rh(III)-catalyzed C–H activation of arenes in the coupling with methyleneoxetanones. This strategy takes advantage of the strain in this four-membered ring and offers a highly step-economical access to various 1,2-disubstituted α,β-unsaturated carboxylic acids in excellent *E* selectivity. The coupling occurred under relatively mild conditions with broad substrate scope and functional group tolerance. Further studies on Rh(III)-catalyzed couplings of

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arenes with other unsaturated coupling partners are underway in our laboratories.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02983.

Detailed experimental procedures, characterization of products, crystal data of **3aa**, and copies of NMR spectra (PDF)

Crystallographic data for **3aa** (CIF)

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Notes

The authors declare no competing financial interest.

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