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Ruthenium catalyzed desymmetrization of diazabicyclic olefins to access heteroaryl substituted cyclopentenes through C–H activation of phenylazoles

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ABSTRACT

The first ruthenium catalyzed redox-neutral C–H activation strategy for the ring-opening of diazabicyclic olefins via C–H bond cleavage of phenyl azoles is reported. The developed method offers a novel route to functionalized cyclopentenes by employing less-expensive ruthenium catalyst and readily accessible biologically significant heteroarenes. The present protocol is a merger of the C–H activation of phenyl substituted heteroaromatics and subsequent β-nitrogen elimination of diazabicyclic olefins.

Transition metal catalyzed direct carbon–carbon bond formation via cleavage of inert C–H bonds represents a proficient atom-economical and environmentally friendly strategy in organic synthesis.[1] Notably, C–H bond activation of various substrates mediated by less-expensive ruthenium catalysts have recently been emerged as a powerful and promising synthetic tool.[2] $[RuCl_2(p\text{-cymene})]_2$ catalyzed direct functionalization reactions of substituted arenes with various alkenes as well as alkynes have been independently investigated by Ackermann et al.,[3] Dixneuf and co-workers,[4] Jeganmohan and co-workers,[5] and Miura and co-workers.[6] for the synthesis of many valuable scaffolds. Ackermann et al. reported a Ru catalyzed regioselective direct alkylation of 2-phenyl pyridines and 1-phenylpyrazoles with alkyl halides through C–H bond activation.[3g] Later, the same group demonstrated the first ruthenium-catalyzed oxidative annulation of alkynes with 1*H*-pyrazoles by C–H/N–H bond functionalizations.[3j] Miura and co-workers reported the direct alkenylation of 1-phenylpyrazoles with alkenes under ruthenium catalysis.[7] At the same time, Dixneuf, Bruneau and co-workers described the Ru catalyzed dehydrogenative alkenylation of *N*-arylpyrazoles[5f] and 2-phenyl oxazolines[5e] under air. Jeganmohan et al. reported a ruthenium catalyzed alkenylation of *ortho* C–H bond of aryl carbamates with alkynes to afford substituted alkene derivatives.[5h] Even though, very limited number of reports are available on the rhodium catalyzed C–H activation/ring-opening of strained systems[8,9] there have been no reports for the ruthenium catalyzed ring-opening of strained bicyclic olefins via C–H activation of substituted arenes.

Metal catalyzed synthetic transformations of versatile synthons, diazanorbornenes[10] via ring-opening reactions[11–16] have been well investigated with various organometallic reagents, aryl iodides, and soft nucleophiles for the preparation of a variety of biologically significant substituted cyclopentenes.[17] Recently, we have developed a rhodium catalyzed oxidative coupling of salicylaldehydes with diazabicyclic alkenes for the synthesis of cyclopentene fused chromanone derivatives by a one-pot ring opening-ring closing strategy.[18] A recent work on Rh(III)-catalyzed ring-opening of diazabicycles through the C–H activation of arenes was reported by Cui et al.[8] Compared to palladium and rhodium catalyzed ring-opening reactions of diazanorbornenes, detailed investigations under ruthenium catalysis remain less explored. Very recently, Simon and Darses demonstrated a ruthenium catalyzed co-dimerization of bicyclic alkenes and Michael acceptors to provide the *exo*-(*E*) adducts (Scheme 1).[19] To the best of our knowledge there has been no report on the C–N bond cleavage of diazabicyclic olefins via C–H activation of phenyl substituted heteroarenes by employing less-expensive ruthenium catalyst. Herein we wish to report the first ruthenium catalyzed ring-opening of diazabicyclic olefins via C–H activation of phenylazoles to access functionalized cyclopentene derivatives in a redox neutral fashion.

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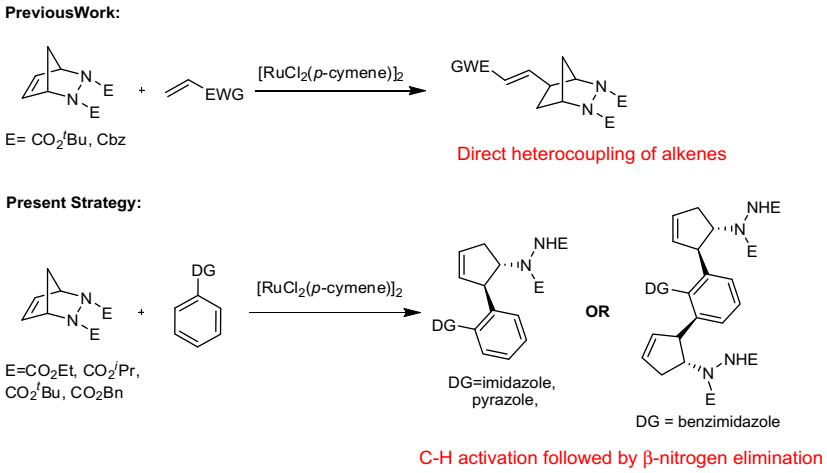


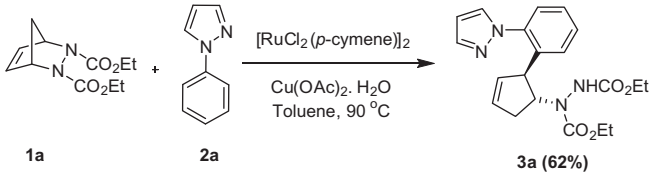
Scheme 1. Ruthenium catalyzed coupling reactions of diazabicyclic olefins.

Our investigations commenced with the reaction of diazabicyclic olefin **1a** and 1-phenylpyrazole **2a** in the presence of $[RuCl_2(p\text{-cymene})]_2$ (5 mol %) and $Cu(OAc)_2{\cdot}H_2O$ (1.5 equiv) in toluene at 90 °C. As expected, we observed the formation of the desired 3,4-disubstituted cyclopentene **3a** in 62% yield (Scheme 2). The structure of the product was established by usual spectroscopic techniques.[20]

Detailed optimization studies were performed to obtain the best reaction conditions for the formation of **3a** (Table 1). Screening of various solvents such as toluene, xylene, 1,4-dioxane, DMF, and DMSO displayed toluene as the most favorable reaction medium for the transformation. In the next stage, a number of additives such as $Cu(OAc)_2{\cdot}H_2O$, NaOAc, CsOAc, AgOAc, and Ag_2CO_3 were tested for their efficiency in the present protocol. Among them the non-acetate source, Ag_2CO_3 inhibited the reactivity and $Cu(OAc)_2{\cdot}H_2O$ was found to be the most proficient one. When the reaction was conducted in the presence of NaOAc or CsOAc, it resulted in the formation of **3a** in lower yields along with a minor amount of homocoupled product of *N*-phenylpyrazole as reported by Dixneuf et al. The effect of temperature was finally studied and the results revealed that the reaction proceeded more efficiently at elevated temperature, 110 °C. Eventually, diazabicyclic olefin **1a** (1 equiv) and 1-phenylpyrazole **2a** (1 equiv) in the presence of $[RuCl_2(p\text{-cymene})]_2$ (5 mol %) and $Cu(OAc)_2{\cdot}H_2O$ (1.5 equiv) in toluene at 110 °C was accomplished as the optimal reaction conditions for the formation of [21].

The scope of various diazabicyclic olefins in the present protocol was proved by the reaction with *N*-phenylpyrazole under optimal catalytic conditions. Ring-opening of bicyclic olefins underwent smoothly to afford the corresponding cyclopentene derivatives in good yields (Table 2).

To explore the generality and scope of the developed chemistry, diazabicyclic olefin **1a** was treated with 2-(2-chlorophenyl)-benzo[*d*]imidazole **2b**, another class of phenyl azoles under the



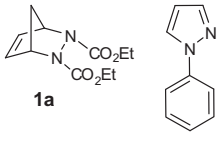
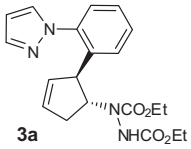
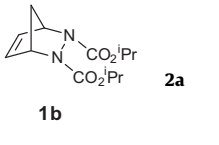
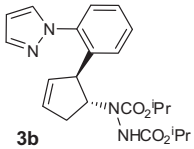
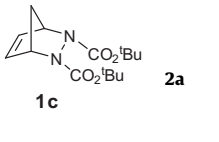
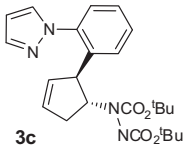
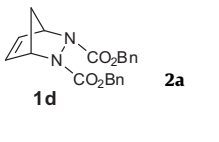
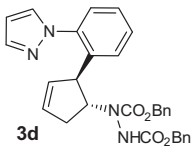
Scheme 2. Ruthenium catalyzed ring-opening of diazabicyclic olefin **1a** with 1-phenyl pyrazole **2a**.

Table 1
Optimization for a suitable catalyst system

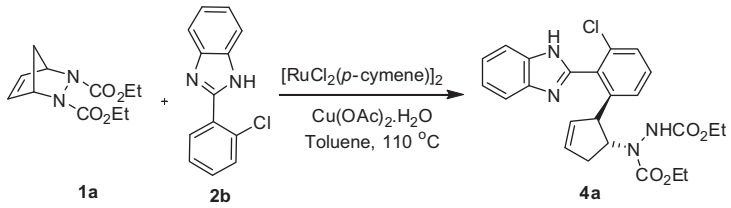
Entry	Catalyst	Additive	Solvent	Yield (%)
1	$[RuCl_2(p\text{-cymene})]_2$	$Cu(OAc)_2{\cdot}H_2O$	DMF	50
2	$[RuCl_2(p\text{-cymene})]_2$	$Cu(OAc)_2{\cdot}H_2O$	1,4-Dioxane	49
3	$[RuCl_2(p\text{-cymene})]_2$	$Cu(OAc)_2{\cdot}H_2O$	Xylene	46
4	$[RuCl_2(p\text{-cymene})]_2$	$Cu(OAc)_2{\cdot}H_2O$	1,2-DCE	23
5	$[RuCl_2(p\text{-cymene})]_2$	$Cu(OAc)_2{\cdot}H_2O$	CH_3CN	No reaction
6	$[RuCl_2(p\text{-cymene})]_2$	$Cu(OAc)_2{\cdot}H_2O$	Toluene	62
7	$[RuCl_2(p\text{-cymene})]_2$	NaOAc	Toluene	19
8	$[RuCl_2(p\text{-cymene})]_2$	CsOAc	Toluene	14
9	$[RuCl_2(p\text{-cymene})]_2$	AgOAc	Toluene	25
10	$[RuCl_2(p\text{-cymene})]_2$	Ag_2CO_3	Toluene	No reaction
11[a]	$[RuCl_2(p\text{-cymene})]_2$	$Cu(OAc)_2{\cdot}H_2O$	Toluene	73

Reaction conditions: alkene (1.0 equiv), 1-phenylpyrazole (1.0 equiv), catalyst (5 mol %), additive (1.5 equiv), solvent (2 mL), 90 °C, 12 h.
[a] At 110 °C.

Table 2
Scope of various diazabicyclic olefins with **2a**

Entry	Bicyclic olefin	1-Phenyl pyrazole	Product	Yield (%)
1	 **1a**	**2a**	 **3a**	73
2	 **1b**	**2a**	 **3b**	72
3	 **1c**	**2a**	 **3c**	52
4	 **1d**	**2a**	 **3d**	60

Reaction conditions: alkene (1.0 equiv), **2a** (1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (5 mol %), $Cu(OAc)_2{\cdot}H_2O$ (1.5 equiv), toluene (2 mL), 110 °C, 12 h.



Scheme 3. C–H activation of 2-(2-chlorophenyl)-benzo[*d*]imidazole with **1a**.

Table 3
Scope of various diazabicyclic olefins and 2-phenyl benzimidazoles

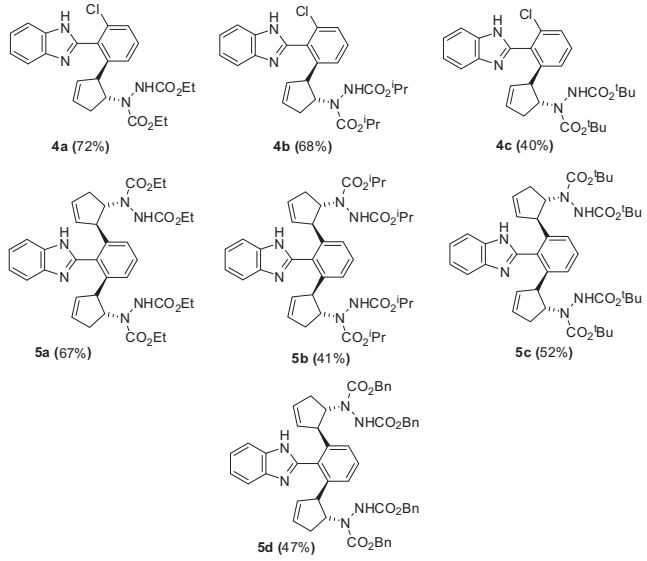
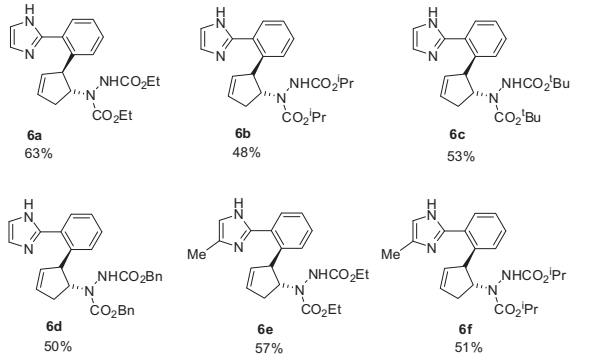


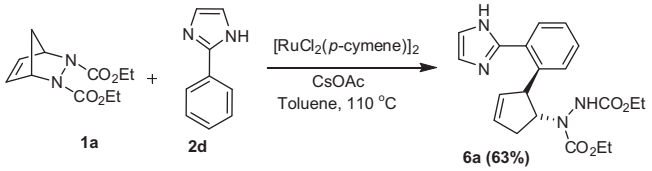
Table 4
Scope of various 2-phenyl imidazoles in the C–H activation strategy



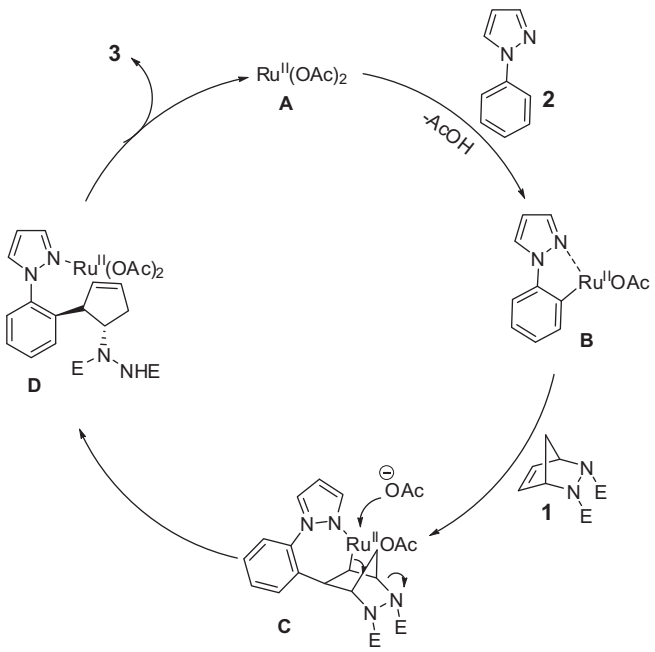
same catalytic conditions (Scheme 3). Unfortunately, the desired functionalized cyclopentene was formed only in very low yields. To our delight, switching the additive from $Cu(OAc)_2{\cdot}H_2O$ to CsOAc, resulted in the formation of mono-cyclopentenyl derivative in 72% yield. The reaction is tolerant of various diazabicyclic olefins under the improved reaction conditions and furnished the corresponding mono-cyclopentenyl products in good yields (Table 3).

In contrast, the reaction of diazanorbornene **1a** with 2-phenyl benzimidazole furnished bis-cyclopentenyl functionalized benzimidazole **5a** in 67% yield via twofold coupling by dual C–H bond activation. Diazabicyclic olefins **1b–d** smoothly underwent ring opening through dual C–H activation of 2-phenylimidazole and provided the products in good yields (Table 3).

We were also interested to investigate the scope of 2-phenyl imidazole in the developed redox-neutral strategy for the desymmetrization of diazabicyclic olefins. Treatment of **1a** with 2-phenylimidazole **2d** resulted in the formation of mono-cyclopentenyl derivative **6a** in 63% yield along with a trace amount of bis-cyclopentenyl derivative (Scheme 4). Ring-opening of various bicyclic



Scheme 4. C–H activation of 2-phenyl imidazoles with **1a**.



Scheme 5. Plausible mechanism.

olefins **1b–d** proceeded efficiently with 2-phenylimidazole and 4-methyl-2-phenylimidazole and gave *trans*-3,4-disubstituted products **6b–f** in good yields (Table 4).

A plausible mechanism for the ring-opening of diazanorbornenes is outlined in Scheme 5 on the basis of the literature reports on the ruthenium catalyzed C–H bond functionalization reactions.[2b] Catalytic cycle is initiated by the generation of an active ruthenium acetate species A by ligand exchange with an acetate

source. In the next step, nitrogen atom of phenylazole is co-ordinated to species A followed by cyclometalation to give a five membered metallacycle B with the liberation of a molecule of acetic acid. Insertion of bicyclic olefin into the metallacycle provides an intermediate C and subsequent β-nitrogen elimination with the assistance of acetate ion furnishes the product **3** with the regeneration of active catalytic species.

In summary, we have developed for the first time a ruthenium catalyzed redox-neutral C–H activation of phenylazoles toward the ring-opening of diazabicyclic olefins. The reaction provides an efficient access to heteroaryl substituted cyclopentenes by employing less-expensive ruthenium catalyst. Further investigations to explore the scope of the developed protocol with other aromatic substrates are currently underway.

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20. *Spectral data for* ***3a***. Yield: 73% as colourless viscous liquid. R_f: 0.53 (7:3 hexane/EtOAc). IR (neat) ν_{max}: 3369, 2922, 2851, 2730, 1740, 1649, 1541, 1513, 1458, 1398, 1211, 1164, 1128, 1046, 939, 689, 597, 558 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.84–7.76 (m 2H), 7.59 (s, 1H), 7.44–7.41 (m, 2H), 7.31–7.26 (m, 1H), 7.19–7.18 (m, 1H), 6.48 (s, 1H), 5.84 (s, 1H), 5.48 (s, 1H), 4.79–4.78 (m, 1H), 4.17–3.93 (m, 5H), 2.67–2.47 (m, 2H), 1.31–1.17 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.6, 155.6, 140.5, 139.5, 132.4, 131.5, 129.9, 129.2, 127.1, 126.1, 106.8, 69.8, 62.0, 61.6, 45.5, 35.1, 14.5. HRMS (ESI): Calcd for $C_{20}H_{24}N_4O_4$, (M+Na): 407.16952; Found: 407.16980
21. *Typical experimental procedure for the reaction of diazabicyclic olefin* ***1a*** *with N-phenylpyrazole* ***2a****:* A mixture of diazabicyclic olefin (50 mg, 0.2083 mmol, 1.0 eqiuv), *N*-phenylpyrazole (30 mg, 0.2083 mmol, 1.0 eqiuv), $[RuCl_2(p\text{-cymene})]_2$ (6 mg, 0.0104 mmol, 5.0 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (62.46 mg, 0.3123 mmol, 1.5 equiv) was weighed in a Schlenk tube and degassed for 10 min. Dry toluene (2 mL) was added and the reaction mixture was purged with argon and allowed to stir at 110 °C for 12 h. The reaction mixture on silica gel column chromatography using mixtures of EtOAc–hexane yielded functionalized cyclopentene **3a** in 73% yield (58 mg).