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Redox-Divergent Hydrogen-Retentive or Hydrogen-Releasing Synthesis of 3,4-Dihydroisoquinolines or Isoquinolines

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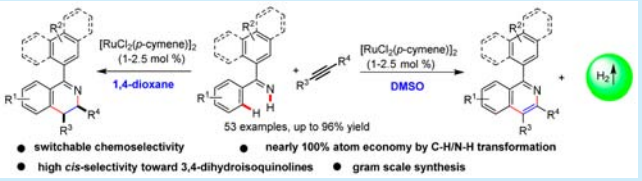
Supporting Information

ABSTRACT: A rare Ru-catalyzed highly selective synthesis of 3,4-dihydroisoquinolines or isoquinolines is accomplished via a redox-divergent hydrogen-retentive or hydrogen-releasing fashion. Notably, high *cis*-selectivity of 3,4-dihydroisoquinolines is achieved. Potential applications are shown by gram-scale reactions and very concise synthesis of N-containing polycyclic aromatic compounds. Primary mechanistic investigations indicate that the sequence of the major pathway involves Ru-catalyzed C−H activation, alkyne insertion, and subsequent 6π-electrocyclization.

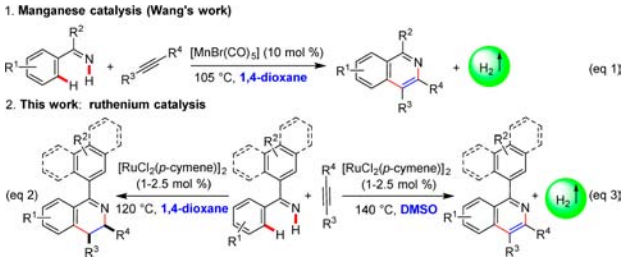


Coupling reactions are a cornerstone in organic chemistry as they are widely used in efficient synthesis of value-added functional molecules.[1] From classical transition-metal (TM)-catalyzed coupling reactions to C−H transformations,[2,3] several generations of synthetic methods have been developed. Ideal couplings should be H_2-releasing with nearly 100% atom-economy via inert R−H bond cleavage to produce H_2 as the sole byproduct.[4−8] In very recent years, construction of C−C, C−N, C−P, C−S, and S−S bonds via this dehydrogenative strategy started to be increasingly explored[5−7] as did C−Si coupling systems.[8] Despite the progress, H_2-releasing couplings remain largely under-explored. Thus, there is a strong incentive to develop novel coupling systems.

Heterocycles are prevalent motifs in bioactive compounds and organic functional materials.[9] Consequently, increasing efforts have been made in their synthesis via a C−H activation pathway.[10] The strategies of these methods are oxidative or redox-neutral processes. The former requires a stoichiometric amount of oxidants, such as Cu(II)/Ag(I) salts, while the latter needs an internal N−O or N−N oxidizing group, which has to be preinstalled on the substrate and has tedious synthesis. To meet the goals of environmental friendliness and atom-economy, the ideal strategy of heterocycle synthesis would be a H_2-releasing coupling with oxygen/air as an oxidant.[11]

Due to the high activity of Ru complexes in C−H transformations[10,12] and hydrogen production,[13] we anticipate ample potential for these complexes in H_2-releasing coupling reactions. Herein, we report the first highly selective synthesis of 3,4-dihydroisoquinolines or isoquinolines via Ru-catalyzed redox-divergent hydrogen-retentive or hydrogen-releasing processes (Scheme 1, eqs 2 and 3). Notably, synthesis of the former directly from alkynes is rare (Scheme 1, eq 2).[14] Moreover, the reactions feature an extraordinarily high *cis*-selectivity. Compared

Scheme 1. Annulations between N−H Imines and Alkynes



with the reported seminal Mn catalysis (Scheme 1, eq 1),[6] switchable chemoselectivity is achieved.

The studies commenced with the coupling of bis(4-methoxyphenyl)methanimine (**1a**) and 1,2-diphenylacetylene (**2a**).[6] Investigation of the reaction parameters (e.g., solvents, reaction temperature/time, and catalyst loading) disclosed that the annulation gave *cis*-dihydroquinoline **3a** in 86% yield with 1 mol % of $[RuCl_2(p\text{-cymene})]_2$ at 120 °C in 1,4-dioxane (Table S1, entry 18). The structure of **3a** was unambiguously confirmed by X-ray crystallography (Scheme 2). The Ru catalyst proved necessary for the reaction system (Table S1, entry 19). To the best of our knowledge, there are few reports on the preparation of 3,4-dihydroisoquinolines from alkynes.[14] The substrate scope was next investigated under the optimized conditions. Substrates bearing electron-donating and weak electron-withdrawing groups on the phenyl ring of ketimines led to reactions with high efficiency (**3a−d**). Introduction of strong electron-withdrawing groups decreased the reaction yields slightly (**3e,f**). Compound **3g** was isolated in 49% yield as the major regioisomer

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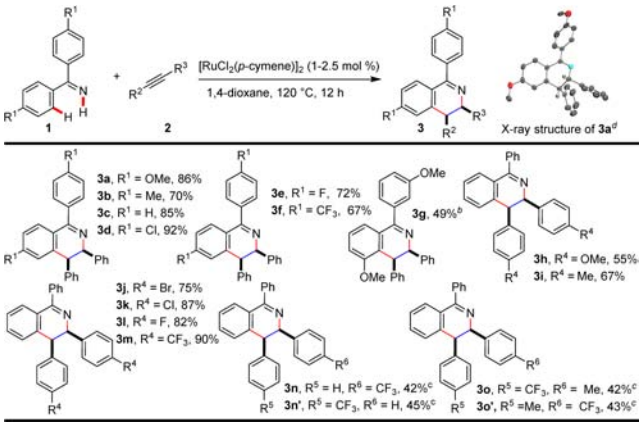
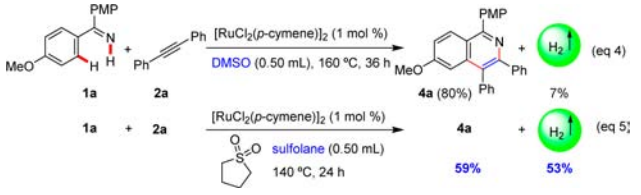
Scheme 2. Synthesis of 3,4-Dihydroisoquinolines[a]



[a]Reaction conditions: **1** (0.20 mmol), **2a** (0.30 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (1 mol %), 1,4-dioxane (2.0 mL), isolated yields. [b]With 2.5 mol % of catalyst, only the regioisomer shown was isolated, and the presence of the other regioisomer could not be confirmed. [c]^{1}H NMR yields. [d]Thermal ellipsoids are drawn at 30% probability with most H atoms omitted for clarity.

and the favored, more hindered *ortho*-C−H activation product, which should be attributed to the secondary directing effect of *meta*-methoxy.[6] The scope of the alkynes was further explored. First, symmetric electron-rich diarylacetylenes (**2h,i**) gave reaction activities lower than those of electron-poor ones (**2j−m**). Electronically biased diarylacetylenes, however, coupled with poor regioselectivity (ca. 1:1 for **3n**/**3n′** and **3o**/**3o′**).

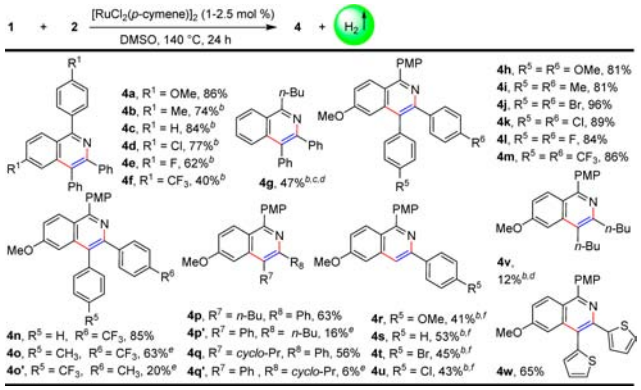
Surprisingly, the chemoselectivity was totally switched from 3,4-dihydroisoquinolines to an isoquinoline as a result of H_2-releasing coupling when the solvent was replaced by DMSO (Table S1, entry 13). Further optimization of reaction conditions (Table S2) improved the isolated yield of **4a** to 86%. [$RuCl_2$(*p*-cymene)]$_2$ also proved necessary for this coupling (Table S2, entry 7). The yield of H_2 was 7% for a gram-scale reaction with 80% yield of **4a** (eq 4). Traces of H_2 were accepted by 1,2-



diphenylethyne as 2.5% of *cis*-1,2-diphenylethene was observed in the reaction mixture. It should be noted that when using sulfolane as solvent under similar conditions, **4a** was obtained in 59% yield with 53% yield of H_2 (eq 5). These results suggested that DMSO acted as a partial hydrogen acceptor. The low yield of H_2 is likely caused by subsequent hydrogen reduction of CO_2 to CH_4 as both CO_2 and CH_4 have been observed. The CO_2 likely originated from the decomposition of small amounts of DMSO by Ru catalysis [see Supporting Information (SI), Scheme S1].[13c,d,15,16] DMSO was thus used as an optimal solvent for further investigations with higher reaction yield.

The substrate scope was studied (Scheme 3). Variation of groups on the phenyl rings of diaryl ketimines from 4-OMe to 4-CF_3 decreased the yield from 86 to 40% (**4a−f**). Notably, 1-phenylpentan-1-imine gave moderate yield (**4g**). Substituted 1,2-diphenylacetylenes bearing both electron-donating and electron-withdrawing groups on the phenyl rings afforded desired

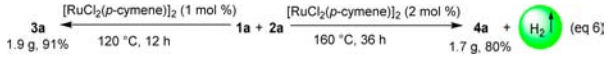
Scheme 3. Synthesis of Isoquinolines[a]



[a]Reaction conditions: **1** (0.20 mmol), **2a** (0.24 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (1 mol %), DMSO (0.5 mL), isolated yields. [b]With 2.5 mol % of catalyst. [c]With 3 equiv of alkyne. [d]Reaction was performed at 160 °C. [e]^{1}H NMR yield. [f]With 2 equiv of alkyne.

products in good to excellent yields (**4h−o**). In contrast to the selectivity of the corresponding 3,4-dihydroisoquinolines (**3n**, **3n′**, **3o**, **3o′**), higher regioselectivity was obtained (**4n** as the only isomer, **4o**/**4o′** = 3.1:1; see SI for the single X-ray crystallography of **4n**). Alkyl phenyl-disubstituted alkynes gave two regioisomers in good yields (**4p**, **4p′**, **4q**, **4q′**). Substituted phenylacetylenes achieved moderate yields (**4r−u**). Dialkyl-substituted alkyne displayed low activity (**4v**). Moreover, dithienylacetylene was compatible (**4w**).

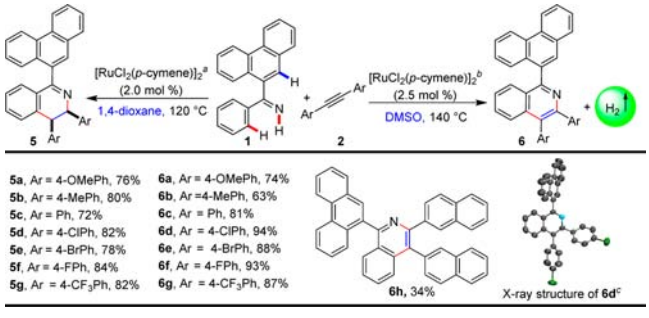
To explore the potential application of the synthetic method, gram-scale synthesis of **3a** (91%) and **4a** (80%) was demonstrated (eq 6). Furthermore, a series of useful polycyclic



aromatic products (**5a−g**, **6a−h**) were synthesized in moderate to excellent yields (Scheme 4).[17] The regioselectivity of the imines was confirmed by the X-ray crystallography of **6d**.

To gain insight into the redox-switchable chemoselectivity and reaction mechanism, a series of experiments were conducted. Monitoring of the synthesis of **3a** (Figure 1a) showed no apparent stable intermediates or byproducts during the reaction. Notably, two major intermediates, **3a** and bis(4-methoxyphenyl)methanone (**7a**), were observed for preparation

Scheme 4. Synthesis of Polycyclic Aromatic Products



[a]Reaction conditions: **1** (0.20 mmol), **2** (0.30 mmol), 1,4-dioxane (1.0 mL), isolated yields. [b]**1** (0.20 mmol), **2** (0.24 mmol), DMSO (0.4 mL), isolated yields. [c]Thermal ellipsoids are drawn at 30% probability, and H atoms are omitted for clarity.

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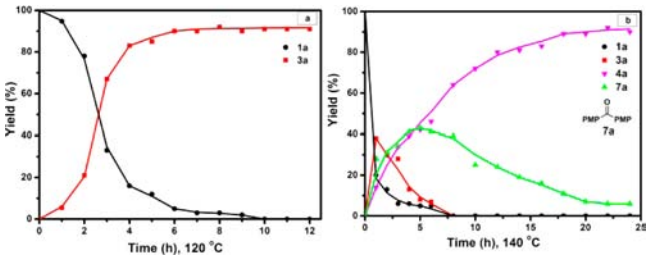
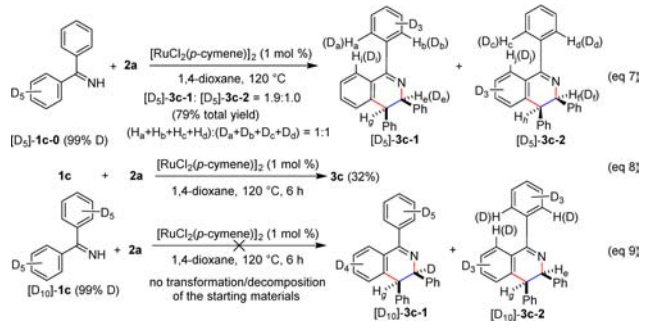


Figure 1. Yield/time diagram for preparation of **3a** (a) and **4a** (b). Yields were reported as ^{1}H NMR yields using $Cl_2CHCHCl_2$ as an internal standard (see Tables S3 and S4 for details).

of **4a** (Figure 1b). This observation indicated that 3,4-dihydroisoquinoline led to the corresponding isoquinoline via dehydrogenation. It was further confirmed by the unidirectional conversion of **3a** to **4a** (eqs S4 and S5). Moreover, intermediate **7a** was confirmed in this reaction, and labeling experiments using ^{18}O-DMSO showed that the oxygen atom of **7a** originates from DMSO. The detected ammonia suggested that the nitrogen atom of **1a** is converted into ammonia (eqs S6 and S7).

Next, different factors related to the chemoselectivity were studied. First, a comparable experiment (eq S8) with the reported Mn catalysis (eq 1) disclosed that catalysts directly affected the chemoselectivity. Second, a set of experiments with variable amounts of DMSO in 1,4-dioxane showed that traces of DMSO sharply inhibited the catalyst activity toward 3,4-dihydroisoquinolines at both 120 and 140 °C (Figure S1a,b). Meanwhile, with more than 20 equiv of DMSO in the reaction mixture, the chemoselectivity showed an inversed tendency. Third, increasing reaction temperature improved the selectivity toward dihydroisoquinolines, while the yield of the isoquinolines was essentially unaffected (Figure S1c). Fourth, the chemoselectivity toward isoquinolines is increased at a higher concentration, accompanied by the reduced selectivity toward dihydroisoquinolines (Figure S1d). These investigations show that the exhibited chemoselectivity is collectively effected by catalysts, solvents, reaction temperature, and the concentration of reactants.

Kinetic isotope experiments were then conducted. H/D scrambling in intramolecular isotopic experiments for the synthesis of **3c** suggests the reversibility of the C−H cleavage (eqs 7 and S9). Labeling studies offered important hints to the



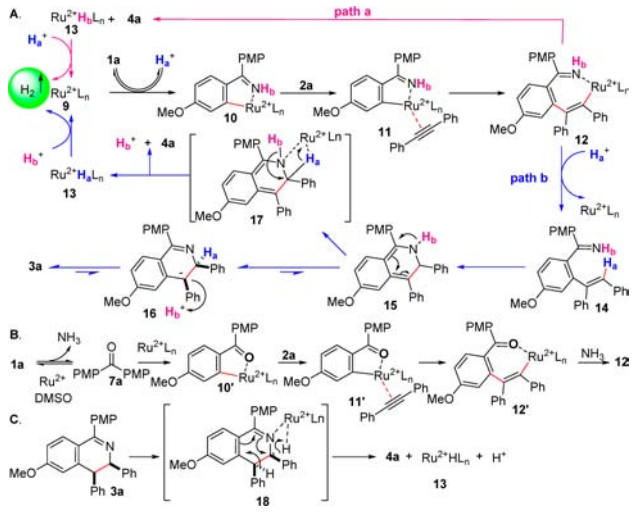
reaction pathway. No deuterium incorporation at the g and h position was observed for products [D_5]-**3c-1** and [D_5]-**3c-2** derived from [D_5]-**1c**. This observation was further consistently made by trace product in the coupling of [D_{10}]-**1c** at 140 °C (eq S10). These data suggest that the H(g) and H(h) should originate from the NH group. However, essentially no formation of [D_{10}]-**3c-1** and [D_{10}]-**3c-2** was detected at 120 °C (eq 9). This result was in sharp contrast to the smooth coupling of **1c** at 120 °C (eq 8), which indicated that the reversible C−H activation is rate-limiting.

For the preparation of isoquinolines, [D_5]-**1c-0** was decomposed to the corresponding ketone in DMSO with catalytic [$RuCl_2$(*p*-cymene)]$_2$ in the absence of **2a** (eq S11). H/D scrambling in the intramolecular kinetic isotope experiment also suggests the reversible C−H activation (eq S12). However, no further information was obtained.

Additionally, a set of experiments was conducted using intermediate **8** [(*E*)-(2-(1,2-diphenylvinyl)phenyl)(phenyl)-methanimine] under similar conditions with/without [$RuCl_2$(*p*-cymene)]$_2$ (eqs S13−S16). The yields of **3c** (59%) and **4c** (24%) with catalyst (eq S13) and **3c** (74%) under TM-free conditions in 1,4-dioxane (eq S15) suggest that 6π-electrocyclization is involved in the catalytic cycle. This deduction is also supported by the results of experiments in DMSO (eqs S14 and S16). The observation of **4c** and traces of H_2 in the absence of Ru should be attributed to DMSO as a hydrogen acceptor (eq S16).[15]

Based on these investigations, a proposed reaction mechanism is shown in Scheme 5. Catalyst precursor [$RuCl_2$(*p*-cymene)]$_2$

Scheme 5. Proposed Reaction Mechanism



produces active Ru complex **9**. Then a reversible electrophilic substitution between imine **1a** and **9** affords intermediate **10**. A subsequent coordination of **2a** with **10** and the following alkyne insertion leads to **12**. The σ-bond metathesis between C(sp^2)−Ru and N−H bonds in **12** leads to **4a** and Ru species **13** (Scheme 5A, path a). Then **13** reacts with the proton generated in situ at the initiating step to produce H_2 with release of **9**. On the other hand, protonation of **12** affords **15** by **14** via 6π-electrocyclization (Scheme 5A, path b). Isomerization of **15** via deprotonation of N−H and protonation of the anion in **16** affords **3a**. The *cis*-selectivity should be explained by the steric factor. An alternative pathway for the formation of **3a** from **15** is by a [1,5]-sigmatropic hydrogen shift.[18] These pathways agree with the observation of the retentive hydrogen source in **3c** (see eqs 7 and S10). **4a**, Ru species **13**, and the proton are generated via transition state **17** from **15**. Notably, using DMSO as solvent, the possible apparent equilibration between **1a** and diaryl ketone **7a** is shifted by the subsequent steps, and **12** generation via C−H activation of ketone **7a** cannot be ruled out at this stage (Scheme 5B). The transformation of **3a** to **4a** is realized via **18**. As mentioned above,

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Org. Lett. 2016, 18, 2840−2843

13 is protonated to release H_2 and regenerate **9** to close the catalytic cycle (Scheme 5C).

In conclusion, we developed a chemoselective annulation of N−H imines and alkynes for synthesis of 3,4-dihydroisoquinolines or isoquinolines using the same Ru catalyst. The valuable assets of the couplings are exhibited by switchable chemoselectivity, nearly 100% atom-economy, high *cis*-selectivity for the synthesis of 3,4-dihydroisoquinolines and further possible applications. Mechanistic investigations indicate a new strategy toward constructing various chemical bonds via H_2 release. The established method will attract wide interest in developing various catalysis systems for these highly concise cross-couplings.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01091.

Experimental procedure, characterization data, computational details (PDF)
Copies of ^{1}H and ^{13}C NMR spectra (PDF)
X-ray data for **3a** (CIF)
X-ray data for **4n** (CIF)
X-ray data for **6d** (CIF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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