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# C−H Activation-Based Traceless Synthesis via Electrophilic Removal of a Directing Group. Rhodium(III)-Catalyzed Entry into Indoles from *N*-Nitroso and α-Diazo-β-keto Compounds

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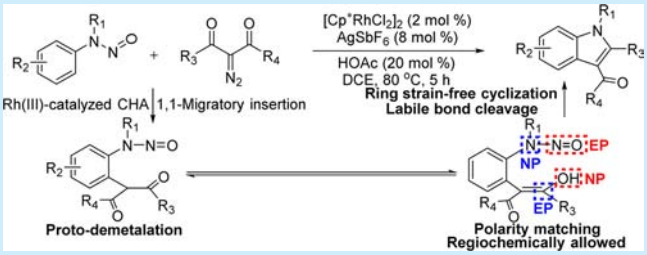
Supporting Information

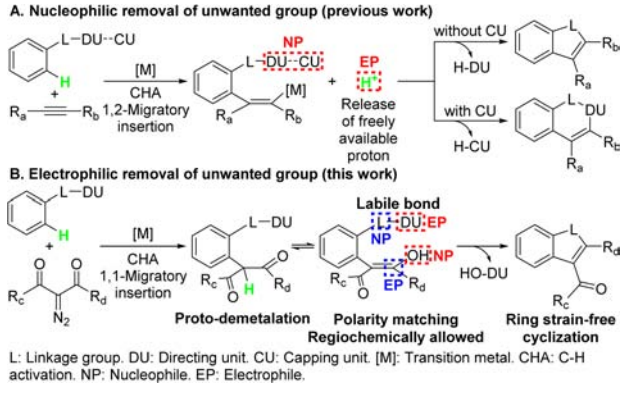
**ABSTRACT:** A distinct C−H activation-based traceless synthetic protocol via electrophilic removal of a directing group is reported, complementing the currently exclusively used nucleophilic strategy. Rh(III)-catalyzed, *N*-nitroso-directed C−H activation allows the development of a traceless, atom- and step-economic, cascade approach for the synthesis of indole skeletons, starting from readily available *N*-nitroso and α-diazo-β-keto compounds. Importantly, the cyclization/denitrosation reaction represents a hitherto unobserved reactivity pattern for the *N*-nitroso group.




Transition-metal-catalyzed C−H activation (CHA)[1] provides a handy tool for the synthesis of heterocycles. A directing group[2] is typically critical in the control of regioselectivity, but can be, in part or as a whole, undesired for intended applications. An ideal synthetic system should allow the generation of target product in a traceless,[3] atom- and step-economic manner under CHA conditions (either on-cycle[4] or off-cycle,[5] one-pot/cascade[6]). Thus, far, essentially all of the unwanted portion of the directing group is removed as a nucleophile, with a proton acting as the formal partner electrophile. Mechanistically, a typical traceless CHA-based synthetic protocol utilizes a 1,2-migratory insertion-generated intermediate for cyclization and the initially extruded proton remains as a freely available electrophile until being sequestered at a later stage, by the removed group (Scheme 1A). This reaction mode has enabled the synthesis of a variety of heterocycles but can impose significant restriction on the substrate scope. We envisioned that an umpolung,[7] complementary reaction mode, with the directing group acting as an electrophile at the removal stage, could be achieved through forward reactivity analysis (Scheme 1B). In particular, electrophilic removal can be a viable strategy by achieving the following prerequisites: (1) freely available electrophilic proton is sequestered at an early stage, prior to cyclization, by the CHA-installed group through a proto-demetalation process; (2) polarity-matched partners are positioned in a regiochemically allowed manner; (3) a sufficiently labile bond exists in the directing group; (4) cyclization can proceed in a ring-strain-free fashion.

We have recently initiated a research program on *N*-nitroso-directed CHA reactions.[8] This labile directing group has allowed the traceless synthesis of indoles by using alkynes as the coupling partner.[8a,9] In this on-cycle cyclization circumstance, the final C−N bond formation is accomplished by the nucleophilic attack of Rh(III)-bound C atom toward the amino N atom, accompanied by simultaneous trapping of the nitroso group with electrophilic proton. This is, however, not a typical reactivity pattern observed for the *N*-nitroso group (under off-cycle, metal-coordination-free conditions), where the amino N atom is nucleophilic and the nitroso N atom is electrophilic. We expect that this polarity can be matched by a cyclization partner containing an electrophilic C atom and a nucleophilic heteroatom. Herein, we report an unprecedented CHA-based

**Scheme 1. Schematic of CHA-Based Traceless Synthesis Strategy via Electrophilic Removal of Directing Group**[a]




[a]L: Linkage group. DU: Directing unit. CU: Capping unit. [M]: Transition metal. CHA: C−H activation. NP: Nucleophile. EP: Electrophile.

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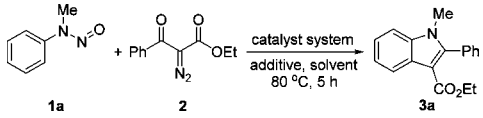
traceless synthetic protocol through electrophilic removal of directing group. In particular, we wish to disclose a traceless indole synthetic protocol by using *N*-nitroso and *α*-diazo-*β*-keto compounds[10] as the reaction partner. Although an *α*-diazo-*β*-keto compound has been previously employed in the synthesis of indoles,[11] the directing group cannot be removed, as expected, due to mismatched polarity and/or low bond lability. The proposed CHA/carbenoid 1,1-migratory insertion/proto-demetalation allows subsequent tautomerization and generation of an enolization intermediate containing an electrophilic alkenyl C atom and a nucleophilic hydroxyl group. The matching of polarity from the *N*-nitroso group and lability of the N−N bond provides the possibility of simultaneous C−N cyclization and N−N bond cleavage. Notably, this cyclization/denitrosation reaction mode has never been observed for the *N*-nitroso group.

We commenced the initial condition-screening experiments by using *N*-nitrosoaniline **1a** (0.4 mmol) and diazo compound **2** (0.6 mmol) as the model substrates. An initial test with $[Cp^*RhCl_2]_2$ (2 mol %) and $AgSbF_6$ (8 mol %) furnished a desired target cyclized indole derivative **3a** in a promising 35% yield after 5 h of reaction at 80 °C in MeOH (entry 1, Table 1).

**Table 1. Optimization of Reaction Conditions**[a,b]




1a 2 3a

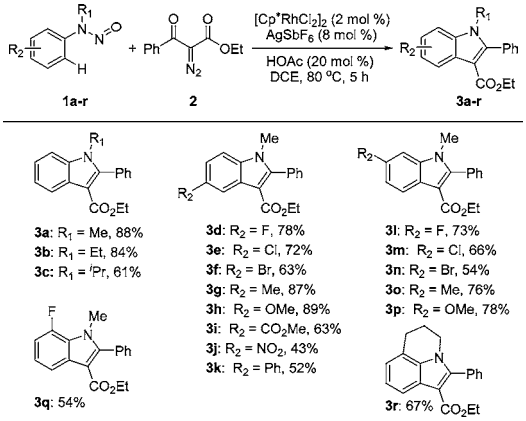
| entry | catalyst system | additive (mmol %) | solvent | yield (%) |
|---|---|---|---|---|
| 1 | $[RhCp^*Cl_2]_2/AgSbF_6$ | | MeOH | 35 |
| 2 | $[RhCp^*Cl_2]_2/AgSbF_6$ | | DCE | 52 |
| 3 | $[RhCp^*Cl_2]_2/AgSbF_6$ | | THF | 30 |
| 4 | $[RhCp^*Cl_2]_2/AgSbF_6$ | | MeCN | 42 |
| 5 | $[RhCp^*Cl_2]_2/AgSbF_6$ | | DMF | 0 |
| 6 | $[RhCp^*Cl_2]_2/AgSbF_6$ | | DMSO | 0 |
| 7 | $[RhCp^*Cl_2]_2/AgSbF_6$ | AgOAc (100) | DCE | 35 |
| 8 | $[RhCp^*Cl_2]_2/AgSbF_6$ | $Na_2CO_3$ (100) | DCE | 33 |
| 9 | $[RhCp^*Cl_2]_2/AgSbF_6$ | NaOAc (100) | DCE | 42 |
| 10 | $[RhCp^*Cl_2]_2/AgSbF_6$ | HOAc (100) | DCE | 68 |
| 11 | $[RhCp^*Cl_2]_2/AgSbF_6$ | HOAc (20) | DCE | 88 |
| 12 | $[RhCp^*Cl_2]_2$ | HOAc (20) | DCE | 0 |
| 13 | $AgSbF_6$ | HOAc (20) | DCE | 0 |
| 14 | $[Cp^*CoI_2]_2/AgSbF_6$ | HOAc (20) | DCE | 20 |
| 15 | $[(p\text{-cymene})RuCl_2]_2$/ $AgSbF_6$ | HOAc (20) | DCE | 0 |
| 16 | $[Cp^*IrCl_2]_2/AgSbF_6$ | HOAc (20) | DCE | 50 |

[a]Reaction conditions: **1a** (0.4 mmol), **2** (0.6 mmol), $[Cp^*RhCl_2]_2$ (2 mol %), $AgSbF_6$ (8 mol %), additive, solvent (2 mL). [b]Isolated yields.

The switching of solvent from MeOH (entries 1−6) to various other reaction media proves DCE as the optimum solvent, where the yield of **3a** could be increased to 52% (entry 2). Further screening of additives shows that acidic conditions are more favored in promoting the transformation (entries 7−10). Investigation on an array of representative acids proves HOAc as the best additive. With the addition of 100 mol % HOAc, the yield of **3a** could be further increased to 68% (entry 10 and Table S1). Systematic optimization with respect to the amount of HOAc, within the 5−200 mol % range, enables the pinpointing of its optimum quantity, 20 mol %, under which conditions **3a** was obtained in 88% yield (entry 11 and Table S2). No further improvement in the yield was observed with the change of catalyst amount, reaction temperature, or reaction time (Table S3). No reaction occurs in the absence of either $[Cp^*RhCl_2]_2$ or $AgSbF_6$ (entries 12, 13), suggesting, most likely, the participation of a cationic Rh(III) complex in the catalytic cycle. The replacement of $[Cp^*RhCl_2]_2$ by $[Cp^*CoI_2]_2$, $[Ru(p\text{-cymene})Cl_2]_2$, or $[Cp^*IrCl_2]_2$ under otherwise identical conditions proves to be detrimental (entries 14−16).

With the optimized conditions established, the scope of *N*-nitrosoanilines was then examined by employing **2** as the coupling partner (Table 2). A variety of *N*-nitrosoaniline

**Table 2. Reaction Scope for *N*-Nitroanilines**[a,b]




[a]Reaction conditions: **1a**−**1s** (0.4 mmol), **2** (0.6 mmol), $[Cp^*RhCl_2]_2$ (2 mol %), $AgSbF_6$ (8 mol %), HOAc (20 mol %), DCE (2 mL). [b]Isolated yields.

derivatives react smoothly to furnish the corresponding indole derivatives in good to excellent yields. The bulkiness of the *N*-alkyl substituent apparently exerts an effect on the reactivity. Substrates containing methyl and ethyl groups (**1a** and **1b**) react equally well, and an isopropyl group (**1c**) affords a slightly lower 61% yield. The reaction is also sensitive to the steric features in the arenes. Both *para* and *meta* derivatives show higher reactivity toward the sterically less hindered C−H bond. For an *ortho* substitution, only small-sized fluorine (**1q**) allows the generation of product in an acceptable 54% yield. The electronic property of arene is another factor that can affect the reaction outcome. An electron-rich substituent (Me, OMe) shows a better reactivity compared with an electron-poor substituent (halogen, $CO_2Me$, $NO_2$, phenyl). Thus, methyl and methoxy groups (**3g**, **3h**, **3o**, and **3p**) give the respective product in excellent yields, ranging from 76% to 89%, whereas halogen atoms (**3d**−**3f** and **3l**−**3n**) and methyl ester (**3i**) afford apparently lower yields. Significantly, a synthetically demanding reaction can proceed for a substrate (**3j**) bearing a very electron-withdrawing group ($NO_2$). In addition, the reaction also works well for *N*-nitroso-tetrahydroquinoline and gives the product **3r** in good yield. Subsequently, the scope of the diazo compounds was investigated using *N*-nitrosoaniline **1a** as one of the substrates. As shown in Table 3, a diversified range of indole derivatives could be synthesized in good to excellent yields. Specifically, ethyl 2-diazo-3-oxo-3-phenylpropanoate bearing electron-donating or -withdrawing groups at a variety of different positions of the phenyl ring (**2a**−**2o**) react smoothly with **1a** to give the desired products **4a**−**4o** (51−88%). Methyl 3-alkyl-2-diazo-3-oxopropanoate (**2p**, **2q**), 2-



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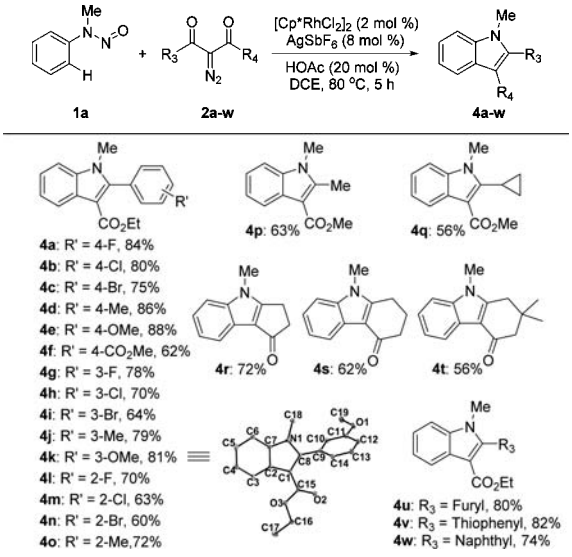
**Table 3. Reaction Scope for Diazo Compounds**[a,b]

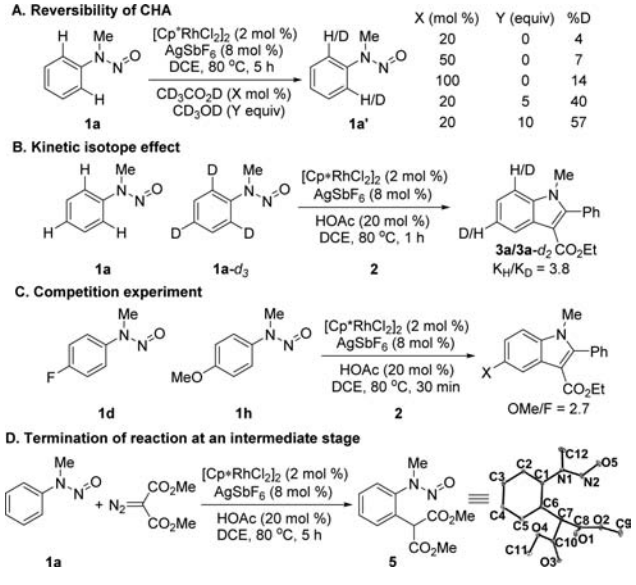



[a]Reaction conditions: **1a** (0.4 mmol), **2a**−**w** (0.6 mmol), $[Cp^*RhCl_2]_2$ (2 mol %), $AgSbF_6$ (8 mol %), HOAc (20 mol %), DCE (2 mL). [b]Isolated yields.

diazocycloalkane-1,3-diones (**2r**−**2t**), and furyl, thiophenyl, and naphthyl diazo esters (**2u**, **2v**, and **2w**) also provide the corresponding products in good yields.

We further performed several experiments to gain insight into the reaction mechanism (Scheme 2). The ready

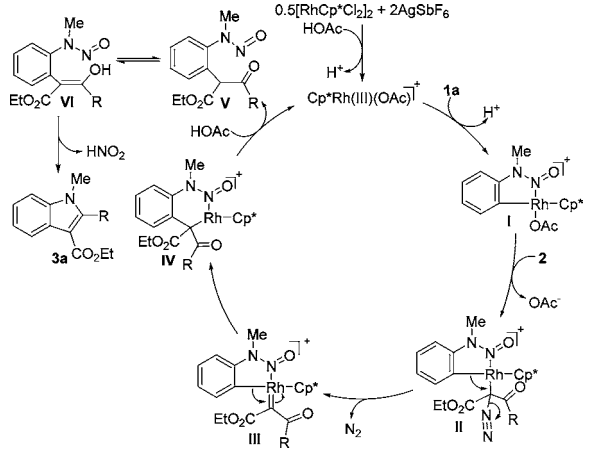
**Scheme 2. Mechanistic Experiments**




observation of H/D scrambling with the addition of a standard amount of $CD_3CO_2D$ (20 mol %) suggests that the CHA and *ortho*-rhodation step is reversible. The reversibility is further highlighted by an elevated degree of scrambling upon the use of an increased amount of $CD_3CO_2D$ or when in combined use with $CD_3OD$. Similarly as expected, D/H scrambling occurs for **1a**-$d_3$ with the addition of HOAc. A kinetic isotope effect value of 3.8 was obtained when using an equimolar mixture of **1a** and **1a**-$d_3$ in the coupling with **2** at a low degree of conversion, supporting CHA as the rate-limiting step. Competition experiments were performed using substrates with different electronic characteristics, and the electron-rich substrate (**1h**) reacts 2.7 times faster than the electron-poor substrate (**1d**). This is consistent with a slightly asynchronous C−H insertion and an electrophilic aromatic substitution mechanism, with Ar−Rh interaction, rather than the acidity of an *ortho*-C−H bond, as the predominant factor dictating the efficiency of the CHA step. The ability to stall the reaction at an intermediate stage with a less reactive dimethyl 2-diazo malonate is consistent with an initial CHA/carbenoid 1,1-migratory insertion/proto-demetalation step and a subsequent separate off-cycle intramolecular cyclization process.

On the basis of these experiments and literature precedents, a plausible mechanism for the indole synthesis process is proposed in Scheme 3: generation of a cationic Rh(III) species

**Scheme 3. Proposed Reaction Pathway**




by $[RhCp^*Cl_2]_2$ and $AgSbF_6$, coordination of $OAc^-$, CHA of *N*-nitrosoaniline with Rh(III) to afford rhodacycle **I**, coordination with a diazo compound to form diazonium intermediate **II**, extrusion of $N_2$ from **II** to afford Rh(III)-carbene **III**, 1,1-migratory insertion to generate Rh(III) species **IV**, proto-demetalation of **IV** to give intermediate **V**, and release of the Rh(III) catalyst simultaneously for a new catalytic cycle. Then tautomerization of intermediate **V** generates in situ an enol intermediate **VI**, which undergoes cyclization/denitrosation to afford the indole product **3a**.

In conclusion, a distinct electrophilic directing group removal strategy has been proposed and demonstrated for a CHA-based synthetic protocol. The protocol allows for the synthesis of indole derivatives from readily available *N*-nitroso and *α*-diazo-*β*-keto compounds. The annulation reaction, involving tandem CHA and a hitherto elusive cyclization/denitrosation step for the *N*-nitroso group, proceeds in a traceless, atom- and step-economic manner, and the corresponding indole derivatives could be obtained with a broad range of substitution patterns.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00310.

Experimental procedure, characterization of the products (PDF)



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Copies of the $^{1}H$ and $^{13}C$ NMR spectra of selected products (PDF)
Crystallographic data for complex **4k** (CIF)
Crystallographic data for complex **5** (CIF)

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### Author Contributions

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### Notes

The authors declare no competing financial interest.

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