

Catalyst-Controlled Regiodivergence in Rearrangements of Indole-Based Oxonium Ylides

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ABSTRACT: We have developed catalyst-controlled regiodivergent rearrangements of oxonium-ylides derived from indole substrates. Oxonium ylides formed *in situ* from substituted indoles selectively undergo [2,3]- and [1,2]-rearrangements in the presence of a rhodium and copper catalyst, respectively. The combined experimental and density functional theory (DFT) computational studies indicate divergent mechanistic pathways involving a metal-free ylide in the rhodium catalyzed reaction favoring [2,3]-rearrangement, and a metal-coordinated ion-pair in the copper catalyzed [1,2]-rearrangement that recombines in the solvent-cage. The application of our methodology was demonstrated in the first total synthesis of the indole alkaloid (±)-sorazolon B, which enabled the stereochemical reassignment of the natural product. Further functional group transformations of the rearrangement products to generate valuable synthetic intermediates were also demonstrated.

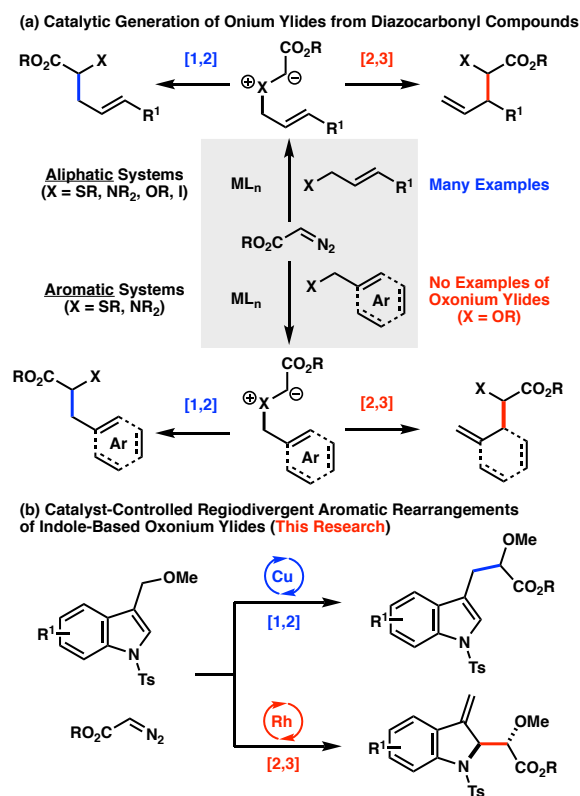
INTRODUCTION

Molecular rearrangements are arguably some of the most effective reactions for the generation of new carbon–carbon bonds in the synthesis of complex molecules.¹ In recent years, advances in catalytic oxonium ylide rearrangements have paved the way for catalyst control of rearrangements that are traditionally unselective.^{2,3} In this context, catalytic generation of oxonium ylides from diazocarbonyl compounds has served as a versatile platform for selective rearrangements (Scheme 1a). Despite many reports of catalytic oxonium ylide rearrangements of *aliphatic* systems,⁴ catalyst-controlled *aromatic* rearrangements are underdeveloped. The challenge of developing this class of rearrangements is partially due to the energetic penalty associated with disruption of aromaticity in the sigmatropic [2,3]-rearrangement (Scheme 1a).⁵ Elegant examples of catalytic aromatic rearrangements of sulfonium (X=SR) and ammonium (X=NR₂) ylides have appeared in the literature.⁶ The selectivity for [1,2]- vs. [2,3]-rearrangement in these methods is largely controlled by subtle differences in substrate structure. Alternatively, catalytic ylide-formation and aromatic [2,3]-rearrangements of oxonium systems (X=OR) are not known, presumably because these more reactive ylides are prone to competing side reactions through non-ylide pathways.⁷ Moreover, the completely catalyst-controlled regiodivergent aromatic rearrangements of any oxonium ylides have not been reported in the literature. Catalytic methods for the selective formation of either [1,2]- or [2,3]-rearrangement products of aromatic systems from the same starting materials would provide a valuable new strategy for the synthesis of complex molecules.

Herein, we report the first catalyst-controlled regiodivergent aromatic rearrangements of indole-based oxonium ylides (Scheme 1b). With the proper choice of catalyst system, we can selectively generate the [1,2]- or [2,3]-rearrangement product. As our initial target for the rearrangements, we chose the indole-scaffold because of its prevalence in many natural products and medicinally valuable compounds.⁸ In addition to exploring the scope of this reaction, we also performed DFT calculations to examine mechanisms and the origins of catalyst-controlled regiodivergence. Finally, to showcase the utility of our method,

we demonstrated the conversion of rearrangement products into the indole alkaloid sorazolon B and several valuable building blocks for drug discovery.

Scheme 1. Catalyst Control of Regioselectivity in Oxonium Ylide Rearrangements



RESULTS AND DISCUSSION

Development of Regiodivergent Rearrangements. Our initial investigations began with the screening of various catalysts

that are generally applied in carbene chemistry,⁹ using 3-(methoxymethyl)-1-tosyl-1*H*-indole (**1a**) and benzyl diazoester (**2a**) as substrates (Table 1). While we did not observe any reactivity in the presence of palladium, silver, or gold catalysts (entries 1–3), CuOTf•benzene (5 mol%) afforded a mixture of [1,2]- and [2,3]-rearrangement products **3a** and **4a** (82:18 rr), respectively, in low yield (entry 4). Moreover, we were pleased to note that indoline **4a** bearing an exomethylene moiety (presumably from the [2,3]-rearrangement) was formed with excellent diastereoselectivity (>20:1 dr). Moving forward with this initial result that gave **3a** as the major product, we began optimizing the [1,2]-rearrangement of the oxonium ylides by screening additional copper sources. Other copper catalysts such as CuCl, CuCl₂, and CuOAc/NaBARF gave similar or slightly improved yields, but relatively lower regioselectivities (entry 5–7). We were delighted to see an improved yield (38%) as well as regioselectivity (86:14 rr) with [Cu(MeCN)₄]PF₆ as catalyst (entry 8). The use of Cu(hfacac)₂ to perform the rearrangement further enhanced the yield (52%) and regioselectivity (92:8 rr) (entry 9). An examination of the conversion of the starting materials under these conditions revealed that the yield was limited by the incomplete consumption of indole **1a**, whereas the diazoester **2a** was completely consumed to give the desired products along with minor amounts of dibenzyl fumarate and dibenzyl maleate as the side products resulting from homodimerization. Increasing the amount of benzyl diazoester **2a** to 2.4 equivalents resulted in >95% conversion of **1a** to provide the [1,2]-rearrangement product **3a** in 78% yield and >95:5 rr (entry 10).

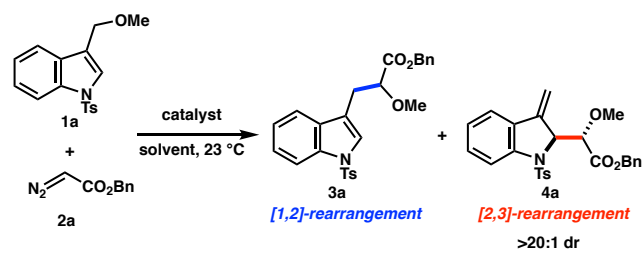
Alternatively, when Rh₂(OAc)₄ (2 mol%) was used as the catalyst, we observed a switch in the regioselectivity that gave [2,3]-rearrangement product **4a** as the major product (>95:5 rr) in 42% yield and >20:1 dr (entry 11). Screening of several other dirhodium carboxylate catalysts commonly used in metal-carbene transformations, such as Rh₂(cap)₄, Rh₂(TFA)₄, Rh₂(TPA)₄, and Rh₂(oct)₄,¹⁰ failed to improve the yield for the reaction (entries 12–15). Similar to the copper-catalyzed [1,2]-rearrangement, an incomplete consumption of indole **1a** was identified as the reason for the moderate yields. Although increasing the amount of diazoester **2a** to 2.4 equivalents provided higher conversion of **1a** (92%), the yield of the [2,3]-rearrangement product **4a** was diminished (26%) (entry 16). We speculated that the reason for the lower yield with excess diazoester might be the propensity of the exomethylene group in **4a** to undergo cyclopropanation with excess highly reactive rhodium-carbene, as suggested by ¹H NMR analysis. Further screening of different solvents also did not provide improvement in the yield (entries 17–19). As a result, the conditions with Rh₂(OAc)₄ (2 mol%) in CH₂Cl₂ at 23 °C were identified as optimal for the catalytic ylide-formation/aromatic [2,3]-rearrangement (entry 11).

Substrate Scope of Regiodivergent Rearrangements. With the optimized reaction conditions for both the copper-catalyzed ylide-formation/[1,2]-rearrangement and rhodium-catalyzed ylide-formation/[2,3]-rearrangement in hand (entries 10 and 11, Table 1), we next explored reaction scope (Table 2).

Indole substrates with a broad range of substituents at various positions on the heteroaromatic ring (**3a–3p**) worked efficiently under the [1,2]-rearrangement conditions. Electron-rich 5- and 6-substituted indole substrates provided high yields and excellent regioselectivities (**3b–3e**). Substitution at the 2-position generated the desired [1,2]-rearrangement product **3f**, albeit in slightly lower yield, likely due to steric hindrance from the 2-

methyl substituent, but nonetheless gave excellent regioselectivity (>95:5 rr). Several electron-withdrawing substituents on the indole ring, including fluoro, bromo, trifluoromethyl, and ester groups (**3g–3m**), provided good yields and high regioselectivities. The reaction also progressed smoothly to generate dihalogenated product **3n** in 51% yield and >95:5 rr. In addition, other alkyl and aryl diazoesters were shown to be competent in generating [1,2]-rearrangement products in moderate to good yields (**3o** and **3p**).

Table 1. Optimization of [1,2] and [2,3]-Rearrangements^a



| Entry | Catalyst | Solvent | Conversion ^b (%) | Yield ^c (%) | 3a:4a |
|-----------------|---|---------------------------------|-----------------------------|------------------------|-------|
| 1 | PdCl ₂ | CH ₂ Cl ₂ | <5 | <5 | - |
| 2 | AgOTf | CH ₂ Cl ₂ | <5 | <5 | - |
| 3 | Ph ₃ PAuCl | CH ₂ Cl ₂ | <5 | <5 | - |
| 4 | Cu(OTf)•benzene | CH ₂ Cl ₂ | 5 | 5 | 82:18 |
| 5 | CuCl | CH ₂ Cl ₂ | 5 | 5 | 71:29 |
| 6 | CuCl ₂ | CH ₂ Cl ₂ | 8 | 7 | 75:25 |
| 7 | CuOAc/NaBARF | CH ₂ Cl ₂ | 26 | 18 | 76:24 |
| 8 | [Cu(MeCN) ₄]PF ₆ | CH ₂ Cl ₂ | 42 | 38 ^d | 86:14 |
| 9 | Cu(hfacac) ₂ | CH ₂ Cl ₂ | 67 | 52 ^d | 92:8 |
| 10 ^e | Cu(hfacac) ₂ | CH ₂ Cl ₂ | >95 | 78 ^d | >95:5 |
| 11 | Rh ₂ (OAc) ₄ | CH ₂ Cl ₂ | 55 | 42 ^d | <5:95 |
| 12 | Rh ₂ (cap) ₄ | CH ₂ Cl ₂ | <5 | <5 | - |
| 13 | Rh ₂ (TFA) ₄ | CH ₂ Cl ₂ | 30 | <5 | - |
| 14 | Rh ₂ (TPA) ₄ | CH ₂ Cl ₂ | 56 | 23 | 32:68 |
| 15 | Rh ₂ (oct) ₄ | CH ₂ Cl ₂ | 44 | 33 | 10:90 |
| 16 ^e | Rh ₂ (OAc) ₄ | CH ₂ Cl ₂ | 92 | 26 | <5:95 |
| 17 | Rh ₂ (OAc) ₄ | DCE | 41 | 36 | <5:95 |
| 18 | Rh ₂ (OAc) ₄ | CHCl ₃ | 51 | 33 | <5:95 |
| 19 | Rh ₂ (OAc) ₄ | toluene | 20 | 16 | <5:95 |

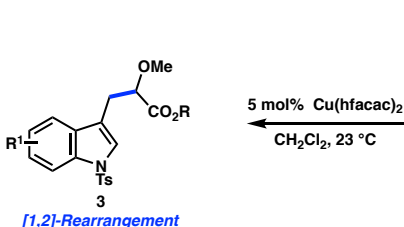
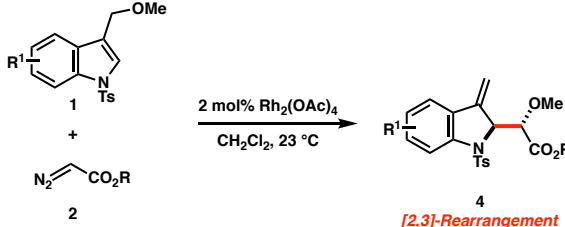
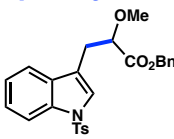
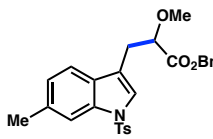
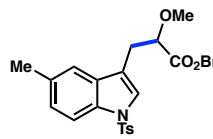
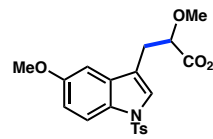
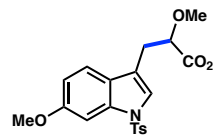
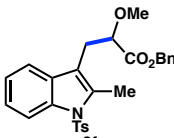
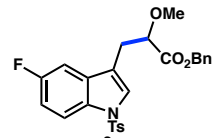
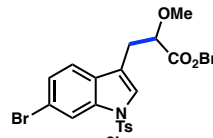
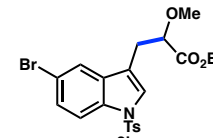
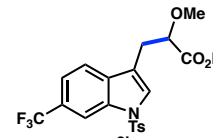
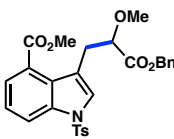
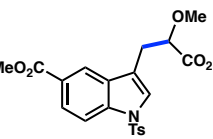
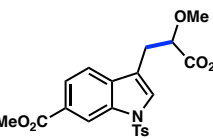
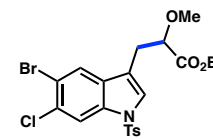
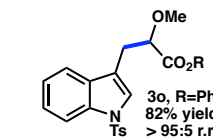
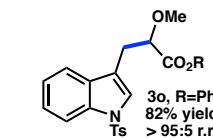
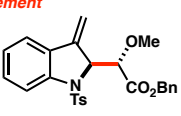
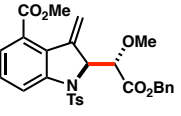
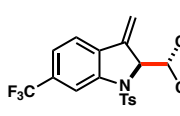
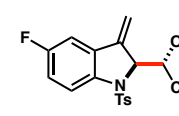
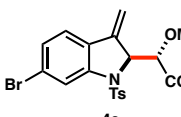
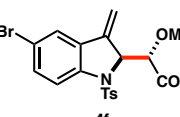
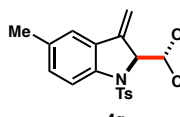
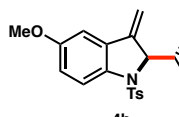
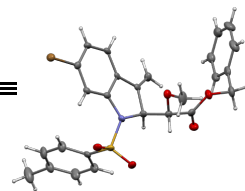
^aReaction conditions: indole **1a** (0.16 mmol), benzyl diazoester **2a** (1.2 equiv, added using syringe pump as 0.2M solution in solvent at a rate of 1mL/h), copper catalyst (5 mol%) or rhodium catalyst (2 mol%). ^bConversion of **1a**. ^cNMR yield using 1,3,5-trimethoxybenzene as internal standard. ^dIsolated yield. ^e2.4 equiv of **2a** was used.

Next, we explored the scope of the rhodium-catalyzed ylide-formation/[2,3]-rearrangement to provide various substituted indolines (**4**) that would be difficult to access in high selectivity by conventional methods.¹¹ Several electron-deficient indole

rings with different substitution patterns underwent selective aromatic [2,3]-rearrangement to generate indolines (**4b-4f**) in moderate yields and with excellent regioselectivities. Electron-donating substituents on the indole ring led to comparatively lower isolated yields of the products (**4g** and **4h**), however the [2,3]-rearrangement proceeded with excellent regioselectivity. The rearrangement products were generally stable to rearomatization, presumably because of the electron-withdrawing tosyl

protecting group similar to other known indolines.^{11b-c} Notably, the [2,3]-rearrangement of all the substrates exhibited high diastereoselectivity. The relative stereochemistry of the major *anti*-diastereomer of product **4e** was confirmed by X-ray crystallography, and the relative stereochemistry of the major diastereomer of all other 2-substituted indolines was assigned by analogy.

Table 2. Products Generated by Regiodivergent [1,2]- and [2,3]-Rearrangements

| [1,2]-Rearrangement | | [2,3]-Rearrangement | | |
|---|---|--|---|---|
|  [1,2]-Rearrangement | |  [2,3]-Rearrangement | | |
|  3a 78% yield > 95:5 rr |  3b 70% yield > 95:5 rr |  3c 81% yield > 95:5 rr |  3d 81% yield 95:5 rr |  3e 85% yield > 95:5 rr |
|  3f 45% yield > 95:5 rr |  3g 81% yield > 95:5 rr |  3h 78% yield > 95:5 rr |  3i 66% yield > 95:5 rr |  3j 77% yield > 95:5 rr |
|  3k 85% yield > 95:5 rr |  3l 59% yield > 95:5 rr |  3m 69% yield > 95:5 rr |  3n 51% yield > 95:5 rr |  3o , R=Ph 82% yield > 95:5 r.r. |
|  3p , R=Et 66% yield 92:8 rr | | | | |
| [2,3]-Rearrangement | | | | |
|  4a 42% yield, >20:1 dr >95:5 rr |  4b 46% yield, >20:1 dr >95:5 rr |  4c 32% yield, >20:1 dr >95:5 rr |  4d 30% yield, >20:1 dr >95:5 rr | |
|  4e 41% yield, >20:1 dr >95:5 rr |  4f 38% yield, >20:1 dr >95:5 rr |  4g 29% yield, >20:1 dr >95:5 rr |  4h 24% yield, >20:1 dr >95:5 rr |  |

Mechanistic Studies. To gain insight into the divergent mechanisms of the catalyst controlled ylide-formation/rearrangement reactions, a series of computational studies were performed using density functional theory at the IEFFPCM(CH₂Cl₂)-UB3LYP-D3(BJ)/6-31+G(d,p),SDD//

IEFFPCM(CH₂Cl₂)-UB3LYP/6-31G(d),LANL2DZ level (see Supporting Information for details).¹² 3-(Methoxymethyl)-1-tosyl-1*H*-indole **1a** was selected as the model substrate.

For the rhodium-catalyzed ylide-formation/[2,3]-rearrangement, we first examined the structure of the metal-bound oxonium ylide (Figure 1). Formation of the carbon-bound ylide **5** is predicted to be endergonic by 6.4 kcal/mol, whereas formation of the oxygen-bound ylide **6** is endergonic by 23.7 kcal/mol. Given the magnitude of this energy difference (essentially a preference for a C-bound rather than O-bound enolate), we did not consider the O-bound structure further.

Our proposed pathway for a concerted [2,3]-rearrangement process is summarized in Figure 1. Dissociation of $\text{Rh}_2(\text{OAc})_4$ prior to rearrangement generates free oxonium ylide **7**, as our computations predicted essentially no binding energy for $\text{Rh}_2(\text{OAc})_4$ with the ylide (see Supporting Information for details). Early dissociation of rhodium(II) complexes from ylides has been reported for other diazocarbonyl-mediated reactions.^{4a,13} The most probable pathway to the product involves a

ΔG (kcal mol⁻¹; 298 K)

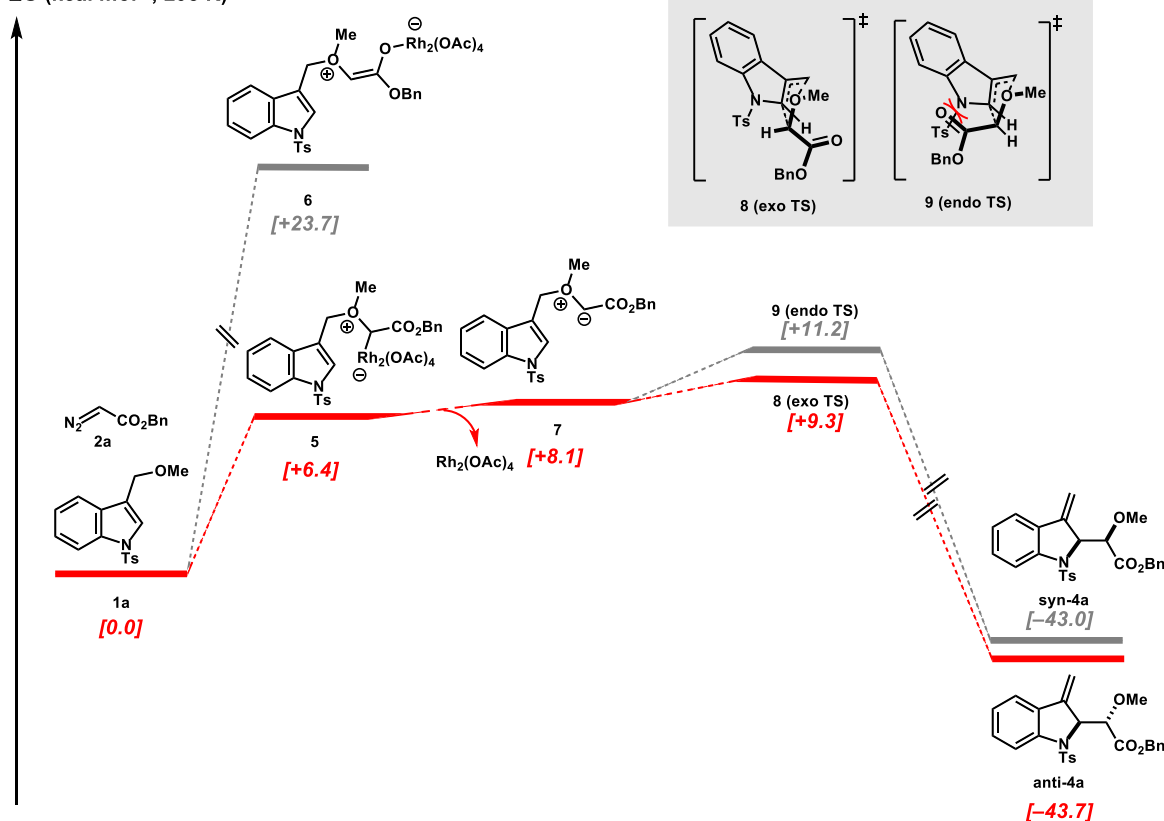


Figure 1. Computed (IEFPCM(CH_2Cl_2)-UB3LYP-D3(BJ)/6-31+G(d,p),SDD//IEFPCM(CH_2Cl_2)-UB3LYP/6-31G(d),LANL2DZ) relative free energies (kcal/mol, italics) for minima and TSSs involved in the Rh-promoted reaction of **1a** and **2a**. Computed relative free energies (IEFPCM(C_6H_6)-UB3LYP-D3(BJ)/6-31+G(d,p),SDD//IEFPCM(C_6H_6)-UB3LYP/6-31G(d),LANL2DZ) in benzene can be found in the Supporting Information.

For the copper-catalyzed ylide-formation/[1,2]-rearrangement, we propose a mechanism that involves a stepwise process (Figure 2A).^{4e,17} The preference for the formation of [1,2]-rearrangement product **3a** over [2,3]-rearrangement product **4a** argues against pathways involving early dissociation of copper from the initially generated metal-coordinated ylide **11**, since metal-free [1,2] rearrangement is predicted to have an extremely high barrier compared to the [2,3]-rearrangement (see Supporting Information). Based on our computational results, we favor an ion-pair fragmentation/recombination pathway for the copper-catalyzed reactions.¹⁸ Other possible pathways were explored but were not consistent with our experimental results (see Supporting Information). For example, formation of simple

metal-free [2,3]-rearrangement of oxonium ylide **7**, which leads to the observed product **4a** with the experimentally observed relative stereochemistry.¹⁴ As expected, we were not able to find a transition state structure for the symmetry-forbidden metal-free [1,2]-rearrangement of oxonium ylide **7**.¹⁵ The *relative* stereochemistry of the major diastereomer of products arising from the [2,3]-rearrangement of indole-based onium ylides **1** is consistent with a preference for an *exo* transition state structure (**8**), similar to typical metal-free concerted [2,3]-rearrangements in allylic systems.^{4d,16} Relative free energies calculated for the *exo* and *endo* transition states predicted a lower energy barrier for *exo* transition state **8** leading to the observed diastereomer *anti-4a*.

radical-pairs cannot be ruled out on the basis of our computational results, but our experimental data argues against it. Specifically, cyclopropane containing substrate **1q** reacted with diazoester **2a** to yield [1,2]-rearrangement product **3q** with the radical probe intact (Figure 2B).^{19,20}

To gain insight into the key carbon-carbon bond forming event in the copper-catalyzed reaction, we considered ion-pair complexes (**12a**, **12b**, **12c**, **12d**, and **12e**) that could lead to [1,2]-rearrangement product **3a** or [2,3]-rearrangement product diastereomers *syn-4a* and *anti-4a* with minimal reorganization (optimized structures are shown in Figure 3).²¹ In principle, these ion-pairs would be in equilibrium with each other and

could recombine to form copper-bound recombination products (e.g., **13a**, Figure 2A and Figure 3).²² However, recombination in a solvent cage is expected to be faster than equilibration between ion-pairs, which could involve a non-statistical dynamic effect.^{18g,23} Although a solvent cage was not explicitly modeled in our calculations, the formation of ion-pairs in a solvent cage is consistent with experimentally determined results. When substrates **1h** and **1r** were simultaneously subjected to the [1,2]-rearrangement conditions, we did not detect crossover products **3s** and **3a** (Figure 2C).

We were able to find a transition state structure (TS_{12a}) converting ion-pair **12a** to **13a**, the Cu(hfacac)₂-bound experimentally observed product, with a negligible barrier. Subsequent

dissociation of Cu catalyst yields **3a**. If **12a** were formed preferentially on dissociation of copper-coordinated oxonium ylide **11**, we propose that this ion-pair could rapidly recombine to the experimentally observed product (**12a** → **3a**) before equilibration with other ion-pairs. Comparisons of the various ion-pairs and metal-ylide intermediate **11** do indeed reveal greater conformational similarity between **11** and **12a** than either **12b**, **12c**, **12d**, or **12e** (Figure 3, see Supporting Information for details). We also investigated the proposed stepwise ion-pair mechanism with other copper catalysts (Cu(acac)₂, CuCl₂, Cu(hfacac)⁺ and Cu(acac)⁺), and all lead to similar results (see Supporting Information for details).

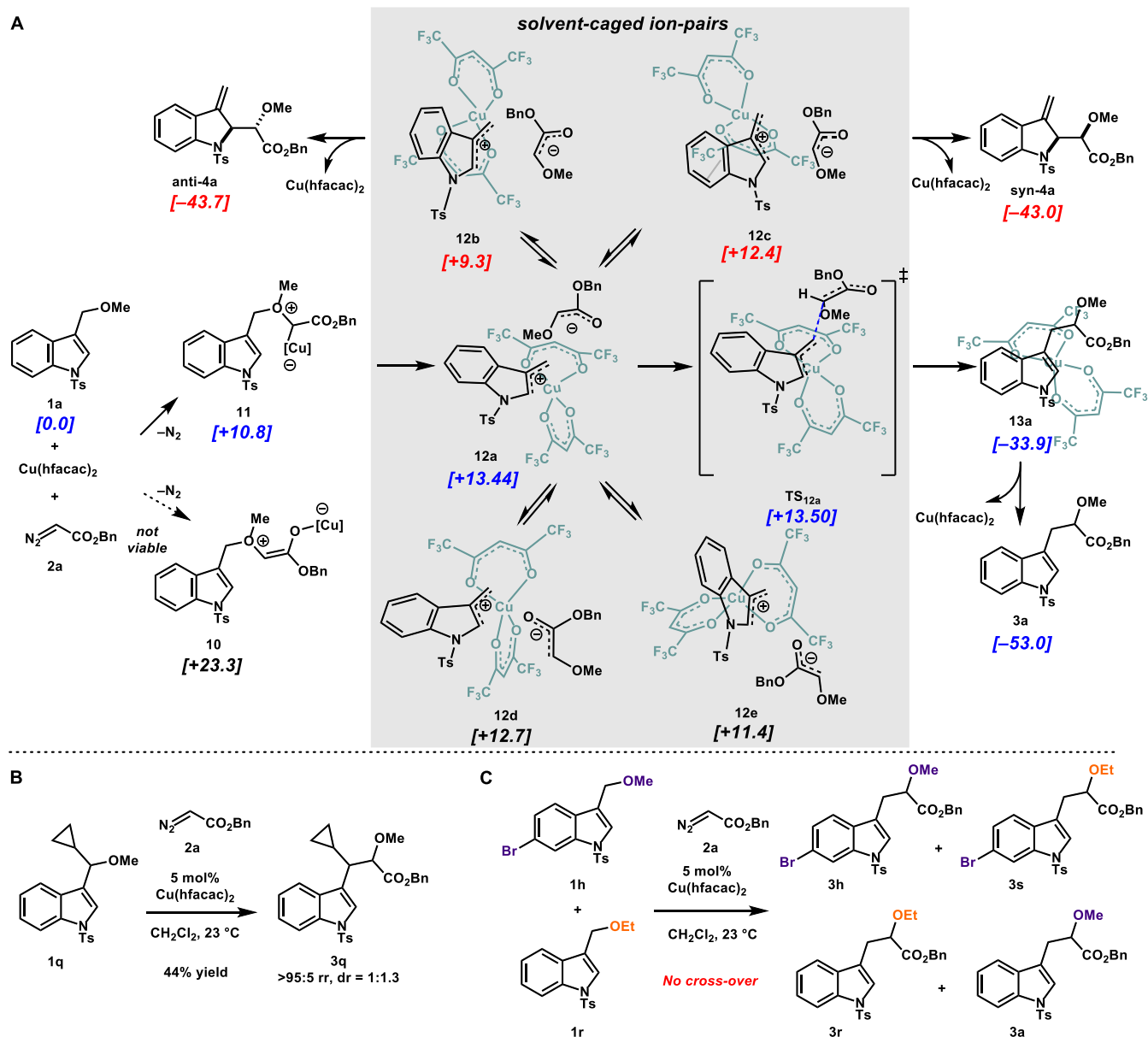


Figure 2. **A.** Computed (IEFPCM(CH₂Cl₂)-UB3LYP-D3(BJ)/6-31+G(d,p),SDD//IEFPCM(CH₂Cl₂)-UB3LYP/6-31G(d),LANL2DZ) relative free energies (kcal/mol, italics) for minima and TSSs involved in the Cu-promoted reaction of **1a** and **2a**. The energies for ion pairs **12a-12e** are based on optimized complexes. Computed relative free energies (IEFPCM(C₆H₆)-UB3LYP-D3(BJ)/6-31+G(d,p),SDD//IEFPCM(C₆H₆)-UB3LYP/6-31G(d),LANL2DZ) in benzene can be found in the Supporting Information. **B.** Results from radical probe experiment. **C.** Results from cross-over experiment.

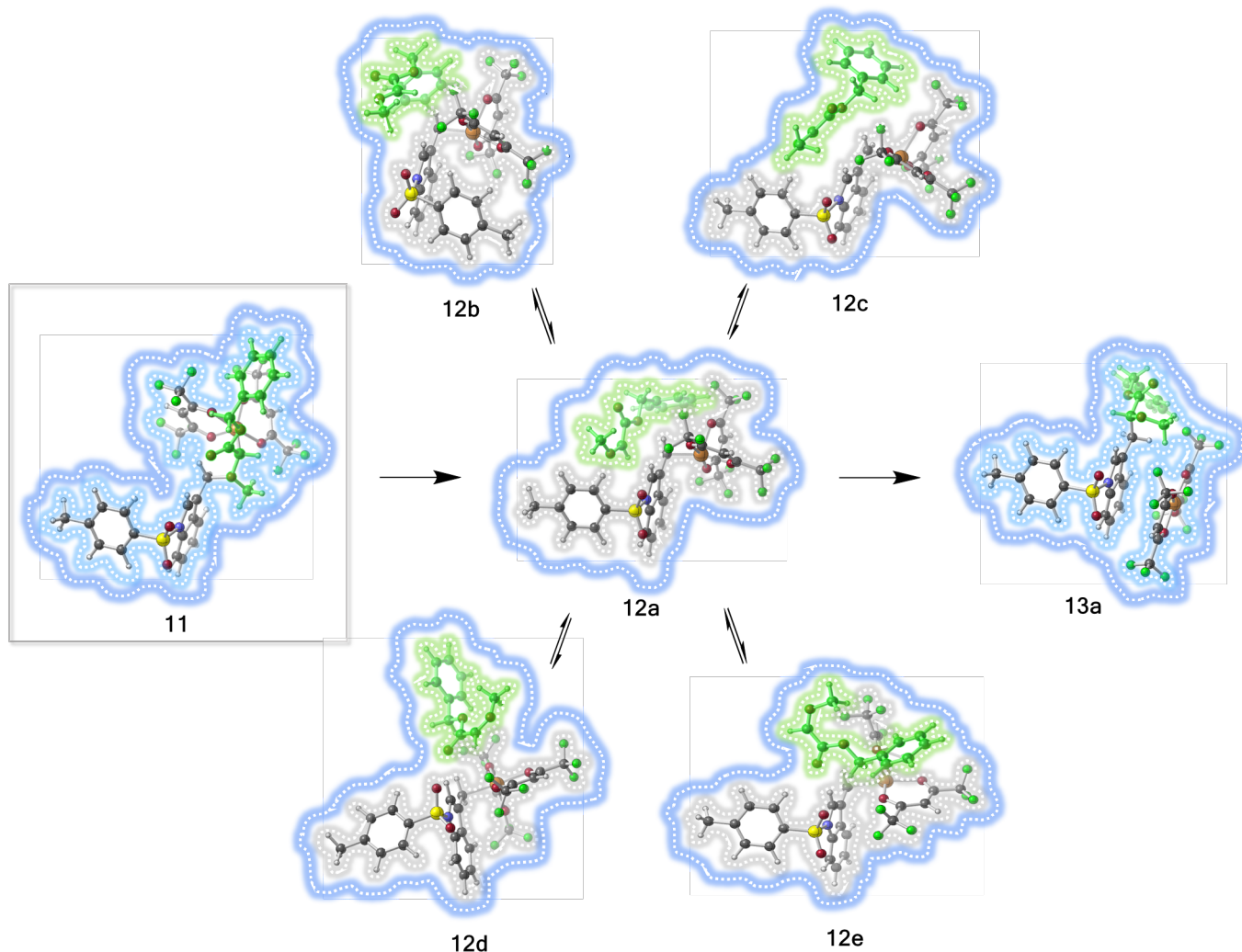
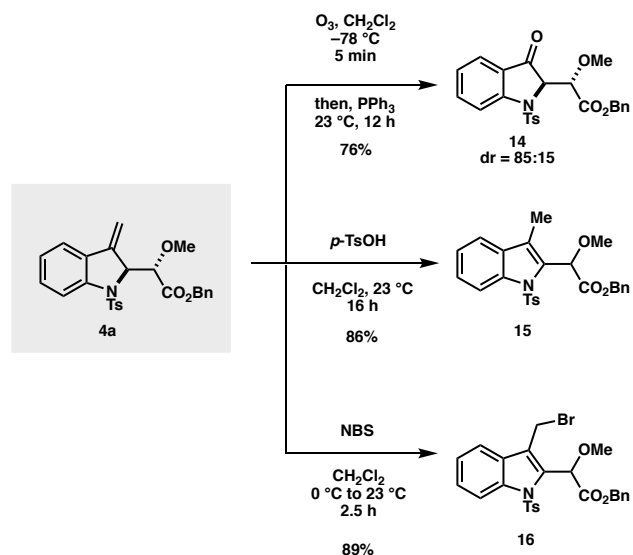


Figure 3. Geometries of the $\text{Cu}(\text{hfacac})_2$ -bound ion-pair complexes, their preceding zwitterion **11** and the recombination product **13a** for qualitative structural comparison (IEFPCM(CH_2Cl_2)-UB3LYP/6-31G(d),LANL2DZ). For clarity in visual comparison, the enolate part of the ion-pair is highlighted in green and the indolyl part (highlighted in grey) is positioned the same way for each structure above. The solvent cage (not modeled explicitly) is depicted in blue with dotted lines.

In summary, based on our combined experimental and computational data, we favor a mechanism for the rhodium-promoted reaction where early catalyst dissociation occurs at the ylide stage, and products are formed via a metal-free [2,3]-sigmatropic rearrangement. For the copper-promoted reaction, we favor a mechanism where a copper-coordinated ion-pair is formed and rapidly recombines in a solvent cage to form the observed [1,2]-rearrangement product.

Synthetic Applications of Regiodivergent Rearrangements. The products generated through the [2,3]-rearrangement proved to be versatile substrates to access building blocks that are potentially useful for the synthesis of complex molecules (Scheme 2). For example, rearrangement product **4a** can undergo ozonolysis to yield indoxyl product **14**. In the presence of acid, rearrangement product **4a** rearomatizes to furnish 2,3-disubstituted indole **15**. In the presence of an electrophilic source of bromine, it is selectively converted to 3-bromomethyl indole **16**.

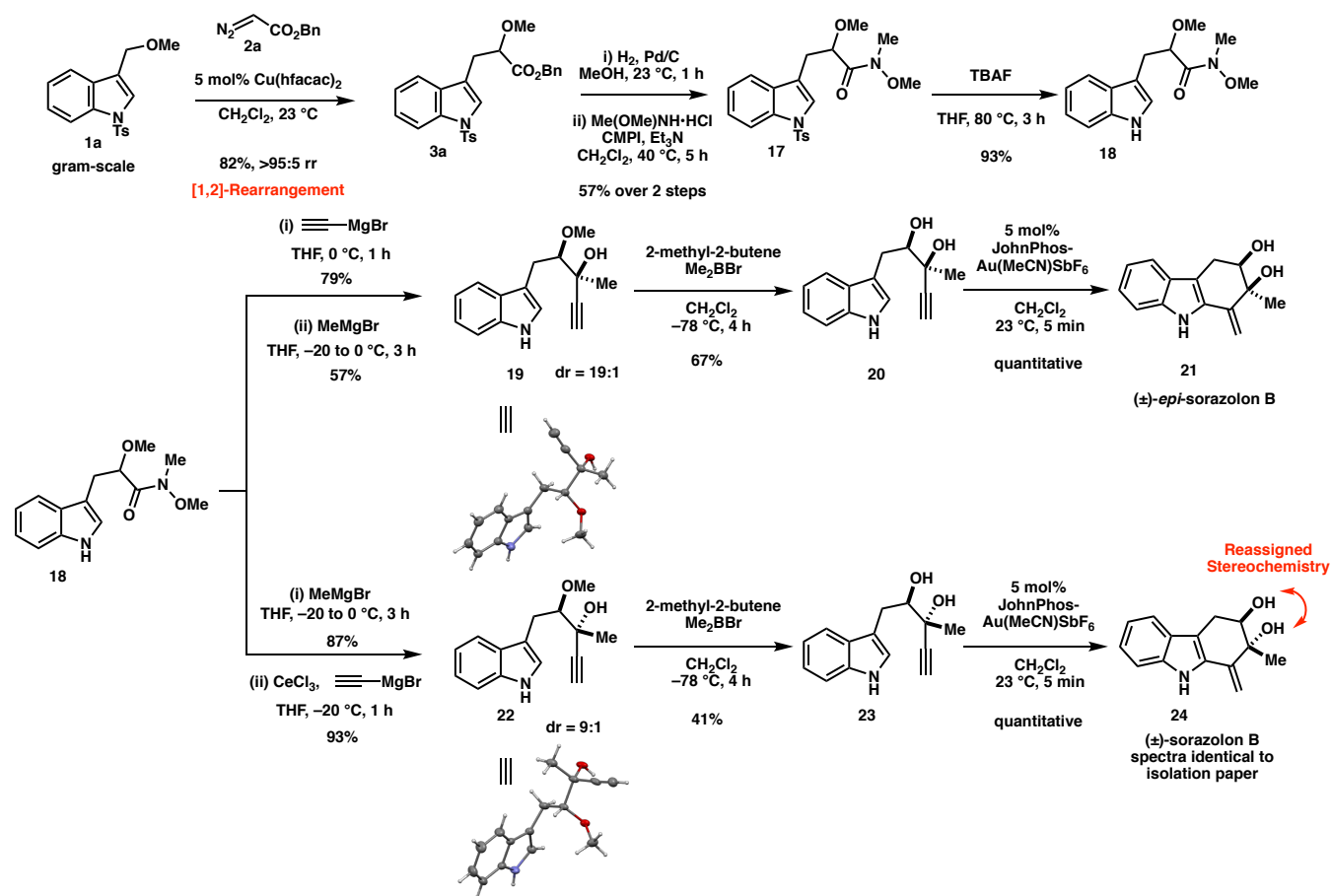
Scheme 2. Synthetic Derivatization of [2,3]-Rearrangement Product



To demonstrate the synthetic utility of the [1,2]-rearrangement products, we incorporated this transformation into the first total synthesis of the indole alkaloid sorazolon B, which enabled a stereochemical reassignment of the natural product's structure that was reported in the original isolation paper (Scheme 3).²⁴ To commence the total synthesis, 3-(methoxymethyl)-1-tosyl-1*H*-indole (**1a**) was coupled with diazoester **2a** under the [1,2]-rearrangement conditions to furnish benzylester **3a** in 82% yield and >95:5 rr. The efficiency of the reaction was maintained on gram scale. A two-step procedure converted benzylester **3a** to Weinreb amide **17**. Subsequent removal of the *N*-tosyl group provided *N*-H indole **18** in 93% yield. To access the

relative configuration for the proposed structure of sorazolon B (**21**), we treated Weinreb amide **18** first with ethynylmagnesium bromide followed by methylmagnesium bromide, which generated tertiary alcohol **19** in 19:1 dr and 57% yield over the two steps. The relative configuration of the major diastereomer, which was confirmed by X-ray crystallography, was consistent with a Felkin-Anh addition of methylmagnesium bromide.²⁵ Alcohol **19** was then converted to diol **20**, which was subjected to gold catalyzed 6-endo cyclization.²⁶ Although the resulting tricyclic skeleton of **21** was consistent with the proposed structure of sorazolon B, the NMR data of our synthetic sample did not match the corresponding data for the natural product.

Scheme 3. Synthesis and Stereochemical Reassignment of (±)-Sorazolon B via [1,2]-Rearrangement



We hypothesized that the relative configuration of the two stereogenic centers in sorazolon B may have been misassigned. To test this hypothesis, we switched the order of addition of Grignard reagents to Weinreb amide **18**. Initial addition of methylmagnesium bromide followed by Felkin-Anh addition of ethynylmagnesium bromide yielded tertiary alcohol **22** in 9:1 dr. The relative configuration of the major diastereomer was confirmed by X-ray crystallography. Treatment of methyl ether **22** with bromodimethylborane and 2-methyl-2-butene resulted in the formation of diol **23**. In the presence of $\text{Au}(\text{MeCN})\text{SbF}_6$ and JohnPhos, diol **23** was converted to tricycle **24**, which had spectroscopic data that were identical with the data reported for sorazolon B in the original isolation paper.²⁴

CONCLUSION

We have developed catalyst-controlled regiodivergent rearrangements of onium-ylides derived from indole methylethers and diazoesters. Whereas a copper catalyst promotes a regioselective [1,2]-rearrangement, a rhodium catalyst facilitates a regioselective and diastereoselective [2,3]-rearrangement. We present experimental and computational studies that support divergent mechanistic pathways for the two rearrangement processes. We also describe the synthetic utility of the two rearrangements by demonstrating the functional group tolerance

and scope of the reactions, as well as transforming the rearrangement products to several indole-containing products. Finally, we applied the copper-catalyzed [1,2]-rearrangement in the first total synthesis of the indole alkaloid sorazolon B, which enabled the stereochemical reassignment of the natural product.

ASSOCIATED CONTENT

Supporting Information.

This material is available free of charge via the Internet at <http://pubs.acs.org>. Experimental details, characterization data, spectral data, and computational results.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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¹⁴ In addition, when two distinct substrates were simultaneously subjected to the [2,3]-rearrangement conditions, no crossover products were detected (see Supporting Information for details). These observations are consistent with a metal-free symmetry-allowed, concerted, and unimolecular process.

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which is used to more accurately capture dispersion effects, but the accuracy of the computed energies is limited because explicit solvent was not included.

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