OL | Organic Letters

Letter

Cite This: Org. Lett. 2019, 21, 9217−9222

pubs.acs.org/OrgLett

Rhodium(III)-Catalyzed Annulative Coupling of Sulfoxonium Ylides and Allenoates: An Arene C−H Activation/Cyclopropanation Cascade

Jiang Lou,[†,‡] Quannan Wang,[†,‡] Yong-Gui Zhou,*[,†] and Zhengkun Yu*[,†,§]

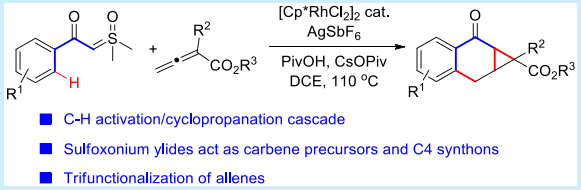
[†]Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China

[‡]University of Chinese Academy of Sciences, Beijing 100049, P. R. China

[§]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China

Supporting Information

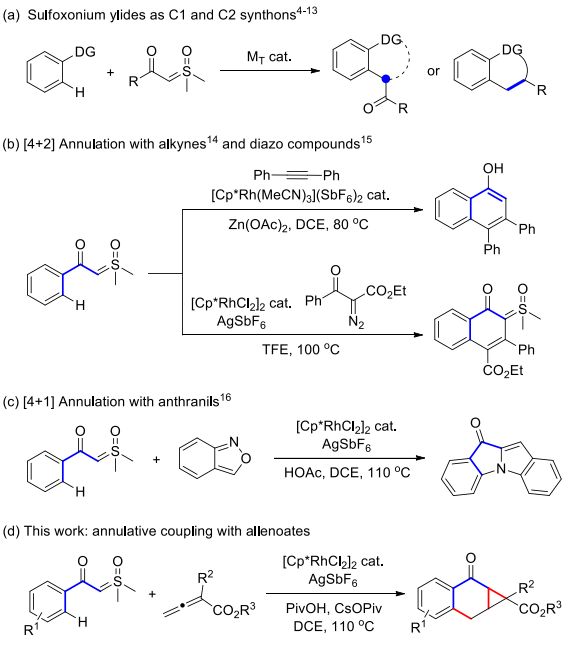
ABSTRACT: Rhodium(III)-catalyzed annulative coupling of sulfoxonium ylides with allenoates was achieved, forming highly functionalized cyclopropanes with a quaternary carbon center by means of the sulfoxonium ylide functionality as a traceless bifunctional directing group and C4 synthon via an arene C−H activation and cyclopropanation cascade. The protocol features simultaneous formation of three new C−C bonds in one pot with excellent diastereoselectivity. The resultant cyclopropanation products could be further transformed to diverse synthetically useful compounds.



Cyclopropane is a structural element in many biologically active compounds, and it can also act as a versatile building block in organic synthesis.[1] Many efforts have been devoted to the synthesis of cyclopropane derivatives by means of Simmons−Smith cyclopropanation reaction and the well-defined and most widely used transition-metal-catalyzed carbene transfer processes.[2] However, the carbene precursors, that is, diazo compounds, face the potential explosion issue and inconvenience to preserve, and the monosubstituted and aliphatic diazo compounds are hardly applicable.[2,3] Thus, development of new cyclopropanation methods with the suitable surrogates of diazo compounds has been highly desirable.

Sulfoxonium ylides have been widely used as the carbene surrogates in organic transformations under transition-metal catalysis due to their facile preparation and operational safety.[4] In this regard, a domino reaction strategy of transition-metal-catalyzed C−H activation and cyclization with sulfoxonium ylides has recently attracted much attention. Diverse carbene-involving methods have been developed to realize the acylmethylation of arenes[5] and synthesis of acyclic,[6] carbocyclic,[7] and heterocyclic compounds such as furans,[8] indoles,[9] quinolines,[10] pyrroles,[11] pyrimidines,[12] and others[13] by means of iridium, rhodium, ruthenium, cobalt, palladium, and other metal catalytic systems. In all these cases, sulfoxonium ylides served as the C1 or C2 synthons with the assistance of a nucleophilic directing group (Scheme 1a).[4−13] In 2017, Li et al. disclosed Rh(III)-catalyzed [4 + 2] annulation of sulfoxonium ylides with alkynes to afford naphthols by using sulfoxonium ylides as the C4 synthons,[14] and the Fan group reported the synthesis of highly functionalized naphthalenones via rhodium(III)-catalyzed [4 + 2] reaction of sulfoxonium ylides with α-diazocarbonyls[15] (Scheme 1b). Recently, rhodium(III)-catalyzed [4 + 1] annulation of sulfoxonium ylides with anthranils toward

Scheme 1. Catalytic Transformations of Sulfoxonium Ylides



Received: October 11, 2019
Published: November 5, 2019

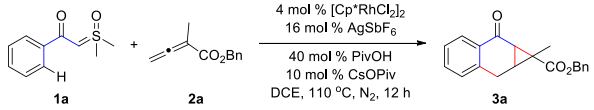
DOI: 10.1021/acs.orglett.9b03589
Org. Lett. 2019, 21, 9217−9222

indoloindolones was also achieved by Cheng et al. (Scheme 1c).[16] Continuous efforts have been made to explore the coupling partners for these reactions, including internal alkynes, diazo compounds, or *N*,*O*-heterocycles. Although much progress has been achieved, the development of other coupling partners is still highly desirable. Allenes have been proved to be highly valuable building blocks for the construction of complex molecules.[17] However, transition-metal-catalyzed cyclopropanation of allenes has seldomly been documented.[17,18] All the attempts within this category were focused on the intramolecular cyclization of allenes[19] and their intermolecular reactions with diazo compounds.[20]

Taking into account the development of new cyclopropanation methods, the potential application of sulfoxonium ylides in the synthesis of cyclic compounds, and our interest in domino reactions of allenes involving C−H and C−S bond activation,[21] we envisioned that a transition-metal-catalyzed C−H activation and cyclopropanation cascade might be established by the precise combination of the allene and sulfoxonium ylide substrates and rendering the latter to serve as both the traceless bifunctional directing group and a carbene precursor. Herein, we disclose rhodium(III)-catalyzed annulative coupling of sulfoxonium ylides with allenoates through an arene C−H activation/cyclopropanation cascade toward the synthesis of 2*H*-cyclopropa[*b*]-naphthalen-2-ones bearing three continuous stereogenic centers including a quaternary carbon atom (Scheme 1d).

Initially, the reaction of benzoyl sulfoxonium ylide (**1a**) with benzyl 2-methylbuta-2,3-dienoate (**2a**) was conducted to screen the reaction conditions (Table 1). After systematic

Table 1. Optimization of the Reaction Conditions[a]



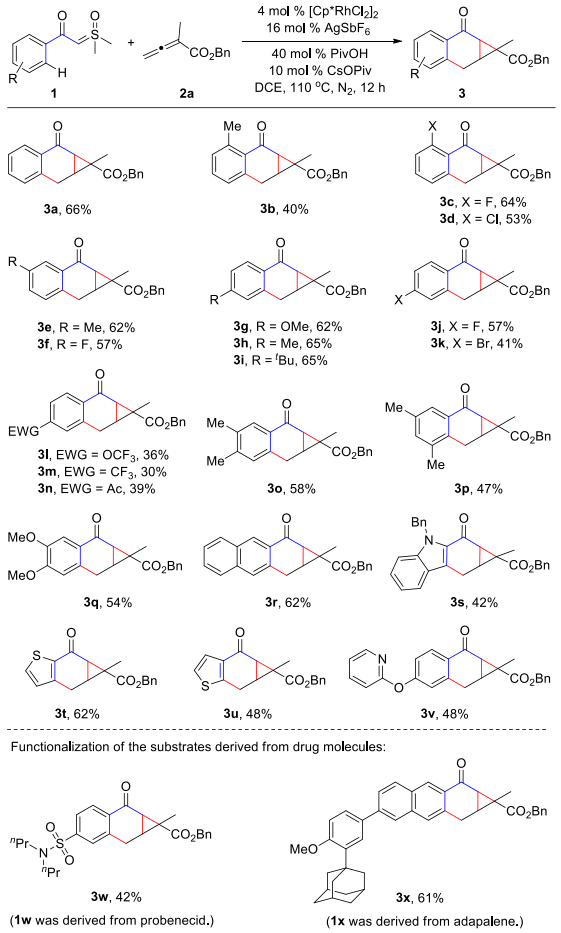
entry	variation	yield[b] (%)
1	none	66 (62)[c]
2	$[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %)	66
3	$[Cp^*RhCl_2]_2$ (3 mol %), $AgSbF_6$ (12 mol %)	59
4	PivOH (1 equiv)	62
5	PivOH (2 equiv)	55
6	**2a** (3 equiv)	63
7	120 °C	66
8	100 °C	57
9	without $[Cp^*RhCl_2]_2$	0
10	without $AgSbF_6$	trace
11	without PivOH	trace
12	without CsOPiv	40

[a]Conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), PivOH (40 mol %), CsOPiv (10 mol %), DCE (3 mL). [b]Isolated yields. [c]**1a** (1 mmol), **2a** (2 mmol), and DCE (10 mL). DCE = 1,2-dichloroethane.

experiments, the optimal reaction conditions were identified (see the Supporting Information for details). In the presence of 4 mol % of $[Cp^*RhCl_2]_2$/16 mol % of $AgSbF_6$ with 40 mol % of PivOH and 10 mol % of CsOPiv as the additives in 1,2-dichloroethane (DCE) at 110 °C, the reaction gave the target product **3a** as a single diastereomer in 66% yield, and **3a** could be obtained in 62% yield on a 1 mmol scale (Table 1, entry 1). The yield could not be further improved by increasing the catalyst loading (Table 1, entry 2) but using less amount of the catalyst, or an excessive amount of the acid PivOH diminished the yield to 55−62% (Table 1, entries 3−5). Increasing the loading of allenoate **2a** or elevating the reaction temperature could not further enhance the reaction efficiency either, while lowering the temperature to 100 °C led to the product in 57% yield (Table 1, entries 6−8). Other acids and additives proved to be much less effective (see the Supporting Information for details). The control experiments revealed that the rhodium(III) catalyst, silver salt, and acid were essential for the reaction (Table 1, entries 9−11). It is noteworthy that the reaction was obviously inhibited to form **3a** in only 40% yield in the absence of cesium trimethyl acetate (CsOPiv) (Table 1, entry 12). The asymmetric synthesis of polysubstituted cyclopropanes was also tried by adding various chiral ligands such as chiral BINOL-based Brønsted acids, C_2-symmetric carboxylic acids, and chiral phosphine ligands in the reaction system,[22] but no enantioselectivity was observed for the isolated product (see the Supporting Information for details).

Under the optimized reaction conditions, the protocol generality was explored by means of a variety of aroyl- and heteroaroyl-based sulfoxonium ylides to react with **2a** (Scheme 2). A negative steric effect was observed from the *o*-Me substituent in the aroyl moiety of the *ortho*-methyl-benzoyl

Scheme 2. Scope of Sulfoxonium Ylides (1)[a]



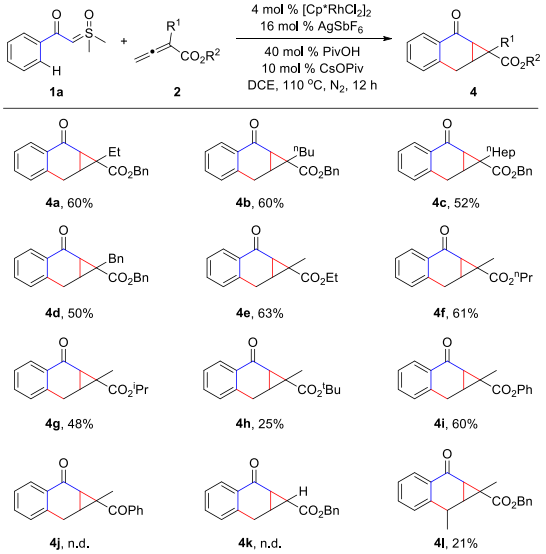
[a]Conditions: **1** (0.3 mmol), **2a** (0.6 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), PivOH (40 mol %), CsOPiv (10 mol %), and DCE (3 mL).

DOI: 10.1021/acs.orglett.9b03589
Org. Lett. 2019, 21, 9217−9222

sulfoxonium ylide **1b**, and its reaction with **2a** gave the target product **3b** in 40% yield. The *ortho*-fluoro group only exhibited a negligible steric effect, leading to the corresponding product **3c** (64%), while *ortho*-chloro-functionalized sulfoxonium ylide **1d** gave the target product **3d** in 53% yield. *meta*-Methyl- and fluoro-substituted benzoyl sulfoxonium ylides could be effectively converted to products **3e** and **3f** (57−62%). Introducing an electron-donating group such as methoxy, methyl, and *tert*-butyl or a fluoro substituent to the *para*-position of the phenyl ring rendered the reaction to give products **3g**−**3j** in 57−65% yields, whereas 4-Br and the electron-withdrawing groups such as trifluoromethoxy, trifluoromethyl, and acetyl showed an obvious negative electronic impact on the product yields of **3k**−**3n** (30−41%), suggesting that the reaction is highly dependent on the steric and electronic effects from the aroyl-based sulfoxonium ylide substrates. Dimethyl- and dimethoxy-substituted benzoyl sulfoxonium ylides afforded the corresponding cyclopropanation products **3o**−**3q** in moderate yields (47−58%). 2-Naphthoyl sulfoxonium ylide (**1r**) could also efficiently react with **2a** to execute the C−H activation at the less sterically hindered 3-position, affording product **3r** in 62% yield. The heterocyclic substrates, that is, *N*-benzyl-2-indoloyl, 2-thienoyl, and 3-thienoyl-based sulfoxonium ylides, reacted under the same conditions to form the target products **3s**−**3u** in 42−62% yields. The 4-(2-pyridyloxy)-bearing benzoyl sulfoxonium ylide (**1v**) underwent the cyclopropanation reaction selectively at the *ortho* position of the carbonyl group, giving **3v** in 48% yield, although the pyridyloxy moiety could act as a potential directing group for the C−H activation procedure. This result implicates that the C−H activation/cyclopropanation sequence can overcome the limitation of C−H activation involving strong coordinating *N*-heterocycle functionalities.[23] The potential utility of the synthetic protocol was exemplified by functionalizing the ylide substrates **1w** and **1x** derived from the drug molecules such as probenecid and adapalene, affording the target products **3w** and **3x** in 42−61% yields.

Next, the scope of allenoates was investigated in the reaction with benzoyl sulfoxonium ylide (**1a**) (Scheme 3). 2-Ethyl- and *n*-butyl-substituted allenoates **2b** and **2c** underwent the reaction smoothly to afford the target products **4a** (60%) and **4b** (60%), respectively, while 2-(*n*-heptyl) and benzyl substituents exhibited a negative steric effect on the product yields of **4c** and **4d** (50−52%). Both ethyl and *n*-propyl 2-methylbuta-2,3-dienoates **2f** and **2g** also reacted with **1a** under the stated conditions, giving the corresponding cyclopropanation products **4e** (63%) and **4f** (61%). *iso*-Propoxycarbonyl and *tert*-butoxycarbonyl functionalities on the allene backbone exhibited an obvious steric impact on the reaction efficiency to render the formation of **4g** and **4h** in low to moderate yields (25−48%). However, phenyl 2-methylbuta-2,3-dienoate (**2j**) could efficiently react to give the target cyclopropanation product **4i** in 60% yield. Unexpectedly, neither allenone **2k** nor the unsubstituted allenoate **2l** could undergo the cyclopropanation reaction to afford the products **4j** and **4k**, respectively, under the standard conditions, indicating the necessity of both the alkyl and ester groups at the same terminus of the allene backbone. The ester group may weakly coordinate with the catalytically active metal center, and the alkyl group exhibits a steric effect, which ensures the regioselectivity of the reaction. The 4-methyl-substituted allenoate **2m** exhibited a negative steric effect, leading to the target product **4l** in 21% yield. It is noteworthy that all the

Scheme 3. Scope of Allenoates (2)[a]

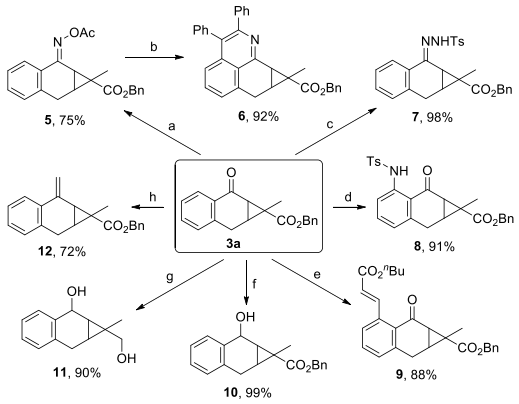


[a]Conditions: **1a** (0.3 mmol), **2** (0.6 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), PivOH (40 mol %), CsOPiv (10 mol %), and DCE (3 mL).

cyclopropanation products **3** and **4** were obtained as the single diastereomers. In addition, the molecular structures of the target products were further confirmed by the X-ray single-crystal structural determination of compound **4e** (see the Supporting Information for details).

Further derivatizations of the cyclopropanation products were performed to demonstrate the potential applications of the present synthetic method (Scheme 4). Treatment of **3a**

Scheme 4. Derivatizations of Cyclopropanation Product 3a[a]



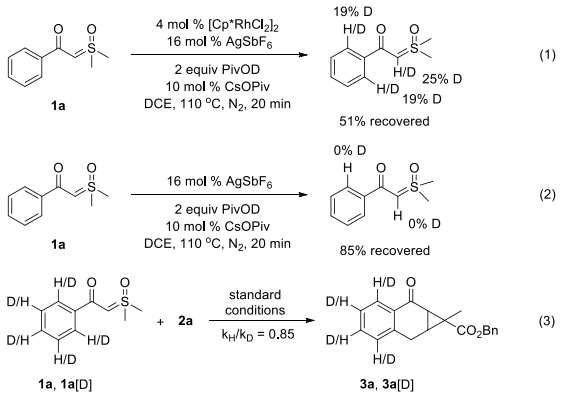
[a]Conditions: (a) **3a** (3 mmol), $NH_2OH{\cdot}HCl$ (2 equiv), pyridine (1 mL), EtOH (2 mL), 60 °C, 1 h, then Ac_2O (2 equiv), DMAP (10 mol %), pyridine (3 mL), rt, 1 h; (b) **5** (0.2 mmol), diphenylacetylene (1.2 equiv), $[Cp^*RhCl_2]_2$ (2.5 mol %), NaOAc (30 mol %), MeOH (1 mL), 60 °C, N_2, 12 h; (c) **3a** (2 mmol), $TsNHNH_2$ (1 equiv), MeOH (5 mL), 60 °C, 36 h; (d) **3a** (0.2 mmol), *p*-toluenesulfonyl azide (1 equiv), $[Cp^*IrCl_2]_2$ (4 mol %), $AgNTf_2$ (16 mol %), HOAc (15 mol %), Li_2CO_3 (15 mol %), DCE (1 mL), 50 °C, N_2, 12 h; (e) **3a** (0.2 mmol), *n*-butyl acrylate (3 equiv), $[Cp^*RhCl_2]_2$ (2 mol %), $AgSbF_6$ (8 mol %), $Cu(OAc)_2$ (1.2 equiv), 1,4-dioxane (1 mL), 120 °C, N_2, 5 h; (f) **3a** (0.2 mmol), $NaBH_4$ (1.01 equiv), MeOH (2 mL), rt, N_2, 20 min; (g) **3a** (0.2 mmol), $LiAlH_4$ (2 equiv), THF (2 mL), rt, N_2, 20 min; (h) **3a** (0.2 mmol), methyltriphenylphosphonium bromide (1.5 equiv), ^{t}BuOK (1.5 equiv), THF (3 mL), rt, N_2, 40 min.

DOI: 10.1021/acs.orglett.9b03589
Org. Lett. 2019, 21, 9217−9222

with hydroxylamine hydrochloride and acetic anhydride afforded *O*-acetyl oxime ester **5** in 75% yield, which proved to be a useful building block in transition-metal-catalyzed cross coupling.[24] Thus, fused 8,9-dihydro-7*H*-benzo[*de*]quinoline (**6**) was efficiently synthesized in 92% yield via rhodium(III)-catalyzed *ortho*-C−H activation of the intermediate compound **5**. **3a** was quantitatively converted to *N*-tosylhydrazone **7**, which can serve as a versatile carbene precursor.[2] The ketone carbonyl of **3a** can act as an effective directing group which enabled efficient amination and alkenylation at the *ortho*-C−H position of the aryl moiety under iridium(III) or rhodium(III) catalysis, giving the corresponding products **8** and **9** in 88−91% yields, respectively. The ketone carbonyl of **3a** was selectively reduced to hydroxyl with $NaBH_4$ as the reductant, and the ester group could be further reduced by $LiAlH_4$ to give diol **11** (90%). Compound **3a** underwent the Wittig reaction with methyltriphenylphosphonium bromide to afford alkene **12** (72%) with tolerance of the ester group. It is noteworthy that all the products **5**−**12** were obtained as the single diastereomers.

Control experiments were then conducted to probe into the reaction mechanism (Scheme 5). Deuterium incorporation was

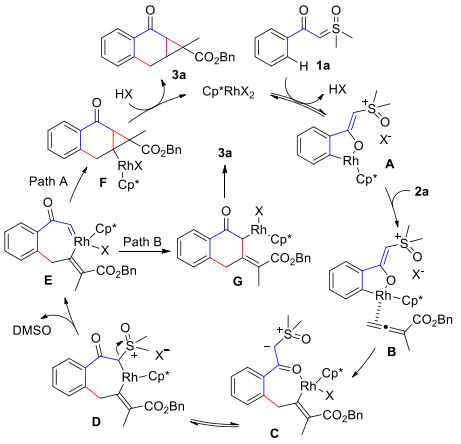
Scheme 5. Control Experiments



observed at the *ortho*-C−H position of the phenyl functionality and the *α*-position of the carbonyl in **1a** when it was treated with deuterated pivalic acid (PivOD, 2 equiv) in the absence of an allenoate substrate (eq 1), while no deuterium incorporation occurred in the absence of the Rh(III) catalyst (eq 2). These results indicate that the C−H bond cleavage process is reversible during the reaction.[14−16] The kinetic isotope effect (KIE) was measured from the parallel reactions of **1a** and its deuterated form **1a**[D] with **2a** (eq 3), and a primary isotope effect was observed with k_H/k_D = 0.85, suggesting that C−H bond activation/cleavage is not likely involved in the rate-determining step in the overall catalytic cycle.

A plausible mechanism is proposed in Scheme 6.[14−16] Initially, interaction of benzoyl sulfoxonium ylide **1a** and the Rh(III) catalyst generates the five-membered rhodacycle complex **A** via arene C−H activation. Coordination of allenoate **2a** to the rhodium center forms species **B**, followed by C═C insertion into the Rh−C bond to form the Rh(III)−sulfoxonium ylide complex intermediate **C**. Intramolecular rearrangement gives species **D** which releases DMSO to yield the rhodium carbenoid intermediate **E**. Intramolecular cyclopropanation thus occurs to form species **F** (Path A), which is then protonated to produce the target product **3a** and regenerate the catalyst, establishing a catalytic annulative

Scheme 6. Proposed Mechanism



coupling cycle. Species **E** may also undergo migratory insertion to furnish the [4 + 2] annulation toward intermediate **G** (Path B), followed by intramolecular nucleophilic attack of the *α*-C at the proximal carbon to give the target product **3a**.

In summary, a Rh(III)-catalyzed annulative coupling of sulfoxonium ylides with allenoates was successfully developed to access 2*H*-cyclopropa[*b*]naphthalen-2-ones with excellent diastereoselectivity via an arene C−H activation/cyclopropanation cascade. The protocol features construction of three new C−C bonds to deliver highly functionalized tricyclic carbocycles in one pot, exhibiting high compatibility with functional groups and broad substrate scopes. The resultant cyclopropanation products can be readily converted to potentially important synthetic intermediates under mild conditions. This work provides a useful method to access carbocycle-fused cyclopropane derivatives.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b03589.

Experimental materials and procedures, NMR of compounds, and X-ray crystallographic analysis (PDF)

Accession Codes

CCDC 1868910 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: zkyu@dicp.ac.cn.
*E-mail: ygzhou@dicp.ac.cn.

ORCID

Jiang Lou: 0000-0002-5653-1359
Quannan Wang: 0000-0002-4136-0016
Yong-Gui Zhou: 0000-0002-3321-5521
Zhengkun Yu: 0000-0002-9908-0017

DOI: 10.1021/acs.orglett.9b03589
Org. Lett. 2019, 21, 9217−9222

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China (21672209 and 21871253) and the National Basic Research Program of China (2015CB856600) for financial support of this research.

■ REFERENCES

(1) (a) Ebner, C.; Carreira, E. M. Cyclopropanation Strategies in Recent Total Syntheses. *Chem. Rev.* **2017**, *117*, 11651−11679. (b) Dalpozzo, R.; Lattanzi, A.; Pellissier, H. Applications of Chiral Three-membered Rings for Total Synthesis: A Review. *Curr. Org. Chem.* **2017**, *21*, 1143−1191. (c) Ganesh, V.; Chandrasekaran, S. Recent Advances in the Synthesis and Reactivity of Vinylcyclopropanes. *Synthesis* **2016**, *48*, 4347−4380.

(2) (a) Dian, L. Y.; Marek, I. Asymmetric Preparation of Polysubstituted Cyclopropanes Based on Direct Functionalization of Achiral Three-Membered Carbocycles. *Chem. Rev.* **2018**, *118*, 8415−8434. (b) Wu, W. Q.; Lin, Z. M.; Jiang, H. F. Recent Advances in the Synthesis of Cyclopropanes. *Org. Biomol. Chem.* **2018**, *16*, 7315−7329. (c) Xia, Y.; Wang, J. B. *N*-Tosylhydrazones: Versatile Synthons in the Construction of Cyclic Compounds. *Chem. Soc. Rev.* **2017**, *46*, 2306−2362. (d) Gurmessa, G. T.; Singh, G. S. Recent Progress in Insertion and Cyclopropanation Reactions of Metal Carbenoids from α-Diazocarbonyl Compounds. *Res. Chem. Intermed.* **2017**, *43*, 6447−6504.

(3) Proctor, L. D.; Warr, A. J. Development of a Continuous Process for the Industrial Generation of Diazomethane. *Org. Process Res. Dev.* **2002**, *6*, 884−892.

(4) (a) Vaitla, J.; Bayer, A.; Hopmann, K. H. Vinyl Sulfoxonium Ylide: A New Vinyl Carbenoid Transfer Reagent for the Synthesis of Heterocycles. *Synlett* **2019**, *30*, 1377−1383. (b) Wu, X. P.; Sun, S.; Yu, J.-T.; Cheng, J. Recent Applications of α-Carbonyl Sulfoxonium Ylides in Rhodium and Iridium-Catalyzed C−H Functionalizations. *Synlett* **2019**, *30*, 21−29. (c) Vaitla, J.; Bayer, A. Sulfoxonium Ylide Derived Metal Carbenoids in Organic Synthesis. *Synthesis* **2019**, *51*, 612−628. (d) Neuhaus, J. D.; Oost, R.; Merad, J.; Maulide, N. Sulfur-Based Ylides in Transition-Metal-Catalysed Processes. *Top. Curr. Chem.* **2018**, *376*, 15. (e) Lu, L.-Q.; Li, T.-R.; Wang, Q.; Xiao, W.-J. Beyond Sulfide-Centric Catalysis: Recent Advances in the Catalytic Cyclization Reactions of Sulfur Ylides. *Chem. Soc. Rev.* **2017**, *46*, 4135−4149.

(5) (a) Yu, J.; Wen, S.; Ba, D.; Lv, W. W.; Chen, Y. H.; Cheng, G. L. Rhodium(III)-Catalyzed Regioselective C3−H Acylmethylation of [2,2′-Bipyridine]-6-carboxamides with Sulfoxonium Ylides. *Org. Lett.* **2019**, *21*, 6366−6369. (b) Ji, S. Y.; Yan, K. L.; Li, B.; Wang, B. Q. Cp*Co(III)-Catalyzed C−H Acylmethylation of Arenes by Employing Sulfoxonium Ylides as Carbene Precursors. *Org. Lett.* **2018**, *20*, 5981−5984. (c) You, C.; Pi, C.; Wu, Y. J.; Cui, X. L. Rh(III)-Catalyzed Selective C8−H Acylmethylation of Quinoline *N*-Oxides. *Adv. Synth. Catal.* **2018**, *360*, 4068−4072. (d) Barday, M.; Janot, C.; Halcovitch, N. R.; Muir, J.; Aïssa, C. Cross-Coupling of α-Carbonyl Sulfoxonium Ylides with C−H Bonds. *Angew. Chem., Int. Ed.* **2017**, *56*, 13117−13121. (e) Xu, Y. W.; Zhou, X. K.; Zheng, G. F.; Li, X. W. Sulfoxonium Ylides as a Carbene Precursor in Rh(III)-Catalyzed C−H Acylmethylation of Arenes. *Org. Lett.* **2017**, *19*, 5256−5259.

(6) (a) Li, C. S.; Li, M.; Zhong, W. T.; Jin, Y. B.; Li, J. X.; Wu, W. Q.; Jiang, H. F. Palladium-Catalyzed Oxidative Allylation of Sulfoxonium Ylides: Regioselective Synthesis of Conjugated Dienones. *Org. Lett.* **2019**, *21*, 872−875. (b) Neuhaus, J. D.; Bauer, A.; Pinto, A.; Maulide, N. A Catalytic Cross-Olefination of Diazo Compounds with Sulfoxonium Ylides. *Angew. Chem., Int. Ed.* **2018**, *57*, 16215−16218. (c) Yuan, Y.; Wu, X.-F. Direct Access to 1,1-Dicarbonyl Sulfoxonium Ylides from Aryl Halides or Triflates: Palladium-Catalyzed Carbonylation. *Org. Lett.* **2019**, *21*, 5310−5314. (d) Yuan, Y.; Wu, X.-F. Synthesis of Esters from Stable and Convenient Sulfoxonium Precursors under Catalyst- and Additive-Free Conditions. *Synlett* **2019**, *30*, 1820−1824.

(7) (a) Clare, D.; Dobson, B. C.; Inglesby, P. A.; Aïssa, C. Chemospecific Cyclizations of α-Carbonyl Sulfoxonium Ylides on Aryls and Heteroaryls. *Angew. Chem., Int. Ed.* **2019**, *58*, 16198−16202. (b) Hu, P. J.; Zhang, Y.; Xu, Y. W.; Yang, S.; Liu, B. X.; Li, X. W. Construction of (Dihydro)naphtho[1,8-*bc*]pyrans *via* Rh(III)-Catalyzed Twofold C−H Activation of Benzoylacetonitriles. *Org. Lett.* **2018**, *20*, 2160−2163. (c) Zhou, C. F.; Fang, F. F.; Cheng, Y. L.; Li, Y. Z.; Liu, H.; Zhou, Y. Rhodium(III)-Catalyzed C−H Activation of Benzoylacetonitriles and Cyclization with Sulfoxonium Ylides to Naphthols. *Adv. Synth. Catal.* **2018**, *360*, 2546−2551. (d) Wang, P. Y.; Xu, Y. W.; Sun, J. Q.; Li, X. W. Rhodium(III)-Catalyzed Chemodivergent Couplings of Sulfoxonium Ylides with Oxa/azabicyclic Olefins. *Org. Lett.* **2019**, *21*, 8459−8463.

(8) Wen, S.; Lv, W. W.; Ba, D.; Liu, J.; Cheng, G. L. Ruthenium(II)-Catalyzed Chemoselective Deacylative Annulation of 1,3-Diones with Sulfoxonium Ylides *via* C−C Bond Activation. *Chem. Sci.* **2019**, *10*, 9104−9108.

(9) (a) Lai, R. Z.; Wu, X. H.; Lv, S. Y.; Zhang, C.; He, M. Y.; Chen, Y. C.; Wang, Q. T.; Hai, L.; Wu, Y. Synthesis of Indoles and Quinazolines *via* Additive-Controlled Selective C−H Activation/Annulation of *N*-Arylamidines and Sulfoxonium Ylides. *Chem. Commun.* **2019**, *55*, 4039−4042. (b) Wu, C. L.; Zhou, J. H.; He, G. X.; Li, H. H.; Yang, Q. L.; Wang, R.; Liu, H. Ruthenium(II)-Catalyzed Selective C−H Bond Activation of Imidamides and Coupling with Sulfoxonium Ylides: An Efficient Approach for the Synthesis of Highly Functional 3-Ketoindoles. *Org. Chem. Front.* **2019**, *6*, 1183−1188. (c) Hu, P. J.; Zhang, Y.; Liu, B. X.; Li, X. W. Facile Construction of Hydrogenated Azepino[3,2,1-*hi*]indoles by Rh(III)-Catalyzed C−H Activation/[5 + 2] Annulation of *N*-Cyanoacetylindolines with Sulfoxonium Ylides. *Org. Chem. Front.* **2018**, *5*, 3263−3266. (d) Vaitla, J.; Bayer, A.; Hopmann, K. H. Synthesis of Indoles and Pyrroles Utilizing Iridium Carbenes Generated from Sulfoxonium Ylides. *Angew. Chem., Int. Ed.* **2017**, *56*, 4277−4281.

(10) (a) Chen, P.; Nan, J.; Hu, Y.; Ma, Q.; Ma, Y. M. Ru^{II}-Catalyzed/NH_2-Assisted Selective Alkenyl C−H [5 + 1] Annulation of Alkenylanilines with Sulfoxonium Ylides to Quinolines. *Org. Lett.* **2019**, *21*, 4812−4815. (b) Xu, Y. W.; Zheng, G. F.; Yang, X. F.; Li, X. W. Rhodium(III)-Catalyzed Chemodivergent Annulations Between *N*-Methoxybenzamides and Sulfoxonium Ylides *via* C−H Activation. *Chem. Commun.* **2018**, *54*, 670−673. (c) Wu, X. P.; Xiong, H.; Sun, S.; Cheng, J. Rhodium-Catalyzed Relay Carbenoid Functionalization of Aromatic C−H Bonds toward Fused Heteroarenes. *Org. Lett.* **2018**, *20*, 1396−1399.

(11) Vaitla, J.; Bayer, A.; Hopmann, K. H. Iron-Catalyzed Carbenoid-Transfer Reactions of Vinyl Sulfoxonium Ylides: An Experimental and Computational Study. *Angew. Chem., Int. Ed.* **2018**, *57*, 16180−16184.

(12) (a) Halskov, K. S.; Witten, M. R.; Hoang, G. L.; Mercado, B. Q.; Ellman, J. A. Rhodium(III)-Catalyzed Imidoyl C−H Activation for Annulations to Azolopyrimidines. *Org. Lett.* **2018**, *20*, 2464−2467. (b) Hoang, G. L.; Streit, A. D.; Ellman, J. A. Three-Component Coupling of Aldehydes, Aminopyrazoles, and Sulfoxonium Ylides *via* Rhodium(III)-Catalyzed Imidoyl C−H Activation: Synthesis of Pyrazolo[1,5-*a*]pyrimidines. *J. Org. Chem.* **2018**, *83*, 15347−15360.

(13) (a) Zheng, G. F.; Tian, M. M.; Xu, Y. W.; Chen, X. H.; Li, X. W. Rhodium(III)-Catalyzed Annulative Coupling Between Arenes and Sulfoxonium Ylides *via* C−H Activation. *Org. Chem. Front.* **2018**, *5*, 998−1002. (b) Xie, H. S.; Lan, J. Y.; Gui, J.; Chen, F. J.; Jiang, H. F.; Zeng, W. Ru(II)-Catalyzed Coupling-Cyclization of Sulfoximines with *alpha*-Carbonyl Sulfoxonium Ylides as an Approach to 1,2-Benzothiazines. *Adv. Synth. Catal.* **2018**, *360*, 3534−3543. (c) Liang, Y.-F.; Yang, L.; Rogge, T.; Ackermann, L. Ruthenium(IV) Intermediates in C−H Activation/Annulation by Weak O-Coordination. *Chem. - Eur. J.* **2018**, *24*, 16548−16552. (d) Oh, H.; Han, S.; Pandey, A. K.; Han, S. H.; Mishra, N. K.; Kim, S.; Chun, R.; Kim, H. S.; Park, J.; Kim, I. S. Synthesis of (2*H*)-Indazoles through Rh(III)-

DOI: 10.1021/acs.orglett.9b03589
Org. Lett. 2019, 21, 9217−9222

Catalyzed Annulation Reaction of Azobenzenes with Sulfoxonium Ylides. *J. Org. Chem.* **2018**, *83*, 4070−4077.
(14) Xu, Y. W.; Yang, X. F.; Zhou, X. K.; Kong, L. H.; Li, X. W. Rhodium(III)-Catalyzed Synthesis of Naphthols *via* C−H Activation of Sulfoxonium Ylides. *Org. Lett.* **2017**, *19*, 4307−4310.
(15) Chen, X.; Wang, M. H.; Zhang, X. Y.; Fan, X. S. Rh(III)-Catalyzed Cascade Reactions of Sulfoxonium Ylides with α-Diazocarbonyl Compounds: An Access to Highly Functionalized Naphthalenones. *Org. Lett.* **2019**, *21*, 2541−2545.
(16) Wu, X. P.; Xiao, Y.; Sun, S.; Yu, J.-T.; Cheng, J. Rhodium-Catalyzed Reaction of Sulfoxonium Ylides and Anthranils toward Indoloindolones *via* a (4 + 1) Annulation. *Org. Lett.* **2019**, *21*, 6653−6657.
(17) (a) Mascarenas, J. L.; Varela, I.; López, F. Allenes and Derivatives in Gold(I)- and Platinum(II)-Catalyzed Formal Cycloadditions. *Acc. Chem. Res.* **2019**, *52*, 465−479. (b) Huang, X.; Ma, S. M. Allenation of Terminal Alkynes with Aldehydes and Ketones. *Acc. Chem. Res.* **2019**, *52*, 1301−1312. (c) Yang, B.; Qiu, Y. A.; Backvall, J. E. Control of Selectivity in Palladium(II)-Catalyzed Oxidative Transformations of Allenes. *Acc. Chem. Res.* **2018**, *51*, 1520−1531. (d) Holmes, M.; Schwartz, L. A.; Krische, M. J. Intermolecular Metal-Catalyzed Reductive Coupling of Dienes, Allenes, and Enynes with Carbonyl Compounds and Imines. *Chem. Rev.* **2018**, *118*, 6026−6052.
(18) (a) Shu, X. Z.; Shu, D.; Schienebeck, C. M.; Tang, W. Rhodium-Catalyzed Acyloxy Migration of Propargylic Esters in Cycloadditions, Inspiration from the Recent "Gold Rush". *Chem. Soc. Rev.* **2012**, *41*, 7698−7711. (b) Ma, S. M. Electrophilic Addition and Cyclization Reactions of Allenes. *Acc. Chem. Res.* **2009**, *42*, 1679−1688.
(19) (a) Ikeuchi, T.; Inuki, S.; Oishi, S.; Ohno, H. Gold(I)-Catalyzed Cascade Cyclization Reactions of Allenynes for the Synthesis of Fused Cyclopropanes and Acenaphthenes. *Angew. Chem., Int. Ed.* **2019**, *58*, 7792−7796. (b) Yasui, M.; Ota, R.; Tsukano, C.; Takemoto, Y. Total Synthesis of Avenaol. *Nat. Commun.* **2017**, *8*, 674. (c) Tang, Y.; Yu, Q.; Ma, S. M. Efficient Trifluoromethylation *via* the Cyclopropanation of Allenes and Subsequent C−C Bond Cleavage. *Org. Chem. Front.* **2017**, *4*, 1762−1767.
(20) (a) Chen, Y. Z.; Liu, T.; Zhu, J.; Zhang, H.; Wu, L. Transition-Metal-Free Radical Cleavage of a Hydrazonyl N−S Bond: Tosyl Radical-Initiated Cascade C(sp^3)−OAr Cleavage, Sulfonyl Rearrangement and Atropisomeric Cyclopropanation. *Org. Chem. Front.* **2018**, *5*, 3567−3573. (b) McCabe, S. R.; Wipf, P. Eight-Step Enantioselective Total Synthesis of (−)-Cycloclavine. *Angew. Chem., Int. Ed.* **2017**, *56*, 324−327. (c) Gregg, T. M.; Farrugia, M. K.; Frost, J. R. Rhodium-Mediated Enantioselective Cyclopropanation of Allenes. *Org. Lett.* **2009**, *11*, 4434−4436.
(21) (a) Wang, Q. N.; Lou, J.; Huang, Z. L.; Yu, Z. K. Rhodium(III)-Catalyzed Annulation of Acetophenone *O*-Acetyl Oximes with Allenoates through Arene C−H Activation: An Access to Isoquinolines. *J. Org. Chem.* **2019**, *84*, 2083−2092. (b) Wang, Q. N.; Liu, Z. Q.; Lou, J.; Yu, Z. K. Palladium-Catalyzed C−S Bond Cleavage with Allenoates: Synthesis of Tetrasubstituted 2-Alkenylfuran Derivatives. *Org. Lett.* **2018**, *20*, 6007−6011.
(22) Pesciaioli, F.; Dhawa, U.; Oliveira, J. C. A.; Yin, R. X.; John, M.; Ackermann, L. Enantioselective Cobalt(III)-Catalyzed C−H Activation Enabled by Chiral Carboxylic Acid Cooperation. *Angew. Chem., Int. Ed.* **2018**, *57*, 15425−15429.
(23) (a) Shang, M.; Wang, M.-M.; Saint-Denis, T. G.; Li, M.-H.; Dai, H.-X.; Yu, J.-Q. Copper-Mediated Late-Stage Functionalization of Heterocycle-Containing Molecules. *Angew. Chem., Int. Ed.* **2017**, *56*, 5317−5321. (b) Wang, H.; Lorion, M. M.; Ackermann, L. Overcoming the Limitations of C−H Activation with Strongly Coordinating *N*-Heterocycles by Cobalt Catalysis. *Angew. Chem., Int. Ed.* **2016**, *55*, 10386−10390.
(24) (a) Rej, S.; Chatani, N. Rhodium-Catalyzed C(sp^2)− or C(sp^3)−H Bond Functionalization Assisted by Removable Directing Groups. *Angew. Chem., Int. Ed.* **2019**, *58*, 8304−8329. (b) Piou, T.; Rovis, T. Electronic and Steric Tuning of a Prototypical Piano Stool Complex: Rh(III) Catalysis for C−H Functionalization. *Acc. Chem. Res.* **2018**, *51*, 170−180.

DOI: 10.1021/acs.orglett.9b03589
Org. Lett. 2019, 21, 9217−9222