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$RhCl_3·3H_2O$-Catalyzed Ligand-Enabled Highly Regioselective Thiolation of Acrylic Acids

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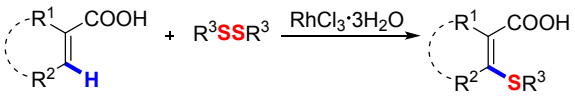
Supporting Information Placeholder

ABSTRACT: A simple inorganic rhodium salt $RhCl_3·3H_2O$ was used as the catalyst to achieve the thiolation of acrylic acids, with a series of (*Z*)-alkenyl sulfides obtained exclusively. It is noteworthy that $[Cp^*RhCl_2]_2$ was not as efficient as $RhCl_3·3H_2O$ in this strategy. Furthermore, the product could be transferred to biological and pharmacological thioflavone conveniently.

KEYWORDS: $RhCl_3·3H_2O$, carboxylate-directed, alkenyl sulfide, C-H activation, regioselectivity

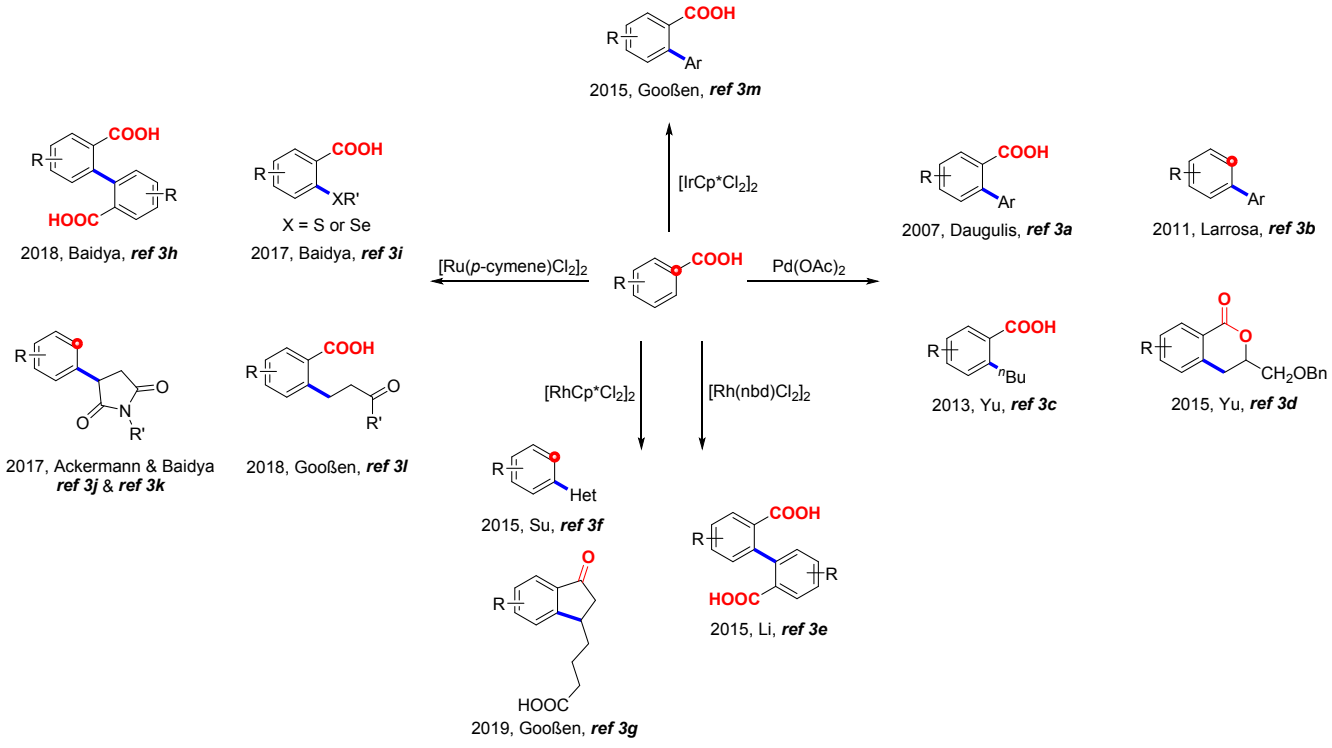


** Higher catalytic efficiency than $[Cp^*RhCl_2]_2$*
** Easier derivative carboxyl group as DG*

■ INTRODUCTION

C-H activation has attracted much attention in recent years due to its high atom economy and diversity of reaction, and has become one of the important strategies of organic synthesis. However, in order to ensure regioselectivity, directing group (DG) is usually indispensable. Strong directing groups such as pyridine, pyrimidine and 8-aminoquinoline were first used in C-H activation reactions.[1] Soon after, weak guiding groups such as oxime ether, ketone and amide have also been reported.[2] Since 2007, carboxyl group has been initially used as directing group of C-H activation reaction because of its non-toxicity, easy removal, widespread existence in nature and abundant derivative reactions. During the past decade, carboxyl group show extraordinary talents in this field. Palladium-, rhodium-, ruthenium- and iridium-catalyzed systems have been developed successfully to achieve arylation, alkylation, alkenylation, thiolation and selenation (Scheme 1).[3] Nevertheless, limited research has been conducted on non-aromatic $C(sp^2)$-H activation, and aromatic reaction still predominates in current research. Therefore, developing carboxylate-directed non-aromatic $C(sp^2)$-H activation has important practical significance.

$[Cp^*RhCl_2]_2$ (Cp^* = 1,2,3,4,5-pentamethylcyclopentadienyl) is the most used catalyst in existing rhodium-catalyzed C-H activation reactions. The Cp* ligand is believed to be helpful in stabilizing rhodium intermediates, as well as promoting eliminating processes due to the steric hindrance effect. Indeed, a large number of reported facts prove that the catalyst has high efficiency, regioselectivity and excellent functional group tolerance.[4] $[Cp^*RhCl_2]_2$ is generally prepared from the coordination reaction of $RhCl_3·3H_2O$ with excess 1,2,3,4,5-pentamethylcyclopentadiene in methanol under an inert atmosphere. However, as the precursor of $[Cp^*RhCl_2]_2$,

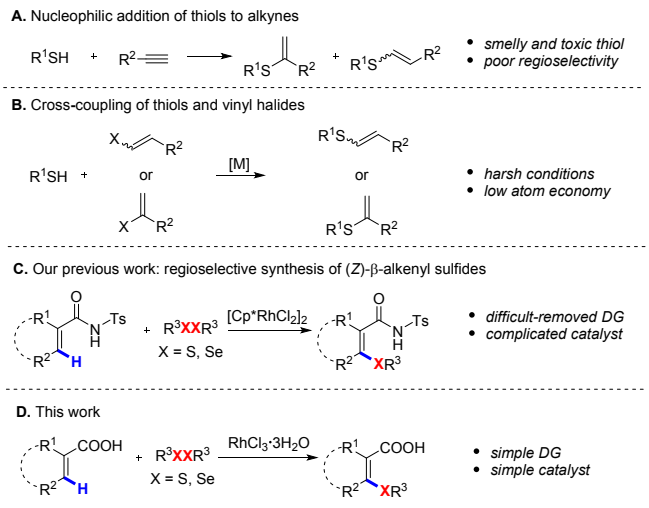


Scheme 1. Carboxylate-directed C-H activation of benzoic acids under Pd, Rh, Ru and Ir catalysis

$RhCl_3·3H_2O$ was used to be the catalyst of C-H activation rarely.[5] In 1990, the $RhCl(PPh_3)_3/Cu^{2+}$ redox couple was used in carboxylation of aromatic rings. Inspired by this work, Witulski and cooperators used $RhCl_3·3H_2O$ and Cu(II) salts to achieve intramolecular C-H/C-H Coupling.[6] Since then, there are only a few articles which have reported $RhCl_3·3H_2O$-catalyzed C-H activation and relevant research.[7]

Alkenyl sulfides are a class of important sulfur-containing compounds, which are widely used in organic synthesis, material science and biopharmaceuticals.[8] With the development of related research, its synthesis is becoming more simple and efficient. Initial synthetic strategies required unfriendly sulfur sources, low atomic economy, poor selectivity and harsh reaction conditions (Scheme 2, A & B),[9] but now these shortcomings have been overcome. In 2018, we reported an N-tosylamide-assisted synthesis of (*Z*)-β-alkenyl sulfides through $[Cp^*RhCl_2]_2$-catalyzed thiolation of alkenes with high efficiency and good substrate tolerance (Scheme 2, C).[10] However, we failed to remove the directing group, which hinders the subsequent application. Therefore, we hope to develop a system with directing group which is easier to remove or derive. Meanwhile, we also desire to apply $RhCl_3·3H_2O$ to this system with the help of ligand. Herein, we demonstrated a $RhCl_3·3H_2O$-catalyzed ligand-enabled highly regioselective thiolation of acrylic acids to afford (*Z*)-β-alkenyl sulfides(Scheme 2, D).

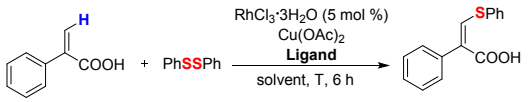
Scheme 2. Synthesis of alkenyl sulfides through different processes.



■ RESULTS AND DISCUSSION

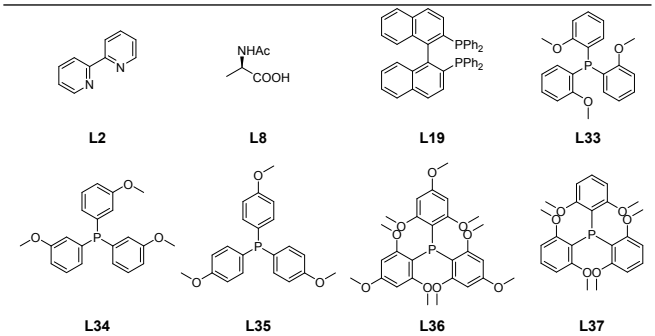
Initially, atropic acid **1a** and diphenyl disulfide **2a** were chose to investigate the reaction conditions (Table 1, see Supporting Information for more details). Rh catalyst could not be replaced by other transition metals such as Pd, Co, Ni, Ru. The reaction could not undergo in common solvents such as ether, benzene and alcohols other than amide solvents and MeCN. The amount and type of Cu salts are key factors of the reaction. The yield peaked when 1 equiv $Cu(OAc)_2$ was added (Table 1, entry 5). Subsequently, different ligands were applied to the reaction. Phosphine ligands were found to be beneficial to the reaction. The desired product could be obtained in 68% yield when 30 mol % tris(2,4,6-trimethoxyphenyl)phosphane (**L36**) was added. And the yield would increase to 71% when the amount of ligand reduced to 15 mol % (Table 1, entry 13). The increment of **2a** also brings the yield up to 75% further (Table 1, entry 16). By the following investigation, reaction time and temperature were determined to 6 h and 120 °C, respectively. Under this condition, the ligand was replaced by cheaper tris(2,6-dimethoxyphenyl)phosphane (**L37**), and the yield could still maintain at 79% (Table 1, entry 20). In addition, when $[Cp^*RhCl_2]_2$ was employed in this reaction, the yield decreased to 69% (Table 1, entry 21).

Table 1. Optimization of the Rh-catalyzed thiolation of 1a with 2a[a]



1a 2a 4a

Entry	$Cu(OAc)_2$ (mol %)	ligand	T (°C)	Time(h)	LC-Yield(%)[b]
1	/	/	120	12	0
2	10	/	120	12	17
3	20	/	120	12	27
4	50	/	120	12	40
5	100	/	120	12	49
6	150	/	120	12	38
7	100	**L2**	120	12	25
8	100	**L8**	120	12	25
9	100	**L19**	120	12	52
10	100	**L33**	120	12	57
11	100	**L34**	120	12	59
12	100	**L35**	120	12	37
13	100	**L36**	120	12	71
14	100	**L36**	80	12	Trace
15	100	**L36**	100	12	73
16[c]	100	**L36**	120	12	75
17[c]	100	**L36**	140	12	72
18[c]	100	**L36**	120	6	80
19[c]	100	**L36**	120	18	75
20[c]	100	**L37**	120	6	79(77[d])
21[c,e]	100	**L37**	120	6	69

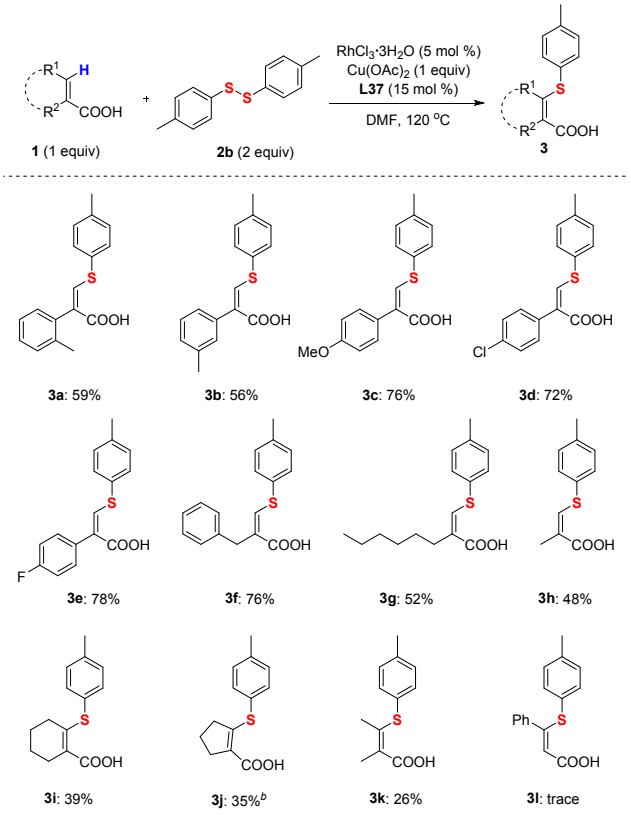


[a]Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.1 mmol, 1.0 equiv), $RhCl_3·3H_2O$ (5 mol %), ligand (15 mol %), $Cu(OAc)_2$(1 equiv), DMF (1 mL), 120 °C, 12 h. [b]LC yield using biphenyl as the internal standard. [c]PhSSPh 2 equiv. [d]Isolated yield. [e]$[Cp^*RhCl_2]_2$ (2.5 mol %). DMF = *N*,*N*-dimethylformamide.

With the optimal conditions in hand, we explored the substrate scope of acrylic acids (Table 2). *Ortho*- and *meta*-substituted substrates could undergo the reaction but the yield went down (**3a** and **3b**). Electron effect did not show obvious effect on this reaction, corresponding products were obtained in 72-78% yield,

respectively (**3c-3e**). Benzyl acrylic acid could also react smoothly with 76% yield (**3f**). Unactivated alkyl acrylic acids could also adapt to this system to give desired products in moderate yield (**3g** and **3h**). It is worth mentioning that this strategy could also be applied to the thiolation of nonterminal alkenes, although the yields were not so ideal (**3i-3k**). However, cinnamic acid could not afford products successfully (**3l**). We assume that it is due to the steric hindrance effect.

Table 2. Substrate scope of acrylic acids[a]

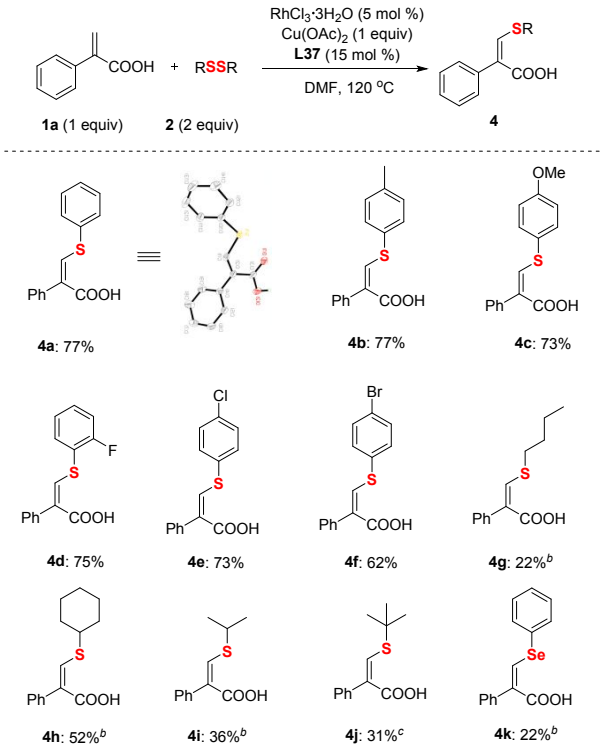


[a]Reaction conditions: **1** (0.3 mmol), **2b** (0.6 mmol), $RhCl_3{\cdot}3H_2O$ (5 mol %), $Cu(OAc)_2$ (1 equiv), **L37** (15 mol %), DMF (3 mL), 120 °C, 6 h. [b]140 °C, 12 h.

Next, we investigate the tolerance of disulfides (Table 3). For electron-rich substrates such as methyl- (**4b**) and methoxy- (**4c**), weak electron-deficient substrates such as F-, Cl-, Br-substituted disulfides (**4d-4f**), the reaction underwent smoothly, and the corresponding target products could be obtained in 62-77% yields, respectively. But for strong electron-deficient nitro-substituted disulfides, the reaction could not occur. For alkyl disulfides, the reaction temperature should be increased to 140 °C, and the yield decreased in varying degrees (**4g-4j**). We also tried to apply diselenides to this system, but the result was not ideal. The target product (**4k**) was merely obtained in 22% yield.

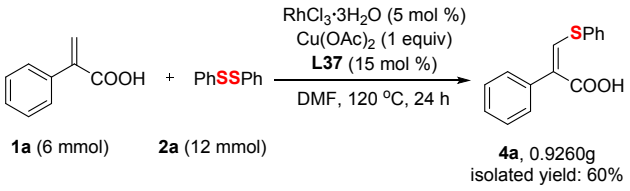
Meanwhile, we attempted to amplify the template reaction to gram level. With reaction time prolonged to 24 h, **4a** could be obtained in 60% isolated yield (scheme 3), which implies the possibility of large-scale industrial production.

Table 3. Substrate scope of disulfides[a]



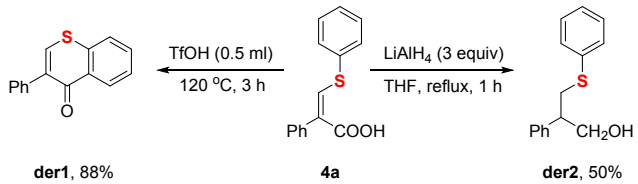
[a]Reaction conditions: **1** (0.3 mmol), **2b** (0.6 mmol), $RhCl_3{\cdot}3H_2O$ (5 mol %), $Cu(OAc)_2$ (1 equiv), L37 (15 mol %), DMF (3 mL), 120 °C, 6 h. [b]140 °C, 12 h. [c]$RhCl_3{\cdot}3H_2O$ (10 mol %), **L37** (30 mol %), 140 °C, 12 h.

Scheme 3. Scale-up synthesis.



Thioflavone is the core moiety of various natural products with biopharmaceutical activities. In addition, thioflavone and its oxide can be further derived to protect many light-unstable functional groups[11]. Based on the structure of aforementioned products, Friedel-Crafts acylation was considered to achieve the construction of thioflavone. When **4a** was stirred in 0.5 mL trifluoromethanesulfonic acid for 3 hours under 120 °C heating, the derivative thioflavone could be obtained in 88% yield. Meanwhile, **4a** was successfully reduced to corresponding alcohol in 50% yield (Scheme 4).

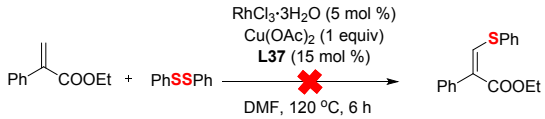
Scheme 4. Derivative reaction.



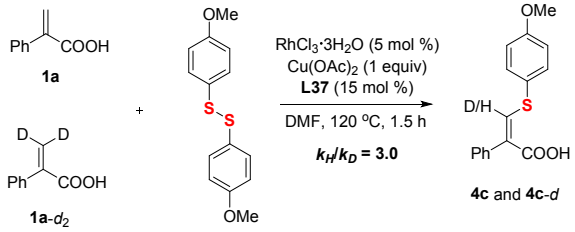
To explore the plausible mechanism, a series controlled experiments were conducted. Under standard condition, atropic acid **1a** was replaced by ethyl 2-phenylacrylate to undergo the reaction (Scheme 5, A). However, corresponding product was not obtained, which reveals the direction of carboxyl group is indispensable. At the same time, the path of Michael addition-elimination was ruled out. Next, we investigated Kinetic Isotope Effect (KIE) of the system (Scheme 5, B). Through a competitive experiment between **1a** and **1a-*d*$_2$**, the KIE value was calculated as 3.0, which suggested a concerted metalation deprotonation (CMD) process. In addition, it was found that a large amount of precipitate was produced after the reaction. The yellow precipitate is poorly soluble in organic solvents, but it can dissolve in concentrated acids to generate diphenyl disulfide. Therefore, we speculate that the solid may be a low valent copper species bound to disulfide. By X-ray photoelectron spectroscopy (XPS) characterization, from the survey spectrum (Scheme 6, a), we could confirm the existence of copper. From the high resolution XPS spectrum (Scheme 6, b), characteristic satellite peaks of Cu(II) (standard spectra see Scheme 6, c) did not appear, which indicated the precipitate did not contain Cu(II). By Auger Electron Spectroscopy (AES) characterization (Scheme 6, d), two groups of peaks were found, which reveals the existence of Cu(0) and Cu(I). That is to say, the precipitate is the mixture of low valence copper species.

Scheme 5. Controlled experiments.

A. Replaced by ethyl 2-phenylacrylate



B. Competitive experiment between 1a and 1a-*d*$_2$

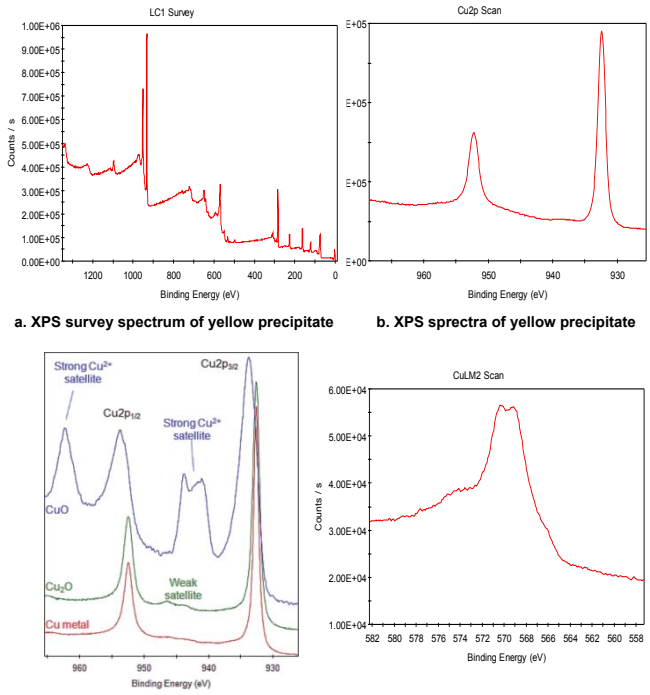


Based on above experimental results and related literatures, we proposed a plausible mechanism (Scheme 7). Ligand and $Cu(OAc)_2$ enabled $RhCl_3{\cdot}3H_2O$ to form the active Rh^{III} species **A**. **A** reacts with substrate **1a** to generate five-membered rhodacycle **B** through a CMD process. Then, product **4a** and intermediate **C** are obtained by the nucleophilic substitution of **B** and disulfide. At last, the active species **A** is regenerated through oxidation of inactive intermediate **C** by $Cu(OAc)_2$, and the low valence Cu species is formed simultaneously.

■ CONCLUSION

In summary, a $RhCl_3{\cdot}3H_2O$-Catalyzed thiolation of acrylic acids was reported. With higher efficiency than $[Cp^*RhCl_2]_2$, this strategy provides a novel way to construct C-S bond through C-H activation. The reaction can be successfully enlarged to gram scale, and the product can be efficiently converted into thioflavone with potential biopharmaceutical activity, which shows practical application in industrial production.

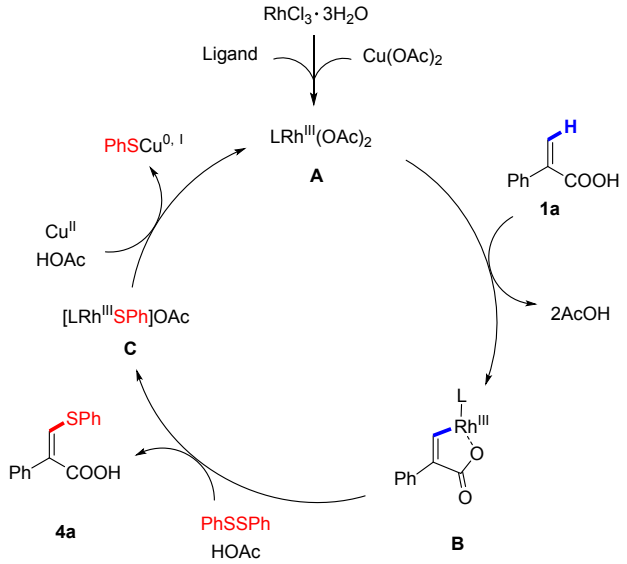
Scheme 6. XPS & AES spectra of yellow precipitate.



a. XPS survey spectrum of yellow precipitate b. XPS sprectra of yellow precipitate

c. Standard XPS spectra of different kinds of Cu d. AES sprectra of yellow precipitate

Scheme 7. Plausible mechanism.



■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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■ REFERENCES

(1) (a) Liu, T.; Zhou, W.; Wu, J. Palladium-Catalyzed Direct C–H Functionalization of Indoles with the Insertion of Sulfur Dioxide: Synthesis of 2-Sulfonated Indoles. *Org. Lett.*, **2017**, *19*, 6638−6641. (b) Parthasarathy, G.; Julian, K.; Lutz, A. Expedient C–H Chalcogenation of Indolines and Indoles by Positional-Selective Copper Catalysis. *ACS Catal*., **2017**, *7*, 1030–1034. (c) Lin, C.; Yu, W.-L.; Yao, J.-Z.; Wang, B.-J.; Liu, Z.-X.; Zhang, Y.-H. Nickel-Catalyzed Direct Thioetherification of β-C(sp^3)–H Bonds of Aliphatic Amides. *Org. Lett.* **2015,** *17,* 1340−1343. (d) Yan, S.-Y.; Liu, Y.-J.; Liu, B.; Liu, Y.-H.; Shi, B.-F. Nickel-catalyzed thiolation of unactivated aryl C–H bonds: efficient access to diverse aryl sulfides. *Chem. Commun.*, **2015**, *51*, 4069-4072.

(2) (a) Korkit, K.; Nikolaos, K.; Torben, R.; Svenja, W.; A. Claudia, S.; Lutz, A. Sequential meta-/ortho-C–H Functionalizations by One-Pot Ruthenium(II/III) Catalysis. *ACS Catal.* **2018**, *8*, 886−892. (b) Yuan, C.-C.; Zhu, L.; Zeng, R.-S.; Lan, Yu. Zhao, Y.-S. Ruthenium(II)-Catalyzed C−H Difluoromethylation of Ketoximes: Tuning the Regioselectivity from the meta to the para Position. *Angew. Chem. Int. Ed.* **2018**, *57*, 1277 –1281. (c) Hojoon, P.; Nikita, C.; Shen, P.-X.; Yu, J.-Q. Ligand-Enabled, Palladium-Catalyzed β-C(sp^3)–H Arylation of Weinreb Amides. *ACS Catal.* **2018**, *8*, 9292−9297. (d) Desta, D. B.; Cody, R. P.; Fereshte, G.; Stefan, A. H.; Joseph N. C.; Maxime, A. S.; Thomas, L. Ketones as directing groups in photocatalytic sp^3 C–H fluorination. *Chem. Sci.* **2017**, *8*, 6918-6923.

(3) (a) Hendrich, A. C.; Quynh-Nhu, P.; Olafs, D. Two Methods for Direct ortho-Arylation of Benzoic Acids. *J. Am. Chem. Soc*. **2007**, *129*, 9879-9884. (b) Josep, C.; Marika, R.; Igor, L. Carboxylic Acids as Traceless Directing Groups for Formal meta‐Selective Direct Arylation. *Angew. Chem. Int. Ed*. **2011**, *50*, 9429-9432. (c) Peter, S. T.-B.; Giorgio, V.; Devin, D.; Paul, R.; Su, S.; Yu, J.-Q. Ligand-Accelerated ortho-C–H Alkylation of Arylcarboxylic Acids using Alkyl Boron Reagents. *J. Am. Chem. Soc*. **2013**, *135*, 17508-17513. (d) Cheng, G.-L.; Li, T.-J.; Yu, J.-Q. Practical Pd(II)-Catalyzed C‐H Alkylation with Epoxides: One-Step Syntheses of 3,4-Dihydroisocoumarins. *J. Am. Chem. Soc.* **2015**, *137*, 10950-10953. (e) Gong, H.; Zeng, H.-Y.; Zhou, F.; Li, C.‐J. Rhodium(I)‐Catalyzed Regiospecific Dimerization of Aromatic Acids: Two Direct C-H Bond Activations in Water. *Angew. Chem. Int. Ed.* **2015**, *54*, 5718 - 5721. (f) Zhang, Y.-F.; Zhao, H.-Q.; Zhang, M.; Su, W.-P. Carboxylic Acids as Traceless Directing Groups for the Rhodium(III)‐Catalyzed Decarboxylative C-H Arylation of Thiophenes. *Angew. Chem. Int. Ed.* **2015**, *54*, 3817 ‐3821. (g) Zhang, G.-D.; Hu, Z.-Y.; Florian, B.; Ou, Y.; Nico, P.; Lukas. J. G. Rhodium‐Catalyzed Annelation of Benzoic Acids with α,β‐Unsaturated Ketones with Cleavage of C−H, CO−OH, and C−C Bonds. *Angew. Chem. Int. Ed.* **2019**, *58*, 6435 –6439. (h) Suman, D.; Deepan, C.; Anup, M.; Francis, A. S. C.; Mahiuddin, B. Ruthenium(II) Catalysis/Noncovalent Interaction Synergy for Cross-Dehydrogenative Coupling of Arene Carboxylic Acids. *ACS Catal.* **2018**, *8*, 10173−10179. (i) Anup, M.; Suman, D.; Harekrishna, S.; Gowri, S. G.; Mahiuddin, B. Ruthenium(II)-Catalyzed ortho-C–H Chalcogenation of Benzoic Acids via Weak O-Coordination: Synthesis of Chalcogenoxanthones. *Org. Lett*. **2017**, *19*, 2430−2433. (j) N. Y. Phani, K.; Torben, R.; Santhivardhana, R. Y.; Alexander, B.; Eric, C.; Lutz, A. Mild Decarboxylative C−H Alkylation: Computational Insights for Solvent-Robust Ruthenium(II) Domino Manifold. *Chem. Eur. J.* **2017**, *23*, 17449-17453. (k) Anup MandalHarekrishna SahooSuman DanaMahiuddin Baidya. Ruthenium(II)-Catalyzed Hydroarylation of Maleimides Using Carboxylic Acids as a Traceless Directing Group. *Org. Lett*. **2017**, *19*, 4138−4141. (l) Guodong Zhang Fan Jia Prof. Dr. Lukas J. Gooßen. Regioselective C−H Alkylation via Carboxylate-Directed Hydroarylation in Water. *Chem. Eur. J*. **2018**, *24*, 4537 – 4541. (m) Huang, L.-B.; Dagmar, H.; Lukas, J. G. Iridium-Catalyzed ortho-Arylation of Benzoic Acids with Arenediazonium Salts. *Angew. Chem. Int. Ed*. **2015**, *54*, 12607 –12611.

(4) (a) Tian, M.-M., Bai, D.-C., Zheng, G.-F., Chang, J.-B., Li, X.-W. Rh(III)-Catalyzed Asymmetric Synthesis of Axially Chiral Biindolyls by Merging C–H Activation and Nucleophilic Cyclization. *J. Am. Chem. Soc*. **2019**, *141*, 9527-9532. (b) Tian, M.-M., Liu, B.-X., Sun, J.-Q., Li, X.-W. Rh(III)-Catalyzed C-C Coupling of Diverse Arenes and 4-Acyl-1-sulfonyltriazoles via C-H Activation. *Org. Lett.* **2018**, *20*, 4946-4949. (c) Xia, J.-T., Huang, Z.-P., Zhou, X.-K., Yang, X.-F., Wang F., Li, X.-W. Rh(III)-Catalyzed Acceptorless Dehydrogenative Coupling of (Hetero)arenes with 2-Carboxyl Allylic Alcohols. *Org. Lett*. **2018**, *20*, 740-743.

(5) She, Z.-J.; Wang, Y.; Wang, D.-P.; Zhao, Y.-S.; Wang, T.-B.; Zheng, X.-S.; Yu, Z.-X.; Gao, G.; You, J.-S. Two-Fold C−H/C−H Cross-Coupling Using $RhCl_3{\cdot}3H_2O$ as the Catalyst: Direct Fusion of N-(Hetero)arylimidazolium Salts and (Hetero)arenes. *J. Am. Chem. Soc.* **2018**, *140*, 12566−12573.

(6) Bernhard, W.; Torsten, S.; Synthesis of Indolo[2,3-a]pyrrolo[3,4-c]carbazoles by Oxidative Cyclization of Bisindolylmaleimides with a Rhodium(III) Copper(II) Catalytic System. *Synthesis* **2005**, 1959–1966.

(7) (a) Vladimir, V. G.; William, J. M.; David L. T. A New, Highly Selective Rh(III) Catalytic System for Carboxylation of Arenes via C±H Activation under Mild Conditions. *Adv. Synth. Catal.* **2001**, *343*, 161-165. (b) Wang, P.; Rao, H.-H.; Hua, R.-M.; Li, C.-J. Rhodium-Catalyzed Xanthone Formation from 2-Aryloxybenzaldehydes via Cross-Dehydrogenative Coupling (CDC). *Org. Lett*. **2012**, *14*, 902-905. (c) Tiffany, P.; Fedor, R.-M.; Maria, R.-M.; Kelvin, E. J.; Natthawat, S.; Trevor, D. T.; Brian, S. N.; Christopher, D. R.; Robert, S. P.; Tomislav, R. Correlating Reactivity and Selectivity to Cyclopentadienyl Ligand Properties in Rh(III)-Catalyzed C−H Activation Reactions: An Experimental and Computational Study. *J. Am. Chem. Soc*. **2017**, *139*, 1296−1310. (d) Ran, Y.; Yang, Y.-D.; You, H.-S.; You, J.-S. $RhCl_3$-Catalyzed Oxidative C−H/C−H Cross-Coupling of (Hetero)aromatic Sulfonamides with (Hetero)arenes. *ACS Catal*. **2018**, *8*, 1796−1801. (e) Shi, Y.; Zhang, L.-Q.; Lan, J.-B.; Zhang, M.; Zhou, F.-L.; Wei, W.-L.; You, J.-S. Oxidative C-H/C-H Cross-Coupling Reactions between N-Acylanilines and Benzamides Enabled by a Cp^*-Free $RhCl_3$/TFA Catalytic System. *Angew. Chem. Int. Ed.* **2018**, *57*, 9108 – 9112. (f) Zhao, K.; Du, R.-R.; Wang, B.-Y.; Liu, J.-H. Xia, C.-G. Yang, L. $RhCl_3{\cdot}3H_2O$-Catalyzed Regioselective C(sp^2)−H Alkoxycarbonylation: Efficient Synthesis of Indole- and Pyrrole-2-carboxylic Acid Esters. *ACS Catal.* **2019**, *9*, 5545-5551.

(8) (a) Dvorak, C. A.; Schmitz, W. D.; Poon, D. J.; Pryde, D. C.; Lawson, J. P.; Amos, R. A.; Meyers, A. I. The Synthesis of Streptogramin Antibiotics: (−)-Griseoviridin and Its C-8 Epimer. *Angew. Chem., Int. Ed*. **2000**, *39*, 1664−1666. (b) Sader, H. S.; Johnson, D. M.; Jones, R. N. In Vitro Activities of the Novel Cephalosporin LB 11058 against Multidrug-Resistant Staphylococci and Streptococci. *Antimicrob. Agents Chemother*. **2004**, *48*, 53−62. (c) Johannesson, P.; Lindeberg, G.; Johansson, A.; Nikiforovich, G. V.; Gogoll, A.; Synnergren, B.; Le Grèves, M.; Nyberg, F.; Karlén, A.; Hallberg, A. Vinyl Sulfide Cyclized Analogues of Angiotensin II with High Affinity and Full Agonist Activity at the AT1 Receptor. *J. Med. Chem.* **2002**, *45*, 1767−1777.

(9) (a) Lee, C.-F.; Liu, Y.-C.; Badsara, S. S. Transition-Metal Catalyzed C−S Bond Coupling Reaction. *Chem. - Asian J.* **2014**, *9*, 706−722. (b) Beletskaya, I. P.; Ananikov, V. P. Transition-Metal Catalyzed C−S, C−Se, and C−Te Bond Formation via Cross- Coupling and Atom-Economic Addition Reactions. *Chem. Rev.* **2011**, *111*, 1596−1636. (c) Dondoni, A.; Marra, A. Metal-Catalyzed and Metal-Free Alkyne Hydrothiolation: Synthetic Aspects and Application Trends. *Eur. J. Org. Chem.* **2014**, *2014*, 3955−3969. (d) Castarlenas, R.; Di Giuseppe, A.; Pérez-Torrente, J. J.; Oro, L. A. The Emergence of Transition-Metal-Mediated Hydrothiolation of Unsaturated Carbon−Carbon Bonds: A Mechanistic Outlook. *Angew. Chem., Int. Ed.* **2013**, *52*, 211−222. (e) Strydom, I.; Guisado-Barrios, G.; Fernández, I.; Liles, D. C.; Peris, E.; Bezuidenhout, D. I. A Hemilabile and Cooperative N-Donor Functionalized 1,2,3-Triazol-5- ylidene Ligand for Alkyne Hydrothiolation Reactions. *Chem. - Eur. J.* **2017**, *23*, 1393−1401. (f) Degtyareva, E. S.; Burykina, J. V.; Fakhrutdinov, A. N.; Gordeev, E. G.; Khrustalev, V. N.; Ananikov, V. P. Pd−NHC Catalytic System for the Efficient Atom-Economic Synthesis of Vinyl Sulfides from Tertiary, Secondary, or Primary Thiols. *ACS Catal.* **2015**, *5*, 7208−7213. (g) Di Giuseppe, A.; Castarlenas, R.; Pérez-Torrente, J. J.; Crucianelli, M.; Polo, V.; Sancho, R.; Lahoz, F. J.; Oro, L. A. Ligand-Controlled Regioselectivity in the Hydrothiolation of Alkynes by Rhodium N-Heterocyclic Carbene Catalysts. *J. Am. Chem. Soc*. **2012**, *134*, 8171−8183. (h) Weiss, C. J.; Marks, T. J. Organozirconium Complexes as Catalysts for Markovnikov-Selective Intermolecular Hydrothiolation of Terminal Alkynes: Scope and Mechanism. *J. Am. Chem. Soc.* **2010**, *132*, 10533−10546. (i) Cao, F.; Fraser, L. R.; Love, J. A. Rhodium Catalyzed Alkyne Hydrothiolation with Aromatic and Aliphatic Thiols. *J. Am. Chem. Soc.* **2005**, *127*, 17614−17615. (j) Pan, X.-Q.; Zou, J.-P.; Yi, W.-B.; Zhang, W. Recent Advances in Sulfur- and Phosphorous-Centered Radical Reactions for the Formation of S−C and P−C Bonds. *Tetrahedron* **2015**, *71*, 7481− 7529. (k) Kao, H.-L.; Lee, C.-F. Efficient Copper-Catalyzed SVinylation of Thiols with Vinyl Halides. *Org. Lett*. **2011**, *13*, 5204−5207. (l) Kabir, M. S.; Lorenz, M.; Van Linn, M. L.; Namjoshi, O. A.; Ara, S.; Cook, J. M. A Very Active Cu-Catalytic System for the Synthesis of Aryl, Heteroaryl, and Vinyl Sulfides. *J. Org. Chem.* **2010**, *75*, 3626−3643. (m) Velasco, N.; Virumbrales, C.; Sanz, R.; Suárez Pantiga, S.; Fernández-Rodríguez, M. A. General Synthesis of Alkenyl Sulfides by Palladium-Catalyzed Thioetherification of Alkenyl Halides and Tosylates. *Org. Lett.* **2018**, *20*, 2848−2852. (n) Rao, W.-H.; Shi, B.-F. Copper(II)-Catalyzed Direct Sulfonylation of C(sp2)−H Bonds with Sodium Sulfinates. *Org. Lett.* **2015**, *17*, 2784−2787. (o) Chen, F.-J.; Liao, G.; Li,

X.; Wu, J.; Shi, B.- F. Cu(II)-Mediated C−S/N−S Bond Formation via C−H Activation: Access to Benzoisothiazolones Using Elemental Sulfur. *Org. Lett.* **2014**, *16*, 5644−5647. (p) Liu, S.-L.; Li, X.-H.; Shi, T.-H.; Yang, G.- C.; Wang, H.-L.; Gong, J.-F.; Song, M.-P. Copper-Promoted Thiolation of C(sp2)−H Bonds Using a 2-Amino Alkylbenzimidazole Directing Group. *Eur. J. Org. Chem.* **2017**, *2017*, 2280−2289. (q) Lin, C.; Li, D.-Y.; Wang, B.-J.; Yao, J.-Z.; Zhang, Y.-H. Direct ortho- Thiolation of Arenes and Alkenes by Nickel Catalysis. *Org. Lett*. **2015**, *17*, 1328−1331. (r) Yang, L.; Wen, Q.; Xiao, F.-H.; Deng, G.-J. Silver-Mediated Oxidative Vinylic C−H Bond Sulfenylation of Enamides with Disulfides. *Org. Biomol. Chem.* **2014**, *12*, 9519−9523.

(10) Liu, C.; Fang, Y.; Wang, S.-Y.; Ji, S.-J. Highly Regioselective RhIIICatalyzed Thiolation of *N*-Tosyl Acrylamides: General Access to (Z)-*β*- Alkenyl Sulfide. *Org. Lett.* **2018**, *20*, 6112-6116.

(11) Subramani, S.; Govindasamy, S.; Copper-Catalyzed One-Pot Synthesis of 2-Arylthiochromenones: An in Situ Recycle of Waste Byproduct as Useful Reagent. *Org. Lett.* **2019**, *21*, 75−79.