Organic LETTERS

Letter

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Divergent Functionalization of Indoles with Acryloyl Silanes via Rhodium-Catalyzed C−H Activation

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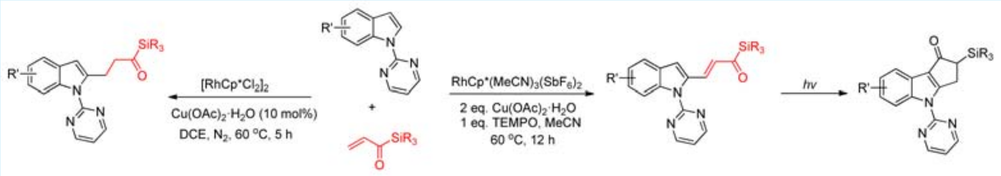
Ⓢ *Supporting Information*



ABSTRACT: A protocol enabled by rhodium-catalyzed C−H functionalization of indoles with acryloyl silanes was developed, providing a convenient and highly effective method for the synthesis of functionalized acylsilane derivatives. By tuning the reaction condition, this C−H-activation-initiated reaction proceeds divergently with acryloyl silianes to selectively afford alkylation or alkenylation products via hydroarylation or oxidative cross-coupling, respectively. The mild reaction conditions employed in both cases enable the tolerance of a wide scope of functionalities as well as high reaction efficiency. Furthermore, polycyclic indole derivatives were easily accessed from 2-alkenylation products through a visible-light-induced reaction cascade.

Acylsilanes represent a class of very important structural motifs, which find widespread use in the fields of synthetic organic chemistry, materials science, and photochemistry.[1] The unique reactivity of acylsilane to act as oxycarboanion,[2] uncoventional acyl anion,[3] or siloxycarbene[4] equivalents under certain reaction conditions stems from the thermodynamically favored 1,2-silyl migration process (Brook rearrangement).[5] Furthermore, the steric and electronic properties of the embeded silyl group could also be capitalized to steer the reaction selectivity on C−C bond formations.[6] While reliable synthetic sequences for the acylsilane synthesis exist, traditional linear synthetic protocols suffer from either low step economy or harsh reaction conditions, which potentially limited the scope of acylsilane attainable, especially of those highly functionalized ones.[7] Therefore, the development of a novel synthetic protocol, which streamlines the synthetic access of functionalized acylsilanes, is still highly desirable and of academic importance.

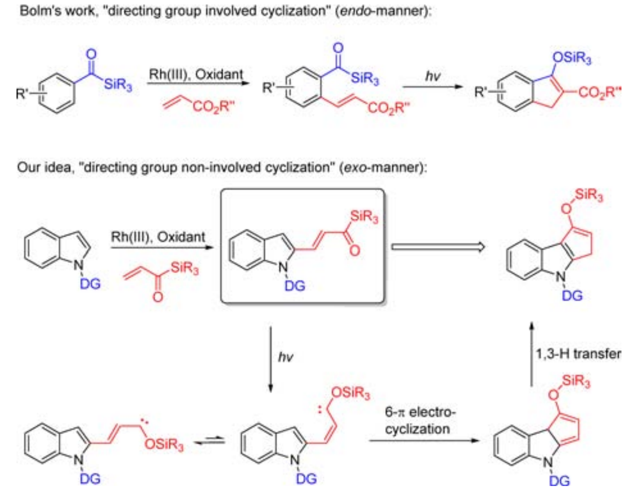
In the past several years, the Rh(III)-catalyzed C−H functionalization has witnessed an explosive evolvement and diverse transformations such as C−C,[8] C−heteroatom[9] bond formation, and annulation reactions[10] in either a redox-neutral or an oxidative manner were disclosed by many research groups as well as our group.[11] Notwithstanding the advancements obtained, the development of an effective protocol in the realm of Rh(III)-catalyzed C−H transformation, which allows easy access of synthetically useful or bioactive relevant structural motifs, is still highly sought after in the synthetic organic community. Recently, by using the acylsilane as the directing group, the Bolm group reported an elegant work of Rh(III)-catalyzed C−H alkenylation of aroylsilanes.[12] The alkenylation product of aroylsilanes could in turn be employed in the photoirradiation for the synthesis of indanone derivatives via siloxycarbenes. While this strategy is effective, the prerequisite of using aroylsilanes as substrates more or less detracts from its synthetic potential, especially in cases where the acylsilane derivatives were not readily accessible. Therefore, we envisage tackling this problem by obviating the use of acylsilane as a directing group but instead introducing the acryloyl silane moiety onto arenes through oxidative alkenylation using traditional functionality as the directing group. Considering the importance of indole derivatives and their ubiquity as the key fragments in various biologically active alkaloids, our privileged endeavor was made in the functionalization of indoles.[13] As exemplified in Scheme 1, oxidative cross-coupling between *N*-protected indole and acryloyl silane is conceived to afford a 2-alkenylation product, which may undergo a cascade sequence encompassing 6-π electrocyclization and a 1,3-hydrogen shift to deliver a polycyclic indole derivative via a photogenerated alkenyl siloxycarbene intermediate.[14]

To make our envisaged reaction sequence work effectively, the identification of suitable reaction conditions for oxidative cross-coupling between indole and acryloyl silane is the premise. To this end, the model reaction between 2-pyrimidyl indole **1a** and TBS-derived acryloyl silane **2a** was systematically examined. Unexpectedly, when substrates **1a** and **2a** were treated with $[RhCp^*Cl_2]_2$ as catalyst and 1 equiv $Cu(OAc)_2 \cdot H_2O$ as oxidant under air atmosphere, no alkenylation product but the alkylation

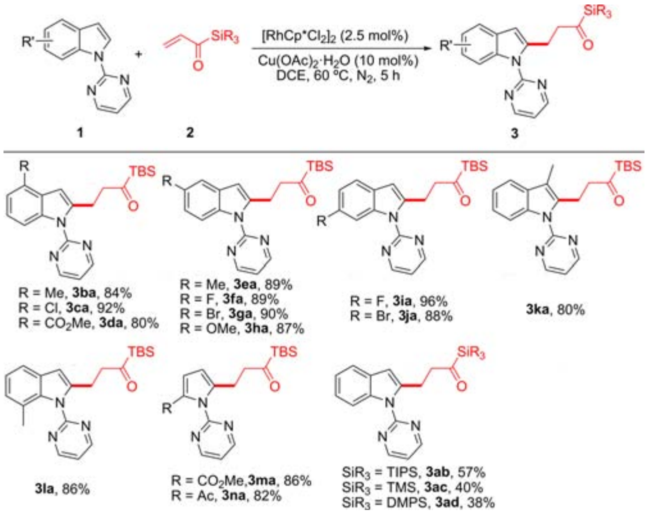
Received: April 29, 2015
Published: June 23, 2015

DOI: 10.1021/acs.orglett.5b01258
Org. Lett. 2015, 17, 3210−3213

Scheme 1. Rhodium Catalyzed Synthesis of Functionalized Acylsilanes and Visible-Light-Induced Electrocyclization



Scheme 2. Reaction Scope of Hydroarylation[a]



[a] Unless otherwise noted, the reactions were carried out at 60 °C using **1** (0.1 mmol), **2** (0.15 mmol), $Cu(OAc)_2·H_2O$ (0.01 mmol), $[RhCp^*Cl_2]_2$ (0.0025 mmol) in DCE (1 mL) under a N_2 atmosphere for 5 h. Yields of isolated products are given.

product **3aa** was obtained in 74% yield (refer to Supporting Information, Table S1, entry 1). Notably, compared to the well-studied Rh(III)-catalyzed hydroarylation of alkynes,[15] related hydroarylation of alkenes, however, were much underdeveloped.[16] The scarcity of this transformation may be in part due to a) the relative slow protonation of $C(sp^3)$-Rh intermediate compared with that of $C(sp^2)$-Rh counterpart; b) the presence of β-hydrogen atoms, which are inclined to undergo elimination. Subsequent attempts revealed that the hydroarylation reaction could be advanced to afford product **2a** in 88% yield by using 10 mol % amount of $Cu(OAc)_2·H_2O$ and under N_2 atmosphere (Table S1, entry 3). To our surprise, copper salt and N_2 protection (in case of using catalytic amount of copper acetate) were identified to be two crucial factors for the success of hydroarylation (Table S1, entries 2, 4).[17] These outcomes implicated that in the hydroarylation reaction the copper salt should have an intimate effect on the rhodium catalyst turnover and the active copper species mediating this process is most likely the Cu(I). Further exploration of reaction parameters led to the optimal reaction condition for the hydroarylation to be using DCE as solvent and 10 mol % $Cu(OAc)_2·H_2O$ as additive under N_2 atmosphere (refer to Supporting Information). It also needs to be noted that during the optimization of hydroarylation reaction condition trace amount of oxidative alkenylation product was often observed, which prompted us toward further investigations, aiming at the realization of controllable divergent functionalization of indole derivatives through C−H activation. Fortunately, we found that alkenylation product **4aa** could be increased to 24% yield simply using MeCN as reaction solvent (Table S1, entry 7).[18] Changing the catalyst to $RhCp^*(MeCN)_3(SbF_6)_2$ further increase the yield of **4aa** to 62% (Table S1, entry 8). Further improvement was obtained when adding additional TEMPO as an additive, which delivered the product **4aa** in 71% yield.[19] A control experiment revealed that rhodium catalyst was essential for both hydroarylation reactions and olefination reactions, without which no reaction occurred.

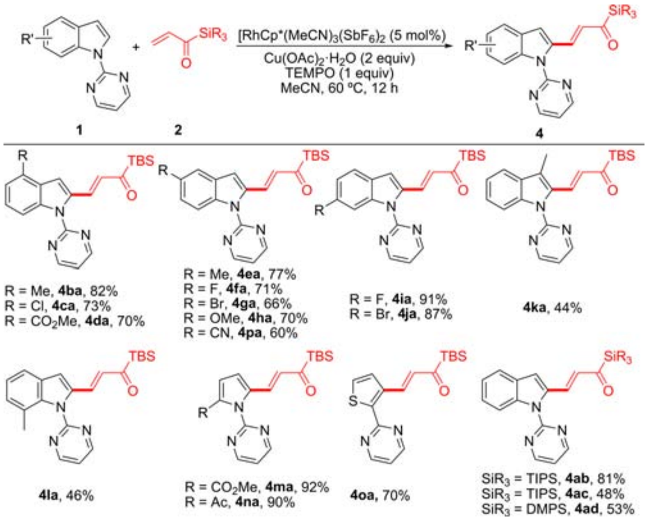
With the optimal reaction conditions for the divergent functionalization of indole established, the substrate scopes with respect to indole and acryloyl silane for hydroarylation reaction were investigated first and the results are summarized in Scheme 2. It turns out that the reaction showed both high efficiency and good functional group tolerance. When indole derivatives **1** containing electron-donating groups, irrespective of their substitution patterns on the indole core, were employed, the reaction occurred smoothly to provide the desired products in high yield (**3ba**, **3ea**, **3ha**, **3ka**, **3la**). Taking the steric hindrance of 3-methyl substituent into account, the outcome of the reaction between **1k** and **2a** was quite noteworthy. A substrate bearing ester group also worked nicely to provide product **3da** in 80% yield. Pleasingly, halogen substituents were also well compatible with the reaction conditions and afforded the desired products in excellent yields (**3ca**, **3fa**, **3ga**, **3ia**, **3ja**), which provide the synthetic handles for further elaboration. It needs to be pointed out that the reaction was not restricted to indole substrates and when pyrroles were subjected to the reaction, the corresponding alkylation products could also be obtained in high yield (**3ma**, **3na**). Finally, acryloyl silanes containing different silyl groups such as TMS, TIPS, and DMPS were examined, which delivered the desired hydroarylation products in moderate yields (**3ab**, **3ac**, and **3ad**).

Subsequently, the oxidative alkenylation reactions are explored, and the results were summarized in Scheme 3. Indole derivatives containing an electron-donating group, such as 4-Me, 5-Me, and 5-OMe, provided the olefination product in good to high yield (**4ba**, **4ea**, **4ha**). Substrates with electron-withdrawing groups delivered the desired products in moderate yields (**4da**, **4pa**). It appears that the oxidative alkenylation was somewhat steric sensitive, and when **1k**, **1l** were employed, the reactions afforded desired products in diminished yields (**4ka**, **4la**). In accordance with hydroarylation reaction, halogen atoms were also well tolerated in the olefination reaction (**4ca**, **4fa**, **4ga**, **4ia**, **4ja**). Gratifyingly, pyrroles derivatives also provided the desired products in excellent yield (**4ma**, **4na**). Moreover, when a thiophene derivative was employed, the olefination product was obtained in 70% yield. In addition, acryloyl silanes with different silyl groups were examined again. A substrate with TIPS substitution gave the olefination product in 81% yield (**4ab**), while substrates bearing TMS and $SiMe_2Ph$ groups afforded the products in moderate yield (**4ac**, **4ad**).

With the olefination products in hand, the subsequent visible-light-induced reaction cascade was examined (Scheme 1). When 2-alkenylation product **4aa** was irradiated with a 23 W compact

DOI: 10.1021/acs.orglett.5b01258
Org. Lett. 2015, 17, 3210−3213

Scheme 3. Reaction Scope of Olefination Reaction[a]

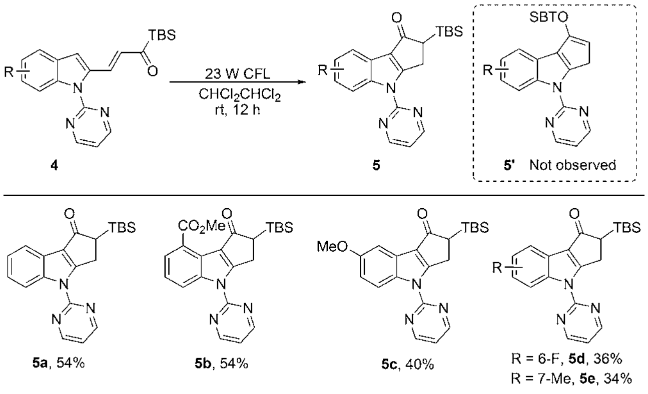


[a]Unless otherwise noted, the reactions were carried out at 60 °C using **1** (0.1 mmol), **2** (0.15 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.2 mmol), TEMPO (0.1 mmol), $RhCp^*(MeCN)_3(SbF_6)_2$ (0.005 mmol) in MeCN (1 mL) under air for 12 h. Yields of isolated products are given.

fluorescent lamp in $CHCl_2CHCl_2$ as solvent, the expected cyclization indeed happened; however, not the silyl enol eher **5a′** but product **5a** was obtained in 54% yield, indicating the involvement of a 1,3-silicon shift process (Scheme 4). By using these preliminary reaction conditions, several other indole functionalized acryloyl silanes were tested.

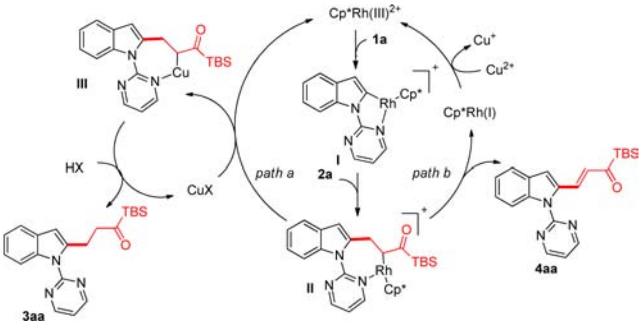
Substrates containing functional groups such as ester, fluorine, and methoxyl were compatible with the reaction conditions, albeit producing the cyclization products in low to moderate yields (**5b**−**5e**).

Scheme 4. Visible-Light-Induced Electrocyclization of Products 4



In order to gain more insight into the reaction mechanism of this divergent C−H functionalization, some control experiments were carried out. A hydroarylation reaction carried out with an additional 0.1 mL of CH_3OD for 2 h delivered **3aa-*d1*** with 33% deuteration content on the α-position of the acylsilane functional group, while no deuterium incorporation was observed when **3aa** was submitted to the same conditions. These results indicate that in the hydroarylation reaction (a) the β-H elimination/reinsertion process was not involved and (b) a protonation of the carbon−metal bond step is present during the catalytic process. On the other hand, deuterium was not incorporated into the alkenylation product when the oxidative coupling reaction was carried out in CD_3CN. It was also found that there is no deuterium incorporation on the recovered indole substrate in both hydroarylation and oxidative alkenylation reactions performed in either CH_3OD or CD_3CN. In addition, when the hydroarylation product **3aa** was subjected to the optimized reaction conditions of oxidative alkenylation, no transformation into product **4aa** was observed, indicating the independent nature of these two reaction pathways. Based on these results, the reaction mechanism for the hydroarylation and olefination reactions was proposed and presented in Scheme 5. Both the hydroarylation and olefination reactions start with directing group assisted irreversible C−H activation of indole **1a** with the Rh(III) catalyst to generate rhodacycle **I**,[20] which underwent further alkene insertion to afford intermediate **II**.[21] In view of the indispensability of Cu salt in the hydroarylation reaction, a Rh−Cu transmetalation process was envisioned to produce intermediate **III** and regenerate the active Rh(III) catalyst (Scheme 2, path a).[22] Protodecupration in **III** would produce the alkylation product **3aa** and regenerate the copper catalyst. For the olefination reaction, intermediate **II** goes through path b via β-H elimination to deliver product **4aa** accompanied by the generation of Rh(I),[23] which in turn is oxidized by copper acetate to complete the catalytic cycle.

Scheme 5. Proposed Reaction Mechanism



In conclusion, we have reported a novel strategy for the synthesis of indole functionalized acylsilane derivatives by taking advantage of the Rh(III)-catalyzed C−H activation manifold. Besides the advantage of using readily available reaction substrates, the controllable nature of chemoselectively generating either hydroarylation or oxidative alkenylation products greatly boosts the synthetic utility of this protocol. Furthermore, the amenability of a wide variety of functional groups and practicality of this reaction provide a straightforward pathway for the synthesis of functionalized acylsilane derivatives. For the 2-alkenylation product obtained, facile access to polycyclic indole derivatives could be gained by taking advantage of visible-light-induced 6-π electrocyclization.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experiment procedures and compound characterization data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01258.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the National Natural Science Foundation of China (Nos. 21372210, 21432009), the Nanyang Technological University for the funding of this research. The authors are grateful to Mr. Koh Peng Fei Jackson (from Nanyang Technological University, Singapore) for his careful proofreading of the final manuscript.

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(17) When the reaction was performed under air using a stoichiometric amount of $[\mathrm{RhCp^*Cl_2}]_2$ or $[\mathrm{RhCp^*Cl_2}]_2/\mathrm{AgSbF_6}$ (1:4) but without $\mathrm{Cu(OAc)_2 \cdot H_2O}$, no reaction occurred.

(18) Performing the reaction under air and using MeCN as reaction solvent, which could either inhibit the formation of reactive Cu(I) species or sequester the in situ formed acid, were believed to be two key factors guaranteeing the selective formation of alkenylation product.

(19) The beneficial effect of TEMPO on the oxidative alkenylation reaction was assumed to be due to the inhibition of polymerization of acryloyl silane and assistance of the oxidative turnover of Rh(III) catalyst. For the Rh(III) catalyzed C−H activation reaction in which TEMPO employed as oxidant, see: Park, S.; Seo, B.; Shin, S.; Son, J. Y.; Lee, P. H. *Chem. Commun.* **2013**, *49*, 8671.

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NOTE ADDED AFTER ASAP PUBLICATION

Schemes 2 and 3 were corrected on June 24, 2015.