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ROYAL SOCIETY OF CHEMISTRY View Article Online
DOI: 10.1039/C7CC07086A

Journal Name

COMMUNICATION

Regiocontrolled Direct C4 and C2-Methyl Thiolation of Indoles under Rhodium Catalyzed Mild Conditions

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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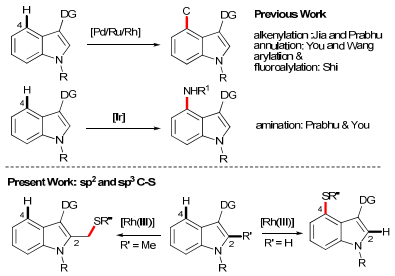
A straightforward Rh(III)catalyzed general strategy was developed for the site selective remote C4 (sp^2) and C2 (sp^3)-methyl thiolation of indole core keeping the oxime directing group at the C3 position. The transformation was accomplished under mild conditions with wide scope and functional group tolerance. The directing group can easily be removed after operation. Methyl substitution at the C2 position of indole core led to C2 (sp^3)-methyl thiolation.

Among many nitrogen containing heterocyclic scaffolds, indole motif is one of the most ubiquitous structure in the natural products and fourth most prevalent heteroatomic in marketed pharmaceuticals.[1] Thus, in current years, significant efforts have been devoted to the transition metal catalyzed direct functionalizations at the C2 and C3 positions due to its inherent reactivity.[2] In sharp contrast, site-selective functionalization of remote less activated C-H bonds in the benzene core of indole derivatives continue to be challenging.[3-6] Hence, selective C-H functionalization at the poor nucleophilic C4 position of indole has been explored recently due to the limitations of earlier two successful approaches (Scheme 1).[7, 8] After the major breakthrough by Jia and co-workers in Pd-catalyzed C4 olefination of tryptophan derivatives,[8a] Prabhu and co-workers published Ru catalyzed C4 olefination of indole derivatives using the aldehyde and ketone directing group.[8b,c] Recently, Jia's group extended this concept with Rh catalyzed conditions on NH free indole derivatives.[8d] After the development of Rh catalyzed regioselective C-H bond activation/annulation of indolyl aldehydes at the C4 position by You's group,[9a] Wang and co-workers also developed Rh catalyzed oxidative annulation reaction of 3-(1*H*-indol-3-yl)-3-oxopropanenitriles with internal alkynes.[9b] In recent significant advancements, Shi's group established Pd catalyzed C4 arylation and fluoroalkylation of indole derivatives with the aid of keto directing group at the C3 position.[4,10]



Scheme 1: Direct C4 functionalization of indole derivatives.

A biomimetic Fridel-Crafts type C4 alkyaltion of 7-methoxyindole derivatives was achieved by Dethe's group.[11] Very recently, Prabhu's group and You's group independently reported the Ir catalyzed C4 amination of indole derivatives with the assist of C3-aldehyde group.[12, 13]

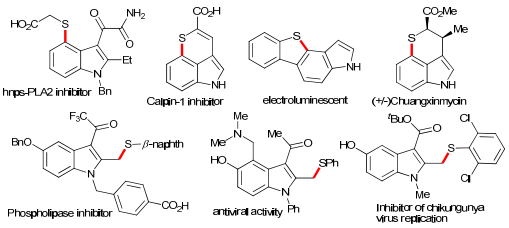


Fig. 1: Biologically relevant scaffold containing C4 and 2-methylthio-substituted indoles.

The thioether moiety is prevalent in bioactive compounds.[14] Transition metal catalyzed direct thiolation of inactivated C-H bonds has emerged as an attractive strategy due to the known limitations of sulfur compounds like catalyst deactivation properties and its over oxidation in the presence of oxidant.[15] Interestingly, 4-thioindoles and 2-thiomethyl indoles are common in pharmaceuticals, natural products and organic materials (Figure 1). Nevertheless, despite significant progresses in transition metal catalyzed direct C2 and C3 selective thiolation in indole core,[16, 17] there is no direct sp^2-C4

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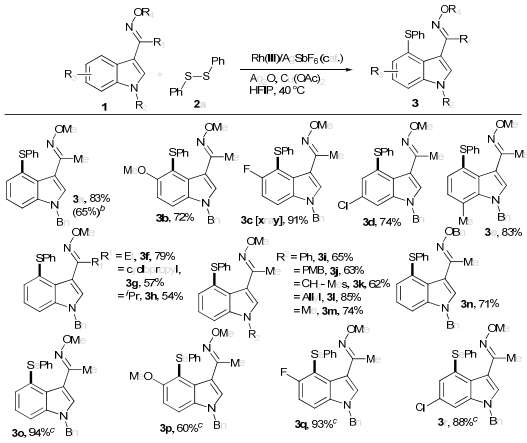
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

thiolation and sp^3-2-methylthiolation report to the best of our knowledge. Intrigued by the recent direct remote functionalizations of indole core[3] and our studies on C-H functionalizations[18], we assumed a suitably placed appropriate, easily removable directing group in indole core would serve the desired site selective thiolation. The challenge of C4-selectivity for this strategy comes from the possibility of C2 selective five membered metallacycle formation over C4 selective six membered metallacycle.[8,19] Herein, we report a direct Rh(III) catalyzed mild, site selective C4 (sp^2)-thiolation and C2 (sp^3)-methyl thiolation of indole core using removable oxime directing group at the C3 position.

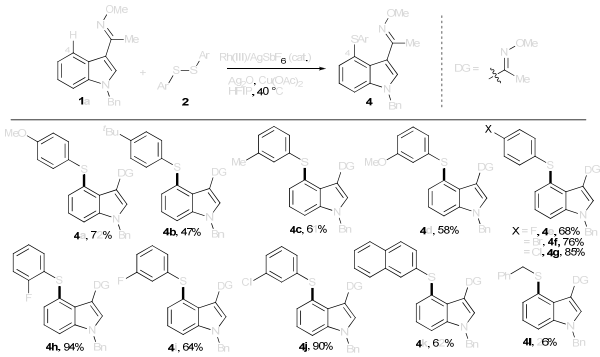
Initially, we explored the thiolation of methyl oxime derivative of *N*-benzyl-3-acetylindole (**1a**) with diphenyldisulfide (**2a**) using catalytic $[Cp^*RhCl_2]_2$/$AgSbF_6$ and stoichiometric copper acetate in 1,2-DCE at 80 °C. This resulted in the formation of the 4-phenylthioindole derivative **3a** in 36% isolated yield (see SI, Table S1, entry 1). The efficiency of the reaction was immediately increased up to 65% isolated yield of the desired product by the choice of Ag_2CO_3 as oxidant (see SI, Table S1, entry 2). Further, screening of other solvents with different polarity, led to lower yield or even no desired product (see SI, Table S1, entries 3-8). When the other silver salts were tested, the yield of the desired product **3a** was increased upto 72% for Ag_2O (see SI, Table S1, entries 9-12). To improve the yield further, the reactions were carried out in presence of various acetate additives (see SI, Table S1, entries 13-15). Satisfyingly, the yield of the desired product **3a** was improved to 77% in presence of $Cu(OAc)_2$ (see SI, Table S1, entry 15). Desired product was obtained with comparable yield in trifluoroethanol solvent (see SI, Table S1, entry 16). Incidentally, lower yield was obtained when the reaction was performed in DCE at 40 °C (see SI, Table S1, entry 17). Furthermore, the efficacy of the reaction was drastically improved as the reaction proceeded at 40 °C with 83% isolated yield under HFIP (see SI, Table S1, entry 18) and decreased amount of oxidant Ag_2O.



Scheme 2 Scope using various indoles: [a]Reaction conditions: **1** (0.1 mmol), **2a** (0.15 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), Ag_2O (0.05 mmol), $Cu(OAc)_2$ (0.1 mmol), HFIP (0.1 M), 40 °C, 8-16 h. Mes = mesityl. [b]reaction was done in 1 gm scale using 1 mol% Rh(III) catalyst. [c]diphenyldiselenide was used in spite of **2a**.

Interestingly, in the absence of $Cu(OAc)_2$ the reaction did not proceed well in HFIP solvent (see SI, Table S1, entry 19). This result indicates that more likely $Cu(OAc)_2$ is highly necessary to obtain this mild optimized reaction conditions. Other transition metal catalysts like $[Cp^*IrCl_2]_2$ or $[Ru(p\text{-cymene})Cl_2]_2$ either provided no yield or poor yield of desired product (see SI, Table S1, entries 20-21).

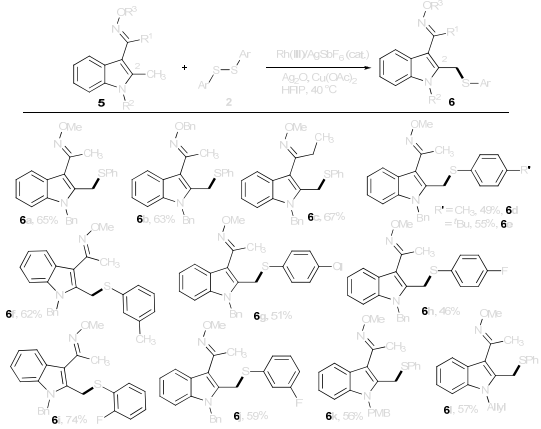
With the optimized conditions in hand, a wide array of indoles with various protecting groups and functionalities were explored (Scheme 2) for C4-thiolation. The reaction worked smoothly with indoles having various electronically and sterically variable functional groups at C5, C6 or C7 positions (Scheme 2, **3a**-**3e**). Further, satisfying product's yield was obtained during the exchange of C3-acetyl oxime with the more sterically crowded oximes (Scheme 2, **3f-3h**). To make this reaction more general, various *N*-protecting groups were explored. We were also pleased to see that the other *N*-protected indole derivatives offered very good yield with admirable degree of selectivity (Scheme 2, **3i**-**3m**). When the methyl oxime was changed with benzyl oxime, the desired product was obtained in 71% yield (Scheme 2, **3n**). Moreover, the robustness of this C4-thiolation method was further extended by the C4-selenylation of indole derivatives **1** that was obtained under otherwise optimized reaction conditions (Scheme 2, **3o**-**3r**). Notably, no desired product was obtained when the reaction was carried out on indole substrate with free NH group. To observe the scalability of the optimized method, **1a** was C4- thiolated in 1 gram scale with 65% isolated yield using only 1 mol% Rh(III) catalyst (Scheme 2, **3a**). Next, the reaction was extended with wide range of disulfides (Scheme 3).



Scheme 3 Scope of C4-thiolation with various disulfides. [a]Reaction conditions: **1a** (0.1 mmol), **2** (0.15 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), Ag_2O (0.05 mmol), $Cu(OAc)_2$ (0.1 mmol), HFIP (0.1 M), 40 °C, 14-16 h.

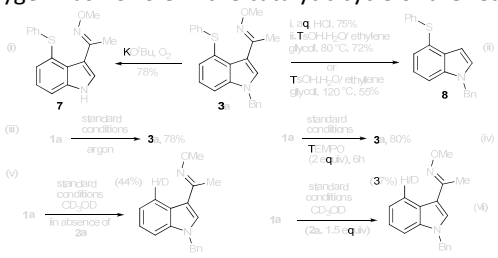
Electron dontating groups at *meta* and *para* positions of aryl ring in diaryldisulfides provided moderate to good yield (Scheme 3, **4a**-**4d**). Very good yields of the desired products were obtained for *para*-halogen substituted diarylsulfides (Scheme 3, **4e**-**4g**). Gladly, halogens at the *ortho* and *meta*-positions of the aryl ring in diaryldisulfides provided excellent yields (Scheme 3, **4h**-**4j**). Incidentally, the thiolation could be extended to obtain sterically more crowded naphthylthioindole derivative in good yield (Scheme 3, **4k**). When dibenzyldisulfide was explored under our developed

conditions, desired thiolated product was isolated in very poor yield (Scheme 3, **4l**). Unfortunately, no desired or trace amounts of desired products were obtained from the other aliphatic disulfides under the optimized conditions.



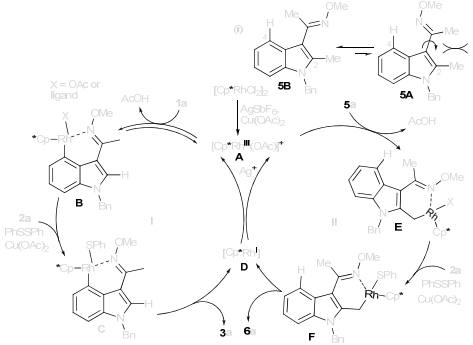
Scheme 4 Scope of sp^3-thiolation of 2-methylindoles: [a]Reaction conditions: **5** (0.1 mmol), **2** (0.15 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), Ag_2O (0.05 mmol), $Cu(OAc)_2$ (0.1 mmol), HFIP (0.1 M), 40 °C, 14-16 h.

In comparison to C(sp^2)-H, direct thiolation of C(sp^3)-H remains a great challenge.[20] Significantly, a large number of bioactive compounds are available with 2-methylthiolated indole core (Figure 1). Arguably, one of the easiest methods to construct such scaffold is direct thiolation at the C2-methyl group of 2-methylindole via C(sp^3)-H activation. To achieve this in regioselective fashion, we envisaged that the steric interaction between R^1 and C2-methyl group in indole derivative **5** might bring the necessary conformation to activate C2-methyl group *via* oxime directed Rh(III) catalyzed C(sp^3)-H bond functionalization. Gratifyingly, 2-methylthiolated indole derivative **6a** was obtained from the 2-methylindole derivative **5a** in 65% yields under the optimized reaction conditions (Scheme 4). Substrate with benzyloxime in the place of methyloxime also worked smoothly (Scheme 4, **6b**) to provide the desired product. Good reactivity was seen when steric bulk in keto group was increased (Scheme 4, **6c**). To our pleasure, various diaryldisulfides demonstrated good reactivities, irrespective of electronic and steric properties of the substituents on the phenyl ring (Scheme 4, **6d**-**6j**). Notably, we found no systematic influence of substituents in the *ortho*-, *meta*-, or *para*-positions. Other indole NH-protecting groups like *para*-methoxybenzyl or allyl group were also found to be useful in this thiolation reaction (Scheme 4, **6k**-**6l**). Furthermore, removal of protecting group was carried out to increase the synthetic utility of the developed protocol. The debenzylated product **7** was obtained from compound **3a** in very good yield (Scheme 5i). Next, the directing ketoxime group was removed from **3a** in two consecutive steps like removal of oxime group followed by reverse Friedel-Crafts acylation to obtain indole **8** (Scheme 5ii)**.** [4,10] Alternatively, the ketoxime group was directly eliminated in single step (Scheme 5ii). Presumably, this reaction does also proceed in similar fashion. Further, the reaction was not much influenced under strict inert conditions (Scheme 5iii).This reflects that more likely oxygen has no role in the catalytic cycle of the reaction.



Scheme 5 Product modifications and control experiments.

Next, to know the radical intermediates involvement, the reaction was carried out in the presence of stoichiometric amount of radical trapping reagent 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO) (Scheme 5iv). The reaction proceeded smoothly and the desired product was isolated in 80% yield. This result suggests that most likely the reaction does not follow a single electron transfer pathway. Moreover, treatment of indole oxime **1a** with CD_3OD as the co-solvent in the presence or absence of disulfide **2a** offered 37-44% deuterium incorporation at the C4 position exclusively (Scheme 5v-vi). This outcome reveals that the C-H activation at the C4 position is reversible. Furthermore, there was no deuterium incorporation observed at the C2-methyl of **5a** in the presence or absence of disulfide **2a.** However, no desired product formation was observed during the use of thiophenol as the thiolating partner.



Scheme 6 Plausible mechanisms for (sp^2) C4 and (sp^3) C2- methyl thiolation of indoles:

On the basis of the control experiments and previous literature reports[15b,20] a tentative mechanism is proposed (Scheme 6). The active catalyst **A** is generated from its precursor by halide abstraction with $AgSbF_6$ followed by acetate transfer. Now for catalytic cycle I, the subsequent formation of 6-membered rhodacycle through oxime directed C4-H bond cleavage provides intermediate **B**. Presumably, in presence of copper salt the disulfide facilitates to afford rhodium thiolate intermediate **C** through the generation of anionic copper complex.[16b,21] Finally, the reductive elimination provides product **3a** with Rh(I) species **D** which is regenerated to Rh(III) active catalyst *via* reoxidation with silver salt. Now, indole oxime **5a** can be present in equilibrium of two different conformers **5A** and **5B**. Presumably, steric interaction between

C2-methyl and C3-ketomethyl (Scheme 6i) group facilitates the higher stability of the conformation **5B**. Evidently for catalytic cycle II, the more stable conformer **5B** provides rhodacycle intermediate **E** through C(sp^3)-H activation. Next, the thiolate transfers to rhodacycle **E** and subsequent reductive elimination affords compound **6a** with Rh(I) species **D**. Finally, reoxidation of Rh(I) species to Rh(III) active catalyst occurs by silver salt.

In summary, we have developed the direct Rh(III) catalyzed regioselective C4 (sp^2) C-H and C2 (sp^3)-methyl thiolation of indoles at mild conditions. The easily available and removable oxime group has been used at the C3 position of indole for the selectivity. Current studies are focused on the synthesis of some relevant natural products using this methodology.

This work is supported by the SERB, India (YSS/2014/000383 and PDF/2016/000242). Fellowship received from IIT Kharagpur (U.K.) is gratefully acknowledged.

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