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COMMUNICATION

DMSO/$SOCl_2$-mediated C(sp^2)–H amination: switchable synthesis of 3-unsubstituted indole and 3-methylthioindole derivatives

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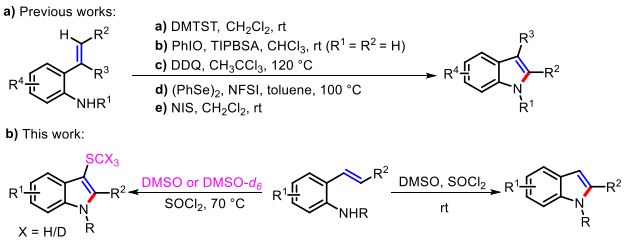
Jingran Zhang,[a] Xiaoxian Li,[a] Xuemin Li,[a] Haofeng Shi,[a] Fengxia Sun,[b] and Yunfei Du*[a]

The reaction of 2-alkenylanilines with $SOCl_2$ in DMSO was found to selectively afford 3-unsubstituted indoles and 3-methylthioindoles. This switchable approach was found to be temperature-dependent: at room temperature, the reaction afforded 3-unsubstituted indoles through intramolecular cyclization and elimination. While at higher temperature, the reaction gave 3-methylthioindoles *via* further electrophilic methylthiolation.

Indole skeleton is one of the most abundant and important motif which widely exists in natural products, such as serotonin and reserpine.[1] In addition, many best-selling small-molecule drugs including tadalafil, rizatriptan, fluvastain and arbidol, all possess the indole framework in their respective structures.[2] Over the past several decades, the synthesis of indole and its derivatives has been a topic of great interests because of their ever-expanding application in synthesis of natural products and pharmaceutical agents.[3] Although numerous methods for their synthesis have been developed, there is still a need to develop efficient and economic strategies that can synthesize functionalized indoles bearing some unique substituents.[4]

Intramolecular oxidative C(sp^2)–H amination of 2-alkenylanilines is one of the straightforward approaches for the construction of indole skeleton. In the past decades, numerous transition metal-mediated methods, by using Pd,[5] Cu,[6] Ru[7] and Ag[8] as catalysts, have been developed for the synthesis of this privileged heterocyclic framework. Most strikingly, the conversion of 2-alkenylanilines to indole compounds *via* intramolecular oxidative cyclization could also be realized under metal-free conditions. For instances, DMTST,[9] PhIO,[10] DDQ,[11] NFSI/$(PhSe)_2$[12] and NIS,[13] have all been utilized to react with 2-alkenylanilines for synthesis of indole products (Scheme 1a). All the above methods have their respective merits in producing the corresponding indoles by using different oxidative systems. In this communication, we reported an alternative oxidative approach for synthesis of indoles by treating 2-alkenylanilines solely with $SOCl_2$ in DMSO. Differing from the above methods which only realize the direct oxidative C(sp^2)-N bond formation for the assemblage of indole framework, this approach can also realize the further functionalization of the indole skeleton with an unique methylthio group at its 3 position.



Scheme 1 Metal-free synthesis of indoles from 2-alkenylanilines

It is well known that DMSO is not only a widely used organic solvent, but also an oxidant in some classical reactions, including Swern oxidation,[14] Pfitzner-Moffatt oxidation,[15] and some other newly discovered reactions.[16] Literature survey indicated that DMSO has been used as sulfur source to introduce thiomethyl group[17] or methylsulfonyl group[18] to olefins, leading to the formation of adducts *via* addition reactions. However, there are few reports describing the direct functionalization/methylthiolation of olefins by using DMSO as sulfur source.[19] In this regard, it is of interest to develop a new method for methylthiolation of olefin compounds.

In our previous work,[20] we have realized the synthesis of 4-(methylthio)isochromenones *via* treating 2-alkynylbenzoates with DMSO/$SOCl_2$. Encouraged by the results, we were interested to investigate whether an alkene substrate can also react with DMSO/$SOCl_2$ to enable the similar oxidative cyclization, affording the corresponding 3-methylthio substituted indoline **2a'**. Alkene **1a** was then used as the modeling substrate to test the feasibility of proposed transformation. Surprisingly, 3-unsubstituted indole **2a**, ranther than the expected indoline was formed by treating *N*-Ts-2-alkenylaniline **1a** (0.5 mmol) with DMSO (1 mL) and $(COCl)_2$ (2.0 equiv) at room temperature. Then we came to optimize the reaction conditions for this newly discovered method. First, we

[a] School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, China. E-mail: duyunfeier@tju.edu.cn
[b] College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology; Hebei Research Center of Pharmaceutical and Chemical Engineering, Shijiazhuang 050018, China.
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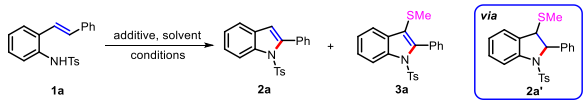
Table 1 Optimization of the reaction conditions[a]

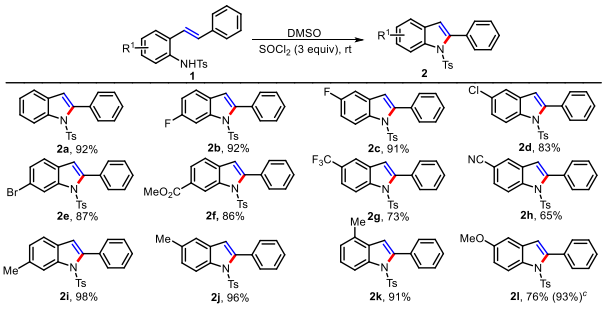


entry	solvent	additive (equiv)	T (℃)	time (h)	yield (%)[b] 2a	3a
1	DMSO	$(COCl)_2$ (2.0)	rt	6	55	0
2	DMSO	$SOCl_2$ (2.0)	rt	3	73	0
3	DMSO	TsCl (2.0)	rt	12	12	0
4	DMSO	AcCl (2.0)	rt	12	16	0
5	DMSO	TFAA (2.0)	rt	12	40	0
6[c]	DCE	$SOCl_2$ (2.0)	rt	12	64	0
7[c]	CH_3CN	$SOCl_2$ (2.0)	rt	12	56	0
8[c]	THF	$SOCl_2$ (2.0)	rt	12	60	0
9[c]	1,4-dioxane	$SOCl_2$ (2.0)	rt	12	67	0
10[c]	toluene	$SOCl_2$ (2.0)	rt	12	49	0
11[c]	DMF	$SOCl_2$ (2.0)	rt	12	62	0
12	DMSO	$SOCl_2$ (2.5)	rt	2	83	0
13	**DMSO**	**$SOCl_2$ (3.0)**	**rt**	**0.5**	**92**	**0**
14	DMSO	$SOCl_2$ (3.5)	rt	0.5	86	0
15	DMSO	$SOCl_2$ (3.0)	70	0.5	80	10
16	DMSO	$SOCl_2$ (3.5)	70	1	43	35
17	**DMSO**	**$SOCl_2$ (4.0)**	**70**	**1**	**0**	**55**

[a] Reaction conditions: **1a** (0.5 mmol) in solvent (1 mL), unless otherwise stated. [b] Isolated yield. [c] Reaction conditions: **1a** (0.5 mmol), DMSO (3.0 equiv) in solvent (1 mL).

began to evaluate the additives including $(COCl)_2$, $SOCl_2$, TsCl, AcCl and TFAA, the results indicated that $SOCl_2$ was the most effective one (Table 1, entries 1-5). Next, solvent screening showed that using DMSO as both reactant and solvent was the most favorable choice, while the reaction led to a much lower yield when using 3.0 equiv of DMSO as reactant and DCE, CH_3CN, THF, 1,4-dioxane, toluene or DMF as respective solvent (Table 1, entries 6-11). Later on, when the dosage of $SOCl_2$ was increased to 3.0 equiv, the yield of **2a** was improved obviously to 92% and the time was greatly shortened. However, when the dosage of $SOCl_2$ was further increased to 3.5 equiv, the reaction did not afford a better result (Table 1, entries 12-14). Next, the reaction temperature was further investigated. When the reaction was carried out at 70 °C, we were surprisingly to find that product **2a** was formed in a much lower yield due to the formation of a predominant byproduct, which was confirmed to be 3-methylthioindole **3a**. This outcome inspired us to further investigate whether this method could be applied to the synthesis of indoles bearing a 3-methylthio substituent. The results revealed that improving reaction temperature was indispensable for the conversion of 2-alkenylaniline **1a** to 3-methylthioindole **3a** (Table 1, entries 13-15). At 70 °C, when the dosage of $SOCl_2$ was increased to 3.5 equiv, the yield of **3a** was further improved to 35% (Table 1, entry 16). Then, we tried to achieve the optimal conditions of **3a** formation through altering the reaction temperature and the dosage of $SOCl_2$ (see the Supporting Information for details). On the basis of the screening results, the optimal conditions of DMSO/$SOCl_2$-mediated synthesis of 3-unsubstituted indoles were confirmed to be 0.5 mmol of **1a** with 3.0 equiv of $SOCl_2$ in DMSO (1 mL) at room temperature, and the best conditions for synthesis of 3-methylthioindoles were concluded to be 0.5 mmol of **1a** with 4.0 equiv of $SOCl_2$ in DMSO (1 mL) at 70 °C.

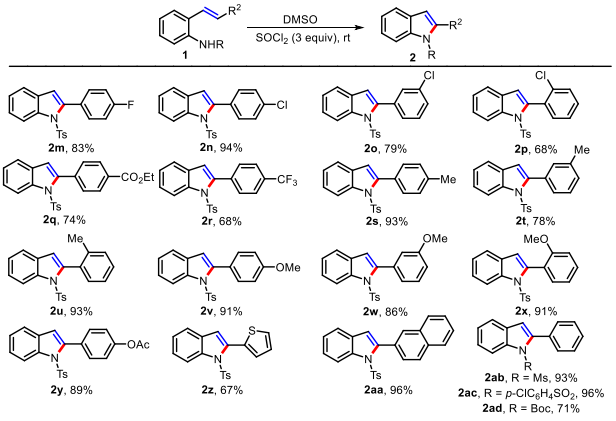
Table 2 DMSO/$SOCl_2$-mediated synthesis of 3-unsubstituted indoles **2**[a, b]



[a] Reaction conditions: **1** (0.5 mmol), $SOCl_2$ (3.0 equiv), DMSO (1 mL), rt, 30 min, unless otherwise stated. [b] Isolated yield. [c] The reaction was carried out at 0 °C for 30 min.

With the optimal conditions in hand, the scope and limitation of this protocol were studied in Table 2. First, we investigated the effects of substituent R^1 residing on the aromatic moiety of *N*-Ts-2-styrylanilines. We found that when R^1 was electron-withdrawing group (F, Cl, Br, CO_2Me), the corresponding starting material could afford the desired products in good to excellent yield (Table 2, **2b-f**). However, when the substrates bearing the electron-withdrawing trifluoromethyl or cyano group were applied (Table 2, **2g-h**), the reaction afforded the corresponding product in a relatively lower yield. Furthermore, when R^1 was a methyl group, all the reactions afforded the target products in excellent yield (Table 2, **2i-k**). It is worth noting that when R^1 was a methoxy group, the corresponding substrate was converted to

Table 3 DMSO/$SOCl_2$-mediated synthesis of 3-unsubstituted indoles **2**[a, b]



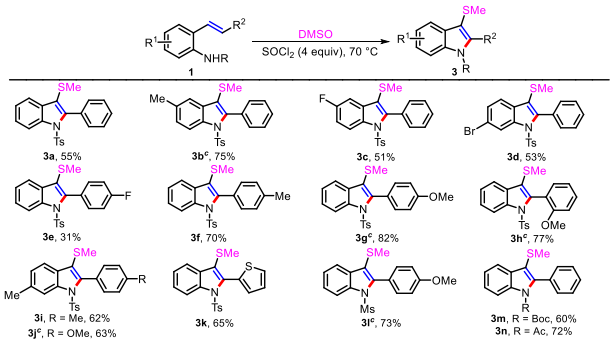
[a] Reaction conditions: **1** (0.5 mmol), $SOCl_2$ (3.0 equiv), DMSO (1 mL), rt, 30 mis. [b] Isolated yield.

3-unsubsitituted indole with concomitant formation of 3-methylthioindole under the standard condition. In order to avoid the formation of 3-methylthioindole byproduct, we carried out the reaction at 0 °C, and the 3-unsubstited indole derivative **2l** was obtained selectively in 93% yield (Table 2, **2l**).

Subsequently, we proceeded to explore the substituent effect at the alkene moiety in the substrates. As shown in Table 3, the

majority of *N*-Ts-2-styrylanilines (R^2 = aryl) could afford the corresponding 3-unsubsitituted indoles in good yield irrespective of the substituent type on phenyl ring (Table 3, **2m-y**). To our delight, it was proved that a thiophene ring or naphthalene linked to the alkene moiety in the substrates was also well tolerated under the standard conditions (Table 3, **2z, 2aa**). Unfortunately, when *N*-Ts-2-styrylaniline bearing a non-aromatic R^2 substituent (R^2 = H, *n*-Pr or Bn) was applied, no desired product was obtained in each case (not shown). Furthermore, the N-Ts group in the substrates could also be replaced with N-Ms, N-*p*-$ClC_6H_4SO_2$ and N-Boc substituent, and the corresponding substrates were converted to the desired products in excellent yield (Table 3, **2ab-ad**). Disappointingly, this method was not applicable to the substrates bearing N-Me, N-Bn or OH moieties, as the reaction in each case gave a complex mixture under the standard conditions (not shown).

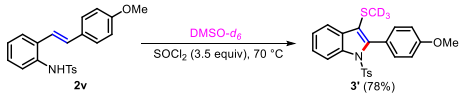
Table 4 DMSO/$SOCl_2$-mediated synthesis of 3-methylthioindoles **3**[a,b]



[a] Reaction conditions: 1 (0.5 mmol), $SOCl_2$ (4.0 equiv), DMSO (1 mL), 70 °C, 50 min. [b] Isolated yield. [c] Reaction conditions: 1 (0.5 mmol), $SOCl_2$ (3.5 equiv), DMSO (1 mL), 70 °C, for 40 min.

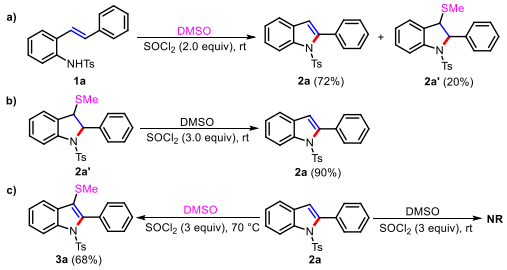
Literature survey indicated that 3-methylthioindole derivatives were widely studied in medicinal chemistry and drug development due to their interesting biological activities.[21] Having this in mind, we came to investigate substrate scope for the synthesis of the biologically interesting 3-methylthioindole **3**. The results listed in Table 4 showed that all substrates **1** employed in this reaction were smoothly converted to the corresponding products **3** in moderate to good yield. When *N*-Ts-2-styrylaniline **1a** was applied, the reaction afforded the desired 3-methylthioindole **3a** in 55% yield, together with the formation of some unidentified byproducts. Specifically, substrates **1** bearing either an electron-donating methyl group, or an electron-withdrawing fluoro or bromo substutent on the left phenyl ring could form the corresponding products **3b-d** in moderate yield. Furthermore, substrates bearing fluoro, methyl or methoxy group on the right phenyl ring, were all conveniently transformed into the corresponding products **3e-j**, with 3-methylthioindole **3e** obtained in relatively lower yield. Meanwhile, the reaction of 2-thienyl-substituted substrate also gave the corresponding product **3k** in satisfactory yield. To our delight, it was found that when Ms, Boc or Ac group were used to take the place of Ts substituents on the N-atom, the corresponding indole products **3l-n** could also be achieved under the standard conditions.

In the past decades, some deuterated pharmaceutical agents have exhibited good biological activity, which has gradually received extensive attention.[22] It is worth noting that DMSO could also be replaced with its deuterated counterpart in our method. As shown in Scheme 2, treating substrate **2v** (0.5 mmol) with 3.5 equiv of $SOCl_2$ in 1 mL of DMSO-d_6 can conveniently afford the desired 3-(d_3-methylthio) indole **3'** in 78% yield.



Scheme 2 DMSO-d_6/$SOCl_2$-mediated synthesis of 3-(d_3-methylthio) indole **3'**

In order to authenticate the reaction mechanism for this transformation, we carried out some control experiments (Scheme 3). First, treating 2-alkenylanilines **1a** with $SOCl_2$ (2.0 equiv) in DMSO under room temperature afforded 3-unsubstituted indole **2a** in 72% yield and 3-methylthioindoline **2a'** in 20% yield at the same time (Scheme 3a). Next, treatment of indoline **2a'** with $SOCl_2$ (3.0 equiv) in DMSO under the standard conditions generated the 3-unsubstituted indole **2a** (Scheme 3b), thus providing further support for the postulate that **2a** was formed through the formation of 3-methylthioindoline **2a'** *via* intramolecular cyclization, followed



Scheme 3 Control experiments

by an elimination process. When 3-unsubstituted indole **2a** was further treated with $SOCl_2$ (3 equiv) in DMSO under 70 °C, it underwent a complete methylthiolation to afford 3-methylthioindole **3a**. However, when the same experiment was carried out at room temperature, no desired product 3a was obtained (Scheme 3c). The results of these control experiments showed that substrates **1** were first converted to the 3-unsubstituted indoles **2,** which could further undergo electrophilic methylthiolation to give 3-methylthioindole **3** at higher temperature.

On the basis of outcomes from these control experiments as well as previous reports,[20] a plausible mechanism for this switchable synthesis of 3-unsubstituted indole and 3-methylthioindole derivatives was purposed in Scheme 4. First, MeSCl **B** was generated *in situ via* intermediate dimethylsulfochlorine cation.[20, 23] Then, the alkene double bond in the substrate reacted with the reactive species MeSCl **B**, through electrophilic addition to afford the sulfonium ion intermediate **C**.[24] Next, 5-exo-tet cyclization occurred in intermediate **C** to give **D**, which was converted to indoline **E** by the abstraction of a proton. Later on, indoline **E** underwent

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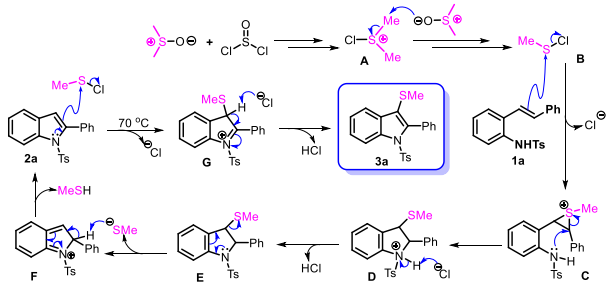
elimination to give **F**, which was converted to 3-unsubstituted indole **2a** *via* deprotonative aromatization. When the reaction was operated at 70 ℃, indole **2a** reacted further with MeSCl **B** *via* electrophilic methylthiolation, *via* intermediate **G**, to afford 3-methylthioindole **3a**.



Scheme 4 Proposed mechanism for the formation of 3-methylthioindoline **2a** and 3-methylthioindole **3a**

In conclusion, we have developed a metal-free oxidative protocol for the switchable synthesis of 3-unsubstituted indoles and 3-methylthioindoles mediated by DMSO/$SOCl_2$. The 3-unsubstituted indoles derivatives could be prepared at room temperature, which was proved to involve intramolecular cyclization followed by elimination process. Besides, 3-methylthioindoles were obtained at higher temperature, through further electrophilic methylthiolation of the obtained 3-unsubstituted indoles. Further investigations on the substrate patterns, e.g., 2-(1-phenylvinyl)anilines and 2-alkynylanilines, as well as reaction mechanism are still in progress in our lab..

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Conflicts of interest

There are no conflicts to declare.

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