Organic LETTERS

Letter

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

pubs.acs.org/OrgLett

Synthesis of 2-(Trifluoromethyl)indoles via Domino Trifluoromethylation/Cyclization of 2-Alkynylanilines

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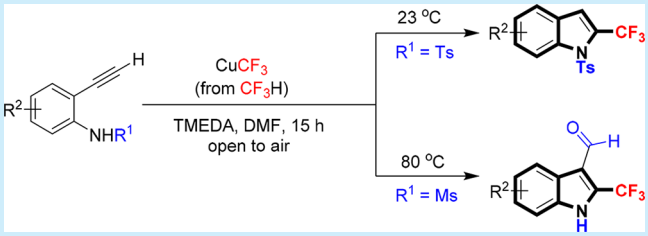
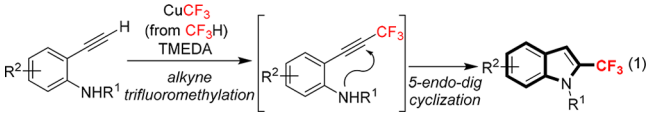
Supporting Information

ABSTRACT: A new method for the synthesis of 2-(trifluoromethyl)indoles using easily accessible 2-alkynylanilines and a well-established fluoroform-derived $CuCF_3$ reagent is described. This method utilizes a domino trifluoromethylation/cyclization strategy to construct the indole cores with no ambiguity of the CF_3 position. The intriguing 3-formyl-2-(trifluoromethyl)-indoles can also be synthesized by this protocol, which are useful intermediates for the preparation of trifluoromethylated drug analogues. The ultimate CF_3 source is the inexpensive industrial byproduct fluoroform.



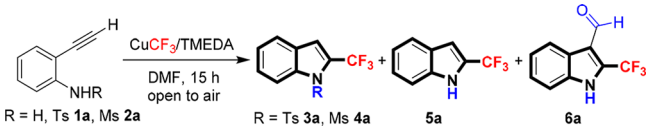
The indole motif is one of the most prevalent and privileged heterocycles in natural products and drug molecules.[1,2] The increasing interest in fluorinated indole derivatives toward drug discovery led to the recent development of methods accessing *trifluoromethylated indoles*, an important class of trifluoromethylated heterocycles.[3] Reports on Fischer indole synthesis[4a,b] as well as other cyclization methods[4c−k] using CF_3-containing building blocks are known, though the synthetic sequences were usually tedious due to the preparation of trifluoromethylated precursors. The majority of current methods are based on trifluoromethylation of existing indole cores.[5,6] Transition-metal-catalyzed cross-coupling of indoles containing boron,[5a−g] halide,[5h−j] and silicon[5k] functional groups have been successfully developed without the need of fluorinated building blocks. However, the reliance of prefunctionalized indoles bearing activating groups at specific positions was inconvenient and equally demanding. More direct C−H trifluoromethylation of indoles using transition-metal-catalyzed,[6a−f] photoredox catalysis,[6g−i] and radical[6j−m] methods has overcome this disadvantage. At the same time, the control of regioselectivity (2-CF_3 vs 3-CF_3) was generally difficult with substrates not containing a blocking group, therefore limiting the reaction scope.[6n−q] In the context of our interest in developing novel trifluoromethylation methods for synthesizing trifluoromethylated heterocycles,[7] we herein describe the preparation of 2-(trifluoromethyl)indoles via a domino trifluoromethylation/cyclization strategy.

We have previously reported an efficient trifluoromethylation method of terminal alkynes using Grushin's fluoroform-derived $CuCF_3$ and TMEDA (tetramethylethylenediamine).[7a] This reaction can potentially be applied to the synthesis of 2-(trifluoromethyl)indoles from readily accessible 2-alknylanilines (eq 1). In a domino fashion,[8] the strategy relies on the trifluoromethylation of terminal alkyne, followed by 5-*endo-dig* cyclization, initiated by the *ortho* nitrogen nucleophilic attack to the triple bond, to construct the indole core. Such a convenient approach has surprisingly not been reported, despite the fact that the synthesis of functionalized indoles via cyclization of 2-alkynylanilines is well-documented.[2]



To test the hypothesis and optimize the reaction conditions (Table 1), the $CuCF_3$ reagent was first prepared according to

Table 1. Optimization Studies[a]



entry	R	conc (M)	temp (°C)	yield of **3a** or **4a**[b] (%)	yield of **5a**[b] (%)	yield of **6a**[b] (%)
1	H	0.06	23		0	0
2	Ts	0.06	23	77	0	0
3	**Ts**	**0.13**	**23**	**81/82**[c]	**0**	**0**
4[d]	Ts	0.13	23	20	0	0
5	Ts	0.13	50	57	7	0
6	Ts	0.13	80	47	6	trace
7	Ms	0.13	80	0	0	70[c]
8	**Ms**	**0.06**	**80**	**0**	**0**	**80**[c]
9[d]	Ms	0.06	80	18	2	0
10	**Ms**	**0.06**	**50**	**8**	**57/58**[c]	**trace**
11	Ms	0.06	23	28/28[c]	53/51[c]	0

[a]General conditions: 2-alkynylaniline (0.1−0.2 mmol), fluoroform-derived $CuCF_3$ (3.0 equiv), TMEDA (3.0 equiv). [b]Determined by ^{19}F NMR analysis using benzotrifluoride as the internal standard. [c]Isolated yield. [d]Without TMEDA.

Received: February 11, 2018

DOI: 10.1021/acs.orglett.8b00509
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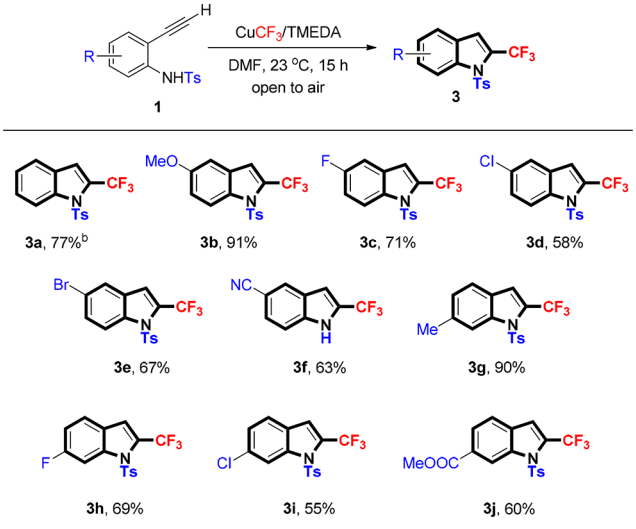
the literature procedures[9] from copper(I) chloride, potassium *tert*-butoxide, and fluoroform in DMF, stabilized with triethylamine trihydrofluoride ($Et_3N{\cdot}3HF$). Under previously developed conditions, 2-ethynylaniline did not provide any indole products (entry 1); only alkyne trifluoromethylation took place (80% yield) without subsequent cyclization.[7a] A drastic change in reactivity was observed when the *N*-tosyl derivative **1a** was employed, which provided the desired 2-(trifluoromethyl)-indole product **3a** in 77% yield (entry 2). Increasing the concentration further improved the yield to 81% (entry 3). The addition of TMEDA was important for the reaction (entry 4). Higher temperatures led to decreased yields with small amounts of desulfonylated product **5a** (entries 5 and 6). To our surprise, when the *N*-mesyl substrate **2a** was used at 80 °C, the 3-formyl 2-CF_3 *N*-H indole product **6a** was obtained exclusively (entry 7). In this case, a lower concentration increased the yield (entry 8). The addition of TMEDA (entry 9) and higher temperature (entries 10 and 11) were crucial for the formation of **6a**, although at 50 °C the desulfonylated product **5a** was isolated in reasonable yield as the major product (entry 10). Overall, three conditions were found to obtain three distinct 2-(trifluoromethyl)-indole products **3a**, **5a**, and **6a** from the common substrate 2-alkynylanilines (entries 3, 10, and 8, respectively). Other *N*-protecting groups were also screened at both 23 and 80 °C (see the Supporting Information for full details). It was found that substrates containing electron-deficient groups, such as −*N*HAc, −*N*HBz, and −*N*HCbz, were more prone to cyclization to give products similar to **3a**/**4a** (albeit in much poorer yields, 3−27%) than electron-rich groups such as −*N*HBn (only alkynyl-CF_3 product obtained). None of these substrates afforded products **5a** and **6a**. We also found that the use of secondary amines such as **1a**/**2a** was important for the reaction. For example, using substrates containing −*N*TsMe and −*N*MsMe did not give any **3a** and **6a**, respectively, under standard conditions (cf. entries 3 and 8). Instead, only alkynyl-CF_3 products were detected.

The scope of 2-(trifluoromethyl)indoles **3** was subsequently investigated (Scheme 1). Indoles **3a**−**j** were prepared from **1** at

Scheme 1. Scope of 2-(Trifluoromethyl)indoles 3[a]

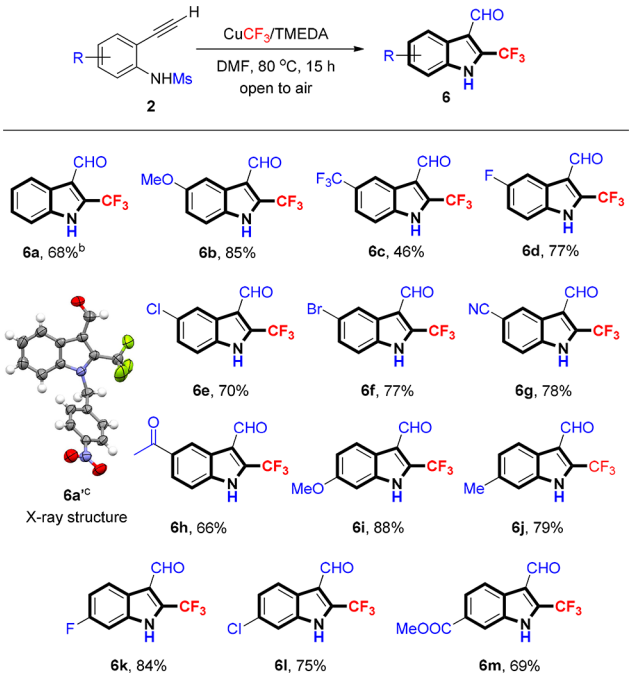


[a]General conditions: **1** (0.2 mmol, 0.13 M in DMF), fluoroform-derived $CuCF_3$ (3.0 equiv), TMEDA (3.0 equiv), isolated yields. [b]1 mmol scale.

room temperature in moderate to good yields tolerating a variety of functional groups. In general, compounds containing electron-withdrawing groups, such as halogens (**3c**−**e**, **h**,**i**), nitrile (**3f**), and ester (**3j**), were obtained in lower yields, compared to those with electron-donating groups (**3b**,**g**), which was mainly due to the formation of desulfonylated side products. In particular, the nitrile-containing *N*-H indole product **3f** was isolated as the major product from the reaction.

On the other hand, the 3-formyl-2-(trifluoromethyl)indoles **6a**−**m** were prepared from **2** at 80 °C in good yields tolerating halogens (**6d**−**f**,**k**-**l**), nitrile (**6g**), ketone (**6h**), and ester (**6m**) (Scheme 2). The lower yield of **6c** was due to the partial

Scheme 2. Scope of 3-Formyl-2-(trifluoromethyl)indoles 6[a]



[a]General conditions: **2** (0.2 mmol, 0.06 M in DMF), fluoroform-derived $CuCF_3$ (3.0 equiv), TMEDA (3.0 equiv), isolated yields. [b]1 mmol scale [c]The *N*-(4-nitrobenzyl) derivative of **6a**.

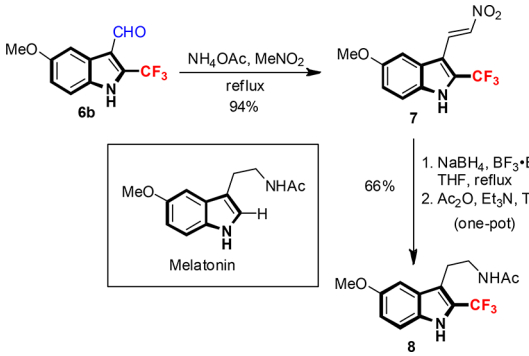
decomposition of the substrate **2c** during the reaction. In all cases, the relatively sensitive formyl group remained intact under the reaction conditions. The structure of **6a** was confirmed by X-ray crystallography through its derivative **6a′**. The C-2 CF_3 group and the C-3 formyl group were unambiguously confirmed.

The formyl functionality of the indole product **6** was versatile for further transformations. To demonstrate its utility, compound **6b** was employed to synthesize the trifluoromethylated analogue of melatonin (Scheme 3), a hormone involved in circadian entrainment and numerous physiological processes.[10a] In two simple operations, condensation with nitromethane, followed by reduction and *N*-acetylation,[10b] the corresponding 2-CF_3 analogue of melatonin **8** was prepared successfully. Such a compound could find useful applications in the structure−activity relationship (SAR) studies.

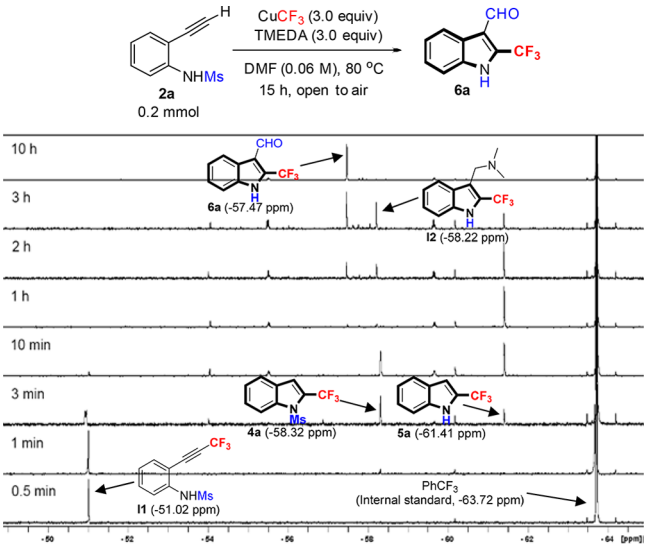
The transformation of **2** to the formylated indoles **6** is intriguing (cf. Scheme 2, vide supra) and, to the best of our knowledge, is unprecedented. Control experiments showed that aerobic conditions were crucial for the formylation process (eq 2). Separately prepared **5a** gave product **6a** in good yield (83%) under standard conditions, thus suggesting its intermediacy (eq 3). By monitoring the reaction of **2a** over time using ^{19}F NMR (Scheme 4), we were able to detect the various intermediates toward product **6a**, including the CF_3-containing alkyne **I1** prior to cyclization, the *N*-mesyl indole **4a**, the *N*-H

DOI: 10.1021/acs.orglett.8b00509
Org. Lett. XXXX, XXX, XXX−XXX

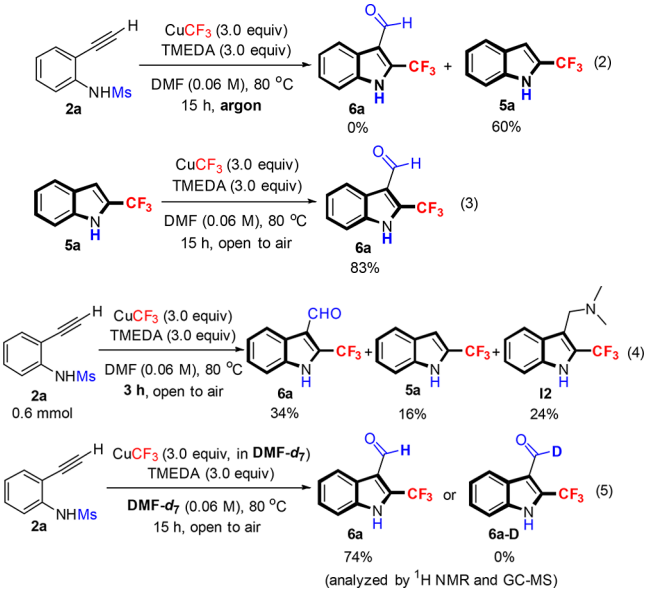
Scheme 3. Synthesis of the Trifluoromethylated Analogue of Melatonin



Scheme 4. ^{19}F NMR Studies of the Conversion of 2a to 6a over Time under Standard Conditions (NMR Solvent = Acetone-d_6)

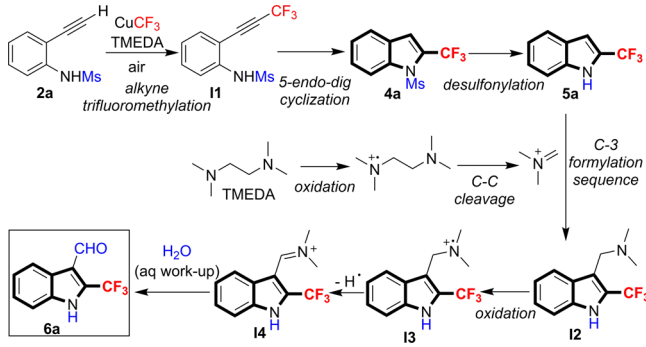


indole **5a**, and a transient intermediate **I2**. When the reaction was stopped after 3 h, we were able to isolate and characterize intermediate **I2** (eq 4). To probe whether the solvent DMF participated in the formylation step, the reaction was carried out in DMF-d_7 and showed no deuterium-incorporated product (eq 5).



On the basis of the above studies and the known literature examples, the following mechanism is proposed for the formation of the 3-formyl-2-(trifluoromethyl)indole **6a** from **2a** (Scheme 5).

Scheme 5. Proposed Mechanism for Domino Trifluoromethylation/Cyclization/Desulfonylation/Formylation of 2a



2-Alkynylaniline **2a** undergoes facile trifluoromethylation at the alkyne terminus to form intermediate **I1**, facilitated by Cu(II)CF_3 and TMEDA under aerobic conditions.[7a] To investigate the subsequent 5-*endo-dig* cyclization and desulfonylation for the formation of **4a** and **5a**, respectively, **I1** was separately prepared and subjected to additives, such as $Et_3N{\cdot}3HF$, Et_3N, KF, and TMEDA, which were likely to be present in the fluoroform-derived $CuCF_3$ reagent[9a,c] and the reaction mixture (see the Supporting Information). The results revealed that simple heating at 80 °C (or with $Et_3N{\cdot}3HF$, Et_3N, and TMEDA) could trigger the cyclization of **I1** to **4a** quantitatively, which might be due to the strong activating (electron-withdrawing) effect by the CF_3 group at the alkyne terminus. In contrast, in the presence of a fluoride such as KF, the desulfonylated product **5a** was obtained exclusively. This observation is consistent with the literature reports,[11] thus suggesting that desulfonylation of **4a** to **5a** is caused by the fluoride used for stabilizing the $CuCF_3$ reagent.[9a]

Copper(II)-catalyzed C-3 formylation of indoles using tertiary amines and molecular oxygen at high temperature (120 °C) is known.[12a] Under the oxidative conditions (aerobic), we expected a copper(II) species to be present after the formation of **I1**.[7a,12b] TMEDA presumably first undergoes one-electron oxidation to the corresponding amine radical cation in the presence of copper and oxygen. Subsequent C−C bond cleavage results in a highly reactive iminium ion.[12c] Attack of iminium by indole **5a** installs one carbon unit at the C-3 position leading to intermediate **I2**.[12d] A second one-electron oxidation takes place to give radical cation **I3**, followed by hydrogen atom abstraction leading to iminium **I4**. Hydrolysis upon aqueous workup eventually provides the 3-formyl-2-(trifluoromethyl)indole **6a**, where the one carbon unit is derived from TMEDA and oxygen comes from water (see the SI for $H_2{}^{18}O$-labeling experiments). The dual role of TMEDA as both a ligand (in the alkyne trifluoromethylation step) and reactant (one carbon donor in the formylation sequence) is worth noting. Overall, a remarkable domino *trifluoromethylation−cyclization−desulfonylation−formylation* sequence is achieved.

In conclusion, we have developed a new synthetic method for the preparation of 2-(trifluoromethyl)indoles from readily available 2-alkynylanilines with no ambiguity of the CF_3 position. An intriguing process for the synthesis of 3-formyl-2-(trifluoromethyl)indoles was discovered that involved a

DOI: 10.1021/acs.orglett.8b00509
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domino sequence for multiple bond formations in one pot without the isolation and purification of intermediates. Such products were useful for the expedient synthesis of trifluoromethylated analogues of pharmaceutically relevant compounds. Further development of efficient domino reactions for the synthesis of novel trifluoromethylated heterocycles is ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00509.

Experimental procedures, characterization data and NMR spectra (PDF)

Accession Codes

CCDC 1571261 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.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Research Grants Council of Hong Kong (CUHK 24301217) and the Chinese University of Hong Kong (the Faculty Strategic Fund for Research from the Faculty of Science and the Direct Grant for Research 4053199).

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DOI: 10.1021/acs.orglett.8b00509
Org. Lett. XXXX, XXX, XXX−XXX