



Cite this: *RSC Adv.*, 2024, 14, 14465

Received 15th March 2024

Accepted 27th April 2024

DOI: 10.1039/d4ra02003k

rsc.li/rsc-advances

Ts₂O mediated deoxygenative C2-dithiocarbamation of quinoline N-oxides with CS₂ and amines†

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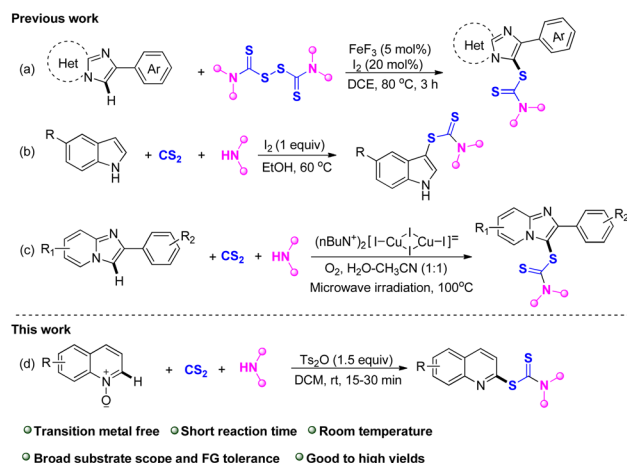
A general, efficient and practical protocol for Ts₂O promoted deoxygenative dithiocarbamation of quinoline N-oxides with *in situ* generated dithiocarbamic acids from CS₂ and amines is reported. The reaction proceeded well under transition-metal free conditions to obtain a variety of novel quinoline-dithiocarbamate compounds with wide functional group tolerance and good to high yields.

Introduction

Dithiocarbamates are a significant class of sulfur-containing organic compounds with diverse biological properties, including anticancer, antibacterial, antioxidation and insecticidal activities.¹ Apart from their essential role in cancer treatment,² rubber industry,³ agricultural chemistry⁴ and polymer chemistry,⁵ they also serve as versatile intermediates in organic synthesis.⁶ Among the various dithiocarbamates, aryl dithiocarbamates have obtained extensive attention due to their intriguing biological behaviors and synthetic applications. Traditionally, aryl dithiocarbamates are primarily synthesized through reactions involving isothiocyanates with thiophenols⁷ or dithiochloroformates with amines.⁸ However, these methods are associated with complex and laborious procedures, the use of hazardous and toxic reagents, and relatively low yields.

In the past few decades, the cross-coupling reaction has emerged as a prominent method for synthesizing aryl dithiocarbamates.⁹ Especially, the three-component cross-coupling reactions based on arylne,¹⁰ aryl halides,¹¹ aryl diazonium fluoroborates,¹² dibenzothiophenium salts¹³ or diaryliodonium triflates¹⁴ with CS₂ and amines to access aryl dithiocarbamates have made great achievements. However, these protocols require the pre-functionalization of the aromatic substrates, and some reactions cannot avoid the use of transition metals and elevated temperature. Most importantly, these developed methods mainly focus on the synthesis of various phenyl-dithiocarbamates. Very limited examples are reported on the synthesis of heterocyclic dithiocarbamates *via* direct C–H functionalization of heterocycles despite that these heterocyclic

dithiocarbamates, such as chromone-dithiocarbamates,¹⁵ indole-dithiocarbamates,¹⁶ triazole-dithiocarbamates,¹⁷ indolizine-dithiocarbamates,¹⁸ benzimidazole-dithiocarbamates,¹⁹ aminosugar-dithiocarbamates²⁰ and quinazolinone-dithiocarbamates,²¹ exhibit exceptional bioactivities. In 2006, Tang *et al.*²² firstly disclosed a C–H thiolation strategy for the incorporation of dithiocarbamates into imidazoheterocycles using I₂ and FeF₃ as co-catalysts (Scheme 1a). Subsequently, In 2018, Halimehjani and co-workers²³ developed a practical and molecular iodine mediated C–H sulfenylation method to introduce dithiocarbamate groups into indole units *via* the three-component reaction involving indoles, carbon disulfide and amines (Scheme 1b). Most recently, Nagula Shankaraiah *et al.*²⁴ reported a one-pot, microwave-assisted, copper-catalyzed dithiocarbamation of imidazo[1,2-*a*]pyridines with carbon disulfide and amines (Scheme 1c). To our knowledge, the incorporation of dithiocarbamate groups into quinoline skeletons *via* C–H functionalization strategy has not been previously



Scheme 1 Representative examples on C–H dithiocarbamation of heterocycles.

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4ra02003k>

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documented. Given the distinct biological properties of quinolines and dithiocarbamates along with their widespread application in pharmaceutical and pesticide industry,²⁵ the development of efficient approaches to simultaneously incorporate quinoline units and the dithiocarbamate groups to a single molecular structure is highly desirable and remains persistent challenges.

In the past few years, great achievements have been made on the C–H functionalization of quinoline *N*-oxides with various nucleophiles for the synthesis of 2-substituted quinolines.²⁶ These nucleophiles mainly include alcohols,²⁷ amines,²⁸ thiols,²⁹ phenols,³⁰ 1,3-dicarbonyl compounds,³¹ RSO_2Na ³² and AgSCF_3 .^{16b,33} However, the utilization of dithiocarbamic acids derived from the reaction of CS_2 and amines as nucleophiles to construct quinoline-dithiocarbamates has never been reported yet. With our continuing research interest in C–H functionalizations of quinoline *N*-oxides,³⁴ we herein report a convenient and practical protocol for the synthesis of quinoline-dithiocarbamates *via* Ts_2O promoted deoxygenative C2–H dithiocarbamation of quinoline *N*-oxides under mild and transition-metal free conditions (Scheme 1d).

Results and discussion

Initially, quinoline *N*-oxide (**1a**), carbon disulfide and diethylamine (**2a**) were selected as model substrates to evaluate this three-component reaction, as shown in Table 1. Performing the

model reaction at room temperature for 0.5 h using *p*-toluenesulfonyl chloride as an electrophilic activating reagent and DCM as a solvent, 11% NMR yield of **3aa** was detected (entry 1). Subsequently, some other electrophilic activating reagents including methyl sulfonyl chloride (entry 2), *p*-toluene sulfonic anhydride (entry 3), methyl sulfonic anhydride (entry 4), trifluoromethanesulfonic anhydride (entry 5), benzoyl chloride (entry 6), acetic anhydride (entry 7) and PyBrop (entry 8) were examined and the results revealed that *p*-toluenesulfonic anhydride gave the best 84% yield of **3aa**. However, other investigated activating agents could only afford the target product in moderate to low yields, among which acetic anhydride, mesulfonic anhydride and PyBroP did not give the desired product likely due to their lower electrophilic activities compared to Ts_2O . Furthermore, the impact of different solvents on the reaction was explored, including CH_3CN (entry 9), THF (entry 10), DCE (entry 11), acetone (entry 12), DMF (entry 13), EtOAc (entry 14), DMSO (entry 15) and water (entry 16). In contrast to DCM, other solvents failed to give better yields of **3aa** and solvent DMSO was found not suitable for the present transformation. Besides, the absence of any activating reagent led to no detection of product **3aa**, highlighting the crucial role of the activating agent in this process (entry 17).

After obtaining the optimized reaction conditions (Table 1, entry 3), the substrate scope and limitations of the present reaction were examined with respect to both quinoline *N*-oxides and amines, as shown in Table 2. Various quinoline *N*-oxides substituted with electron-donating, electron-withdrawing or sterically hindered groups at different positions on the quinoline rings, all reacted well to afford the expected products in moderate to good yields (**3aa–3ra**). Notably, functional groups such as methyl (**3ba**, **3fa**, **3ga**, **3ma** and **3oa**), methoxy (**3ha**), aryl (**3ea** and **3pa**), fluoride (**3ia**), chloride (**3ca** and **3ja**), bromide (**3da** and **3ka**), trifluoromethyl (**3na**) and ester (**3la**) groups were found to be compatible with the reaction. Furthermore, di-substituted quinoline *N*-oxides also served as suitable substrates, providing products **3qa** and **3ra** in 72 and 64% yields, respectively. Some other nitrogen-containing compounds were then investigated, of which 1*H*-pyrrolo[2,3-*b*]pyridine 7-oxide (**1s**) gave the corresponding product **3sa** in 78% yield. In contrast to quinoline *N*-oxides, some substituted pyridine *N*-oxides as potential reaction substrates can also give acceptable results (**3ta–3va**), while isoquinoline *N*-oxide (**1w**), quinoxaline 1-oxide (**1x**), 4-nitroquinoline *N*-oxide (**1y**), 3-cyanoquinoline *N*-oxide (**1z**), pyridine *N*-oxide, and 4-cyanopyridine *N*-oxide failed to give the corresponding products (**3wa–3za**, **4aa** and **4ba**), with most of the starting substrates being recovered in the case of pyridine and 4-cyanopyridine *N*-oxides.

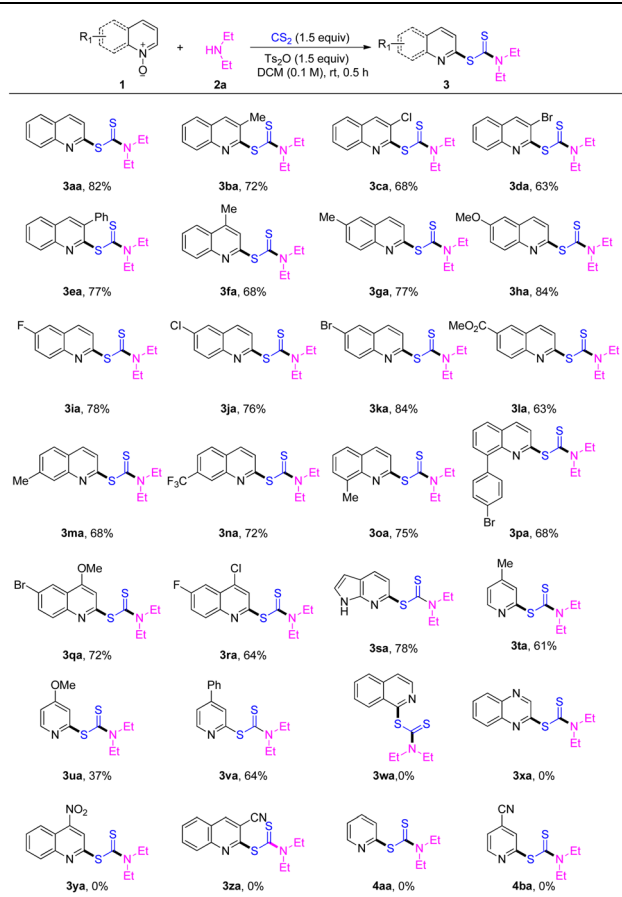
The scope of the three-component coupling reaction between quinoline *N*-oxide (**1a**), CS_2 and different amines was then investigated, as revealed in Table 3. Chain dialkylamines reacted well under standard conditions, yielding the corresponding products in 62–83% yields (**3ab–3af**). Furthermore, some cyclic amines including pyrrolidine (**2g**), piperidines (**2h** and **2i**), morpholine (**2j**) and azocane (**2k**) all reacted readily and gave the desired products (**3ag–3ak**) in good to excellent yields. However, several primary amines such as butan-1-amine (**2l**), 2-

Table 1 Optimization of the reaction conditions^a

Entry	Activating agent	Solvent	Yield ^b (%)
1	TsCl	DCM	11
2	MsCl	DCM	16
3	Ts_2O	DCM	84
4	Ms_2O	DCM	0
5	Tf_2O	DCM	57
6	BzCl	DCM	53
7	Ac_2O	DCM	0
8	PyBroP	DCM	0
9	Ts_2O	CH_3CN	34
10	Ts_2O	THF	26
11	Ts_2O	DCE	82
12	Ts_2O	Acetone	62
13	Ts_2O	DMF	78
14	Ts_2O	EtOAc	31
15	Ts_2O	DMSO	0
16	Ts_2O	H_2O	43
17	None	DCM	0

^a Conditions: **1a** (0.1 mmol, 1 equiv.), **2a** (0.15 mmol, 1.5 equiv.), activating agent (0.15 mmol, 1.5 equiv.), solvent (1 mL), r.t., 0.5 h, air atmosphere. ^b Yield of **3aa** was determined by ^1H NMR. PyBroP: bromotripyrrolidinophosphonium hexafluorophosphate.



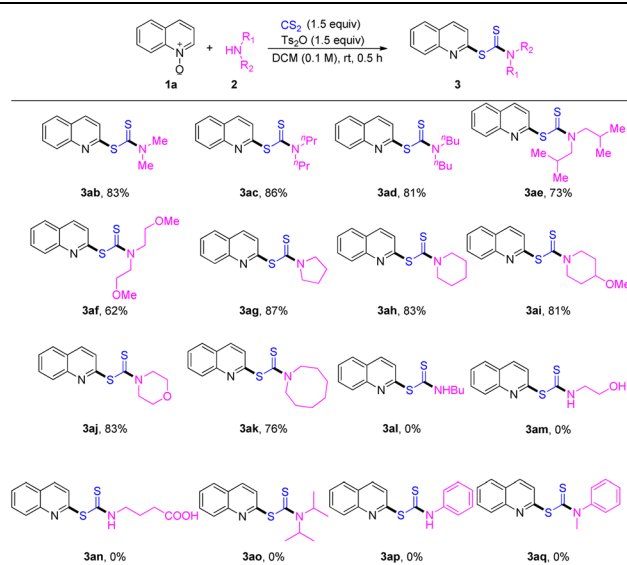
Table 2 Reaction scope^a

^a Reaction conditions: **1** (0.3 mmol), **2a** (0.45 mmol), CS_2 (0.45 mmol), Ts_2O (0.45 mmol), DCM (3 mL), r.t., air, 0.5 h, isolated yields based on **1**.

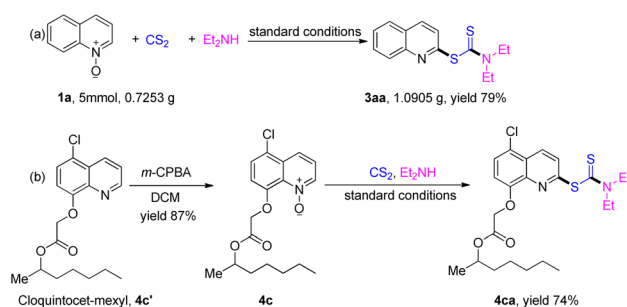
aminoethanol (**2m**), 4-aminobutanoic acid (**2n**), diisopropylamine (**2o**), aniline (**2p**) and *N*-methylaniline (**2q**) failed to deliver the expected products (**3al–3aq**). Notably, *N*-butylquinolin-2-amine was obtained in a 74% isolated yield under standard conditions *via* the direct deoxygenative C2–H amination reaction of quinoline *N*-oxide (**1a**) with butan-1-amine (**2l**).

To better demonstrate the practicability of the three-component reaction, a gram-scale experiment involving **1a** (5 mmol, 0.7253 g), CS_2 and diethylamine (**2a**) was conducted under standard conditions. As expected, the desired product **3aa** was obtained in 79% isolated yield (Scheme 2a). To further show the synthetic utility of the present method, cloquintocet-mexyl, an effective herbicide **4c'**, was oxidized by *m*-CPBA to afford substrate **4c**, which reacted smoothly with CS_2 and diethylamine under standard conditions and gave product **4ca** in 74% isolated yield (Scheme 2b).

To gain further insight into the three-component reaction mechanism, a series of control experiments were conducted, as depicted in Scheme 3. Initially, quinoline **1a'**, carbon disulfide and diethylamine were combined under standard conditions, yet no formation of **3aa** was observed (Scheme 3a). This result shows that quinoline *N*-oxide is crucial for this reaction and the

Table 3 Reaction scope^a

^a Reaction conditions: **1a** (0.3 mmol), **2** (0.45 mmol), CS_2 (0.45 mmol), Ts_2O (0.45 mmol), DCM (3 mL), r.t., air, 0.5 h, isolated yields based on **1a**.

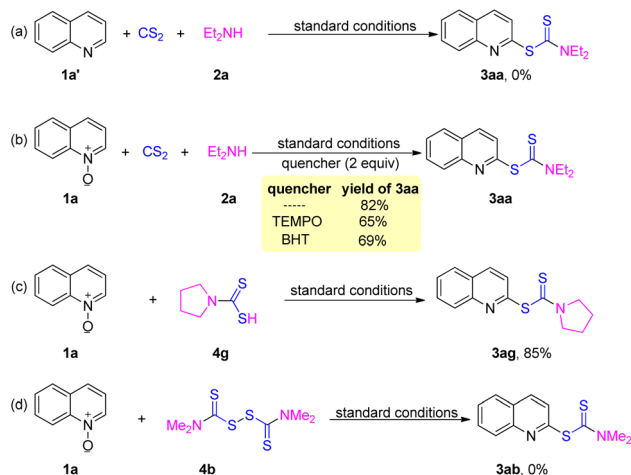


Scheme 2 Gram-scale experiment and late stage functionalization.

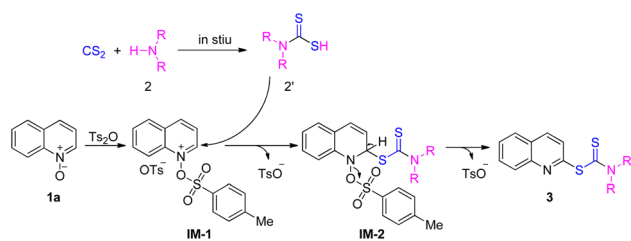
possibility of quinoline as an intermediate during the transformation could be ruled out. Furthermore, two common free radical inhibitors, TEMPO and BHT were added to the reaction system under standard conditions, the yields of **3aa** were not significantly affected, suggesting that free radicals might not be involved in the reaction (Scheme 3b). In addition, a reaction between **1a** and **4g** resulted in the formation of product **3ag** in 85% yield, indicating that the *in situ* generation of dithiocarbamic acid from the reaction of CS_2 and amine could potentially serve as reaction intermediate (Scheme 3c). However, when compound **4b** was utilized instead of CS_2 and amine, and its reaction with **1a** under standard conditions, no product **3ab** was detected (Scheme 3d), effectively ruling out tetraalkylthiuram disulfide as a reaction intermediate.

Based on the control experiment stated above and relevant literature reports,^{26a,29,32c} a possible reaction mechanism was illustrated in Scheme 4. Firstly, quinoline *N*-oxide **1a** was activated by *p*-toluenesulfonic anhydride to produce the activated intermediate **IM-1**, which is further regioselectively nucleophilic





Scheme 3 Control experiments.



Scheme 4 Possible mechanism.

attacked by dithiocarbamic acid **2'** generated *in situ* from carbon disulfide and amine **2** to form another intermediate **IM-2**. Subsequently, the intermediate **IM-2** underwent rearomatization to yield the target product **3**, along with the release of 4-methylbenzenesulfonate anion in the current basic system.

Conclusions

In summary, we have established the first example of Ts_2O promoted three-component reaction involving quinoline *N*-oxides, CS_2 and amines to introduce dithiocarbamates onto the quinoline skeleton at ambient temperature. The *in situ* generated dithiocarbamates from CS_2 and amines act as nucleophiles, attracting the C2 position of quinoline *N*-oxides towards diverse quinoline-dithiocarbamates in satisfactory yields with broad functional group tolerance. The present method may provide a powerful tool for the screening of potential bioactive quinoline molecules bearing dithiocarbamate frameworks.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (22101082), the Science and Technology

Innovation Program of Hunan Province (2022RC1119) and the construct program of applied characteristic discipline in Hunan Province.

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