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Copper-Mediated *ortho*-Nitration of Arene and Heteroarene C–H Bonds Assisted by an 8-Aminoquinoline Directing Group

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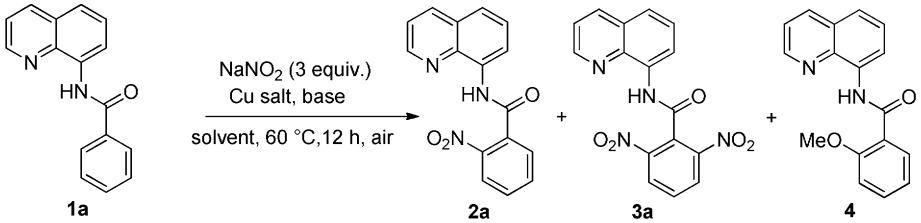
Abstract: A copper-mediated, chelation-assisted *ortho* C–H bond nitration of benzoic acid derivatives using sodium nitrite as the source of the nitro group has been achieved with the aid of an 8-aminoquinoline directing group. Selective mono- or dinitration can be achieved by simply changing the reaction conditions. The method shows excellent functional group tolerance and provides a novel and straightforward route for the preparation of *ortho*-nitrated benzoic acids.

Keywords: arenes; C–H activation; copper; nitration; selectivity

Aromatic nitro compounds are versatile building blocks in the preparation of dyes, pharmaceuticals, plastics, perfumes and explosives.[1] Therefore, much attention has been directed to the development of efficient and practical methods for the nitration of aromatic compounds. The mixed acid system (H_2SO_4/HNO_3) and its derivatives are the benchmark method in the classic electrophilic nitration of arenes. However, in spite of the usefulness of these methods, they tend to suffer from regioselectivity and functional group compatibility issues.[2] Most existing nitrating reagents are strong oxidants, which can limit their application scope for substrates such as phenols and anilines which can be easily oxidized. In order to overcome these problems, several alternative strategies have been developed. For example, nitroarenes can be readily accessed *via* oxidation of aromatic primary amines[3] and azides.[4] Alternatively they can be synthesized from arylmetals *via* nitrodemetallation of aryl C–M bonds (M = B, Li, Sn)[5] or from aryl carboxylic acids[6] *via* nitrodecarboxylation. In addition, transition metal-catalyzed (Pd or Cu) couplings also provide a powerful method for the construction of nitroarenes starting from aryl halides, pseudohalides and arylboronic acids.[7] Since these methods all require the use of prefunctionalized arene starting materials, recent efforts are focused on the development of new methods using the parent arenes as the starting materials. Along this line, significant progress has been made in the transition metal-catalyzed (or promoted), chelation-assisted aromatic C–H nitration.[8] However, the substrate scope of these recent developments is still limited. Thus there remains much room for improvement in the field of selective nitration of arenes.

In recent years, bidentate auxiliaries have attracted considerable attention owing to their unique potential for the activation of C–H bonds.[9] Since the pioneering work of Daugulis and co-workers on the introduction of picolinic acid and 8-aminoquinoline auxiliaries as removable directing groups,[10] extensive research efforts have been devoted to the development of methods for the palladium-catalyzed arylation, alkylation, alkenylation, alkynylation, alkoxylation, borylation, silylation and intramolecular amination of sp^2 and sp^3 C–H bonds.[10,11] Additionally, investigations of these bidentate auxiliaries in C–H bond functionalization based on relatively cheaper metal catalysts such as iron,[12] cobalt,[13] nickel,[14] and ruthenium[15] have also been carried out by several groups. As for the use of Cu salts, Daugulis and co-workers recently discovered the aminoquinoline- and picolinamide-directed, copper-catalyzed sulfenylation, amination, fluorination and etherification of arene and heteroarene C–H bonds[16] while Miura and co-workers discovered the copper-mediated coupling of benzoic acid derivatives and 1,3-azoles with the aid of an 8-aminoquinoline-based double *N*,*N*-coordination strategy.[17] Stahl and co-workers reported the copper-mediated methoxylation of *N*-(8-quinolinyl)benzamide by employing methanol as the solvent.[18] Later on, Niu inde-

Table 1. Optimization of the reaction conditions.[a]



Entry	Cu salt	Base	Solvent	**2a** [%]	**3a** [%]	**4** [%]
1	$Cu(OAc)_2·H_2O$	none	MeOH	38	2	3
2	$Cu(OAc)_2·H_2O$	NaOAc	MeOH	42	3	6
3	$Cu(OAc)_2·H_2O$	K_2CO_3	MeOH	45	6	5
4	$Cu(OAc)_2·H_2O$	KOAc	MeOH	51	4	3
5	$Cu(OAc)_2·H_2O$	K_3PO_4	MeOH	58	2	5
6	$Cu(OAc)_2·H_2O$	KH_2PO_4	MeOH	67	5	3
7	$Cu(OAc)_2·H_2O$	K_2HPO_4	MeOH	78	3	4
8	$Cu(OAc)_2$	K_2HPO_4	MeOH	56	4	5
9	$CuBr_2$	K_2HPO_4	MeOH	0	0	6
10	$CuCl_2$	K_2HPO_4	MeOH	0	0	4
11	CuI	K_2HPO_4	MeOH	0	0	trace
12[b]	$Cu(OAc)_2·H_2O$	K_2HPO_4	MeOH	52	trace	3
13[c]	$Cu(OAc)_2·H_2O$	K_2HPO_4	MeOH	36	trace	2
14	–	K_2HPO_4	MeOH	trace	0	0
15	$Cu(OAc)_2·H_2O$	K_2HPO_4	toluene	trace	0	n.d
16	$Cu(OAc)_2·H_2O$	K_2HPO_4	THF	trace	0	n.d
17	$Cu(OAc)_2·H_2O$	K_2HPO_4	dioxane	trace	0	n.d
18	$Cu(OAc)_2·H_2O$	K_2HPO_4	CH_3CN	trace	0	n.d
19	$Cu(OAc)_2·H_2O$	K_2HPO_4	DMF	16	30	n.d
20[d]	$Cu(OAc)_2·H_2O$	K_2HPO_4	DMF	trace	45	n.d
21[d]	$Cu(OAc)_2·H_2O$	K_2CO_3	DMF	trace	51	n.d
22[d]	$Cu(OAc)_2·H_2O$	Ag_2CO_3	DMF	trace	38	n.d
23[d]	$Cu(OAc)_2·H_2O$	AgOAc	DMF	trace	65	n.d

[a] *Reaction conditions*: amide (0.3 mmol), $NaNO_2$ (0.9 mmol), Cu salt (0.6 mmol), base (0.6 mmol), solvent (1 mL).
[b] $Cu(OAc)_2·H_2O$ (1.5 equiv.).
[c] $Cu(OAc)_2·H_2O$ (1.0 equiv.).
[d] At 80 °C.

pendently reported a copper-mediated direct aryloxylation of benzamides assisted by an *N,O*-bidentate directing group.[19] Very recently, You and co-workers reported a copper-mediated, tandem oxidative alkynylation and annulation of arenes with terminal alkynes by taking advantage of the bidentate-chelation assistance of an 8-aminoquinoline residue[20] while Yu and co-workers discovered the copper-mediated *ortho* C–H alkynylation and trifluoromethylation of arenes by using an amide-oxazoline directing group.[21] In addition, copper-catalyzed intramolecular C(sp^3)–H and C(sp^2)–H amidation with an 8-aminoquinoline or picolinic acid group as the directing group was also developed by several groups.[22] Inspired by these reports, we were tempted to test the use of bidentate auxiliaries in the selective nitration of arenes. Herein we wish to disclose a copper-mediated, aminoquinoline group-assisted nitration of benzoic acid derivatives. (During the preparation of this manuscript, Gooßen reported a similar copper-mediated, *ortho*-nitration of benzamides using NMO as the oxidant, in which only the mononitrated product was observed.[23])

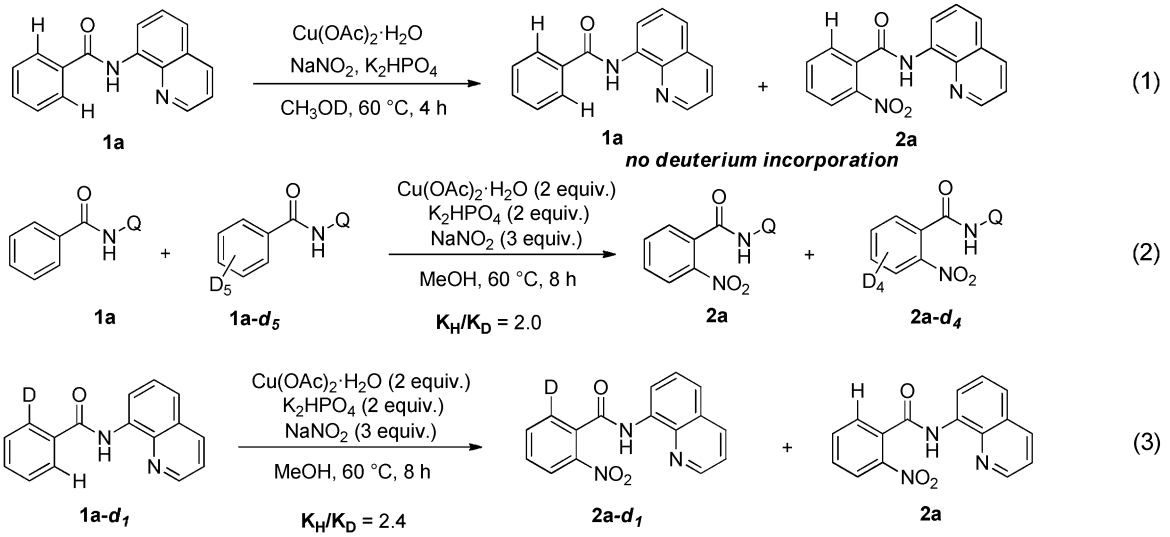
We commenced our studies with the aim to develop a direct *ortho* nitration of benzoic acid derivatives using the aminoquinoline moiety as the coordinating group due to its wide applications in selective C–H functionalizations. *N*-(Quinolin-8-yl)benzamide **1a** was selected as a model substrate for optimizing the reaction conditions, and the results are listed in Table 1 (see the Supporting Information for more extensive screening results). When we treated *N*-(quinolin-8-yl)benzamide **1a** (0.3 mmol) with $NaNO_2$ (0.9 mmol) in the presence of $Cu(OAc)_2·H_2O$ (0.6 mmol) in MeOH (1 mL) under air, the desired mononitrated product **2a** was isolated in 38% yield accompanied by the dinitrated product **3a** in 2% yield (Table 1, entry 1). This showed that the first nitration step is faster than the second nitration step. The yield of **2a** could be increased up to 42% by employing 2 equiv. of NaOAc as the base (Table 1, entry 2). Extensive screening studies showed that the efficiency of the reaction could be significantly affected by the choice of the base used and K_2HPO_4 was determined to be the best base for this reaction (Table 1, entries 2–7). It is important to note that the selectivity

towards mononitration did not change. Other copper salts such as $Cu(OAc)_2$, $CuBr_2$, $CuCl_2$ and CuI were found to be less effective than $Cu(OAc)_2{\cdot}H_2O$ (Table 1, entries 8–11). Decreasing the amount of $Cu(OAc)_2{\cdot}H_2O$ to 1.5 or 1.0 equiv. led to lower yields (Table 1, entries 12 and 13) and the reaction did not work in the absence of copper salts (Table 1, entry 14). Changing the solvent to toluene, THF, dioxane and CH_3CN all gave no product (Table 1, entries 15–18). When the reaction was conducted in DMF, much to our surprise, the selectivity of mononitrated product **2a** *vs.* dinitrated product **3a** was reversed and they are isolated in a 1:2 ratio with a 46% combined yield (Table 1, entry 19). To our delight, highly selective dinitration can be achieved by elevating the reaction temperature to 80 °C and the dinitrated product **3a** was isolated in 45% yield (Table 1, entry 20). Further optimization of base showed the yield of **3a** could be raised to 65% if AgOAc was used as the base (Table 1, entries 21–23).

We next examined the effect of directing groups. No reaction occurred when a series of monodentate directing groups with structures (**A–D**) similar to **1a** were tried in the reaction; which indicated that a bidentate coordinating group is essential for the reaction to proceed. In addition, other *N,N*- or *N,O*-bidentate directing groups (**E–H**) failed to promote this reaction, which showed the indispensable role of the 8-aminoquinoline moiety for this reaction.

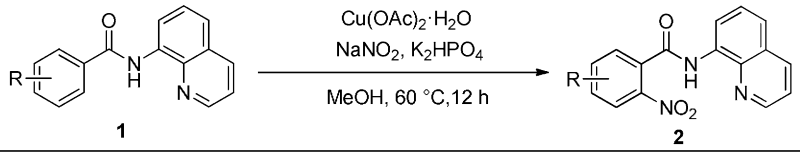
With the optimized conditions in hand, we next set out to examine the scope of mononitration of benzoic acid derivatives and the results are summarized in Table 2. Notably, better results were often achieved when electron-donating groups including methoxy, methyl, ethyl, isopropyl, *tert*-butyl, phenyl groups were placed on the *para*-position of the aromatic ring of the benzoic acid derivatives (**2b–2g**). Benzoic acid derivatives bearing fluoro, chloro, bromo, trifluoromethyl and carboxylate groups on the *para*-position of the benzene ring could also participate in the transformation as well, but the yields were slightly lower (**2h–2l**). In addition, substrates bearing methyl or fluoro group at the *ortho*-position could be used as viable substrates to generate the desired products **2q** and **2r**, showing that the reaction is not sensitive to steric hindrance. Finally, heteroaromatic amides including pyridine and thiophene derivatives can be also efficiently mononitrated (**2s** and **2t**).

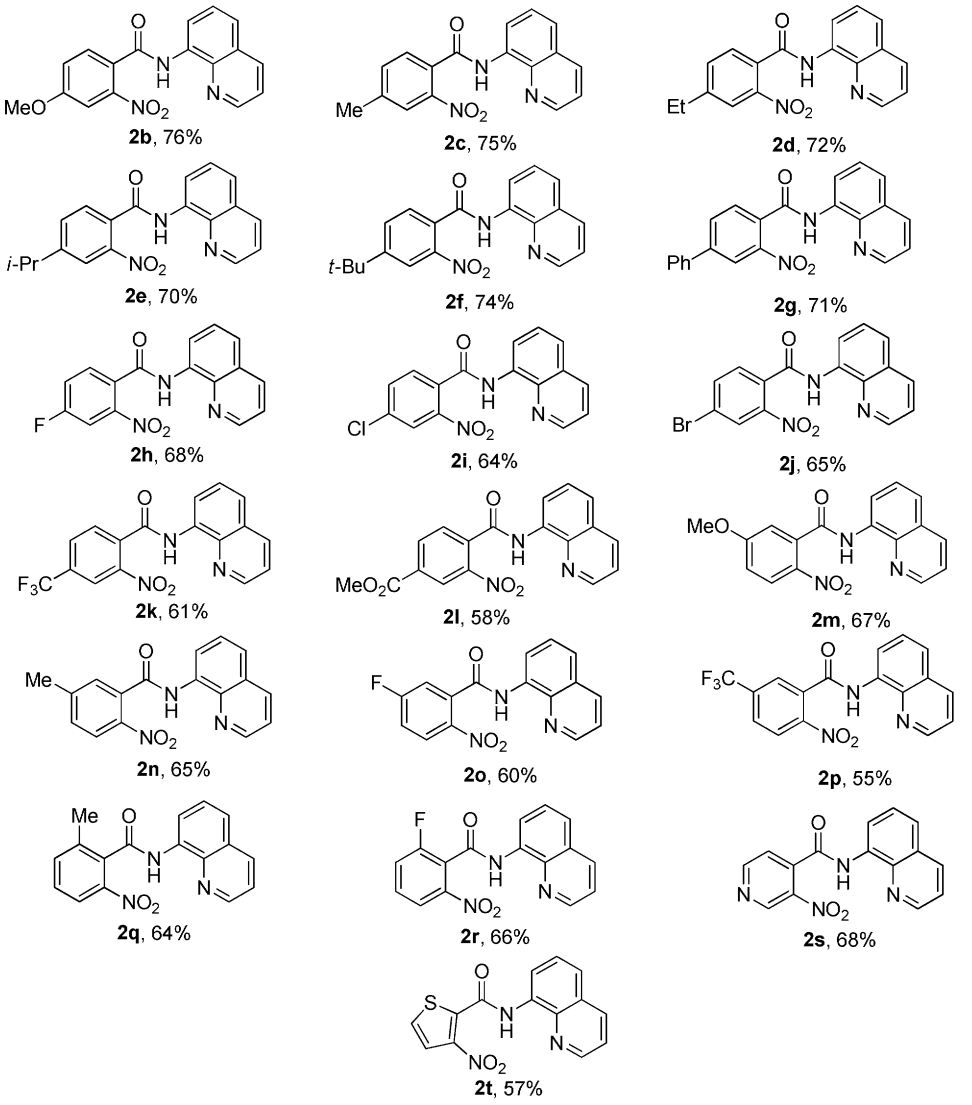
Next, we turned our attention to the selective dinitration of various amides and the results are summarized in Table 3. From this table, we can see that slightly better results were obtained when electron-donating groups including methoxy, methyl, ethyl, isopropyl, *tert*-butyl groups were placed on the *para*-position



Scheme 1. Control reactions.

Table 2. Copper-mediated mononitration of carboxylic acid derivatives.[a]



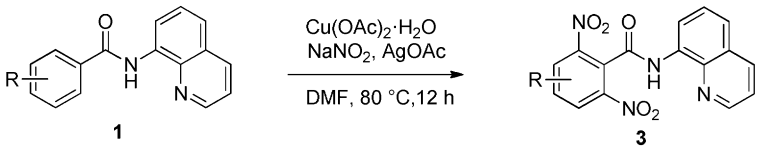


[a] *Reaction conditions*: amide **1** (0.3 mmol), $NaNO_2$ (0.9 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.6 mmol), K_2HPO_4 (0.6 mmol), MeOH (1 mL) under air for 12 h.

(**3b–3f**) whereas lower yields were observed when electron-poor benzamides were used (**3g** and **3h**). It is worthwhile to point out that *meta*-substituted substrates also reacted efficiently with $NaNO_2$ to give the desired products **3i** and **3j** in yields above 50%. Interestingly, a heterocyclic amide such as isonicotinanmide can also be efficiently dinitrated in good yield (**3k**).

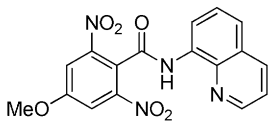
To get some insights into the mechanism of this new transformation, a series of control experiments was performed. When the reaction was conducted in CH_3OD, no deuterium was incorporated into the recovered starting material or the product. This suggested that the C–H activation step is irreversible [Scheme 1, Eq. (1)].[18] The intermolecular K_H/K_D of **1a** to **1a-*d*$_5$** was determined to be 2.0 [Scheme 1, Eq. (2)] and a similar KIE was also obtained from the intramolecular H/D competition experiment [K_H/K_D = 2.4, Scheme 1, Eq. (3)], suggesting that the *ortho* C–H bond cleavage of **1a** was involved in the rate-determining step of the nitration. When the reaction was carried out in the presence of the radical scavenger

Table 3. Copper-mediated dinitration of carboxylic acid derivatives.[a]

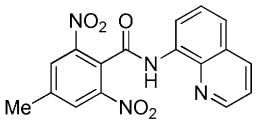


1 → **3**

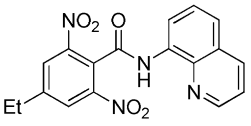
3b, 63%



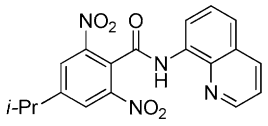
3c, 61%



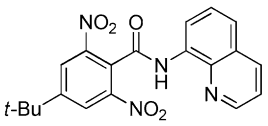
3d, 58%



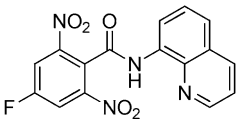
3e, 60%



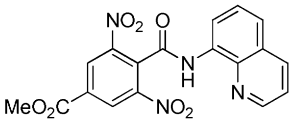
3f, 64%



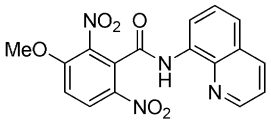
3g, 52%



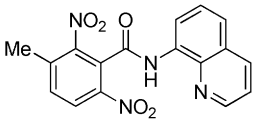
3h, 47 %



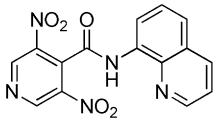
3i, 56%



3j, 53%



3k, 55%

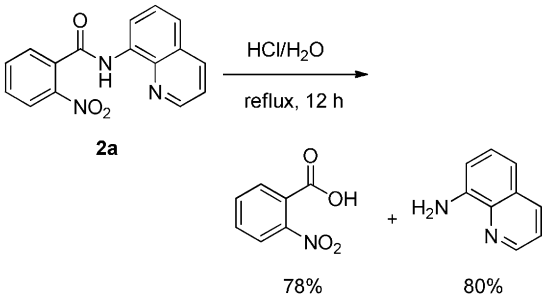


[a] *Reaction conditions*: amide **1** (0.3 mmol), $NaNO_2$ (0.9 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.6 mmol), AgOAc (0.6 mmol), DMF (1 mL) under air for 12 h.

2,2,6,6-tetramethylpiperidine *N*-oxyl (TEMPO, 1 equiv.), the yield of the desired product was only slightly decreased, which ruled out the possibility of a radical mechanism.

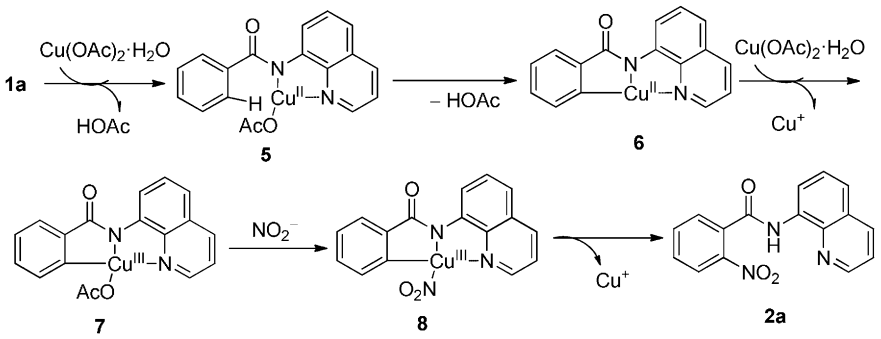
Although the exact mechanism is still not clear at present, on the basis of the above results, a plausible reaction mechanism is proposed and shown in Scheme 2. As depicted in Scheme 2, coordination of **1a** to a copper(II) species followed by ligand exchange generates the copper complex **5**; **5** next undergoes C–H activation to form the aryl/Cu(II) species **6** by a cyclocupration process.[22] Subsequently, the $Cu(OAc)_2$-promoted oxidation of **6** affords a Cu(III) species **7**.[24] Then **7** next reacts with sodium nitrite to generate the copper complex **8**. In the final step, **8** undergoes reductive elimination to produce the desired nitration compound **2a**. Alternatively, the C–H activation step may take place after the center copper(II) ion has been oxidized to copper(III) as proposed by Miura[17] and You.[20]

In order to demonstrate the synthetic utility of our method, **2a** was hydrolyzed with HCl in water and 2-nitrobenzoic acid was isolated in 78% yield. The directing group 8-aminoquinoline could also be recovered in 80% yield [Eq. (4)].



2a → 78% + 80% (4)

In summary, we have developed a novel copper-mediated, chelation-assisted *ortho* C–H bond nitration of benzoic acid derivatives using $NaNO_2$ as the source of the nitro group. The reaction was found to be critically dependent on the use of an 8-aminoquinoline directing group. Selective mono- or dinitration can be achieved by simply changing the reaction conditions. In addition, the auxiliary can be conveniently removed and recovered. Further studies on the mechanistic details of this reaction and efforts to expand the reaction scope are currently underway in our lab; the results will be reported in due course.



Scheme 2. Plausible reaction mechanism.

Experimental Section

General Procedure for Copper-Mediated C–H Mononitration of Benzoic Acid Derivatives

Benzamide **1** (0.3 mmol), $Cu(OAc)_2{\cdot}H_2O$ (120 mg, 0.6 mmol), K_2HPO_4 (105 mg, 0.6 mmol), $NaNO_2$ (62 mg, 0.9 mmol) and anhydrous MeOH (1 mL) were added to a 25-mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. Then the flask was sealed under air and the contents stirred at 60 °C for 12 h. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was then quenched with aqueous 1 M HCl solution (10 mL). The mixture was extracted with ethyl acetate, and the combined organic layer was dried over sodium sulfate. Concentration under vacuum followed by silica gel column purification with petroleum ether/ethyl acetate elutent gave the desired product **2.**

Acknowledgements

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