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Facile Synthesis of 2-Acylthieno[2,3-*b*]quinolines via Cu-TEMPO-Catalyzed Dehydrogenation, sp^2-C−H Functionalization (Nucleophilic Thiolation by S_8) of 2-Haloquinolinyl Ketones

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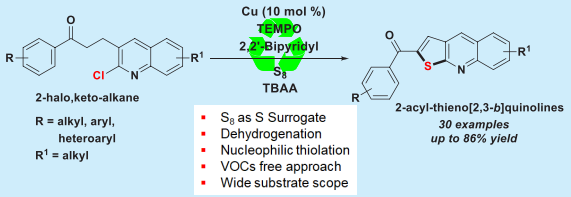
ABSTRACT: An efficient, solvent-free synthesis of 2-acylthieno[2,3-*b*]quinolines is reported from 2-halo-quinolinyl ketones through Cu-TEMPO catalyzed dehydrogenation, sp^2-C−H functionalization using elemental sulfur as thiol surrogate (sulfur source) and tetrabutylammonium acetate as an ionic reaction medium. The optimized reaction conditions give excellent product yields under mild reaction conditions with chemoselectivity and broad functional group tolerance. The synthetic importance of the synthesized molecules is showcased further by Friedländer annulation, reduction, and alkene functionalization reactions.



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In the past few years, nitrogen-containing heterocycles have been considered important due to their engaging biological activities. Among them, quinoline subunits exhibit potential pharmacological activities,[1−3] which are also available in natural products and used as essential intermediates for many organic transformations. In this regard, thienoquinolines are quinoline-fused sulfur-containing heterocycles and are privileged scaffolds available in natural products, pharmaceutical drugs, and also organic light-emitting materials.[4,5] The 2-acylthienoquinoline scaffold is commonly found in various drug molecules and shows its broad range of bioactivities (Figure 1). For example,

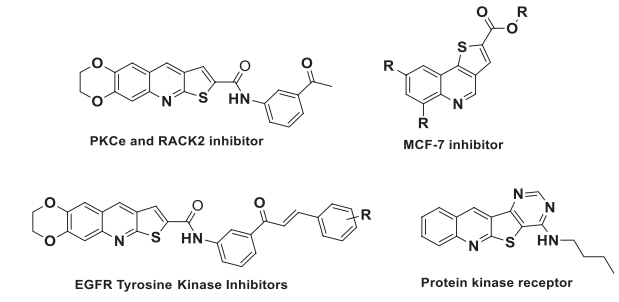

Figure 1. Representative examples of biologically active 2-acylthieno-[2,3-*b*]quinolines.

thienoquinolines are novel disruptors of the PKCε/RACK2 inhibitors.[6] Protein kinase inhibitors in cancer cells show functional interactions with protein kinase receptor against VEGFR1 and CHK2 receptors.[7]

A very few literature reports are available for the synthesis of thienoquinolines (Scheme 1a). Mahadevan and co-workers reported a one-pot reaction of 3-formyl-2-mercaptoquinolines with 1-chloroacetone using K_2CO_3 under microwave conditions, (i).[8] Xie and co-workers reported a domino reaction of o-isothiocyanato-(*E*)-cinnamaldehyde with α-halocarbonyl compounds, utilizing L-proline and DBU in methanol (ii).[4] Koketsu and co-workers reported an iodine mediated synthesis of thieno[2,3-*b*]quinoline derivatives via electrophilic cyclization of 3-alkynyl-2-(methylthio) quinolines. (iii).[9] Doucet and co-workers documented one-pot sequential imination and intramolecular arylation of thiophene-3-carbaldehyde with 2-bromoaniline. (iv)[10] A few other reports have been published.[11,12]

However, the above literature reports show several advantages and limitations, including expensive metal catalysts and external ligands, limited substrate scope, use of the conventional organic solvents at high temperatures, harsh reaction conditions, multistep starting materials, and long reaction intervals to obtain products. To the best of our knowledge, the synthesis of 2-acylthieno[2,3-*b*]quinolines from 2-halo-alkylated ketones is a challenging concern, including less reactive C(sp^2) and C(sp^2) sites, elemental sulfur as a thiol source, and Cu powder as a catalyst for cyclization. Here, we report the synthesis of 2-acylthieno[2,3-*b*]quinolines via Cu-TEMPO catalyzed dehydrogenation and sp^2-C−H functionalization (S_8-thiolation) from 2-haloquinolinyl ketoalkanes (Scheme 1b).

Initially, we started our investigation using 3-(2-chloroquinolin-3-yl)propan-1-one **1a** (2-chloroquinolinyl ketoalkanes) as a substrate for the synthesis of 2-acylthienoquinolines, using $Cu(OAc)_2$ as a catalyst, TEMPO as a novel oxidant, DBU as

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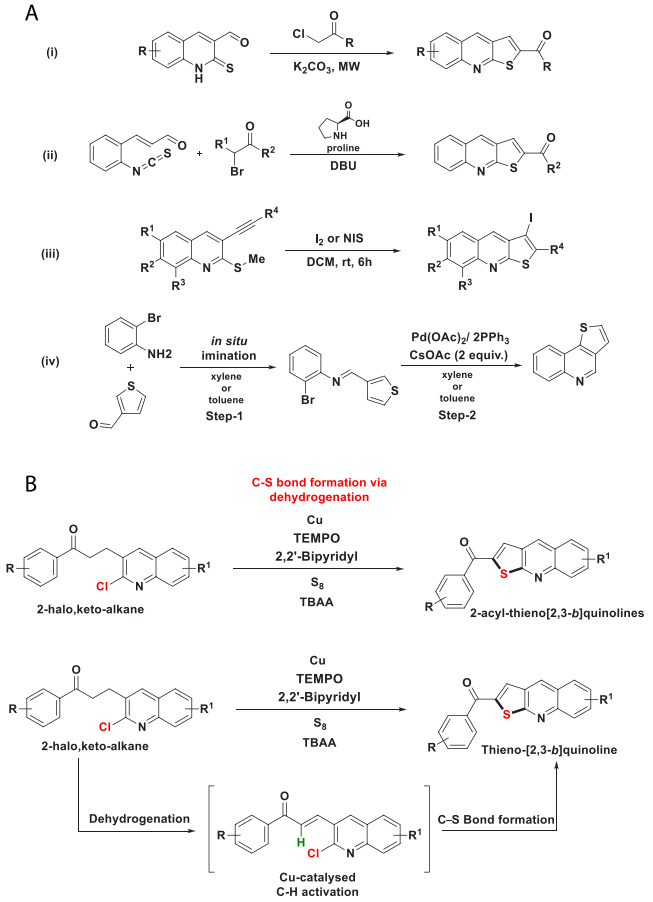
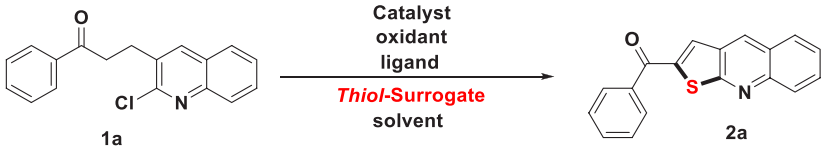
Scheme 1. (A) Previous Reports: Thieno-quinoline Core Motifs. (B) This Report: Cu-Catalyzed Synthesis of 2-Acylthieno[2,3-*b*]quinolines from 2-Haloquinolinyl Ketones through Dehydrogenation and sp^2-C−H Functionalization, Using S_8 as Thiol Source



ligand, and S_8 (elemental sulfur) as a sulfur precursor in DMF at 90 °C and have observed that the reaction yielded a trace amount of the desired product (30%) **2a** (Table 1, entry 1). The exchange of ligand to DABCO, 2,2-bipyridyl, and 1,10-phenanthroline was carried out (entries 2−4). Here, we have observed that 2,2-bipyridyl ligand is effective in obtaining **2a** in 45% yield, compared to other ligands, because it is a bidentate chelating ligand that can easily form a complex with transition metals.[13,14] Then change of oxidant to TBHP is effected, and no increment in product yield was observed (entry 5). TEMPO is a well-known radical initiator and oxidant and is used as a mediator for many controlled radical polymerization reactions.[15−18] Further, optimization of the reaction is done to improve the efficiency of the thiol surrogate, explored with Na_2S, $Na_2S_2O_3$, K_2S_5, and KEX (potassium ethyl xanthogenate) as various sulfur precursors (entries 6−9). Though it provided **2a** in trace to moderate yields, S_8 (sulfur) and KEX provided **2a** in 45, 40% of yields (entries 3 and 9). Consequently, S_8 (sulfur) was chosen as a sulfur surrogate because of its cost-effectiveness compared to the expensive KEX. So far, the reaction was attempted with various ligands and oxidants, but the yields were not acceptable. Subsequently, the reaction was screened with Cu salts $CuCl_2$, $CuBr_2$, CuI, $CuSO_4$, $Cu(OTf)_2$, and Cu -powder (entries 10−15). The results show that CuI, $Cu(OTf)_2$, and only Cu provided **2a** in 52%, 56%, and 55% of yields, respectively. Interestingly, Cu itself shows its catalytic activity in terms of product yield compared with other copper catalysts. Cu was chosen as the metal catalyst for further studies. The solvent effect was studied, using DMSO and toluene under Cu catalysis, but there is no improvement in the yield was observed (entries 16 and 17).

Surprisingly, when the reaction was screened using TBA salts as a basic ionic medium in the presence of Cu, a better yield was observed, and it eliminated the use of conventional volatile organic solvent (VOCs). Several literature procedures wherein tetrabutylammonium salts were utilized as ionic

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	oxidant	ligand	solvent	S-surrogate	temp (°C)	time (h)	yield[f] (%)
1	$Cu(OAc)_2$	TEMPO	DBU	DMF	S_8	90	14	30
2	$Cu(OAc)_2$	TEMPO	DABCO	DMF	S_8	90	10	25
3	$Cu(OAc)_2$	TEMPO	2,2′-bipyridyl	DMF	S_8	90	8	45
4	$Cu(OAc)_2$	TEMPO	1,10-phenanthroline	DMF	S_8	90	12	34
5	$Cu(OAc)_2$	TBHP	2,2′-bipyridyl	DMF	S_8	90	15	26
6	$Cu(OAc)_2$	TEMPO	2,2′-bipyridyl	DMF	Na_2S	90	8	38
7	$Cu(OAc)_2$	TEMPO	2,2′-bipyridyl	DMF	$Na_2S_2O_3$	90	8	trace
8	$Cu(OAc)_2$	TEMPO	2,2′-bipyridyl	DMF	K_2S_5	90	8	26
9	$Cu(OAc)_2$	TEMPO	2,2′-bipyridyl	DMF	KEX	90	8	40
10	$CuCl_2$	TEMPO	2,2′-bipyridyl	DMF	S_8	90	10	32
11	$CuBr_2$	TEMPO	2,2′-bipyridyl	DMF	S_8	80	9	41
12	Cu−I	TEMPO	2,2′-bipyridyl	DMF	S_8	80	10	52
13	$CuSO_4$	TEMPO	2,2′-bipyridyl	DMF	S_8	90	15	18
14	$Cu(OTf)_2$	TEMPO	2,2′-bipyridyl	DMF	S_8	100	6	56
15	Cu	TEMPO	2,2′-bipyridyl	DMF	S_8	90	6	55
16	Cu	TEMPO	2,2′-bipyridyl	DMSO	S_8	110	5	51
17	Cu	TEMPO	2,2′-bipyridyl	Toluene	S_8	100	5	46
18	Cu	TEMPO	2,2′-bipyridyl	TBAB	S_8	90	4	81

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Table 1. continued

entry	catalyst	oxidant	ligand	solvent	S-surrogate	temp (°C)	time (h)	yield[f] (%)
19	Cu	TEMPO	2,2′-bipyridyl	TMAB	S_8	90	6	75
20	Cu	TEMPO	2,2′-bipyridyl	TEAB	S_8	90	5	77
21	Cu	TEMPO	2,2′-bipyridyl	TBAI	S_8	90	8	80
22	Cu	TEMPO	2,2′-bipyridyl	TBAA	S_8	90	3	86
23	$PdCl_2$	TEMPO	2,2′-bipyridyl	TBAA	S_8	90	10	
24	$Pd(OCOCH_3)_2$	TEMPO	2,2′-bipyridyl	TBAA	S_8	90	8	
25	$PdCl_2(PPh_3)_2$	TEMPO	2,2′-bipyridyl	TBAA	S_8	100	10	trace
26	$Pd(PPh_3)_4$	TEMPO	2,2′-bipyridyl	TBAA	S_8	100	9	trace
27	$Ru(p\text{-cymene})Cl_2]_2$	TEMPO	2,2′-bipyridyl	TBAA	S_8	90	10	trace
28	$Zn(OTf)_2$	TEMPO	2,2′-bipyridyl	TBAA	S_8	90	12	30
29	$Yb(OTf)_2$	TEMPO	2,2′-bipyridyl	TBAA	S_8	90	8	25
[b]30	Cu	TEMPO	2,2′-bipyridyl	TBAA	S_8	90	3	71
[c]31	Cu	TEMPO	2,2′-bipyridyl	TBAA	S_8	90	3	87
[d]32	Cu	TEMPO	2,2′-bipyridyl	TBAA	S_8	110	3	86
[e]33	Cu	TEMPO	2,2′-bipyridyl	TBAA	S_8	90	3	55
[e]34	Cu	TEMPO	2,2′-bipyridyl	TBAA	S_8	90	3	88

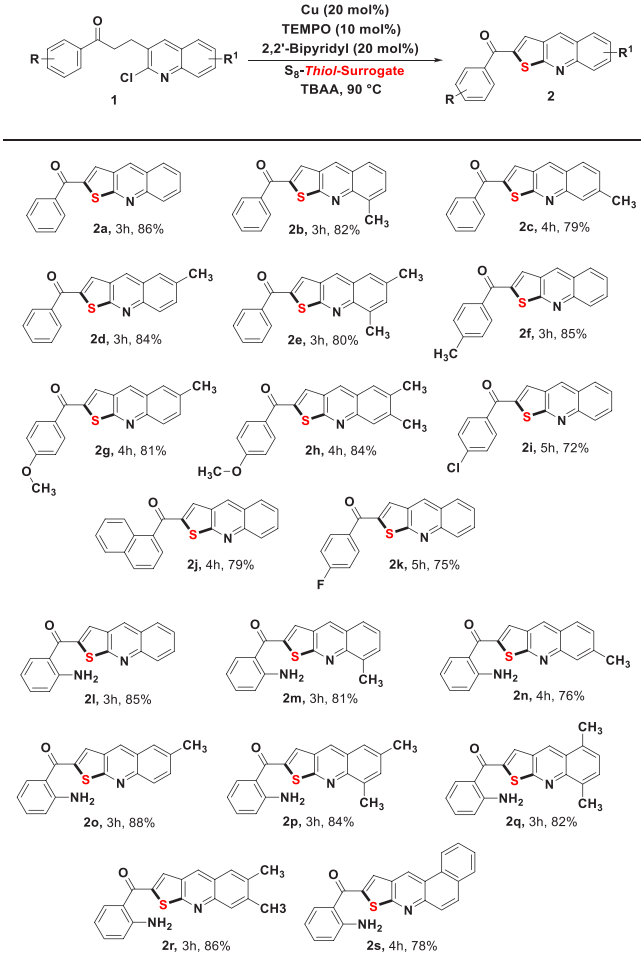
[a]Standard reaction conditions: 2-halo-quinolinyl ketone, **1a** (1.0 mmol), catalyst (20 mol %), TEMPO (10 mol %), ligand (20 mol %), Thiol-surrogate (2 equiv) in 2 mL of solvent in closed reaction vial at 90 °C or 1 equiv of TBA-ILs. [b]Reaction under nitrogen atmosphere. [c]30 mol % of Cu catalyst. [d]Temperature change. [e]Change in the equiv of S_8, [f]Isolated yields.

liquids (ILs) as additive or solvent instead of VOCs in reactions included Heck coupling, Suzuki, Stille, Sonogashira, and other cyclization reactions.[19−26] At first, TBAB (tetrabutylammonium bromide) was tried using Cu as a catalyst (20 mol %), TEMPO (10 mol %), 2,2-bipyridyl (20 mol %), and S_8 thiol-surrogate at 90 °C, the reaction yielded 81% of **2a** (entry 18). To our delight, the dehydrogenation followed by thiolation under TBAB as a reaction medium gave an encouraging result, which was screened further with other TBA salts including TMAB, TEAB, TBAI, and TBAA as ILs using the same optimized conditions, which provided good amounts of desired product **2a** in 75%, 77%, 80%, and 86%, respectively (entries 19−22).

The TBAA (tetrabutylammonium acetate) ionic medium gave the expected product in good yield compared to all other ILs. Further, the reaction under inert N_2 atmosphere gave a lower yield in contrast to the standard conditions (**2a** in 71% yield) (entry 30). When 30 mol % of Cu catalyst was used, there was no improvement in the yield (entry 31). Furthermore, there was no difference in the observed yield when the temperature was increased to 110 °C (entry 32). Additionally, the S_8 equivalent was evaluated, utilizing 1 equiv of S_8 as sulfur surrogate, and a decrease in the product yield (55% of **2a**) was observed, and when 3 equiv of S_8 was used an identical result was observed (entries 33 and 34). Further, dehydrogenation and sp^2-CH functionalization (thiolation) were tried with palladium, ruthenium, and metal triflates, but there is no fruitful result observed (entries 23 and 29). As per known literature reports, copper catalysis is an efficient tool for dehydrogenation and cyclization strategies.[27−30] Compared to other metal catalysts, it is also cost effective. Accordingly, our optimization studies showed that use of Cu (20 mol %) as an efficient catalyst, TEMPO (10 mol %) as an oxidant, 2,2-bipyridyl (20 mol %) as a ligand, S_8 (2 equiv) elemental sulfur as a thiol-surrogate, and 1 equiv of TBAA as an ionic medium or solvent for the reaction gives 2-acylthieno[2,3-*b*]quinoline **2a** in excellent yield up to 86% within 3 h.

Having optimized reaction conditions in hand (Table 1, entry 22), the substrate scope was explored with a wide variety of substrates. For instance, 3-(2-chloroquinolin-3-yl)-1-phenylpropan-1-one, **1**, was prepared from acetophenone and

Scheme 2. Synthesis of 2-Acylthieno[2,3-*b*]quinolines[a,b]



[a]Standard reaction conditions: 2-chloroquinolinyl ketone, **1a** (1.0 mmol), Cu (20 mol %), TEMPO-oxidant, (10 mol %), ligand (20 mol %), thiol-surrogate (2 equiv) in TBAA reaction medium at 90 °C. [b]Isolated yields.

2-chloro-quinolinyl alcohols according to our previous literature procedure.[31] The electron-donating groups from acetophenone

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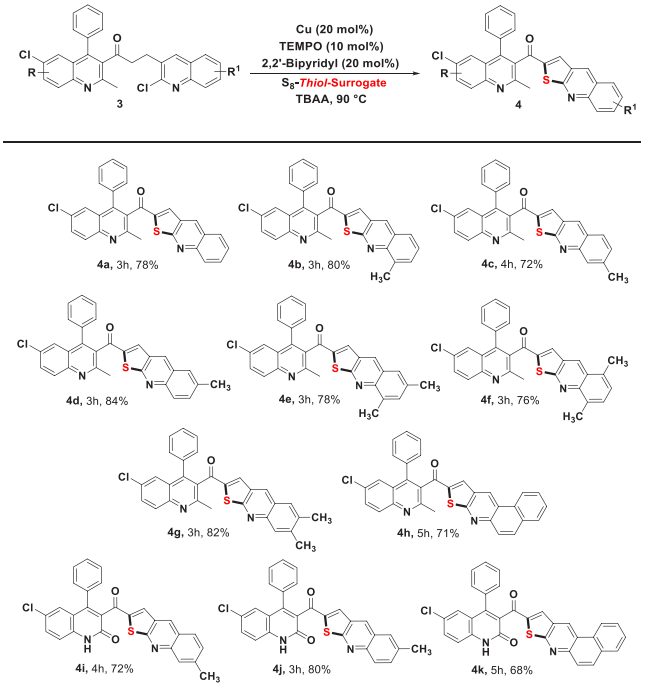
Scheme 3. Synthesis of 4-Phenylquinolin-3-ylthieno[2,3-*b*]quinolin-2-yl)methanones[a,b]



[a]Standard reaction conditions: 4-phenylquinolin-3-yl-3-(2-chloroquinolin-3-yl)propan-1-one **3a** (1.0 mmol), Cu catalyst (20 mol %), TEMPO oxidant, (10 mol %), ligand (20 mol %), thiol surrogate (2 equiv) in TBAA reaction medium at 90 °C. [b]Isolated yields.

substitution (−Me, −OMe, and $-NH_2$) facilitated smoothly to give the corresponding 2-acylthienoquinolines **2f**, **2g**, **2h**, and **2o** in excellent yields (Scheme 2). Likewise, electron-withdrawing groups from acetophenone (−F and −Cl) facilitated the reaction smoothly to provide 2-acylthieno quinolines **2i** and **2k** in good yield. In the quinoline alcohol, methyl groups of phenyl ring at the ortho, meta, and para positions did not affect the product yields (steric effect). The quinoline-substituted ketones instead of acetophenones were also transformed smoothly to product **4**, as given in (Scheme 3). Compared to product **2**, product **4** was obtained in slightly lower yields because of steric effects at the acyl substituent.

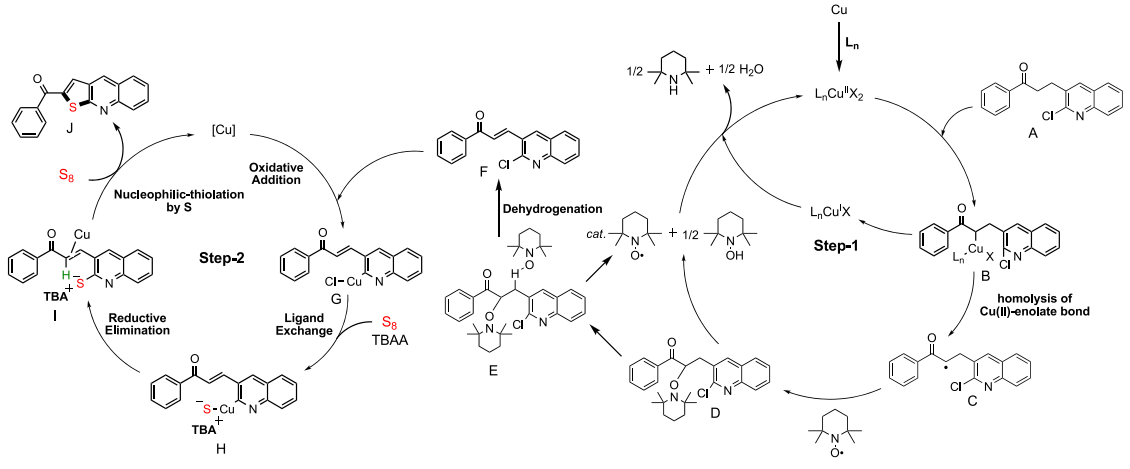
The above results indicate that the electronic and steric effects on 2-chloroquinolinyl ketones do not affect the reaction, and the corresponding products in excellent yields up to 86% were observed. In addition, the control experiments and ^{1}H NMR studies were performed to identify the reaction mechanism. (The results are discussed in Scheme S1).

On the basis of the above experimental studies and previous reports,[27,32−35] a two-step concerted plausible reaction mechanism was proposed for the formation of 2-acylthieno-[2,3-*b*]quinoline (Scheme-4). In step I, initially, Cu as a Lewis acid reacts with ketone **A** to form metal−enolate complex **B**. After homolysis of the Cu(II)−enolate bond which generates Cu(I) species and formation of α-radical intermediate **C** will then react with active TEMPO radical to result in formation of α-TEMPO radical substituted ketone **D**. The α-TEMPO radical undergoes rapid TEMPO−OH elimination to form enone **E**, and TEMPO−OH elimination at the α-position occurs via β-H abstraction assisted by another molecule of TEMPO leading to formation of α,β-unsaturated carbonyl (chalcone) via dehydrogenation **F**. Finally, the oxidation of Cu(I) species by TEMPO or TEMPOH again generates active Cu(II) species with tetramethylpiperidine and water.[27,36] In step II, again the oxidative addition of copper to chalcone intermediate takes place to yield **G** and ligand exchange to leading to Cu−S intermediate **H**, which further undergoes reductive elimination to give sulfur-substituted α-C−H intermediate **I**. Finally, Cu catalyzed nucleophilic thiolation at α-C−H takes place to give thienoquinoline product **J**. However, in-depth mechanistic studies and applications of this newly developed strategy are underway.

The synthesized 2-acylthieno[2,3-*b*]quinoline **2** was further functionalized at active *o*-NH_2-ketone using Friedländer annulation[37] in acidic medium to obtain thieno[2,3-*b*]quinolin-2-yl)quinolin-3-yl)ethan-1-ones **5** in up to 92% yield (a). Likewise, reduction of compound **2** at 2-acyl (ketone) position using $NaBH_4$ in methanol[38] led to thieno[2,3-*b*]quinolin-2-yl)(phenyl)methanol **6** in 96% yield (b). Further, during functionalization of compound **4**, the methyl group at the 2-position was effective to obtain 2-styrylquinolin-3-ylthieno-[2,3-*b*]quinolin-2-yl)methanones **7** in 61% yield using aldehyde in the presence of acidic medium[39] (c) (Scheme 5).

In summary, a solvent-free protocol is reported for the synthesis of 2-acylthieno[2,3-*b*]quinoline from saturated ketones via Cu-TEMPO-catalyzed dehydrogenation followed by

Scheme 4. Proposed Reaction Mechanism



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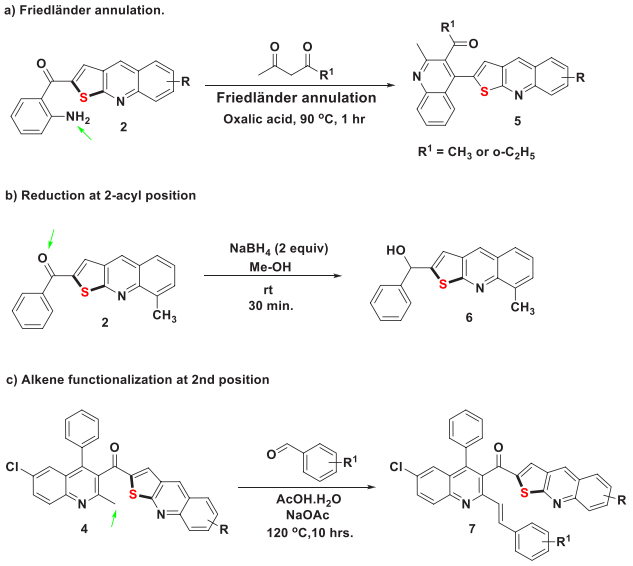
Scheme 5. Synthetic Application of 2-Acylthieno[2,3-*b*]quinolines



nucleophilic thiolation using elemental sulfur as the sulfur source. The TBA ILs were used as the reaction medium to avoid toxic VOCs. This is an efficient protocol in terms of wide substrate scope and broad functional group tolerance, with high regio- and stereoselectivity, resulting in good yields. The synthetic application of the 2-acylthieno[2,3-*b*]quinolines was also showcased by Friedlander's annulation, reduction, and alkene functionalization.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b04598.

Copies of ^{1}H, ^{13}C NMR, Mass and IR spectra of the synthesized products, control experiment, additional data, figures and tables (PDF)

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Notes

The authors declare no competing financial interest.

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