Organic LETTERS

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Transition-Metal-Free Quinoline Synthesis from Acetophenones and Anthranils via Sequential One-Carbon Homologation/Conjugate Addition/Annulation Cascade

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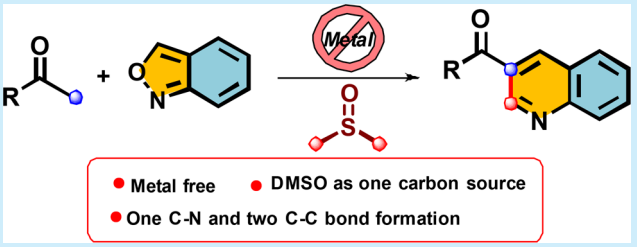
Supporting Information

ABSTRACT: A transition-metal-free method for the construction of functionalized quinolines from readily available acetophenones and anthranils is reported. This one-pot reaction cascade involves in situ generation of α,β-unsaturated ketones from the acetophenone via one-carbon homologation by DMSO followed by the aza-Michael addition of anthranils and subsequent annulation. DMSO acted in this reaction not only as solvent but also as one carbon source, thus providing a highly atom-economical and environmentally benign approach for the synthesis of 3-substituted quinolines.



The 3-substituted quinolines are ubiquitous in various pharmacologically and medicinally relevant molecules displaying a broad range of biological activities (Figure 1).[1,2]

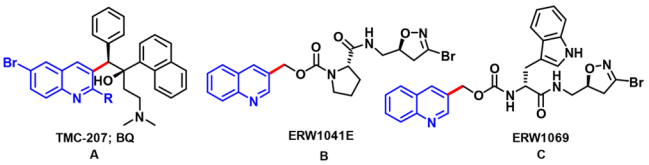


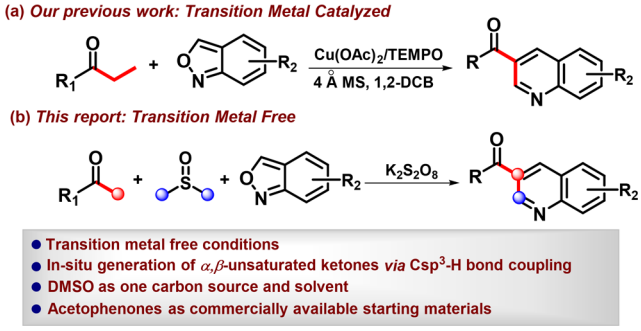
Figure 1. Biologically active molecules containing 3-substituted quinolines.

In addition, they have been exploited as synthetic intermediates in the preparation of drugs and functional materials.[3] Over the past few years, numerous quinoline syntheses have been developed, but most of the existing methods suffer from the requirement of highly functionalized starting materials and expensive transition metals.[4−6] Therefore, development of new synthetic methods for the quinoline synthesis in green, efficient, and metal-free fashion is highly desirable.

α,β-Unsaturated ketones are frequently encountered in various bioactive compounds and generally regarded as versatile synthetic intermediates in the syntheses of fine chemicals, pharmaceuticals, and materials.[7,8] Traditionally, the synthesis of α,β-unsaturated ketones required multiple steps[9,10] and equimolar amounts of reagents such as 2-iodoxybenzoic acid (IBX) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).[11,12] Over the past few years, transition-metal-catalyzed (Pd, Ru, Ir, Ni, and Cu) oxidation of saturated ketones has proven to be a concise, efficient, and atom-economical method for the synthesis of α,β-unsaturated ketones.[8] To eliminate the need for the troublesome isolation of α,β-unsaturated ketones they are in situ subjected to various organic transformations such as arylation, amination, and conjugate addition to get β-functionalized ketones.[13] Very recently, we developed a copper-catalyzed α,β functionalization of saturated ketones with anthranils via sequential dehydrogenation/aza-Michael addition/annulations cascade reactions in one pot (Scheme 1).[13f] Although this method allows a convenient access to 3-ketoquinolines, the requirements of a transition metal and the commercial unavailability of phenylethyl ketones are the key limitations.

In the recent past, both the acetophenone and anthranils have been recognized as good substrates for several organic

Scheme 1. Synthesis of 3-Ketoquinolines



Received: August 7, 2017

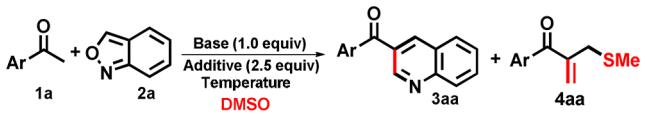
DOI: 10.1021/acs.orglett.7b02429
Org. Lett. XXXX, XXX, XXX−XXX

transformations due to their distinct electronic properties.[14] In this context and in the frame of our current research interest,[15] herein we report the transition-metal-free synthesis of 3-ketoquinolines from readily available acetophenones and anthranils by using DMSO as one carbon source. In this newly developed protocol, the α,β-unsaturated ketones are formed in situ through C(sp^3)−H bonds coupling among two methyl groups of ketones and dimethyl sulfoxide.

Our investigation started with the reaction of readily available acetophenone (**1a**), anthranil (**2a**), and DMSO as model substrates, and the details are summarized in Table 1. Our initial effort of reacting acetophenone (**1a**, 1.0 mmol), anthranil (**2a**, 1.2 mmol), and $K_2S_2O_8$ (2.5 mmol) in the presence of DABCO 1.0 mmol) at room temperature was found to be unsuccessful and did not furnish any desired product **3aa** (entry 1). Unfortunately, a similar result was obtained even after the reaction mixture was heated at 60 °C for 24 h (entry 2). Gratifyingly, when the reaction mixture was heated at 120 °C for 24 h, a mixture of the desired **3aa** in 26% yield along with undesired **4aa** in 45% yield was obtained (entry 3). At this stage, the structures of **3aa** and **4aa** were well characterized using different spectroscopic techniques, and the spectral data of **3aa** exactly matched that of previously reported compounds. In order to reduce the formation of 2-(methylthiomethyl)-1-phenylprop-2-en-1-one (**4aa**), different organic bases, such as DBU and Et_3N, were screened, but they also furnished undesired **4aa** as a major product (entries 4 and 5). Compared to the organic bases, the use of inorganic bases such as K_2CO_3, Cs_2CO_3, and NaOAc showed better selectivity and produced **3aa** as a major product in good yields (entries 6−8). Unexpectedly, **3aa** was obtained as a single product in 76% yield when the reaction was run without any base under similar reaction conditions (entry 9). Various oxidants such as $(NH_4)_2S_2O_8$, $KHSO_4$, TBHP, and TEMPO were also screened, but most of them were found to be less efficient and produced **3aa** in low yields (entries 10−13). The decrease in the amount of $K_2S_2O_8$ (1.5 equiv) furnished a low yield of **3aa** (entry 14). Using different solvents such as DMF, DMA, and NMP also furnished the desired product **3aa**, but in low yield (see the Supporting Information for details).

With the optimal reaction conditions in hand (Table-1, entry 9), the scope of the reaction with respect to various aryl methyl ketones and anthranils was evaluated (Scheme 2). A wide range of aryl methyl ketones and anthranils could be used in this tandem reaction. The aryl methyl ketones containing both electron-withdrawing (EWGs) and electron-donating groups (EDGs) at different positions of the aryl ring readily delivered the corresponding 3-ketoquinolines in good to moderate yields (**3ba**−**ao**). A variety of functional groups such as alkyl (**1b**, **1c**), *tert*-butyl (**1d**), chloro (**1e**), bromo (**1f**), iodo (**1h**), fluoro (**1j**,**k**), trifluoromethyl (**1k**), cyano (**1l**), nitro (**1m**), biphenyl (**1n**), and alkoxy (**1o**,**p**) were well tolerated in this reaction. To our delight, a phenyl ring containing a free hydroxyl group (**1v**) was also tolerated in this reaction and furnished the corresponding 3-ketoquinoline **3va** in 52% yield. This one-pot tandem cascade reaction was further extended to a variety of heteroaryl methyl ketones including 2-acetylthiophene (**1q**), 2-acetylfuran (**1r**), and 2-acetylthiazole (**1s**), and good yields of

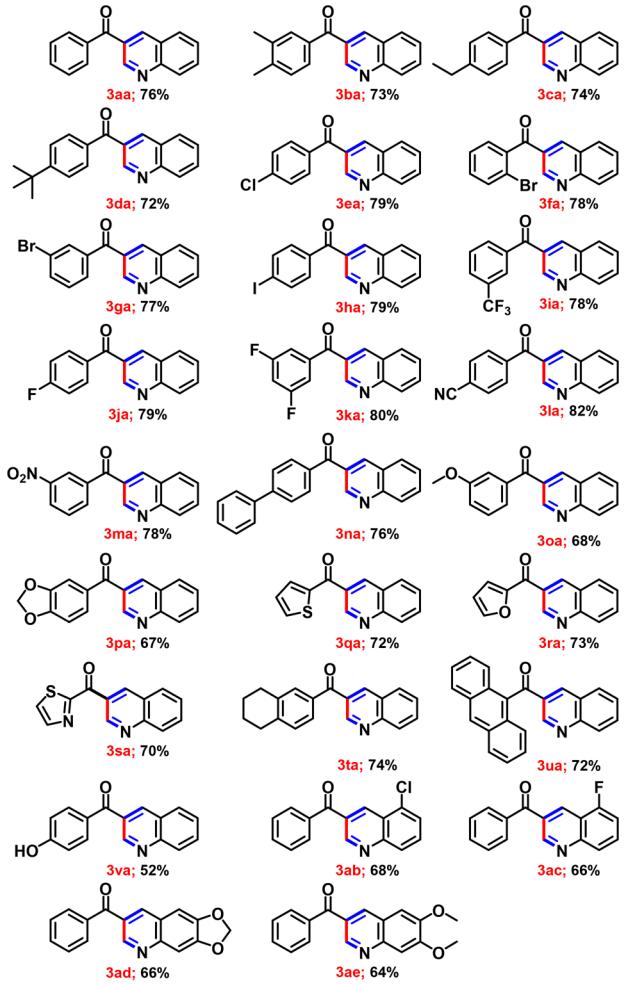
Table 1. Optimization of Reaction Conditions[a]



entry	additive	base	temp (°C)	yield[b] (%) 3aa	4aa
1	$K_2S_2O_8$	DABCO	rt	n.o.	n.o
2	$K_2S_2O_8$	DABCO	60	n.o.	n.o.
3	$K_2S_2O_8$	DABCO	120	26	45
4	$K_2S_2O_8$	DBU	120	21	26
5	$K_2S_2O_8$	Et_3N	120	11	15
6	$K_2S_2O_8$	K_2CO_3	120	54	trace
7	$K_2S_2O_8$	Cs_2CO_3	120	51	trace
8	$K_2S_2O_8$	NaOAc	120	43	trace
9	$K_2S_2O_8$		120	76	n.o.
10	$(NH_4)_2S_2O_8$		120	37	n.o
11	$KHSO_4$		120	n.o	n.o.
12	TBHP		120	n.o.	n.o.
13	TEMPO		120	n.o.	n.o.
14	$K_2S_2O_8$		120	52	n.o.[c]

[a]Reaction was performed using **1a** (1.0 mmol), **2a** (1.1 mmol), DMSO (2.0 mL), and additive (2.5 mmol) under nitrogen 24 h. [b]Isolated yield. [c]When (1.5 equiv) of $K_2S_2O_8$ was used.

Scheme 2. Substrate Scope[a]



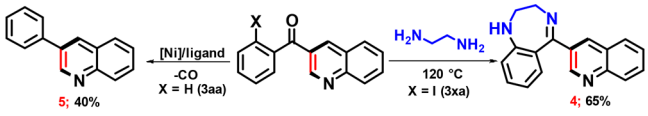
[a]Reaction conditions: aryl methyl ketones (**1a**−**v**; 1.0 mmol), anthranils (**2a**−**e**; 1.1 mmol), DMSO (2.0 mL), and $K_2S_2O_8$ (2.5 mmol) under N_2 at 120 °C for 24 h.

DOI: 10.1021/acs.orglett.7b02429
Org. Lett. XXXX, XXX, XXX−XXX

the corresponding 3-ketoquinolines (**3q–s**) were obtained. Moreover, bicyclic and tricyclic aryl methyl ketones such as 6-acetyltetralin (**1t**) and 9-acetylanthracene (**1u**) smoothly underwent to this reaction and furnished the corresponding **3ta** and **3ua** in 74% and 72% yields, respectively. Furthermore, various substituted anthranils (**2b–e**) were treated with acetophenone (**1a**) under optimized reaction conditions to provide the desired products (**3ba–ea**) in moderate yields (64–66%).

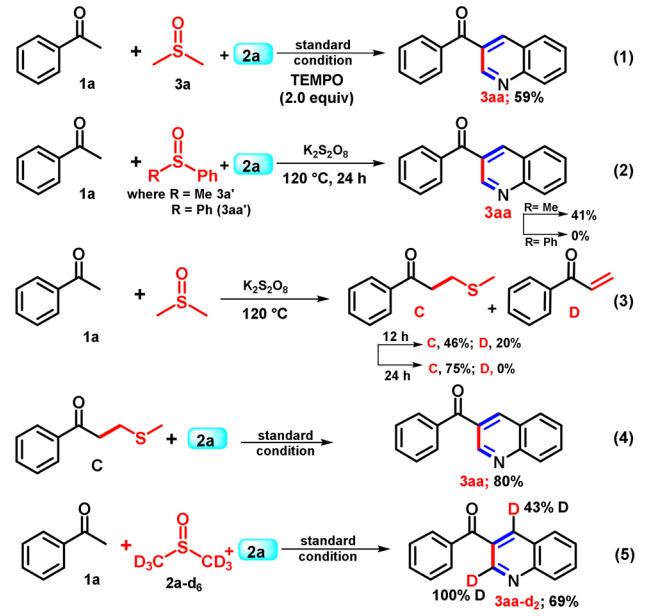
To assess the efficiency and potential for application of this method, we have developed a one-pot sequential synthesis of 2,3-dihydro-5-(3-quinolinyl)-1*H*-1,4-benzodiazepine (**4**),[13f] and nickel-catalyzed decarbonylation of **3aa** to prepare 3-phenylquinoline **5**[16a] (Scheme 3) (for details, see the SI).

Scheme 3. Synthetic Utility



To understand the reaction mechanism, we carried out a series of control experiments (Scheme 4). Initially, when the

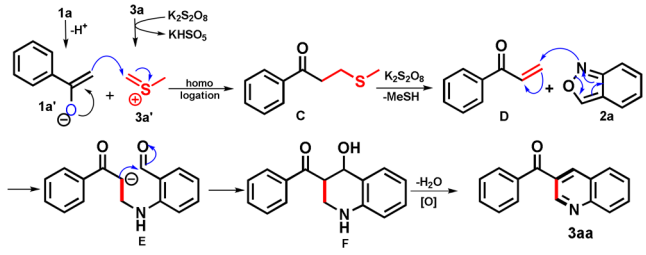
Scheme 4. Mechanistic Insights



reaction was performed in the presence of radical scavenger TEMPO, the desired product **3aa** was obtained in 59% yield, which indicates that the radical species is not involved in this process. To verify the carbon source in this reaction, we carried out reaction in the methyl phenyl sulfoxide solvent that led to formation of **3aa** in 41% yield. However, when the reaction was performed in diphenyl sulfoxide solvent expectedly **3aa** was not formed. Furthermore, when the reaction was performed in the absence of anthranil (**2a**), under the standard condition for 12 h, two products, **C** and **D**, were isolated in 46% and 20% yields, respectively. By further heating the reaction for 24 h, only product D was isolated in 72% yield, indicating that **C** and **D** would be the key intermediates in this reaction. Next, treating the intermediate **C** with **2a** under the standard reaction conditions gave the desired **3aa** in 80% yield. To shed more light on reaction mechanism, we carried out deuterium-labeling experiments by treating **1a** with **2a** in DMSO-d_6 under standard reaction conditions which produced **3aa-d$_2$** in 69% yield. ^{1}H NMR analysis revealed 100% deuteration at the C-2 position, and surprisingly, we also observed 43% of deuteration at the C-4 position.[16b]

On the basis of the preliminary mechanistic experiments and previous literature, a possible mechanism is proposed (Scheme 5). DMSO (**3a**) is activated by $K_2S_2O_8$ to furnish intermediate

Scheme 5. Plausible Reaction Mechanism



3a′, which on reaction with enolate (**1a′**) generated from **1a** furnished intermediate **C**. The intermediate **C** undergoes $K_2S_2O_8$-assisted demethylthioation to form α,β-unsaturated ketone (**D**).[14a,17] The aza-Michael addition by anthranil on intermediate **D** would give intermediate **E**, which eventually cyclizes to form **F**, which upon auto oxidation leads to the formation of 3-ketoquinoline **3aa**.

In conclusion, an efficient three-component reaction cascade has been developed for the synthesis of 3-ketoquinolines from the readily available acetophenones, anthranils, and DMSO in the presence of $K_2S_2O_8$. The present report provides a novel method for the one-carbon homologation of acetophenones to produce α,β-unsaturated ketones that was further utilized in situ for the aza-Michael addition and annulation reactions with anthranils. The reaction is robust enough, and a number of 3-ketoquinolines were synthesized, reflecting the generality of the method.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02429.

Complete experimental details and characterization data for all products (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Department of Science and Technology (DST), New Delhi, India, for financial support in the form of a DST-INSPIRE Faculty grant and a Startup Research Grant for young researchers (GAP 0414 and GAP 0512). S.B.W. thanks the

DOI: 10.1021/acs.orglett.7b02429
Org. Lett. XXXX, XXX, XXX–XXX

CSIR-New Delhi for fellowship. S.B.W., D.K.T., and M.P. gratefully acknowledge the Academy of Scientific and Innovative Research (AcSIR) for Ph.D. registration. We are thankful to Dr. Amit B. Pawar (DST-INSPIRE Faculty, CSIR-IICT) for valuable suggestions. We are also grateful to the Director, CSIR-IICT, for providing the necessary infrastructure.

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DOI: 10.1021/acs.orglett.7b02429
Org. Lett. XXXX, XXX, XXX−XXX