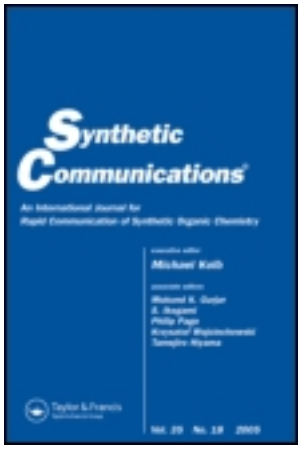

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Vanadium-Catalyzed Synthesis of 4(3H)-Quinazolinones from Anthranilamides and Aryl Aldehydes

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VANADIUM-CATALYZED SYNTHESIS OF 4(3*H*)-QUINAZOLINONES FROM ANTHRANILAMIDES AND ARYL ALDEHYDES

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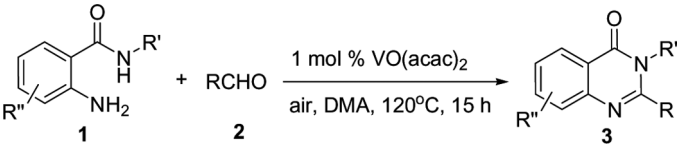
GRAPHICAL ABSTRACT



Abstract *An efficient synthesis of 2-substituted and 2,3-disubstituted quinazolin-4(3-*H*)-ones via tandem reaction of anthranilamides and aromatic aldehydes catalyzed by vanadyl acetylacetonate with 1 mol% loading under an air atmosphere is described. This new method is associated with several advantages such as low catalyst loading (only 1 mol%), use of green oxidant in the form of air, high atom economy, and good to excellent yields. A mechanism of vanadium-catalyzed synthesis of 4(3*H*)-quinazolinones has also been proposed.*

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Keywords Anthranilamides; aromatic aldehydes; domino reaction; quinazolin-4(3-*H*)-ones; vanadyl acetylacetonate

INTRODUCTION

4(3*H*)-Quinazolinones are an important class of nitrogen-containing heterocycles with various pharmacological and therapeutic properties,[1] such as anticancer,[2] anti-inflammatory,[3] antibacterial,[4] antihypertensive,[5] vasopressin V3 receptor

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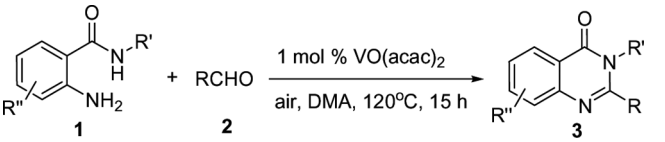
antagonists,[6] and nonpeptide CCK-B antagonists.[7] Hence, the efficient synthesis of quinazolinones derivatives has assumed enormous significance.

Various protocols for the synthesis of quinazolin-4(3*H*)-ones have been investigated in the past. Some common methods include condensation of 2-aminobenzamides and substituted benzoyl chlorides or their equivalents in ionic liquid,[8] tandem condensation, and C-N cross coupling of 2-halobenzoic acids and amidines,[9] cyclization of o-acylaminobenzamides,[10] 2-amino-benzonitrile,[11] N-arylorthanilamides,[12] nitroenes,[13] and aza-Wittig reactions of α-azido-substituted aromatic imides.[14] However, most of these procedures have some drawbacks such as poor atom economy, use of environmentally toxic reagents or media, use of expensive chemicals, and harsh reaction conditions. In addition, some three-component condensation reactions of isatoic anhydride/anthranilic acid, *ortho* esters, and amines have been reported,[15] but these approaches again lack atom economy. Relatively recently, Xu et al. reported CuBr-catalyzed domino synthesis of 2-aryl 4(3*H*)-quinazolinones via Ullmann-type coupling of *ortho*-iodobenzamides and benzyl amines or α-amino acids (decarboxylation of α-amino acids as the substrates), and aerobic oxidative C-H amidation.[16] Unfortunately, both approaches lead to the generation of undesired by-products, such as hydrogen iodide (HI), which consumes K_2CO_3, making the overall process less efficient in terms of atom economy.

In 1994, Abdel-Jalil et al. introduced a new synthetic protocol for 2-substituted 4(3*H*)-quinazolinones: cascade condensation of anthranilamide and aryl, alkyl, and heteroaryl aldehydes and 3 equivalents of $CuCl_2$ as the oxidant and catalyst.[17] Synthesis of the desired product from anthranilamide and aldehydes is not only atom economical but also environmentally-friendly as water is the only water major by-product of the reaction.

Later a similar protocol with 2 equivalents of $FeCl_3$ as the oxidant and catalyst was reported.[18] In 2010, Wang et al. developed an iodine-catalyzed approach in ionic liquid with the same class substrates, that is, anthranilamide and aldehydes, but the loading of iodine was not given in their main article or its supporting information, nor was any mention made in their general procedure for the synthesis of 2-arylquinazolin-4(3*H*)-one and (*E*)-2-arylideneaminobenzamide.[19] Similar to this work, Dabiri et al. reported a one-pot, three-component route to synthesize 2,3-disubstituted 4(3*H*)-quinazolinones in the presence of an equivalent amount of iodine as the catalyst.[20] All the aforementioned methods with anthranilamides and aldehydes as substrates involve using stoichiometric instead of catalytic amounts of various chemicals; usually the reactions required more than 1 equiv. of $CuCl_2$, $FeCl_3$, and iodine. Therefore, in the present study we tried to discover an optimal catalyst for the reaction with appreciably lower loading. Keeping this in mind, in continuation of our research on vanadium-catalyzed sulfide oxidation,[21] herein we report an efficient vanadium-catalyzed synthesis of 4(3*H*)-quinazolinones in the presence of only 1 mol% catalyst (Scheme 1).

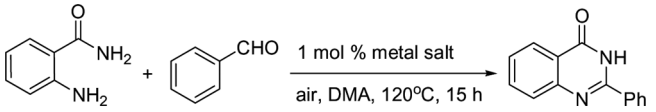


Scheme 1. Vanadium-catalyzed synthesis of 4(3*H*)-quinazolinones.

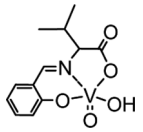
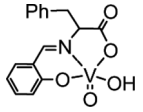
RESULTS AND DISCUSSION

To find a catalytic system for the synthesis of 4(3*H*)-quinazolinones from anthranilamides (**1**) and aldehydes (**2**), anthranilamide and benzaldehyde were used as the model substrates, and various metal salts and complexes were evaluated (Table 1). Because stoichiometric $CuCl_2$ and $FeCl_3$ were reported to be efficient for the synthesis of 4(3*H*)-quinazolinones, they were adopted in our research as potential catalyst candidates. Under air and at 120 °C, $CuCl_2$- and $FeCl_3$-catalyzed tandem condensation and oxidation of anthranilamide and benzaldehyde for 24 h with 1 mol% catalyst loading afforded 2-phenyl-4(3*H*)-quinazolinone (**3a**) with moderate yields of 72% and 64%, respectively (Table 1, entries 1 and 2).

Table 1. Screening of various reaction conditions[a]



1a **2a** **3a**

Entry	Catalyst	Solvent	Time (h)	Yield (%)[b]
1	$CuCl_2$	DMSO	24	72
2	$FeCl_3$	DMSO	24	64
3	$Fe(NO_3)_3 \cdot H_2O$	DMSO	24	80
4		DMSO	24	82
5		DMSO	24	84
6	$VO(SO_4)$	DMSO	24	84
7	$VO(acac)_2$	DMSO	24	88
8	$VO(acac)_2$	DMF	24	68
9[c]	$VO(acac)_2$	Ethanol	15	13
10[d]	$VO(acac)_2$	H_2O	15	6
11	$VO(acac)_2$	DMA	24	95
12	$VO(acac)_2$	DMA	15	97
13	$VO(acac)_2$	DMA	13	88
14	$VO(acac)_2$	DMA	7	53
15	$VO(acac)_2$	DMA	5	34
16[d]	$VO(acac)_2$	DMA	15	77

[a]Reaction conditions: Metal salt (0.01 mmol), anthranilamide (1 mmol), benzaldehyde (1 mmol), and DMA (3 mL), at 120 °C for 15 h, unless otherwise mentioned.

[b]Isolated yield.

[c]78 °C.

[d]100 °C.

As ferric nitrate [$Fe(NO_3)_3$] has already been successfully employed in the aerobic oxidation of alcohols and sulfides,[22] it was attempted by us in this transformation. Ferric nitrate efficiently accomplished the transformation from anthranilamide and benzaldehyde to afford 2-phenyl-4(3*H*)-quinazolinone (**3a**) in 80% yield (entry 3).

Inspired by the study of vanadium-catalyzed oxidative coupling of 2-naphthol to 1,1′-bi-2-naphthol,[23] *N*-salicylidene vanadyl carboxylate-catalyzed enantioselective aerobic oxidation of α-hydroxy esters and amides,[24] and our research of vanadium-catalyzed enantioselective sulfide oxidation,[21] some vanadium complexes and salts were used in the catalytic synthesis of 2-phenyl-4(3*H*)-quinazolinone (**3a**). Vanadyl carboxylates derived from *N*-salicylidene-valine and *N*-salicylidene-phenylalanine gave 2-phenyl-4(3*H*)-quinazolinone with 82% and 84% yields, respectively (entries 4 and 5). A simple vanadyl sulfate gave the same yield (entry 6). Vanadyl acetylacetonate afforded a better yield of 88% (entry 7).

The result is probably attributed to the fact that vanadyl acetylacetonate increases the condensation of anthranilamide and benzaldehyde to form an imide intermediate, and more significantly, hugely promotes aerobic oxidation of the imide intermediate to give 2-phenyl-4(3*H*)-quinazolinone (**3a**). As mentioned, vanadium can efficiently catalyze aerobic oxidative coupling of 2-naphthol,[23] α-hydroxy esters, and amides.[24]

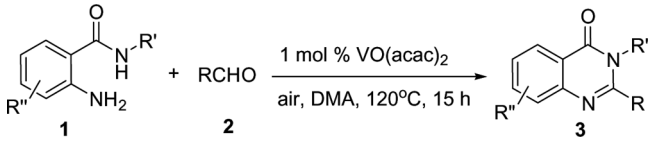
To obtain an ideal result, some other solvents were also screened. While reaction in dimethyl formamide (DMF) at 120 °C gave a lower yield (Table 1, entry 8), water and ethanol were proved to be poor solvents to dissolve anthranilamide and 2-phenyl-4(3*H*)-quinazolinone (**3a**) and gave extremely poor yields at lower temperatures (entries 9 and 10). To our surprise, the solvent DMA (*N,N*-dimethylacetamide) afforded an excellent result with 95% yield (entry 11). The further examination of reaction time demonstrated that longer reaction time of 24 h was not necessary. However, when the reaction time was too short, the starting materials could not be effectively transformed into the product (entries 12 to 15), and the optimized time was set as 15 h (entry 12). Decreasing the temperature resulted in lower yields (entry 16).

With the optimized reaction conditions in hand, a series of anthranilamides and aldehydes were investigated (Table 2, Scheme 1). Under the optimized conditions, vanadyl acetylacetonate–catalyzed cascade condensation and aerobic oxidation of 4-methylbenzaldehyde and anthranilamide afforded 2-(4′-methylphenyl)-4(3*H*)-quinazolinone (**3b**) with a fairly good yield similar to that of benzaldehyde (entry 2 vs. 1).

Aromatic aldehydes with electron-donating groups demonstrate excellent performance in the reaction (Table 2, entries 3 to 5). Reaction of 3-methoxylbenzaldehyde and anthranilamide gave 2-(3′-methoxylphenyl)-4(3*H*)-quinazolinone (**3c**) with the great yield of 99% (entry 3). Reaction of 4-(*N,N*′-dimethyl)benzaldehyde gave the corresponding 4(3*H*)-quinazolinone (**3d**) with a good yield (entry 4). To our surprise, a much more complex aldehyde 3,5-di-*tert*-butylsalicylaldehyde with a free phenolic hydroxyl group also afforded the target product (**3e**) with excellent yield (entry 5).

Vanadium-catalyzed cascade condensation and aerobic oxidation of aromatic aldehydes with electron-withdrawing groups and anthranilamide also afforded the

Table 2. Synthesis of 2-substituted and 2,3-disubstituted quinazolin-4(3*H*)-ones[a][25]



Entry	R	R′	R″	Product	Yield (%)[b]
1	Ph	H	H	**3a**	97
2	4-$CH_3C_6H_4$	H	H	**3b**	95
3	3-$CH_3OC_6H_4$	H	H	**3c**	99
4	4-$N(CH_3)_2C_6H_4$	H	H	**3d**	84
5	3,5-tBu$_2$-2-OHC_6H_2	H	H	**3e**	95
6	4-FC_6H_4	H	H	**3f**	96
7	4-ClC_6H_4	H	H	**3g**	79
8	4-BrC_6H_4	H	H	**3h**	85
9	3-BrC_6H_4	H	H	**3i**	78
10	2-BrC_6H_4	H	H	**3j**	99
11	Furyl	H	H	**3k**	92
12	Ph	C_3H_7	H	**3l**	80
13	Ph	$CH_2C_6H_5$	H	**3m**	63

[a]Reaction conditions: $VO(acac)_2$ (0.01 mmol), anthranilamide (1 mmol), substituted benzaldehyde (1 mmol), and DMA (3 mL), at 120 °C for 15 h.
[b]Isolated yield.

corresponding 4(3*H*)-quinazolinones with good to excellent yields (Table 2, entries 6 to 10). *para*-Fluorobenzaldehyde produced 2-(4′-flurophenyl)-4(3*H*)-quinazolinone (**3f**) with up to 95% yield (entry 6). *para*-Chloro- and *para*-bromo-benzaldehyde also gave the product (**3g, 3h**) with good yields (entries 7 and 8).

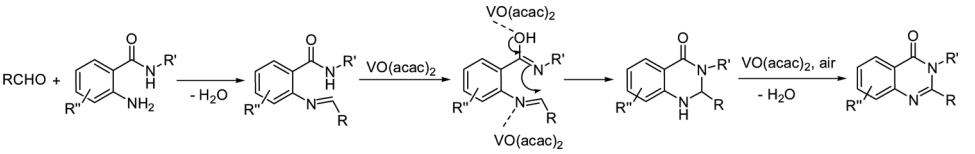
para-, *meta*-, and *ortho*-substituted benzaldehydes all afforded good to excellent yields (Table 2, entries 9 to 11). *para*- and *meta*-bromobenzaldehydes produced the corresponding products (**3i, 3j**) with good yields (entries 9 and 10). Again, surprisingly *ortho*-bromobenzaldehyde afforded 2-(2′-bromophenyl)-4(3*H*)-quinazolinone with up to 99% yield (entry 10).

Furthermore, vanadium-catalyzed cascade condensation and aerobic oxidation of heteroaromatic aldehyde furfural and anthranilamide gave 2-furyl-4(3*H*)-quinazolinone (**3k**) with up to 92% yield (Table 2, entry 11).

Besides nonsubstituted anthranilamide, substitution on the amide group of anthranilamide gave moderate to good yields (Table 2, entries 12 and 13). Perhaps because of the steric hindrance exerted by benzyl and 2-amino-*N*-benzylbenzamide groups, a moderate yield of 2-phenyl-3-benzyl-4(3*H*)-quinazolinone (**3 m**) was achieved (entry 13).

To account for the observed results, we reasoned that the vanadium-catalyzed reaction probably acts through a different mechanistic pathway compared to those reported earlier with other catalytic systems and synthetic methods.[15d,16a,19] The plausible mechanism of vanadium-catalyzed synthesis of 4(3*H*)-quinazolinones is depicted in Scheme 2.

In conclusion, we have demonstrated for the first time that vanadyl acetylacetonate could be used as an efficient catalyst for the selective synthesis of 2-substituted



Scheme 2. Proposed mechanism of vanadium-catalyzed synthesis of 4(3*H*)-quinazolinones.

and 2,3-disubstituted 4(3*H*)-quinazolinones with air as the oxidant. The salient features include environmentally friendly air as the oxidant, low catalyst loading (only 1 mol%), good to excellent yields, high atom economy, cheap and readily available reagents, and easy operation to make the present method superior to the existing methods for the synthesis of 4(3*H*)-quinazolinones. A plausible mechanism has been proposed to support the experimental observations.

EXPERIMENTAL

The purities of all the synthesized compounds were checked by thin-layer chromatography (TLC) using different organic solvents. The infrared (IR) spectra were recorded on a Bruker Tensor-27 Fourier transform (FT)–IR spectrophotometer in KBr discs. ^{1}H NMR spectra were recorded on a Bruker Advance 300-MHz NMR or 400-MHz spectrometer in $CDCl_3$ or dimethylsulfoxide (DMSO-d_6) containing tetramethylsilane (TMS) as an internal standard. Melting points were determined on an Electrothermal melting-point apparatus.

The chemicals and reagents were purchased from Aldrich, Acros, Alfa Aesar, Aladdin, or Kelong chemical companies and were used without further purification.

General Procedure for the Synthesis of 4(3*H*)-Quinazolinones

A mixture of anthranilamide (1.0 mmol), benzaldehyde (1.0 mmol), and catalyst (0.01 mmol vanadyl acetylacetonate) in DMA (3 ml) was stirred in an oil bath at 120 °C for 15 h. After completion of the reaction, the reaction mixture was cooled to room temperature, quenched with a saturated solution of NaCl, extracted with ethyl acetate (3 × 10 mL), and then washed with water. The organic phase was dried over Na_2SO_4 and filtered, and then the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (gradient eluent with a mixed solution of petroleum ether and ethyl acetate) to give the pure 4(3H)-quinazolinone.

2-Phenyl-4(3*H*)-quinazolinone (3a)

White solid. Mp: 239–241 °C. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 11.12 (s, 1H), 8.33 (d, $J = 7.52$ Hz, 1H), 8.20–8.22 (m, 2H) 7.78–7.85 (m, 2H), 7.59 (t, $J = 2.78$ Hz, 3H) 7.51(t, $J = 3.19$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 163.6, 151.6, 149.5, 134.8, 132.8, 131.6, 129.0, 128.0, 127.3, 126.8, 126.5, 120.8. ESI-MS (negative mode), m/z = 221 $[M–H]^-$. IR (KBr), ν (cm^{-1}): 2924, 1730, 1664, 1601, 1451, 1375, 1212, 1045, 942, 752, 694.

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