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Copper-Catalyzed Aerobic Oxidative Annulation and Carbon-Carbon Bond Cleavage of Arylacetamides: Domino Synthesis of Fused Quinazolinones

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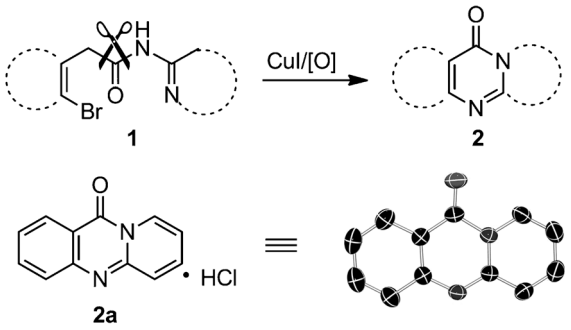
Abstract: An efficient copper-catalyzed tandem aerobic oxidative annulation and carbon-carbon bond cleavage reaction was developed from easily accessible arylacetamides, which provides a direct approach for the domino synthesis of a vast array of tricyclic or tetracyclic fused quinazolinone alkaloid structures. A plausible reaction mechanism is proposed involving an aerobic benzylic oxidation/cyclization/decarbonylation cascade.

Keywords: copper; cyclization; decarbonylation; quinazolinone; tandem reaction

Cleavage of C–C bonds poses great challenges to chemists mainly due to the inherent inertness of C–C σ bonds (*ca.* 350 kJ mol^{-1}),[1] which partially makes their cleavage thermodynamically less favoured than the opposite formation process.[2] In order to facilitate such a transformation, generally two strategies have been exploited to provide the driving forces. One is to raise the energy state of the starting materials, for example, by using strained small-membered ring systems.[3] The other is to lower the energy states of the C–C bond cleavage intermediates, such as through formation of a stable organometallic intermediate by chelating assistance.[4,5] Despite the remarkable achievements to date,[6] new strategies for C–C bond cleavage of unstrained linear substrates have received sustained interest. Alternatively, release of a stable small molecule such as CO or CO_2 could compensate the demanded energy, which is demonstrated by the rapidly growing field of decarboxylative cross-coupling reactions[7] and metal-catalyzed decarbonylations of ketones and aldehydes.[8] Although significant progresses have been achieved with this strategy, most of the C–C bond cleavages were catalyzed by noble metals such as palladium, rhodium and ruthenium, while use of the cheaper and ubiquitous copper for such transformations is quite rare.[9]

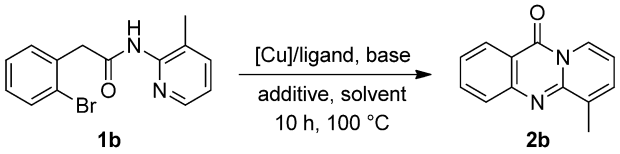
Nitrogen-containing heterocycles are found in numerous natural products and pharmaceutical drugs. Among these azaheterocycles, quinazolinone scaffolds are privileged structures in medicinal chemistry which show a broad spectrum of potent biological activities[10,11] and serve as a crucial category of anticancer agents as exemplified by marketed drugs such as Raltitrexed for colorectal cancer, Tempostatin for bladder cancer, and Ispinesib for solid tumours in its clinic trails. Typically, quinazolinones are constructed from 2-aminobenzoic acids or their derivatives *via* a sequence of acylation and condensation reactions under acidic or basic conditions.[12,13] Although several other methods have been developed to prepare quinazolinones including transition metal-catalyzed reactions,[14,15] the development of novel synthetic methods for quinazolinones as well as their fused derivatives is still highly demanded in term of efficiency and availability of starting materials. Herein, we report an efficient copper-catalyzed tandem aerobic oxidative annulation and carbon-carbon bond cleavage reaction, whereby in sequence one C–O bond and two C–N bonds are formed followed by two C–C bond cleavages for decarbonylation. To the best of our knowledge, the given approach features a novel protocol for sequential chemical bond formation and cleavage of arylacetamides, which provides an efficient approach for the domino synthesis of a vast array of tricyclic or tetracyclic fused quinazolinones from easily available arylacetamides (Scheme 1).



Scheme 1. Copper-catalyzed transformation of arylacetamides to fused quinazolinones, and the X-ray structure of product **2a**. Thermal ellipsoids are set at 50% probability, rendered with POV-Ray. Hydrogen and chlorine atoms are omitted for clarity.

Our preliminary investigation started by examining the reaction of 2-(2-bromophenyl)-*N*-(3-methylpyridin-2-yl)acetamide (**1b**) in the presence of $Cu(OAc)_2$ in dioxane using KOAc as a base in order to synthesize an *N*-pyridyl-substituted isatin. To our surprise, the reaction afforded an unexpected product – 6-methyl-11*H*-pyrido[2,1-*b*]quinazolin-11-one (**2b**) – in 58% yield (Table 1, entry 1). An extensive screening concerning copper sources (entries 2–5), bases (entries 6–9), ligands (entries 10–16), additives (entries 17–19) and solvents (entries 20–22) revealed that the use of CuI and 1,10-Phen as catalyst, KOAc as base and TBAB as additive in DMF at 100 °C under air was the best choice and resulted in **2b** in 87% yield (entry 22). It is worth noting that decreased yields were obtained in the absence of TBAB (entry 23), which was supposed to act as a phase-transfer catalyst for the copper ions by transmitting them in the form of complexes to the organic phase where the reaction takes place[16] or be involved in the benzylic oxidation reaction by adjusting the solu-

Table 1. Optimization of reaction conditions.[a]



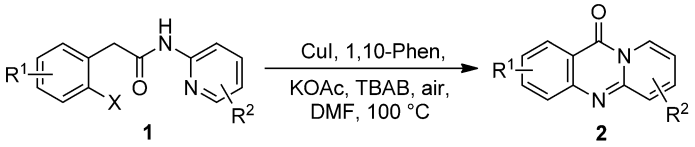
Entry	Cu Source	Base	Solvent	Additive	Ligand	Yield[b] [%]
1	$Cu(OAc)_2$	KOAc	dioxane	TBAB	1,10-Phen	58
2	$Cu(acac)_2$	KOAc	dioxane	TBAB	1,10-Phen	36
3	CuCl	KOAc	dioxane	TBAB	1,10-Phen	65
4	CuBr	KOAc	dioxane	TBAB	1,10-Phen	58
5	CuI	KOAc	dioxane	TBAB	1,10-Phen	84
6	CuI	NaOAc	dioxane	TBAB	1,10-Phen	trace
7	CuI	Cs_2CO_3	dioxane	TBAB	1,10-Phen	36
8	CuI	*t*-BuOK	dioxane	TBAB	1,10-Phen	55
9	CuI	Et_3N	dioxane	TBAB	1,10-Phen	trace
10	CuI	KOAc	dioxane	TBAB	bipyridine	51
11	CuI	KOAc	dioxane	TBAB	L-proline	80
12	CuI	KOAc	dioxane	TBAB	glycine	trace
13	CuI	KOAc	dioxane	TBAB	DMEDA	55
14	CuI	KOAc	dioxane	TBAB	PPh_3	58
15	CuI	KOAc	dioxane	TBAB	IMes·HCl	29
16	CuI	KOAc	dioxane	TBAB	–	40
17	CuI	KOAc	dioxane	Bu_4NCl	1,10-Phen	44
18	CuI	KOAc	dioxane	Bu_4NOAc	1,10-Phen	36
19	CuI	KOAc	dioxane	Et_4NBr	1,10-Phen	36
20	CuI	KOAc	DMSO	TBAB	1,10-Phen	65
21	CuI	KOAc	anisole	TBAB	1,10-Phen	62
22	**CuI**	**KOAc**	**DMF**	TBAB	**1,10-Phen**	**87**
23	CuI	KOAc	DMF	–	1,10-Phen	76
24	CuI	KOAc	DMF	–	–	71
25[c]	CuI	KOAc	DMF	TBAB	1,10-Phen	trace
26	–	KOAc	dioxane	TBAB	1,10-Phen	trace

[a] *Reaction conditions:* **1a** (0.3 mmol), [Cu] (10 mol%), ligand (20 mol%), base (3.0 equiv.) and TBAB (1.4 equiv.) in solvent (2 mL), 10 h, 100 °C, open to air, dried through a calcium chloride tube. DMEDA = *N*,*N*′-dimethylethylenediamine, 1,10-Phen = 1,10-phenanthroline, TBAB = tetrabutylammonium bromide.

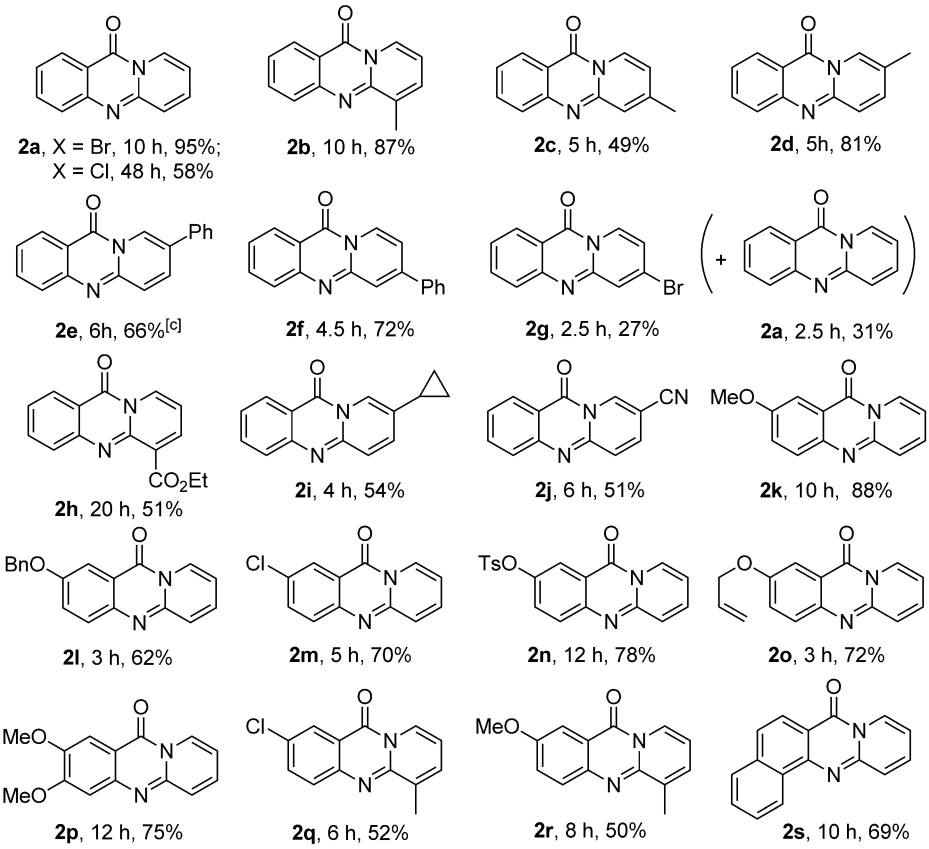
[b] Isolated yield.

[c] Under an N_2 atmosphere.

Table 2. Synthesis of pyridine-derived quinazolines.[a,b]



1 **2**

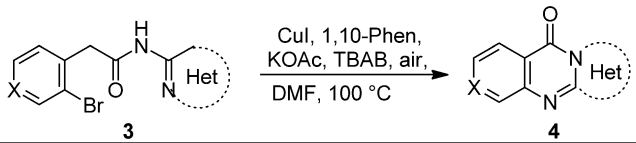


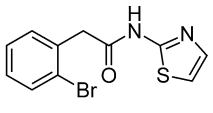
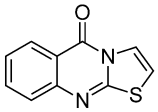
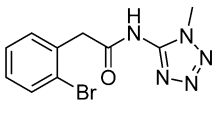
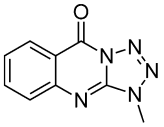
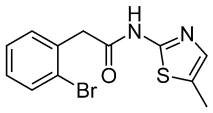
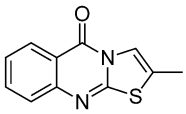
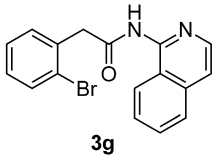
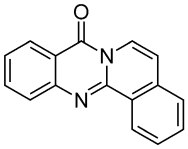
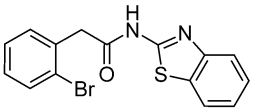
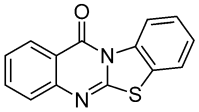
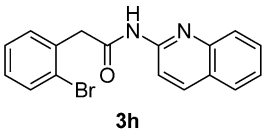
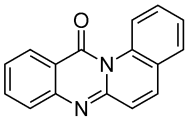
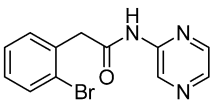
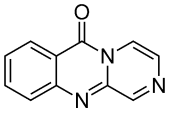
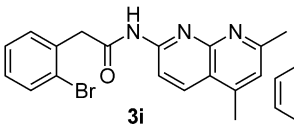
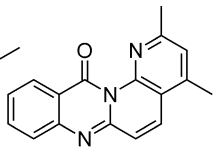
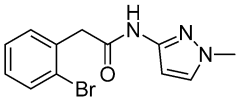
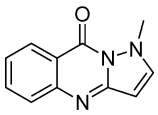
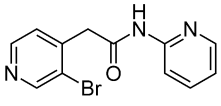
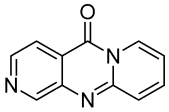
[a] *Reaction conditions:* **1** (0.3 mmol), CuI (10 mol%), 1,10-Phen (20 mol%), KOAc (3.0 equiv.) and TBAB (1.4 equiv.) in DMF (2 mL), 10 h, 100 °C, open to air, dried through a calcium chloride tube.
[b] Isolated yield.
[c] Run at 115 °C.

bility of base in the solvent.[17] The absence of ligand also led to a diminished yield (entry 24). Trace amounts of product was detected when the reaction was conducted under a nitrogen atmosphere (entry 25) or in the absence of CuI (entry 26), which implied that atmospheric oxygen and copper salt are crucial for this transformation.

With the optimized conditions in hand, various *N*-pyridylarylacetamides with different substituents were investigated for the synthesis of fused quinazolinones. As illustrated in Table 2, a wide variety of substitution patterns and functionalities could be tolerated. Substrates bearing different functional groups on both of the phenyl and pyridyl rings, such as alkyl (**2b–d**), aryl (**2e**, **2f**), cycloalkyl (**2i**), alkoxyl (**2k**, **2l, 2o**, **2p, 2r**), halo (**2g, 2m, 2q**), nitrile (**2j**), ester (**2h**), and tosyl (**2n**) were compatible with this reaction and gave moderate to excellent yields, regardless of their different electronic properties and substitution positions. The identity of products, for example **2a** and **2n**, was determined by spectral analysis and further confirmed by X-ray crystallographic analysis.[18] Substrate **1g** with a bromo substituent afforded the corresponding **2g** in diminished yield accompanied with a 31% yield of the debrominated product **2a**. The reaction was not limited to simple benzene-containing aromatics, the naphthyl substrate also gave the desired product in 69% yield (**2s**). It should be noted that the less reactive chloro-substituted substrate, 2-(2-chlorophenyl)-*N*-(pyridin-2-yl)acetamide (**1t**), could still afford product **2a** in 58% yield.

Table 3. Synthesis of quinazolinones from arylacetamides containing various heterocycles.[a,b]



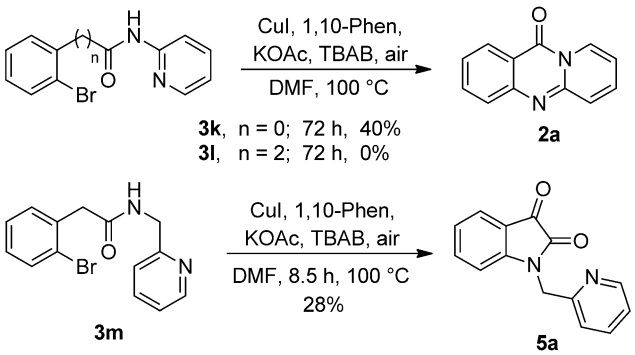
Substrate	Product	Substrate	Product
 **3a**	 **4a**, 3 h, 76%	 **3f**	 **4f**, 7 h, 41%
 **3b**	 **4b**, 3 h, 54%	 **3g**	 **4g**, 10 h, 68%
 **3c**	 **4c**, 3 h, 54%	 **3h**	 **4h**, 10 h, 58%
 **3d**	 **4d**, 5.5 h, 56%	 **3i**	 **4i**, 5 h, 75%
 **3e**	 **4e**, 6 h, 72%	 **3j**	 **4j**, 4 h, 66%

[a] *Reaction conditions:* **3** (0.3 mmol), CuI (10 mol%), 1,10-Phen (20 mol%), KOAc (3.0 equiv.) and TBAB (1.4 equiv.) in DMF (2 mL), 10 h, 100 °C, open to air, dried through a calcium chloride tube.

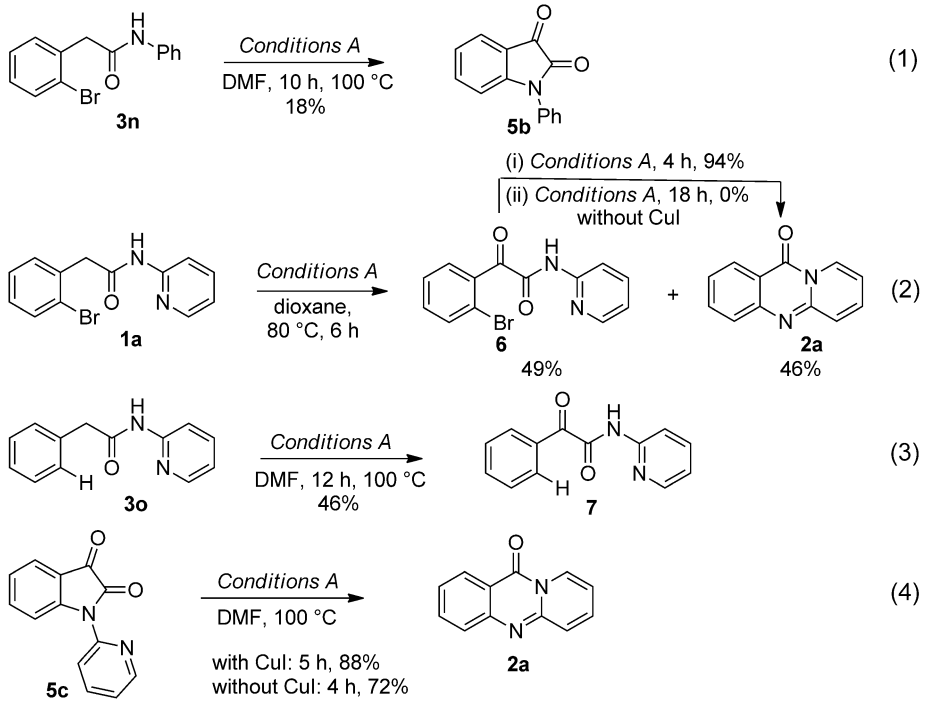
[b] Isolated yield.

To further explore the generality and scope of this method, other substrates were next examined. To our delight, reactions of arylacetamides with *N*-heterocycles other than the pyridyl group proceeded smoothly under the optimized reaction conditions as illustrated in Table 3. Substrates bearing thiazole (**3a**, **3b**), benzothiazole (**3c**), pyrazine (**3d**), pyrazole (**3e**), tetrazole (**3f**), quinoline (**3g**, **3h**) and 1,8-naphthyridine (**3i**) moieties, all gave the desired tricyclic or tetracyclic fused products in moderate to good yields. Notably, some of these products have shown potent biological activities and are difficult to prepare using regular synthetic methods from easily available substrates. Dual pyridine-containing substrate **3j** also showed good reactivity and gave **4j** in good yield, which is of good bactericidal activities.[19]

In comparison, when 2-bromo-*N*-(pyridin-2-yl)-benzamide (**3k**) was treated under the optimized condi-



Scheme 2. Scope of arylacetamides.



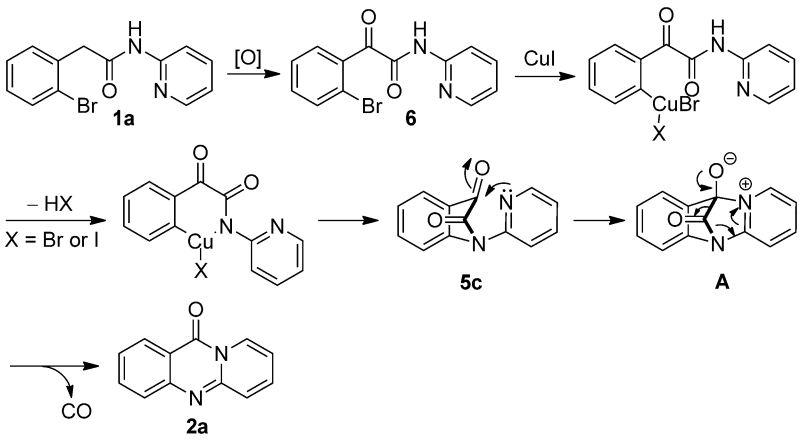
Scheme 3. Mechanistic studies. *Conditions A:* CuI (10 mol%), 1,10-Phen (20 mol%), KOAc (3.0 equiv.) and TBAB (1.4 equiv.), under air.

tions, the reaction could also afford compound **2a** in 40% yield after reaction for 72 h (Scheme 2). The given result might arise from the iminoketene-benzazetinone intermediate formed by direct intramolecular C–N bond formation of **3k**.[20] However, for substrate **3l** with two carbons between the aryl and amide groups, no expected cyclic product was observed and the starting material was recovered quantitatively. When we attempted to conduct the reaction with the one-carbon homologated analogue of **1a**, 2-(2-bromophenyl)-*N*-(pyridin-2-ylmethyl)acetamide (**3m**), it gave only the isatin product **5a** in 28% yield,[21] and no corresponding tricyclic fused product was observed.

To define the reaction mechanism, several control reactions were investigated (Scheme 3). Substrate **3n**, in which the pyridyl substituent in **1a** was replaced by a phenyl group, afforded the isatin product **5b** in 18% yield under the optimized conditions [Eq. (1)]. This result suggested that the isatin product might be the intermediate during the formation of quinazolinone and that the pyridyl substituent played an important role for the subsequent transformation. Treatment of **1a** at lower temperature in dioxane afforded a mixture of **6** and **2a** in 49% and 46% yield, respectively. The isolated **6** could be further transformed to **2a** in 94% yield under the standard conditions, while no reaction happened in the absence of copper catalyst [Eq. (2)]. Substrate **3o** could only give the corresponding benzylic oxidative product **7** without the detection of **2a**, the reason for which may due to the difficult cyclization through an intramolecular C–N bond formation [Eq. (3)]. These results indicated that the decarbonylation may occur through a cyclic intermediate such as isatin **5c** during the formation of **2a** from intermediate **6**, although no **5c** was observed during this transformation. The synthesized **5c** could indeed deliver **2a** smoothly with or without a copper catalyst (88% and 72% yield, respectively), which indicated a thermal process for this transformation and strongly suggested that the isatin **5c** may be the key intermediate for this reaction [Eq. (4)].

On the basis of these investigations, we proposed a plausible mechanism for this transformation as depicted in Scheme 4. Initially, **1a** was aerobically oxidized to α-keto amide **6**,[17] which gave the isatin product **5c** after a copper-catalyzed intramolecular amination reaction. Subsequently, the intramoleular nucleophilic attack of pyridyl to ketone afforded a tricyclic zwitterionic intermediate **A**. The extrusion of carbon monoxide from intermediate **A** led to the formation of quinazolinone **2a**.[22] It is worth noting that decarbonylation of a zwitterionic intermediate like **A** is quite unusual, although expulsion of carbon monoxide from ketone bridged bicycles by a thermal or photochemical route is not surprising.[23]

In conclusion, we have successfully demonstrated an efficient copper-catalyzed tandem reaction through sequential aerobic benzylic oxidation, intramolecular cyclization, and decarbonylation processes. This ap-



Scheme 4. Plausible mechanism for the synthesis of **2a** from **1a** (ligands are omitted for clarity).

proach features a novel protocol for sequential chemical bond formation and cleavage of arylacetamides, and provides a direct approach for the domino synthesis of a vast array of tricyclic or tetracyclic fused quinazolinone analogues from easily available arylacetamides. The characteristics of excellent functional group tolerance and synthesis modularity should provide the described reaction with a broad utility in organic synthesis. Further insights into the mechanism, reaction scope and the synthetic application for bioactivities and material potentials of produced fused quinazolinones are under investigation in our group.

Experimental Section

General Procedure for the Synthesis of Fused Quinazolinones from Arylacetamides

To a 25-mL round-bottom flask equipped with a drying tube and a magnetic stirring bar were charged **1b** (92.0 mg, 0.30 mmol), CuI (5.7 mg, 0.03 mmol), 1,10-phenantholine (11 mg, 0.06 mmol), KOAc (88 mg, 0.90 mmol) and TBAB (135 mg, 0.42 mmol) in anhydrous DMF (2 mL). The mixture was stirred at 100 °C in an oil bath, and monitored by TLC. After 10 h, the reaction mixture was evaporated under vacuum to give the crude product which was purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:5) to afford **2b** as a yellowish solid; yield: 55 mg (87%).

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