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Furan-2-carbaldehydes as C1 building blocks for the synthesis of quinazolin-4(*3H*)-ones via ligand-free photocatalytic C–C bond cleavage

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Furan-2-carbaldehydes, as biomass-derived chemicals, are used as efficient green C1 building blocks to synthesize bioactive quinazolin-4(*3H*)-ones by ligand-free photocatalytic C–C bond cleavage. Notably, protection of hydroxyl, carboxyl, amide, or secondary amino groups is not required. Mechanistic studies suggest that conjugated *N,O*-tridentate copper complexes act as novel photoinitiators under visible light.

The synthesis of quinazolin-4(*3H*)-ones (Fig. 1) has attracted the interest of many organic chemists, owing to their important roles in pharmaceuticals, pesticides, and functional materials.[1] Several traditional C1 building blocks have been reported for the synthesis of quinazolin-4(*3H*)-ones, including formaldehyde/I_2, *N,N*-dimethylformamide/(*t*-Bu-O)$_2$ or $POCl_3$, pivalaldehyde/I_2, carbon dioxide/poly(methylsiloxane)/1,3-bis(2,6-diisopropyl-phenyl)imidazol-2-ylidene, formic acid–triethylamine/Pd, *1H*-imidazole/C:Cu(OAc)/(*t*-Bu-O)$_2$, trimethoxymethane, and ethyl formate.[2] However, the use of these C1 building blocks has many disadvantages, such as the needs for costly and hazardous materials, moisture-sensitive agents, non-green solvents, multistep processes, and high temperatures. For example, trimethoxymethane, which is the most widely used C1 building block, is moisture-sensitive and requires complicated and energy-intensive preparation.[3] (*t*-Bu-O)$_2$ and $POCl_3$ are hazardous materials. Moreover, the reaction yields of these C1 building blocks are sometimes unsatisfactory (27%–55%).[2]

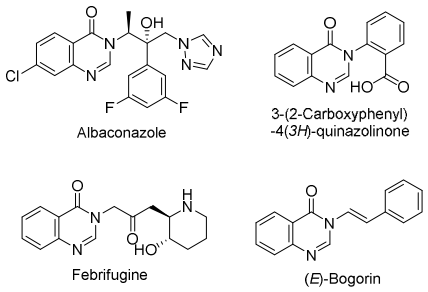
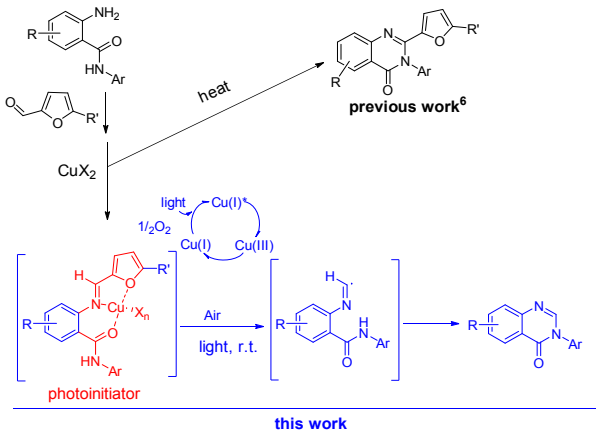


Fig. 1 Structures of selected bioactive quinazolinones.

In this study, we employed furan-2-carbaldehydes, which are biomass agents produced from rice bran or corn hull, as green and renewable C1 building blocks for the synthesis of quinazolin-4(*3H*)-ones via photocatalytic C–C bond cleavage.[4,5] Only moderate reaction conditions were required, and the synthesis could proceed in the presence of various unprotected active functional groups, including hydroxyl, carboxyl, and secondary amino groups (Scheme 1).



Scheme 1 Furan-2-carbaldehydes as C1 feedstocks via photocatalytic C–C bond cleavage, and the proposed reaction mechanism.[7,8]

Photoredox catalysis has emerged as a powerful method for initiating radical reactions under mild conditions using low-

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energy irradiation.[9] However, photocatalysis usually relies on heavy metal-based photocatalysts, e.g. ruthenium,[10] iridium,[11] copper,[7] gold,[12] or cobalt[13] complexes with complicated ligands. For green synthesis, it is essential to develop ligand-free photocatalytic methods.[8,14]

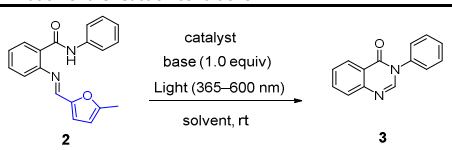
Recently, we found that conjugated *N,O*-bidentate copper(II) complexes act as photoinitiators for intramolecular C–H bond activation via a free radical mechanism.[8] Herein, we envisioned that complexes between conjugated *N,O*-tridentate copper and furan-2-carbaldehydes[15] could function as novel photoinitiators for C1 building blocks in the synthesis of quinazolin-4(*3H*)-one derivatives via a C–C bond cleavage. Therefore, the application of 5-methylfuran-2-carbaldehyde as a C1 building block via ligand-free photocatalytic C–C bond cleavage was first investigated using 2-amino-*N*-phenylbenzamide (**1**) as a model substrate. Compound **1** was reacted with 5-methylfuran-2-carbaldehyde to obtain 2-[(5-methyl-furan-2-ylmethylene)-amino]-*N*-phenylbenzamide (**2**). Based on our previous study, the photoinitiator complex of **2** and copper(II) forms in solution by activating the C–C bond of the furan-2-ylmethylene motif when irradiated by light from a high-voltage mercury lamp commonly used in industry. The desired product **3** was then successfully obtained by intramolecular cyclization, and its structure was characterized using single-crystal X-ray diffraction (Fig. S1).

Encouraged by this result, we optimized the reaction conditions by varying the base, solvent, catalyst, and reaction time. As shown in Table 1, the highest yields of about 90%–91% were obtained when ethanol was used as the solvent, $CuCl_2$ as the catalyst, and CsOAc or TEA as the base. Notably, when CsOAc was used as the base, the reaction was easy to handle.

Further, we examined other green and renewable furan-2-carbaldehydes as potential C1 building blocks. In order to identify abundant, green C1 feedstocks for ligand-free photocatalytic C–C bond cleavage, the comparative cost and availability were considered, and furan-2-carbaldehyde and 5-methylfuran-2-carbaldehyde were chosen as good candidates. To evaluate the effect of electron-withdrawing groups, 5-nitrofuran-2-carbaldehyde was also tested. Kinetic studies showed that 5-methylfuran-2-carbaldehyde and furan-2-carbaldehyde gave similarly high yields and reaction rates. In contrast, the yield of quinazolin-4(*3H*)-one was only about 20% when 5-nitrofuran-2-carbaldehyde was employed instead, although the starting material was almost completely consumed within 6 h (Fig. 2). Hence, both 5-methylfuran-2-carbaldehyde and furan-2-carbaldehyde proved to be excellent C1 building blocks. However, the former, which is used as for food flavoring and hence very safe, has the advantage of reacting with 2-amino-*N*-phenylbenzamides to form easy-to-handle imines in high yields. Therefore, 5-methylfuran-2-carbaldehyde was determined to be an excellent green C1 feedstock candidate.

With the optimized conditions and C1 feedstock candidates in hand, the substrate scope of the reaction was investigated (Fig. 3). Notably, quinazolin-4(*3H*)-ones with an alkyl, fluorine,

Table 1 Optimization of the reaction conditions



2 3

Entry	Solvent	Base	Catalyst	Time (h)	Yield (%)[a]
1	acetone	Cs_2CO_3	20% $CuCl_2$	4	61
2	ethanol	Cs_2CO_3	20% $CuCl_2$	4	84
3	THF	Cs_2CO_3	20% $CuCl_2$	4	65
4	CH_3CN	Cs_2CO_3	20% $CuCl_2$	4	68
5	EtOAc	Cs_2CO_3	20% $CuCl_2$	4	83
6	ethanol	Cs_2CO_3	20% $CuCl_2$	0.5	64
7	ethanol	Cs_2CO_3	20% $CuCl_2$	1	77
8	ethanol	Cs_2CO_3	20% $CuCl_2$	2	81
9	ethanol	Cs_2CO_3	20% $CuCl_2$	5	87
10	ethanol	Cs_2CO_3	20% $CuCl_2$, No light	5	0
11	ethanol	No base	20% $CuCl_2$	5	68
12	ethanol	CsOAc	20% $CuCl_2$	5	91
13	ethanol	K_2CO_3	20% $CuCl_2$	5	87
14	ethanol	TEA[b]	20% $CuCl_2$	5	90
15	ethanol	NMM[c]	20% $CuCl_2$	5	82
16	ethanol	pyridine	20% $CuCl_2$	5	74
17	ethanol	DMAP[d]	20% $CuCl_2$	5	63
18	ethanol	HOBT[e]	20% $CuCl_2$	5	17
19	ethanol	KOH	20% $CuCl_2$	5	89
20	ethanol	DIPEA[f]	20% $CuCl_2$	5	86
21	ethanol	NaOH	20% $CuCl_2$	5	81
22	ethanol	CsOAc	20% CuCl	5	79
23	ethanol	CsOAc	20% CuBr	5	84
24	ethanol	CsOAc	20% CuI	5	73
25	ethanol	CsOAc	20% $CuBr_2$	5	84
26	ethanol	CsOAc	10% $CuCl_2$	5	88
27	ethanol	CsOAc	5% $CuCl_2$	5	90
28	ethanol	CsOAc	1% $CuCl_2$	5	60

[a]HPLC yields. [b]TEA, triethylamine. [c]NMM, 4-methylmorpholine. [d]DMAP, 4-dimethylaminopyridine. [e]HOBT, 1-hydroxybenzotriazole. [f]DIPEA, *N,N*-diisopropylethylamine.

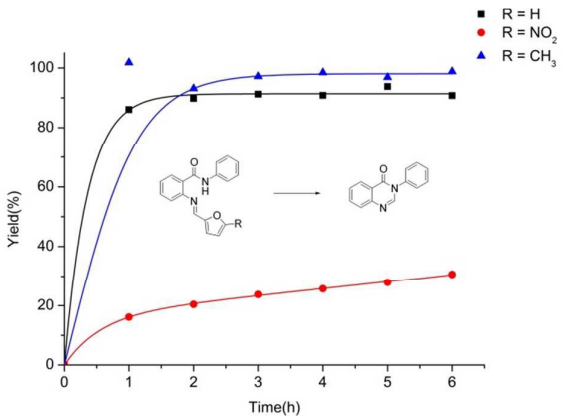


Fig. 2 Kinetic data of various furan-2-carbaldehydes used as C1 building blocks. The yields were determined by HPLC using an internal standard.

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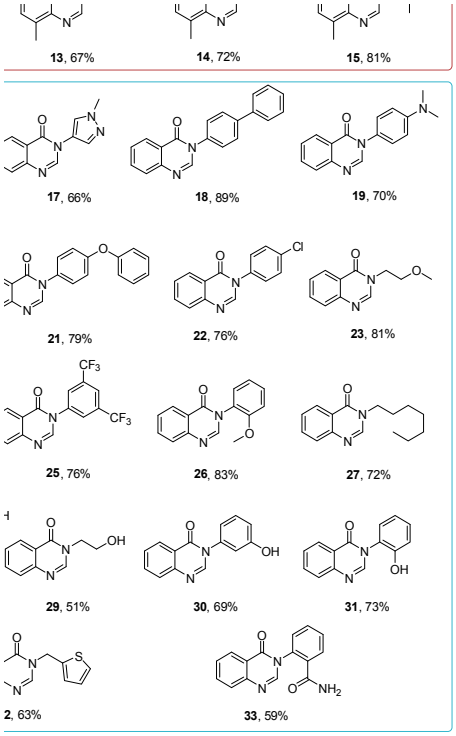

Fig. 3 Reaction scope and isolated yields for the conditions in Table 1, entry 27.

or alkoxy substituent on the phenyl ring were obtained in isolated yields of 59%–82%. Moreover, quinazolin-4(3*H*)-ones with a phenyl, pyrazol-4-yl, or alkyl substituent at the N3-position were also obtained in good to excellent yields. In particular, for substrates with hydroxyl or secondary amino groups, traditional C1 feedstocks require an additional step to protect these groups,[16] whereas 5-methylfuran-2-carbaldehyde can be used directly.

In the aforementioned experiments, a high-voltage mercury lamp was used because of its low cost and durability. However, its spectrum contains some UV light (Fig. S2), therefore, the role of UV light played in the reaction was then explored. Interestingly, the reaction proceeded even in the

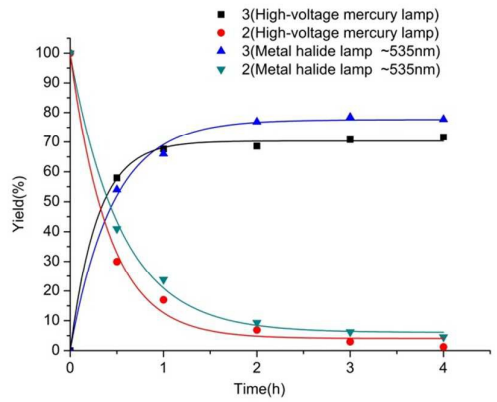

Fig. 4 Reaction kinetics using different light sources (300 W). The yields were determined by HPLC. The curves of **2** are surplus ratio–time curves.

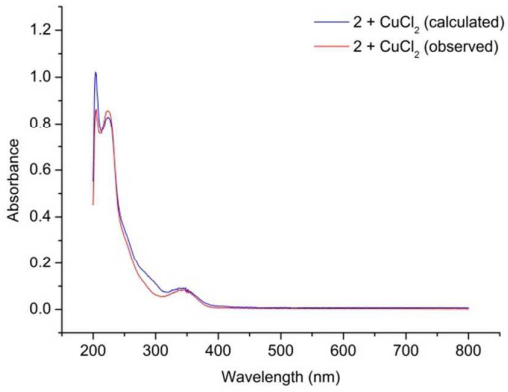

Fig. 5 UV-visible absorption spectrum of a mixed solution of **2** (2×10^{-5} mmol/mL) and $CuCl_2$ (2×10^{-5} mmol/mL) in ethanol (red curve). The blue curve was the sum of absorbances of **2** (2×10^{-5} mmol/mL) and $CuCl_2$ (2×10^{-5} mmol/mL) in ethanol alone.

absence of UV light (the lamp was equipped with an optical filter to remove UV light, < 420 nm). Therefore, the reaction kinetics was compared to that under a metal halide lamp (thallium, ~530 nm). As shown in Fig. 4, similar yields and reaction rates were obtained with the two light sources, indicating that this reaction can be initiated by visible light irradiation.

Next, the reaction mechanism was investigated. UV-visible and IR spectra were recorded to confirm the successful complex formation between compound **2** and copper(II) in solution, as suggested in our previous study.[8] As shown in Fig. 5, the absorption bands observed at around 212 and 300 nm could not be accounted for by summing the spectra of **2** and $CuCl_2$, suggesting the association between these two species. Moreover, the IR peaks (Fig. S3) of **2** at around 768.8, 1405.8, and 1666.9 cm^{-1}, which correspond to the copper(II)-chelating functionalities, were weaker for the mixture of **2** and $CuCl_2$. In particular, the N–H out-of-plane bending vibration (δ_{N-H}: 1551.3 cm^{-1}) observed for the mixture was not detected for the individual solutions (Fig. S4).

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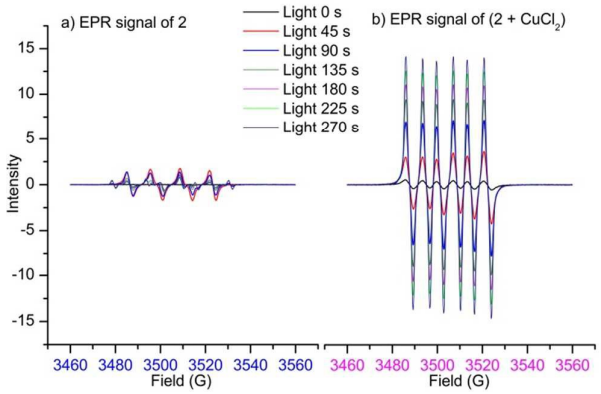
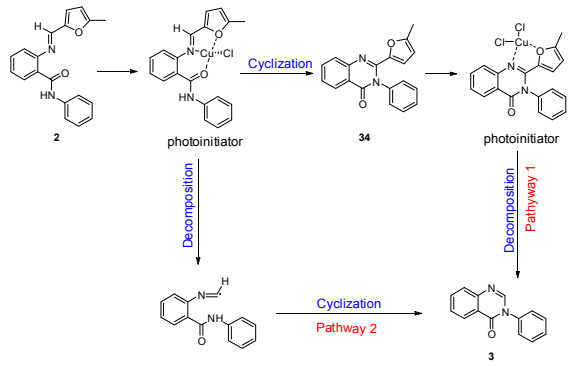


Fig. 6 Electron paramagnetic resonance spectra of (a) **2** in ethanol and (b) the complex of **2** and copper(II) in ethanol. The solutions were irradiated using a high-voltage mercury lamp, and the signals were collected after 0, 45, 90, 135, 180, 225, and 270 s.



Scheme 2 Possible reaction pathways.

These findings confirmed the complex formation between 2 and copper(II) in solution.

Electron paramagnetic resonance (EPR) studies were performed to determine whether the reaction proceeds via a free radical mechanism. Under light irradiation (high-voltage mercury lamp), small amounts of free radicals including superoxide, nitrogen, and carbon radicals were generated in the solution of **2** (Fig. 6a), whereas the $CuCl_2$ solution gave no EPR signals (Fig. S5). In contrast, in the mixed solution of **2** and $CuCl_2$, only carbon free radicals were produced, the amount of which increased with time (Fig. 6b). These results suggest that copper(II) ions play a key role in this reaction. The complex of **2** and copper(II) acts as a photoinitiator, and 5-methylfuran-2-carbaldehyde as a C1 building block via a free radical mechanism.

Based on these observations, two possible reaction pathways were proposed (Scheme 2). In pathway 1, compound **2** forms the photoinitiator by chelating copper(II) ions, and the obtained complex cyclizes to give intermediate **34** (Fig. S6). Next, **34** chelates copper(II) and its furan ring is decomposed under light irradiation to form **3**. In contrast, in pathway 2, the decomposition of the furan ring of the photoinitiator occurs before the cyclization. To determine which pathway was followed, we attempted to monitor the formation of intermediate **34** by HPLC and LC/MS, but no

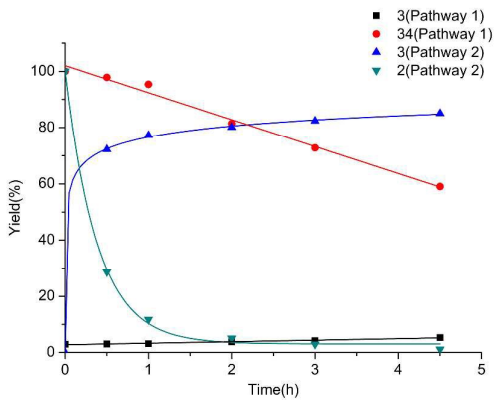


Fig. 7 Kinetics of the two possible reaction pathways. Pathway 1 starts from intermediate **34**, and pathway 2 from intermediate **2**. The curves of **34** and **2** are surplus ratio–time curves. The yields were determined by HPLC using an internal standard.

evidence of it was observed. Next, two kinetic assays were performed: from **34** to **3** and from **2** to **3**. As shown in Fig. 7, **34** decomposed under irradiation from the mercury lamp, but the yield of **3** was below 10%. In contrast, **2** was rapidly converted to **3** at a rate matching that of the free radical formation as revealed by the EPR study. Hence, we concluded that the reaction proceeded via pathway 2.

Conclusions

In summary, we demonstrated two renewable green agents, 5-methylfuran-2-carbaldehyde and furan-2-carbaldehyde, which can be produced from rice bran or corn hull, as efficient C1 building blocks for the synthesis of quinazolin-4*(3H)*-ones by photocatalytic C–C bond cleavage under visible light irradiation. The reaction conditions were more moderate and greener than those using traditional C1 building blocks. In particular, for substrates with hydroxyl, secondary amino, amide, or carboxyl groups, protection reactions are not required before using furan-2-carbaldehydes. Importantly, the complex between 2-[(5-methylfuran-2-ylmethylene)-amino]-*N*-phenylbenzamide and copper(II) was found to be a novel ligand-free photoinitiator that produces a moderate amount of carbon free radicals. Therefore, this study provides a useful tool for constructing new skeletons by intermolecular reactions of in-situ generated carbon radicals.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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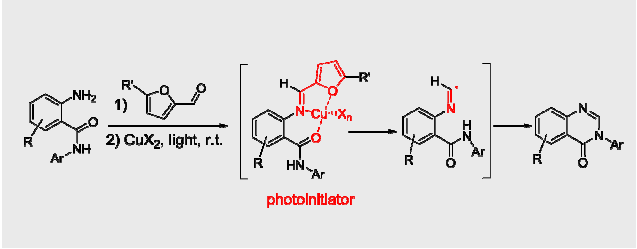

Simple and inexpensive: The biomass-derived chemicals furan-2-carbaldehydes are efficient green C1 building blocks for the synthesis of biologically interesting quinazolin-4(*3H*)-ones via ligand-free photocatalytic C-C bond cleavage.

Wenjia Yu, Xianwei Zhang, Bingjie Qin, Qiyang Wang, Xuhong Ren and Xinhua He**

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