

Cite this: *Chem. Sci.*, 2026, 17, 4632

All publication charges for this article have been paid for by the Royal Society of Chemistry

# Controllable copper-catalysed photo-induced carbonylative cyclization to access dihydroquinolinones and oxindoles

Yan-Hua Zhao,<sup>a</sup> Le-Cheng Wang<sup>ab</sup> and Xiao-Feng Wu<sup>ab</sup> \*<sup>ab</sup>

Oxindoles and dihydroquinolinones are pivotal heterocyclic scaffolds in medicinal and synthetic chemistry. Herein, we describe a controllable visible-light-induced, copper-catalyzed carbonylative cyclization of arylthianthrenium salts with alkenes, enabling the efficient synthesis of structurally diverse oxindoles and dihydroquinolinones. Notably, this transformation proceeds under mild conditions without the need for expensive photocatalysts, and regioselective acyl radical addition is achieved simply by tuning the substitution pattern of the alkene, which enables the switchable synthesis of carbonylated five- and six-membered heterocycles. Mechanistic studies indicate that blue-light irradiation promotes the copper-mediated reduction of arylthianthrenium salts, generating aryl radicals that subsequently capture CO to afford acyl radicals and initiate a tandem cyclization sequence. This method exhibits broad functional-group tolerance and offers a versatile platform for the late-stage functionalization of bioactive molecules.

Received 3rd December 2025  
Accepted 8th January 2026

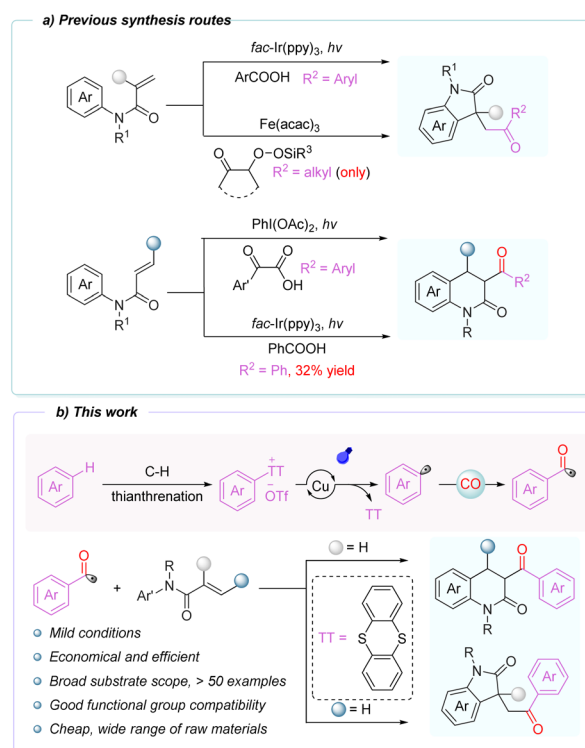
DOI: 10.1039/d5sc09434h

rsc.li/chemical-science

## Introduction

3,3-Disubstituted oxindoles and dihydroquinolinones are important nitrogen-containing heterocycles that are widely found in natural products and bioactive molecules,<sup>1–8</sup> and their efficient synthesis continues to attract significant attention.<sup>9–15</sup> Over the past decades, numerous transition-metal-catalyzed and metal-free oxidative strategies have been developed for assembling these frameworks.<sup>16–20</sup> Among them, the palladium-catalyzed domino-Heck reaction is typically one of the most efficient methods for constructing heterocycles. This approach employs (pseudo)halides, chloroform, aldehydes, and other substrates, coupling them with alkenes to form oxygen-containing indoles and dihydroquinolinones through ring-closure reactions.<sup>21–24</sup> In recent years, significant progress has been made in radical-based cyclizations (Scheme 1a). Wallentin, Banerjee, and others developed visible-light-driven strategies for generating acyl radicals that subsequently undergo transformations with *N*-aryl acrylamides.<sup>25,26</sup> In 2023, the Maruoka group reported an iron-catalyzed method in which alkyl silyl peroxides serve as precursors to acyl radicals, enabling cascade reactions with *N*-aryl acrylamides.<sup>27</sup> Shortly thereafter, Liu and co-workers reported a visible-light-mediated radical cascade between *N*-aryl acrylamides or *N*-methylacrylamide benzamides and carbon dioxide.<sup>28</sup> However, these approaches

still suffer from limitations such as limited substrate scope. Therefore, the development of a direct, efficient, sustainable, and controllable strategy for the construction of carbonyl-containing heterocyclic frameworks remains highly desirable.



Scheme 1 Previous synthesis routes and this work.

<sup>a</sup>Leibniz-Institut für Katalyse e.V., Albert-Einstein-Straße 29a, Rostock 18059, Germany. E-mail: Xiao-Feng.Wu@catalysis.de<sup>b</sup>Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China. E-mail: xwu2020@dicp.ac.cn

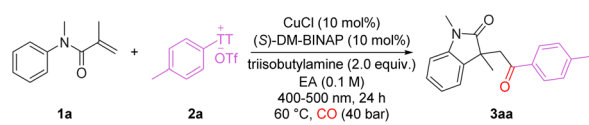
Carbonylation chemistry offers one of the most direct and versatile platforms for accessing carbonyl-containing molecules.<sup>29–35</sup> Since Heck's pioneering report of palladium-catalyzed carbonylation in 1974, carbon monoxide (CO) has become an essential C1 synthon for transforming simple and readily available substrates into diverse carbonylated derivatives.<sup>36–42</sup> Despite its broad synthetic utility, achieving chemoselective and regioselective carbonylation remains challenging, as conventional protocols often rely on noble-metal catalysts, strong Brønsted acids, and high temperatures, thereby limiting functional-group tolerance and substrate scope.<sup>43–49</sup> *N*-arylacrylamides, as structurally privileged activated alkenes, offer an attractive platform for achieving regioselective carbonylation *via* substitution-controlled reactivity, enabling streamlined access to carbonylated oxindoles and dihydroquinolinones.<sup>50–56</sup> Meanwhile, arylthianthrenium salts have attracted considerable interest due to their high reactivity and ready accessibility, which allows them to be readily prepared from simple arenes *via* C(sp<sup>2</sup>)-H thianthrenation.<sup>57–64</sup> In recent years, Ritter and co-workers have systematically investigated thianthrenium salts, revealing their broad utility in diverse C-H functionalization reactions.<sup>65–70</sup> However, only a few examples of carbonylation reactions using thianthrenium salts have been reported, and there are no related reports on the selective controllable carbonylation associated with them.

Building on our previous investigations into the photochemical behavior of thianthrenium salts,<sup>68,71–75</sup> we demonstrated that these reagents undergo efficient visible-light-induced homolytic C(sp<sup>2</sup>)-S bond cleavage to generate aryl radicals. Leveraging this reactivity, we developed a controllable single electron carbonylative cyclization manifold. Under visible-light-promoted copper catalysis, the *in situ* formed aryl radicals readily capture CO to produce acyl radicals, which undergo selective addition with *N*-aryl acrylamides to deliver oxindoles and dihydroquinolinones. *N*-aryl acrylamides are readily accessible from a variety of  $\alpha,\beta$ -unsaturated carboxylic acid derivatives, and their tunable substitution patterns provide an ideal platform for controlling reaction selectivity. Remarkably, tuning the alkene substitution pattern alone dictates the regioselectivity of acyl-radical addition, granting switchable access to carbonylated five- and six-membered heterocycles without altering reaction conditions. This platform thus provides a general, mild, and highly controllable approach to carbonylation, addressing key limitations in current radical carbonylation chemistry (Scheme 1b).

## Results and discussion

We began our investigation using *N*-arylacrylamide **1a** and arylthianthrenium salt **2a** as the model substrates to evaluate the feasibility of the carbonylative cyclization (Table 1). Under blue-light irradiation at 60 °C in EtOAc, with CuCl as the catalyst, (*S*)-DM-BINAP as the ligand, and triisobutylamine as the base under 40 bar CO for 24 h, the desired oxindole **3aa** was obtained in 80% yield (78% isolated, entry 1). Control experiments confirmed that the reaction did not proceed in the absence of the copper catalyst, ligand, base, or light (Table 1,

Table 1 Optimization of reaction conditions<sup>a</sup>



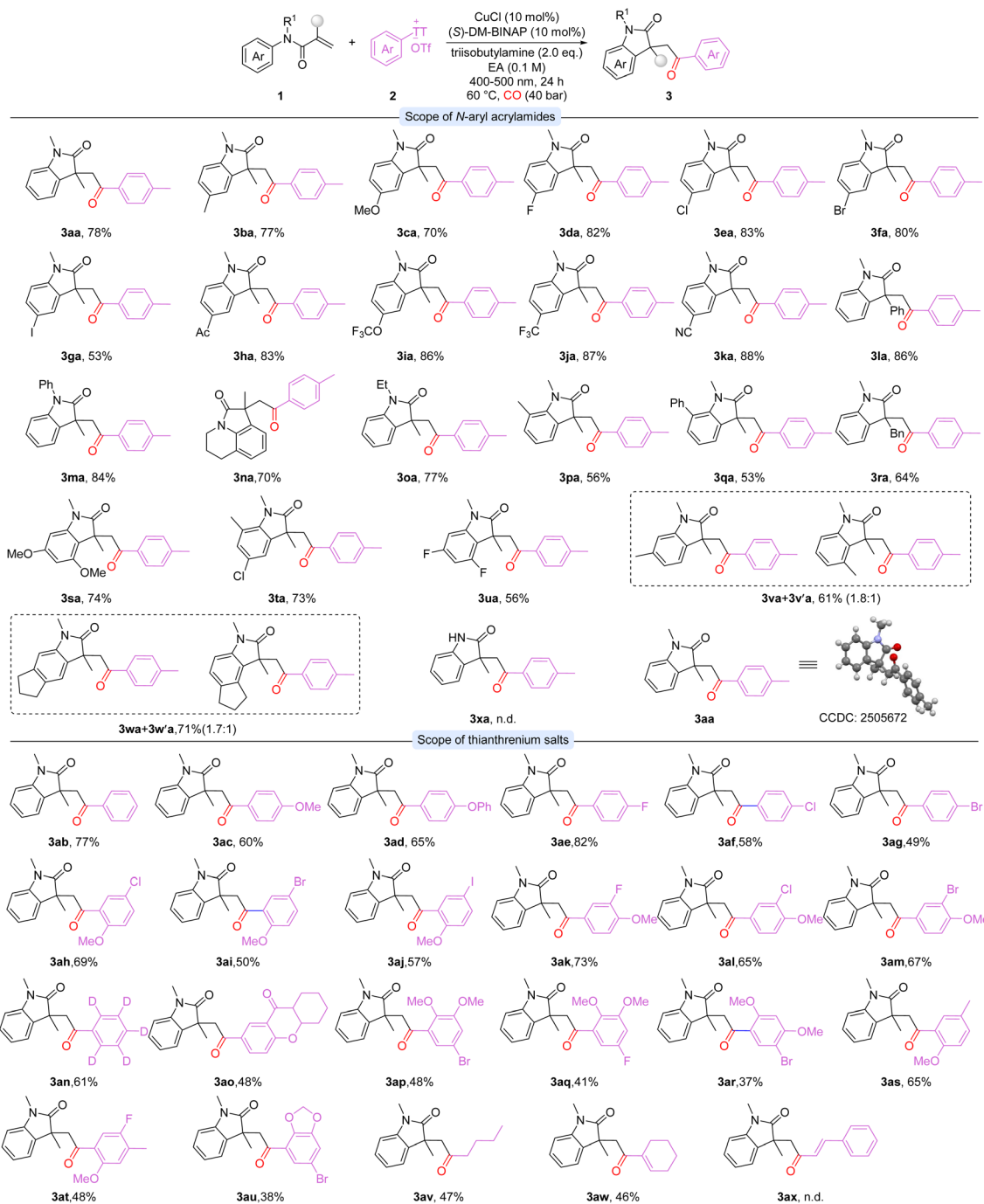
Entry	Variation from the standard conditions	Yield (%) <sup>b</sup>
1	None	80 (78) <sup>c,d</sup>
2	No catalyst	n.d.
3	No ligand	n.d.
4	No base	Trace
5	No light irradiation	n.d.
6	CuBr instead of CuCl	36
7	Cu(CH <sub>3</sub> CN) <sub>4</sub> BF <sub>4</sub> instead of CuCl	56
8	Cu(acac) <sub>2</sub> instead of CuCl	31
9	BINAP instead of ( <i>S</i> )-DM-BINAP	69
10	PCy <sub>3</sub> instead of ( <i>S</i> )-DM-BINAP	n.d.
11	1,10-Phen instead of ( <i>S</i> )-DM-BINAP	n.d.
12	( <i>R</i> )-DM-BINAP instead of ( <i>S</i> )-DM-BINAP	79
13	DIPEA instead of triisobutylamine	74
14	K <sub>3</sub> PO <sub>4</sub> instead of triisobutylamine	16
15	CH <sub>3</sub> CN as solvent	25
16	Toluene as solvent	56
17	1.0 equiv. <b>2a</b>	50
18	0.2 mol L <sup>-1</sup> EA	75
19	40 °C instead of 60 °C	73
20	20 bar CO	69

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), CO (40 bar), catalyst (10 mol%), ligand (10 mol%), base (0.2 mmol), solvent (1.0 mL), blue-light irradiation at 60 °C, 24 h. <sup>b</sup> Yield was determined by GC using <sup>3</sup>Hexadecane as the internal standard. <sup>c</sup> Isolated yield. <sup>d</sup> 70% yield on 10 mmol scale.

entries 3–5). Screening of copper salts revealed that Cu(acac)<sub>2</sub> could also promote the reaction, even with a slightly lower yield, while other copper catalysts gave comparable results (Table 1, entries 6–8). Bidentate phosphine ligands facilitated product formation but did not improve the yield, and the reaction outcomes for (*R*)-DM-BINAP and (*S*)-DM-BINAP were similar (Table 1, entries 9 and 12). In contrast, nitrogen-based or monodentate phosphine ligands failed to produce detectable amounts of **3aa** (Table 1, entries 10 and 11). The choice of base significantly affected the reaction outcome, with organic bases outperforming inorganic bases (Table 1, entries 13 and 14). Solvent screening indicated that EtOAc was the optimal, while acetonitrile or toluene led to decreased yields (Table 1, entries 15 and 16). Reducing the amount of **2aa** or increasing the reaction concentration also lowered the yield (Table 1, entries 17 and 18). The reaction proceeded at 40 °C to give **3aa** in 73% yield (Table 1, entry 19), and lowering the CO pressure similarly decreased the reaction efficiency (Table 1, entry 20). For the reaction time, the conversion cannot be completed after 15 hours and no better yield can be produced if we extend the reaction time to 36 hours.

With the optimal conditions established, the substrate scope of *N*-aryl acrylamides was investigated at the first stage (Scheme 2). Unsubstituted and electron-donating substrates, such as methyl- and methoxy-substituted *N*-aryl acrylamides, were well





Scheme 2 Reaction conditions: **1** (0.1 mmol), **2** (0.15 mmol), CuCl (10 mol%), (*S*)-DM-BINAP (10 mol%), triisobutylamine (0.2 mmol), EA (1.0 mL), CO (40 bar), under blue-light irradiation at 60 °C, 24 h.; isolated yields.

tolerated, affording the desired products in good to high yields (**3aa–3ca**). Halogen-substituted substrates (F, Cl, Br, I) were also compatible, providing the corresponding products in moderate to excellent yields (**3da–3ga**). Notably, substrates bearing electron-withdrawing groups, including acyl, trifluoromethoxy, trifluoromethyl, and cyano, proceeded smoothly to give oxindoles in excellent yields (**3ha–3ka**). Alkenes bearing other substituents delivered products **3la** and **3ra** in 86% and 64% yields, respectively. *N*-protected acrylamides with phenyl or

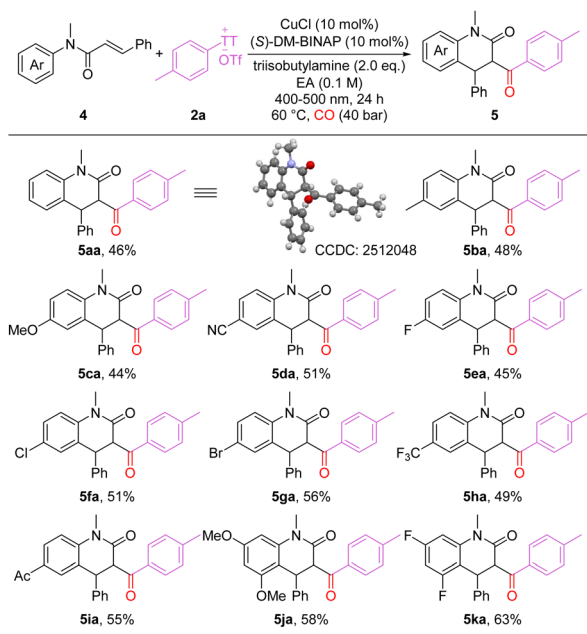
ethyl groups were also compatible, yielding **3ma** and **3oa** in 84% and 77% yields. In contrast, unprotected *N*-aryl acrylamides failed to afford the desired product (**3xa**). The ester analogue was also tested, but no lactone product could be detected. Tetrahydroquinoline derivatives were tolerated, providing the target product **3na** in 70% yield. *Ortho*-Substituted substrates furnished the products **3pa** and **3qa** in moderate yields, while *meta*-substituted substrates led to regioisomeric mixtures (**3va/3v'a** and **3wa/3w'a**). Furthermore, multi-substituted substrates



were also well tolerated, afforded the corresponding products in excellent yields (**3sa-3ua**).

The substrate scope of thianthrenium salts was further investigated (Scheme 2). Unsubstituted and electron-rich aryl thianthrenium salts gave the desired products in good yields (**3ab-3ad**, **3as**). Aryl thianthrenium salts bearing C(sp<sup>2</sup>)-X bonds (X = F, Cl, Br) were also compatible, providing the corresponding products in moderate to excellent yields (**3ae-3ag**). Similarly, di- and tri-substituted aryl thianthrenium salts (**3ah-3am** and **3ap-3ar**, **3at-3au**) performed well under the reaction conditions, delivering the target products in good yields in general. These results highlight the high chemoselectivity of the catalytic system and its potential for subsequent structural modifications. Complex scaffolds, including flavone-derived salts, also participated smoothly, delivering the corresponding product in moderate yield (**3ao**). Deuterated substrates afforded the desired oxindole **3an** in 61% yield. Notably, thianthrenium salts bearing alkyl and alkenyl substituents reacted smoothly under the standard conditions, delivering the desired products (**3av-3aw**) in moderate yields. However, the styrenyl-substituted thianthrenium salt showed no reactivity under the standard reaction conditions (**3ax**). These results indicate that the catalytic system features broad substrate scope and high chemoselectivity. Additionally, instead of thianthrenium salt, iodobenzene was checked as well but lead to no desired product formed.

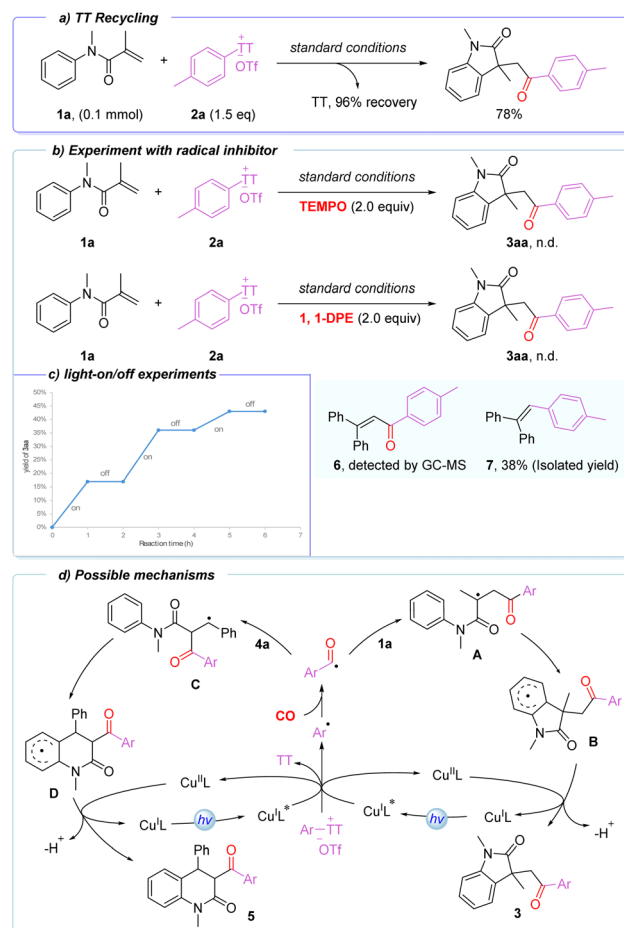
Under the standard reaction conditions, employing alkenes with different substitution patterns, six-membered dihydroquinolinones were selectively obtained rather than five-membered oxindoles (Scheme 3). As shown in the scheme, a variety of carbonylated six-membered heterocycles bearing diverse functional groups were synthesized in moderate to good



Scheme 3 Reaction conditions: **4** (0.1 mmol), **2a** (0.15 mmol), CuCl (10 mol%), (S)-DM-BINAP (10 mol%), triisobutylamine (0.2 mmol), EA (1.0 mL), CO (40 bar), under blue-light irradiation at 60 °C, 24 h.; isolated yields.

yields (**5aa-5ka**). Unsubstituted and electron-rich substrates afforded the corresponding products in moderate yields (**5aa-5ca**). Internal alkenes bearing halogens (F, Cl, Br) or electron-withdrawing groups (cyano, acyl, trifluoromethyl) were compatible with the reaction, delivering the desired products in moderate yields (**5da-5ia**). Multi-substituted substrates also performed well, providing the target products in good yields (**5ja-5ka**). It's worth to mention that non-carbonylation product was the main by-product during this process and response for the moderate yields.

The atom economy of the reaction was also evaluated, and thianthrene was recovered in yields of up to 96% (Scheme 4a). To gain some insight into the reaction mechanism, several mechanistic experiments were conducted. Under the standard conditions, the addition of 2.0 equiv. of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) completely suppressed the formation of the desired product. Similarly, the addition of 2.0 equiv. of 1,1-diphenylethylene (1,1-DPE) led to no detectable target product, while radical adducts **6** and **7** were observed (Scheme 4b). Furthermore, light-on/off experiments revealed that the reaction proceeds only under visible-light irradiation, and no conversion occurs in the dark (Scheme 4c). Collectively, these results indicate that the transformation does not follow a radical chain process, but rather proceeds *via* an aryl radical intermediate.



Scheme 4 Control experiments and possible mechanisms.



Based on the above results and literature precedents, a plausible mechanism is proposed (Scheme 4d).<sup>76–80</sup> Under blue-light irradiation, the Cu<sup>I</sup>L complex is excited to Cu<sup>I</sup>L\*, which reacts with the aryl thianthrenium salt to generate an aryl radical and copper(II) complex Cu<sup>II</sup>L. The aryl radical captures CO to form an acyl radical, which adds to the alkene of *N*-methyl-*N*-phenylacrylamide **1a**, affording intermediate **A**. Intramolecular cyclization on the aryl ring then gives intermediate **B**, which undergoes single-electron transfer with Cu<sup>II</sup>L and subsequent deprotonation to yield oxindole **3**. Similarly, when the acyl radical reacts with *N*-methyl-*N*-phenylcinnamamide, addition to the alkene forms intermediate **C**, followed by intramolecular cyclization to intermediate **D**. Subsequent single-electron transfer with Cu<sup>II</sup>L and deprotonation furnishes the six-membered dihydroquinolinone **5**. This mechanism highlights the key roles of aryl radicals, CO trapping, and Cu-mediated single-electron transfer in enabling selective carbonylative cyclization.

## Conclusions

In summary, we have developed a visible-light-induced, copper-catalyzed controllable carbonylative cyclization that enables selective synthesis of carbonylated five- and six-membered heterocycles by simply tuning the substitution pattern of the starting alkenes. The method employs inexpensive CO as the carbonyl source, proceeds under mild conditions, and allows efficient one-pot access to 3,3-disubstituted oxindoles and dihydroquinolinones. It features broad substrate scope, generally good yields, excellent functional-group tolerance, and potential for downstream derivatization, providing a practical, economical, and sustainable approach to nitrogen-containing carbonylated heterocycles.

## Author contributions

Y. H. Z. and L. C. W. designed and carried out the reactions and analyzed the data. X.-F. W. designed and supervised the project. X.-F. W. and Y. H. Z. wrote and revised the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: general comments, general procedure, analytic data, and NMR spectra. See DOI: <https://doi.org/10.1039/d5sc09434h>.

## Acknowledgements

We thank the Chinese Scholarship Council for financial support. We also thank the analytical department of Leibniz-Institute for Catalysis for their excellent analytical service.

## Notes and references

- J. F. Austin, S.-G. Kim, C. J. Sinz, W.-J. Xiao and D. W. C. MacMillan, Enantioselective organocatalytic construction of pyrroloindolines by a cascade addition–cyclization strategy: Synthesis of (–)-flustramine B, *Proc. Natl. Acad. Sci. U.S.A.*, 2004, **101**, 5482–5487.
- J. J. Badillo, N. V. Hanhan and A. K. Franz, Enantioselective synthesis of substituted oxindoles and spirooxindoles with applications in drug discovery, *Curr. Opin. Drug Discov. Dev.*, 2010, **13**, 758–776.
- N. R. Ball-Jones, J. J. Badillo and A. K. Franz, Strategies for the enantioselective synthesis of spirooxindoles, *Org. Biomol. Chem.*, 2012, **10**, 5165–5181.
- C. Zheng and S.-L. You, Catalytic asymmetric dearomatization (CADA) reaction-enabled total synthesis of indole-based natural products, *Nat. Prod. Rep.*, 2019, **36**, 1589–1605.
- X.-H. Yang, R.-J. Song, Y.-X. Xie and J.-H. Li, Iron Catalyzed Oxidative Coupling, Addition, and Functionalization, *ChemCatChem*, 2016, **8**, 2429–2445.
- M. Chen, X. Wang, P. Yang, X. Kou, Z.-H. Ren and Z.-H. Guan, Palladium-Catalyzed Enantioselective Heck Carbonylation with a Monodentate Phosphoramidite Ligand: Asymmetric Synthesis of (+)-Physostigmine, (+)-Physovenine, and (+)-Folicanthine, *Angew. Chem., Int. Ed.*, 2020, **59**, 12199–12205.
- T. Ma, Y. Chen, Y. Li, Y. Ping and W. Kong, Nickel-Catalyzed Enantioselective Reductive Aryl Fluoroalkenylation of Alkenes, *ACS Catal.*, 2019, **9**, 9127–9133.
- A. D. Marchese, E. M. Larin, B. Mirabi and M. Lautens, Metal-Catalyzed Approaches toward the Oxindole Core, *Acc. Chem. Res.*, 2020, **53**, 1605–1619.
- K. Fang, W. Huang, C. Shan, J. Qu and Y. Chen, Synthesis of 3,3-Dialkyl-Substituted Isoindolinones Enabled by Nickel-Catalyzed Reductive Dicarbofunctionalization of Enamides, *Org. Lett.*, 2021, **23**, 5523–5527.
- Q. Pan, Y. Ping, Y. Wang, Y. Guo and W. Kong, Ni-Catalyzed Ligand-Controlled Regiodivergent Reductive Dicarbofunctionalization of Alkenes, *J. Am. Chem. Soc.*, 2021, **143**, 10282–10291.
- N. Qin, X. Lu, Y. Liu, Y. Qiao, W. Qu, F. Feng and H. Sun, Recent research progress of *Uncaria* spp. based on alkaloids: phytochemistry, pharmacology and structural chemistry, *Eur. J. Med. Chem.*, 2021, **210**, 112960.
- K. Wang, Z. Ding, Z. Zhou and W. Kong, Ni-Catalyzed Enantioselective Reductive Diarylation of Activated Alkenes by Domino Cyclization/Cross-Coupling, *J. Am. Chem. Soc.*, 2018, **140**, 12364–12368.
- J.-X. Yan, H. Li, X.-W. Liu, J.-L. Shi, X. Wang and Z.-J. Shi, Palladium-Catalyzed C(sp<sup>3</sup>)-H Activation: A Facile Method for the Synthesis of 3,4-Dihydroquinolinone Derivatives, *Angew. Chem., Int. Ed.*, 2014, **53**, 4945–4949.
- L. Zhang, Z. Qureshi, L. Sonaglia and M. Lautens, Sequential Rhodium/Palladium Catalysis: Enantioselective Formation of Dihydroquinolinones in the Presence of Achiral and



- Chiral Ligands, *Angew. Chem., Int. Ed.*, 2014, **53**, 13850–13853.
- 15 X. Zheng, Y. Xu, G. Huang and W. Yuan, Catalyst-controlled 5-exo and 6-endo cyclization: regiodivergent access to indolinones and dihydroquinolinones, *Org. Chem. Front.*, 2025, **12**, 5018–5026.
  - 16 P. Biswas, S. Mandal and J. Guin, Aerobic Acylarylation of  $\alpha,\beta$ -Unsaturated Amides with Aldehydes, *Org. Lett.*, 2020, **22**, 4294–4299.
  - 17 P. Biswas, S. Paul and J. Guin, Aerobic Radical-Cascade Alkylation/Cyclization of  $\alpha,\beta$ -Unsaturated Amides: an Efficient Approach to Quaternary Oxindoles, *Angew. Chem., Int. Ed.*, 2016, **55**, 7756–7760.
  - 18 X.-W. Chen, J.-P. Yue, K. Wang, Y.-Y. Gui, Y.-N. Niu, J. Liu, C.-K. Ran, W. Kong, W.-J. Zhou and D.-G. Yu, Nickel-Catalyzed Asymmetric Reductive Carbo-Carboxylation of Alkenes with CO<sub>2</sub>, *Angew. Chem., Int. Ed.*, 2021, **60**, 14068–14075.
  - 19 M. He, Y. Yang, H. Zhang, Z. Guan, Z.-B. Dong, H. Yi and A. Lei, General radical difluoromethylation using difluoroacetic anhydride via photoredox catalysis, *Sci. China Chem.*, 2024, **67**, 2637–2646.
  - 20 M.-Z. Zhang, L. Liu, Q. Gou, Q. Wang, Y. Li, W.-T. Li, F. Luo, M. Yuan, T. Chen and W.-M. He, Synthesis of hydroxyl-containing oxindoles and 3,4-dihydroquinolin-2-ones through oxone-mediated cascade arylhydroxylation of activated alkenes, *Green Chem.*, 2020, **22**, 8369–8374.
  - 21 H. Hu, F. Teng, J. Liu, W. Hu, S. Luo and Q. Zhu, Enantioselective Synthesis of 2-Oxindole Spiro-fused Lactones and Lactams by Heck/Carboxylative Cyclization Sequences: Method Development and Applications, *Angew. Chem., Int. Ed.*, 2019, **58**, 9225–9229.
  - 22 Y. Kobayashi, H. Kamisaki, R. Yanada and Y. Takemoto, Palladium-Catalyzed Intramolecular Cyanoamidation of Alkynyl and Alkenyl Cyanoforamides, *Org. Lett.*, 2006, **8**, 2711–2713.
  - 23 X. Liu, B. Li and Z. Gu, Palladium-Catalyzed Heck-type Domino Cyclization and Carboxylation to Synthesize Carboxylic Acids by Utilizing Chloroform as the Carbon Monoxide Source, *J. Org. Chem.*, 2015, **80**, 7547–7554.
  - 24 D. Wen, Z. Shen, X. Qi and X.-F. Wu, Palladium-Catalyzed Cascade Carbonylative Synthesis of Functionalized Isoquinoline-1,3-diones and Oxindoles Using Dimethyl Carbonate as both Solvent and Reactant, *Eur. J. Org. Chem.*, 2022, **2022**, e202200971.
  - 25 G. Bergonzini, C. Cassani and C.-J. Wallentin, Acyl Radicals from Aromatic Carboxylic Acids by Means of Visible-Light Photoredox Catalysis, *Angew. Chem., Int. Ed.*, 2015, **54**, 14066–14069.
  - 26 C. S. Nishad, P. Suman, H. Saha and B. Banerjee, Visible-Light-Induced Metal- and Photocatalyst-Free Radical Cascade Cyclization of Cinnamamides for Synthesis of Functionalized Dihydroquinolinones, *J. Org. Chem.*, 2023, **88**, 11010–11022.
  - 27 J. Liu, S. Liu, Z. Wang, T. Kato, Y. Liu and K. Maruoka, Synthetic utility of functionalized alkylsilyl peroxides for Fe-catalyzed and visible-light-promoted radical transformation, *Chem. Sci.*, 2024, **15**, 4757–4762.
  - 28 T. Zhang, Z. Chen, F. Xue, X. Ren, B. Wang, W. Jin, Y. Xia, S. Wu, A. Iqbal, Y. Zhang and C. Liu, Visible-Light-Mediated Cascade Arylcarboxylation/Cyclization of *N*-Aryl/Benzoyl Acrylamide with CO<sub>2</sub>, *Org. Lett.*, 2025, **27**, 8423–8428.
  - 29 Z.-P. Bao, L.-C. Wang and X.-F. Wu, Carbonylation: Unlocking Opportunities for Bioactive Molecule and Pharmaceutical Development, *ACS Catal.*, 2025, **15**, 19580–19606.
  - 30 M. Beller and X.-F. Wu, *Transition Metal Catalyzed Carbonylation Reactions*, 2013, pp. 115–145.
  - 31 B. Cornils, W. A. Herrmann and M. Rasch, Otto Roelen, Pioneer in Industrial Homogeneous Catalysis, *Angew. Chem., Int. Ed.*, 1994, **33**, 2144–2163.
  - 32 T. Kawamoto, T. Fukuyama, B. Picard and I. Ryu, New directions in radical carbonylation chemistry: combination with electron catalysis, photocatalysis and ring-opening, *Chem. Commun.*, 2022, **58**, 7608–7617.
  - 33 Q. Tian, X. Yin, R. Sun, X. F. Wu and Y. Li, The lower the better: Efficient carbonylative reactions under atmospheric pressure of carbon monoxide, *J. Coord. Chem.*, 2023, **475**, 214900.
  - 34 L.-C. Wang, H. Yang, Z.-W. Liu, R.-G. Miao, M. Hou and X.-F. Wu, Recent Advances in Single-Electron-Transfer-Mediated Carbonylation, *Chem. Rev.*, 2026, DOI: [10.1021/acs.chemrev.5c00664](https://doi.org/10.1021/acs.chemrev.5c00664).
  - 35 F.-P. Wu, Y. Yang, D. P. Fuentes and X.-F. Wu, Copper-catalyzed carbonylative catenation of olefins: Direct synthesis of  $\gamma$ -boryl esters, *Chem*, 2022, **8**, 1982–1992.
  - 36 J. Falbe, H. Bahrmann and B. Cornils, *New Syntheses with Carbon Monoxide*, Springer, 1980.
  - 37 S. D. Friis, A. T. Lindhardt and T. Skrydstrup, The Development and Application of Two-Chamber Reactors and Carbon Monoxide Precursors for Safe Carbonylation Reactions, *Acc. Chem. Res.*, 2016, **49**, 594–605.
  - 38 B. Gabriele, *Carbon Monoxide in Organic Synthesis: Carbonylation Chemistry*, John Wiley & Sons, 2021.
  - 39 A. Haynes, P. M. Maitlis, G. E. Morris, G. J. Sunley, H. Adams, P. W. Badger, C. M. Bowers, D. B. Cook, P. I. P. Elliott, T. Ghaffar, H. Green, T. R. Griffin, M. Payne, J. M. Pearson, M. J. Taylor, P. W. Vickers and R. J. Watt, Promotion of Iridium-Catalyzed Methanol Carbonylation: Mechanistic Studies of the Cativa Process, *J. Am. Chem. Soc.*, 2004, **126**, 2847–2861.
  - 40 A. Schoenberg and R. Heck, Palladium-catalyzed formylation of aryl, heterocyclic, and vinylic halides, *J. Am. Chem. Soc.*, 1974, **96**, 7761–7764.
  - 41 Q. Tian, X. Yin, R. Sun and Y. Li, The lower the better: Efficient carbonylative reactions under atmospheric pressure of carbon monoxide, *J. Coord. Chem.*, 2023, **475**, 214900.
  - 42 X.-F. Wu, B. Han, K. Ding and Z. Liu, *The Chemical Transformations of C1 Compounds*, John Wiley & Sons, 2022.
  - 43 Z. Li, P. Ma, Y. Wang and J. Wang, Substrate-Controlled Divergent Synthesis of Multisubstituted Cyclopentenones and 1,4-Diketones, *Org. Lett.*, 2025, **27**, 8946–8951.



- 44 B.-X. Liu, S.-C. Li, H.-W. Rao, Q.-Q. Yang, W. Du and Y.-C. Chen, Palladium-Catalyzed Substrate-Controlled Regiodivergent Hydroamination of gem-Difluoroallenes, *Org. Lett.*, 2025, **27**, 8288–8292.
- 45 W. Liu, W. Ren, J. Li, Y. Shi, W. Chang and Y. Shi, A Ligand-Directed Catalytic Regioselective Hydrocarboxylation of Aryl Olefins with Pd and Formic Acid, *Org. Lett.*, 2017, **19**, 1748–1751.
- 46 J.-B. Peng and X.-F. Wu, Ligand- and Solvent-Controlled Regio- and Chemodivergent Carbonylative Reactions, *Angew. Chem., Int. Ed.*, 2018, **57**, 1152–1160.
- 47 X. Wang, J. Zhang, X. Zhao, Y. Wang, J. Sima, Z. Wang, X. Jia, S. Song and F. Yu, Substrate-controlled regioselective dibenzoylation of enaminones, *Org. Chem. Front.*, 2025, **12**, 6209–6214.
- 48 Y. Zhang, S. Torker, M. Sigrist, N. Bregović and P. Dydio, Binuclear Pd(I)–Pd(I) Catalysis Assisted by Iodide Ligands for Selective Hydroformylation of Alkenes and Alkynes, *J. Am. Chem. Soc.*, 2020, **142**, 18251–18265.
- 49 F. Zhao, H.-J. Ai and X.-F. Wu, Copper-Catalyzed Substrate-Controlled Carbonylative Synthesis of  $\alpha$ -Keto Amides and Amides from Alkyl Halides, *Angew. Chem., Int. Ed.*, 2022, **61**, e202200062.
- 50 R. K. Dhungana, S. KC, P. Basnet and R. Giri, Transition Metal-Catalyzed Dicarbofunctionalization of Unactivated Olefins, *Chem. Rec.*, 2018, **18**, 1314–1340.
- 51 Z.-L. Li, G.-C. Fang, Q.-S. Gu and X.-Y. Liu, Recent advances in copper-catalysed radical-involved asymmetric 1,2-difunctionalization of alkenes, *Chem. Soc. Rev.*, 2020, **49**, 32–48.
- 52 J. Lin, R.-J. Song, M. Hu and J.-H. Li, Recent Advances in the Intermolecular Oxidative Difunctionalization of Alkenes, *Chem. Rec.*, 2019, **19**, 440–451.
- 53 J. Xie, P. Xu, H. Li, Q. Xue, H. Jin, Y. Cheng and C. Zhu, A room temperature decarboxylation/C–H functionalization cascade by visible-light photoredox catalysis, *Chem. Commun.*, 2013, **49**, 5672–5674.
- 54 L. Zheng, H. Huang, C. Yang and W. Xia, UV Light-Mediated Difunctionalization of Alkenes through Aroyl Radical Addition/1,4-/1,2-Aryl Shift Cascade Reactions, *Org. Lett.*, 2015, **17**, 1034–1037.
- 55 M.-B. Zhou, R.-J. Song, X.-H. Ouyang, Y. Liu, W.-T. Wei, G.-B. Deng and J.-H. Li, Metal-free oxidative tandem coupling of activated alkenes with carbonyl C(sp<sup>2</sup>)-H bonds and aryl C(sp<sup>2</sup>)-H bonds using TBHP, *Chem. Sci.*, 2013, **4**, 2690–2694.
- 56 M.-B. Zhou, C.-Y. Wang, R.-J. Song, Y. Liu, W.-T. Wei and J.-H. Li, Oxidative 1,2-difunctionalization of activated alkenes with benzylic C(sp<sup>3</sup>)-H bonds and aryl C(sp<sup>2</sup>)-H bonds, *Chem. Commun.*, 2013, **49**, 10817–10819.
- 57 M. J. Cabrera-Afonso, A. Granados and G. A. Molander, Sustainable Thioetherification via Electron Donor–Acceptor Photoactivation Using Thianthrenium Salts, *Angew. Chem., Int. Ed.*, 2022, **61**, e202202706.
- 58 L.-C. Campeau, Thianthrenium ions pair-up for Suzuki–Miyaura reactions, *Nat. Synth.*, 2024, **3**, 1448–1450.
- 59 S. Happy, M. Saleem and D. Yadagiri, Pd-Catalyzed Late-Stage Installation of Nitrile and Carbamoyl Groups via a Cross-Coupling Approach of Thianthrenium Salts with Isonitriles, *ACS Catal.*, 2025, **15**, 13401–13411.
- 60 F. Juliá, Q. Shao, M. Duan, M. B. Plutschack, F. Berger, J. Mateos, C. Lu, X.-S. Xue, K. N. Houk and T. Ritter, High Site Selectivity in Electrophilic Aromatic Substitutions: Mechanism of C–H Thianthrenation, *J. Am. Chem. Soc.*, 2021, **143**, 16041–16054.
- 61 H. Meng, M.-S. Liu and W. Shu, Organothianthrenium salts: synthesis and utilization, *Chem. Sci.*, 2022, **13**, 13690–13707.
- 62 S. Tang, X. Zhao, L. Yang, B. Li and B. Wang, Copper-Catalyzed Carboxylation of Aryl Thianthrenium Salts with CO<sub>2</sub>, *Angew. Chem., Int. Ed.*, 2022, **61**, e202212975.
- 63 K. Targos, A. R. Gogoi, R.-G. Ángel, M. J. Kim, O. Gutierrez and Z. K. Wickens, Mechanism of Z-Selective Allylic Functionalization via Thianthrenium Salts, *J. Am. Chem. Soc.*, 2024, **146**, 13689–13696.
- 64 Y. Yuan, C. Bai, Y. Tao, Y.-N. Zhang, X. Bao, D. Ji, L. Wang, X. Qi and C. Huo, Electrochemical ring-opening oxidation of aryl thianthrenium salts, *Green Chem.*, 2025, **27**, 9777–9786.
- 65 Z. Bai, B. Lansbergen and T. Ritter, Bicyclopentylation of Alcohols with Thianthrenium Reagents, *J. Am. Chem. Soc.*, 2023, **145**, 25954–25961.
- 66 Z. Bai and T. Ritter, Applications of thianthrene chemistry in organic synthesis, *Nat. Synth.*, 2025, **4**, 1187–1199.
- 67 M. Mrozowicz, S. Chatterjee, M. Alikı Mermigki, D. A. Pantazis and T. Ritter, Meta-Dimethylation of Arenes via Catellani Reaction from Aryl Thianthrenium Salts, *Angew. Chem., Int. Ed.*, 2025, **64**, e202419472.
- 68 S. Pandit and T. Ritter, Copper-Photoredox-Catalyzed C(sp<sup>3</sup>)-C(sp<sup>3</sup>) Reductive Cross-Coupling of Alkyl Bromides with BCP-Thianthrenium Reagents, *Angew. Chem., Int. Ed.*, 2025, **64**, e202506785.
- 69 X. Sun and T. Ritter, Decarboxylative Polyfluoroarylation of Alkylcarboxylic Acids, *Angew. Chem., Int. Ed.*, 2021, **60**, 10557–10562.
- 70 J. Zhang, M. Jiao, Z. Lu, H. Lu, M. Wang and Z. Shi, Hydrodeuteroalkylation of Unactivated Olefins Using Thianthrenium Salts, *Angew. Chem., Int. Ed.*, 2024, **63**, e202409862.
- 71 M. Liu, Y. Qian, Y. Wu and F. Zhang, Multicomponent synthesis of di-aryl dithiocarbamates via electron donor–acceptor photoactivation with thianthrenium salts, *Green Chem.*, 2023, **25**, 3852–3856.
- 72 C. M. Panos, A. D. Matthews and Z. K. Wickens, Homologative 1,3-Functionalization of Alkenes via an Iodomethyl Thianthrenium Reagent, *Angew. Chem., Int. Ed.*, 2025, **64**, e202519207.
- 73 R. I. Patel, B. Saxena and A. Sharma, Photoactivation of Thianthrenium Salts: An Electron-Donor–Acceptor (EDA)-Complex Approach, *J. Org. Chem.*, 2025, **90**, 6617–6643.
- 74 K. Sun, C. Ge, X. Chen, B. Yu, L. Qu and B. Yu, Energy-transfer-enabled photocatalytic transformations of aryl thianthrenium salts, *Nat. Commun.*, 2024, **15**, 9693.



- 75 Y. Zhang, J. Mao, Z. Wang, L. Tang and Z. Fan, Visible light-promoted defluorinative alkylation/arylation of  $\alpha$ -trifluoromethyl alkenes with thianthrenium salts, *Green Chem.*, 2024, **26**, 9371–9377.
- 76 K. Cheng, E. W. Webb, G. D. Bowden, J. S. Wright, X. Shao, M. S. Sanford and P. J. H. Scott, Photo- and Cu-Mediated  $^{11}\text{C}$  Cyanation of (Hetero)Aryl Thianthrenium Salts, *Org. Lett.*, 2024, **26**, 3419–3423.
- 77 X. Fan, T. Lei, B. Chen, C.-H. Tung and L.-Z. Wu, Photocatalytic C–C Bond Activation of Oxime Ester for Acyl Radical Generation and Application, *Org. Lett.*, 2019, **21**, 4153–4158.
- 78 Y.-Y. Jiang, Z. Chen, Y.-X. Jiang, W.-J. Zhu, J.-C. Xu, J.-H. Ye, W. Zhang and D.-G. Yu, Visible-Light-Driven Thiolate-Catalyzed Carbo-Carboxylation of Alkenes with  $\text{CO}_2$ : Facile Synthesis of Oxindole-3-acetic Acid Derivatives, *Chin. J. Chem.*, 2025, **43**, 2341–2346.
- 79 N. Kvasovs and V. Gevorgyan, Contemporary methods for generation of aryl radicals, *Chem. Soc. Rev.*, 2021, **50**, 2244–2259.
- 80 W.-P. Mai, G.-C. Sun, J.-T. Wang, G. Song, P. Mao, L.-R. Yang, J.-W. Yuan, Y.-M. Xiao and L.-B. Qu, Silver-Catalyzed Radical Tandem Cyclization: An Approach to Direct Synthesis of 3-Acyl-4-arylquinolin-2(1H)-ones, *J. Org. Chem.*, 2014, **79**, 8094–8102.

