Metallaphotoredox-Catalyzed C–H Activation: Regio-Selective Annulation of Allenes with Benzamide

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Abstract

We have developed an efficient annulation of benzamides with allenes using cobalt and photoredox dual catalysis under an oxygen atmosphere. This reaction provides a mild and environmentally friendly method for the construction of isoquinolinon scaffolds in good to excellent yields, which demonstrates broad substrate scopes, high regioselectivity, and good functional group compatibility. Notably, this transformation feathers an alternative strategy for the regeneration of cobalt catalyst with the aid of Eosin Y. Preliminary mechanism studies reveal that a radical-mediated cascade annulation is involved in this reaction.

Introduction

Transition-metal-catalyzed direct C–H functionalizations have emerged as efficient, powerful, and straightforward approaches for the construction of carbon-carbon and carbon-heteroatom bonds over the past few decades [1–6]. Recently, low-cost and earth-abundant first-row transition metals seem to be an appealing alternative to noble metals [7–10]. Among the first-row transition metals, the unique properties of cobalt in varied oxidation states have witnessed the powerful ability to manipulate various chemical bonds as a result of the chelation-assisted direct metalation of azobenzene [11–16]. Among such elegant transformations, a number of C–H activation and oxidative annulation reactions with various unsaturated coupling partners, such as alkynes and alkenes, have garnered considerable attention for molecule diversity in step- and atom- economical strategies [17].

Allenes, bearing two orthogonal cumulative carbon-carbon double bonds, have been applied into a wide variety of annulations [18–25]. Various noble second- and third-row transition metals such as Pd [26–32], Ir [33], Rh [34–40] and Ru [41], have been employed for the preparation of cyclic scaffolds from simple, nonfunctionalized acyclic starting materials. Moreover, the first-row transition metals, such as Mn [42–47], Fe [48], Ni [49–53] and Co [54–63], have been recognized as cheap, environmentally friendly and reactively effective catalysis for C–H functionalization with allenes. Particularly, cobalt-catalyzed regioselective intermolecular cyclization reactions of arylamides or alkenylamides with allenes were independently reported by the group of Cheng [56–58], VolIa [59], Rao [60], Zhai [61], and Ackermann [62–63], which provide rapid synthetic routes for diverse isoquinolin scaffolds (Scheme 1a). Generally, stoichiometric amounts of metal oxidants (Ag₂CO₃, Mn(OAc)₂, Mn(OAc)₃, etc.), which could re-oxidize low valent cobalt and complete the reaction cycle, were commonly employed in these reported cobalt-catalyzed annulation reactions of arylamides with allenes (Scheme 1a). Recently, Ackermann group disclosed an electrochemical C–H activation with allenes which enabled the high valent cobalt regeneration under the anodic oxidation (Scheme 1a) [62–63].

In recent years, significant progress has been achieved based on visible light-mediated photoredox catalysis [64–70], which emerged as a sustainable and versatile platform for the development of practically synthetic methodologies. Among these, the merge of transition metal catalysis and photocatalysis, termed metallaphotoredox catalysis, affords a distinct reaction environment, with both
oxidation and reduction of organic and organimetallic species simultaneously possible [71–78]. On the basis of the huge advantage of metallaphotoredox catalysis in organic synthesis, we imagined that the development of cobalt-catalyzed C–H annulation of allenes with benzamide could be an important complement to the reported strategies.

Previous cyclic voltammetry study showed that Co(OAc)$_2$ revealed high oxidation potential, which meant the cobalt (III) could not be easily generated from Co(II) with common photocatalysts. However, the in situ generated cobalt catalyst between Co(OAc)$_2$ and benzamide substrate showed a lower oxidation potential at 1.19 V$_{SCE}$, indicating an accessible photoredox mediated cobalt (II/III) single-electron oxidation [79] (Scheme 1b). Thus, we sought to regenerate the cobalt catalyst through a single electron transfer (SET) process assisting with a photocatalyst under the irradiation of light, which might avoid the use of metal oxidants (Scheme 1b). Herein, we reported the application of dual cobalt and photoredox catalysis strategy into annulation of benzamides with allenes, which provided an economic and atom-efficient approach for the synthesis of isoquinolinones (Scheme 1c).

Materials And Methods

In an oven dried Schlenk tube charged with magnetic stirrer, benzamide (0.1 mmol, 1.0 equiv.), Co(acac)$_2$ (0.02 mmol, 20 mol%), potassium trifluoride mesylate (0.02 mmol, 20 mol%) and Eosin Y disodium salt (0.005 mmol, 5 mol%) were added. Freshly prepared allene was subsequently added to the reaction mixture followed by freshly distilled 2,2,2-trifluoroethanol (1.5 mL) as solvent. The Schlenk tube was evacuated and purged with oxygen. Then, the resulted solution was placed under 15 W CFL irradiation at room temperature for 24 h. The reaction process was detected by thin-layer chromatography (TLC). Upon completion, the reaction mixture was evaporated under reduced pressure and passed through the column for purification. Petroleum ether and ethyl acetate mixture was used as an eluent.

Results And Discussion

As illustrated in Table 1, benzamides(1a) and benzyl buta-2,3-dienoate (2a) were exploited as model substrates with 10 mmol % Co(acac)$_2$, 0.2 equiv. of NaOPiv and 5.0 mol % photoredox catalysis under visible light irradiation (15W CFL) for 24 h at room temperature under an oxygen atmosphere. The model reaction was preferentially performed using 2,2,2-trifluoroethanol as a solvent, mainly because of which is facilitated to pair with hydrogen-bond acceptor groups and interfere with the catalytic cycle [80]. To our delight, the desired product 3a could be obtained when [Ru(bpy)$_3$]$^{2+}$Cl$_2$ was used as a photoredox catalyst (entry 1). It was found that [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ did not effectively promote this cyclization (entry 2). Instead of [Ru(bpy)$_3$]$^{2+}$Cl$_2$, Na$_2$-eosin Y slightly increased the annulation yields under the similar reaction conditions (entry 3). Further experiment revealed that the use of KOTf as a base could accelerate the reaction and effectively improve the yield of 3a (entry 5). Interestingly, a slight increase in the amount of cobalt made significant effect in promoting the reaction, and the excellent yield was obtained when the annulation reaction was performed with 20 mmol% Co(acac)$_2$ under the similar
reaction conditions (entry 6). In addition, control experiments indicated that in the absence of either Co(acac)$_2$ or oxygen, the reaction was completely inhibited (entry 9 and 10). It is worthy to note that the light played a crucial role for the annulation reaction, and it stopped at 14% yield when the reaction was performed without photocatalyst in dark (entry 11). Using unprotected benzamides with weaker directing groups instead of 1a, the desired product was not obtained under standard conditions, and the corresponding starting materials were decomposed or fully recovered.

**Table 1 Optimization the reaction conditions**

| Entry | [Co] (mol %) | PS (mol %) | Atmosphere | Base (mol %) | time (h) | Yield (%)$^a$ |
|-------|--------------|------------|------------|--------------|----------|---------------|
| 1     | Co(acac)$_2$ (10) | [Ru] (5) | O$_2$ | NaOPiv (20) | 24 | 32% |
| 2     | Co(acac)$_2$ (10) | Ir (5) | O$_2$ | NaOPiv (20) | 24 | <5%$^b$ |
| 3     | Co(acac)$_2$ (10) | Eosin Y (5) | O$_2$ | NaOPiv (20) | 24 | 39% |
| 4     | Co(acac)$_2$ (10) | Eosin Y (5) | O$_2$ | KOAc (20) | 24 | 41% |
| 5     | Co(acac)$_2$ (10) | Eosin Y (5) | O$_2$ | KOTf (20) | 24 | 55% |
| 6     | Co(acac)$_2$ (20) | Eosin Y (5) | O$_2$ | KOTf (20) | 24 | 87% |
| 7     | Co(acac)$_2$ (20) | Eosin Y (5) | air | KOTf (20) | 24 | 53% |
| 8     | Co(acac)$_2$ (20) | Eosin Y (5) | N$_2$ | KOTf (20) | 24 | <5%$^b$ |
| 9     | - | Eosin Y (5) | O$_2$ | KOTf (20) | 24 | <5%$^b$ |
| 10    | Co(acac)$_2$ (20) | - | O$_2$ | KOTf (20) | 24 | 18% |
| 11    | Co(acac)$_2$ (20) | Eosin Y (5) | O$_2$ | KOTf (20) | 24 | 14%$^c$ |

Note: All reactions were carried out under oxygen atmosphere unless otherwise stated, using 1a (0.2 mmol), 2a (0.4 mmol), cobalt catalyst (10-20 mol %), additive (20 mol %), 2,2,2-trifluoroethanol (2.0 mL) at room temperature under visible light irradiation (15W CFL) for 24 hours. $^a$ isolated yield; $^b$ yield determined by $^1$H NMR analysis using 4-nitrobenzaldehyde as the internal standard; $^c$ without light.

**Optimization the reaction conditions**

With the optimized conditions in hand, the annulation reaction scope was investigated between various substituted benzamides and allenes, and the results were presented in Scheme 1. We found that a number of arylamides bearing different substitutions at the ortho-, meta-, and para-positions were compatible with the optimized conditions (Scheme 2, 3a-3p). For para-substituents in the carboxamides, such as halogen (3f-3 h), acetyl (3i), cyano (3j), or electron-donating methyl (3 k), cyclohexyl (3 l), methoxyl (3 m) groups, the desired isoquinolinones were produced in excellent yields. It was found that
the reaction of meta-substituted benzamide furnished two expected regioisomers in good yields (3n). On the other hand, the ortho-substituted substrates with incorporation of electron-withdrawing substituents, such as halogen (3b-3c) and trifluoromethyl (3d), were efficiently transformed into the corresponding products in excellent yields. Replacing with methoxyl in the ortho-position (3e), the cyclization process took a short reaction time, but slightly reduced product yield was observed. In the case of disubstituted benzamide (3o), this reaction also gave the desired product in good yield. Additionally, the naphthoamide (3p) was smoothly converted into the three rings fused heterocycle in good yield.

**Scheme 2** Scope of benzamides with benzyl buta-2,3-dienoate

Next, the scope of allenes was investigated extensively. As summarized in Scheme 3, various allenes were smoothly reacted with benzamides under the optimal conditions, and the corresponding isoquinolinones were got in good to excellent yields. Notably, it was found that the cyclization reaction featured excellent chemo- and regioselectivity, and solely occurred at the allenes’ terminal position. Various electronically diverged allenes (2b-2f) were efficiently converted into the desired products (4a-4p). Heteroaromatic substrate also showed good reactivity, and thieno[3,2-c]pyridin-4(5H)-one derivative (4h) was efficiently obtained in good yield. Gratifyingly, it is worth mentioning that the excellent yields (4i-4n) were obtained when diphenyl(propa-1,2-dien-1-yl)phosphine (2e) oxide was used. A gram-scale reaction was conducted to assess the efficiency of this protocol, and two isoquinolinones (4l and 4n) could be obtained in 79% and 87% yield, respectively (for details, please see supporting information). The structure and regioselectivity of nitro substituted isoquinolinone (4n) were confirmed unambiguously by the X-ray crystallography. In the case of ethyl penta-3,4-dienoate (2f), the desired isoquinolinones (4o and 4p) were afforded as single regioisomers with moderate yields.

Generally, the electronical properties of allenes have a great influence on the reactivity of annulation. Interestingly, various isoquinolinones with exo-double bonds were obtained by coupling benzamides with propa-1,2-dien-1-ylbenzene (2g), which demonstrated the diverse reactivity of allene. A number of ary amides (5a-5d), and heterocyclic derivative, such as thiophene (5e) showed good compatibility with the reaction condition. To our delight, when terminal di-substituted allene (2h) was used as a coupling partner, the reaction also afforded the corresponding exo-cyclic isoquinolinones (5g-5i) in moderate to good yields. These results might provide an interesting perspective for the mechanism information on the migratory allene insertion/isomerization manifold.

To gain further mechanistic insights, a series of control experiments were carried out. A mixture of benzamide [D5]-1a/1a (1:1) was used to react with allenylphosphonate (2e) under optimized conditions, and the KIE experiments gave a $k_{H}/k_{D}$ value of 1.1. This phenomenon indicated that C – H bond activation might not be involved in the rate-determining step (Scheme 5a). Furthermore, no D/H exchange was observed when [D5]-1a was treated with phosphateallene under standard conditions. Similarly, no deuterium incorporation in the product 4n was observed when 1c was treated with isotopically labelled CD$_3$OD as a cosolvent. These results suggested that the C – H cobaltation step should be irreversible (Scheme 5a). A control reaction was performed in the presence of stoichiometric 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, a common radical scavenger), and no the desired product was obtained under the standard condition (Scheme 5b). This gave some clues that a highly radical species might be involved in the catalytic cycle. Additionally, the cyclization reaction conducted under an oxygen atmosphere in the
absence of Eosin Y did not generate the desired product (Scheme 5c). It excluded the possibility of oxygen acting as a single oxidant which was used to regenerate the cobalt catalyst. On the other hand, intermolecular competition studies suggested that the electron-rich amide was slightly more favorable, which could be rationalized an electrophilic-type substitution C–H metalation. Based on the mechanistic experiments described above and relevant literature reports [81–82], a plausible mechanism for this reaction was proposed in Scheme 6. The first step began with oxidation of Co(II) to give Co(III)-species assisted simultaneously by reduction of Na₂Eosin Y*. A following ligand exchange and coordination of 8-aminoquinoline derived benzamide (1a) generated Co(III)-species (intermediate A). Interestingly, this intermediate was observed by the treating stoichiometric amounts of Co(acac)₂ under the standard conditions (for details, please see supporting information) [59, 77–78, 83–85]. After that, intermediate A activated the inert sp² C–H bond to form the key metallacycle Co(III) intermediate B. Subsequently, allene coordinated with metallacycle intermediate B to give the corresponding C, and regioselective insertion of C–Co bond of intermediate C gave the seven membered cobaltacycle intermediate D or E. The selectivity of the annulation depended on the allene structure and electronic characteristics of the substituents. When R were electronic-withdrawing groups, the insertion took place in the less-substituted double bond of allene leads to the intermediate D. When R was the phenyl group, the addition was apt to occur at a more electron-rich double bond, furnishing the formation of the intermediate E with high selectivity. The reductive elimination gave the cyclic-product (I or G) and intermediate F. The newly obtained cobalt intermediate F (the in situ generated cobalt catalyst between Co(OAc)₂ and benzamide substrate showed a oxidation potential at 1.19 V vs SCE) [79] might be oxidized by the photoexcited Na₂Eosin Y* (0.83 V vs SCE) [77, 86]. Thus the Co(III) species could be regenerated, and a strong reductant, Na₂Eosin Y radical anion (-1.06 V vs SCE) [86] was simultaneously generated. The Na₂Eosin Y radical anion might be oxidized to the ground state by O₂ to complete the photoredox cycle [86]. At last, the intermediate G undergoes 1,3-hydrogen shift to furnish the corresponding final product H.

Conclusion

In conclusion, we have developed an efficient protocol for the construction of isoquinolinones by merging cobalt(II)-catalyzed C–H functionalization with visible light mediated photoredox catalysis. Notably, no metal oxidants are required in this transformation. This reaction provides a mild and environmentally friendly route for the construction of isoquinolinones in good to excellent yields. A wide range of substrate scopes, high level of chemoselectivity and regioselectivity, and broad functional group tolerance were observed. Preliminary mechanism studies reveal that a radical-mediated cascade annulation is involved in this reaction. Further studies about synthetic applications and reaction mechanism are currently ongoing in our laboratory.

Supporting Information

Supporting Information is available and includes synthetic procedures and characterizations of all new compounds, computational details, and additional computational results.
Declarations

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author contributions

Tianlei Li, Jishun Li, Zihao Zhu, Yuyuan Chen, Xueyao Li, and Wenxuan Zhang conducted the experiments and prepared the supporting information. Tianlei Li, Jie Xia and Qingyun Yang characterized and analyzed the X-ray crystal data. Tianlei Li, Song Wu, Weidong Pan and Chao Zhang designed the experiments and wrote the paper. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

References

1. Chen X., Engle K. M., Wang D.-H., Yu J.-Q., Angew. Chem., Int. Ed. 2009, 48, 5094–5115.
2. Colby D. A., Tsai A. S., Bergman R. G., Ellman, J. A., Acc. Chem. Res. 2012, 45, 814–825.
3. Wencel-Delord J., Glorius F., Nat. Chem. 2013, 5, 369–375.
4. Ackermann, L. Acc. Chem. Res. 2014, 47, 281–295.
5. Tobisu, M.; Chatani, N. Cross-Couplings Using Aryl Ethers via C-O Bond Activation Enabled by Nickel Catalysts. Acc. Chem. Res. 2015, 48, 1717–1726.
6. Rej S., Ano Y., Chem. Rev. 2020, 120, 1788–1887.
7. Su B., Cao Z.-C., Shi Z.-J., Acc. Chem. Res. 2015, 48, 886–896.
8. Zweig J. E., Kim D. E., Newhouse T. R., Chem. Rev. 2017, 117, 11680–11752.
9. Gandeepan P., Mueller T., Zell D., Cera G., Warratz S., Ackermann L., Chem. Rev. 2019, 119, 2192–2452.
10. Peng J.-B., Wu F.-P., Wu X.-F., Chem. Rev. 2019, 119, 2090–2127.
11. Gandeepan P., Cheng C.-H., Acc. Chem. Res. 2015, 48, 1194–1206.
12. Moselage M., Li J., Ackermann L., ACS Catal. 2016, 6, 498–525.
13. Kommagalla Y., Chatani N., Coord. Chem. Rev. 2017, 350, 117–135.
14. Yoshino T., Matsunaga S., Asian J. Org. Chem. 2018, 7, 1193–1205.
15. Yoshino, T.; Matsunaga, S. *Adv. Organomet. Chem.* 2019, 68, 197–247.
16. Baccalini A., Vergura S., Dolui P., Zanoni G., Maiti D., *Org. Biomol. Chem.* 2019, 17, 10119–10141.
17. Zhu R.-Y., Farmer M. E., Chen Y.-Q., Yu J.-Q., *Angew. Chem., Int. Ed.* 2016, 55, 10578–10599;
18. Norbert Krause A. S. K. H., Modern Allene Chemistry. *Wiley-VCH, Verlag GmbH & Co. Weinheim, Germany*, 2004.
19. Ma S., *Aldrichimica Acta* 2007, 40, 91–102.
20. Yu S., Ma S., *Angew. Chem., Int. Ed.* 2012, 51, 3074–3112.
21. Alcaide B., Almendros P., Aragoncillo C., *Chem. Soc. Rev.* 2014, 43, 3106–3135.
22. Chu W.-D., Zhang Y., Wang J., *Catal. Sci. Technol.* 2017, 7, 4570–4579.
23. Huang X., Ma S., *Acc. Chem. Res.* 2019, 52, 1301–1312.
24. Larock R. C., Berrios-Pena N. G., Fried C. A., *J. Org. Chem.* 1991, 56, 2615–17.
25. Larock R. C., Zenner J. M., *J. Org. Chem.* 1995, 60, 482–483.
26. Suresh R. R., Swamy K. C. K., *J. Org. Chem.* 2012, 77, 6959–6969.
27. Ye J., Ma S., *Acc. Chem. Res.* 2014, 47, 989–1000.
28. Xia X.-F., Wang Y.-Q., Zhang L.-L., Song X.-R., Liu X.-Y., *Chem. - Eur. J.* 2014, 20, 5087–5091.
29. Rodriguez A., Albert J., Ariza X., Garcia J., Granell J., Farras J., La Mela A., Nicolas E., *J. Org. Chem.* 2014, 79, 9578–9585.
30. Vidal X., Mascarenas J. L., Gulias M., *J. Am. Chem. Soc.* 2019, 141, 1862–1866.
31. Xia X.-F., Zhu S.-L., Hu Q., Li Y., Xu X., *Tetrahedron* 2017, 73, 3529–3535.
32. Qi W., Wu Y., Han Y., Li Y., *Catalysts* 2017, 7, 320–329.
33. Zhang Y. J., Skucas E., Krische M. J., *Org. Lett.* 2009, 11, 4248–4250.
34. Wang H., Glorious F., *Angew. Chem., Int. Ed.* 2012, 51, 7318–7322, S7318/1-S7318/83.
35. Zeng R., Fu C., Ma S., *J. Am. Chem. Soc.* 2012, 134, 9597–9600.
36. Zeng R., Wu S., Fu C., Ma S., *J. Am. Chem. Soc.* 2013, 135, 18284–18287.
37. Gandeepan P., Rajamalli P., Cheng C.-H., *Chem. - Eur. J.* 2015, 21, 9198–9203.
38. Kong D.-S., Wang Y.-F., Zhao Y.-S., Li Q.-H., Chen Y.-X., Tian P., Lin G.-Q., *Org. Lett.* 2018, 20, 1154–1157.
39. Ghosh C., Nagtilak P. J., Kapur M., *Org. Lett.* 2019, 21, 3237–3241.
40. Wang Q., Lou J., Huang Z., Yu Z., *J. Org. Chem.* 2019, 84, 2083–2092.
41. Nakanowatari, S.; Ackermann, L. *Chem. - Eur. J.* 2015, 21, 16246–16251.
42. Chen S.-Y., Li Q., Liu X.-G., Wu J.-Q., Zhang S.-S., Wang H., *ChemSusChem* 2017, 10, 2360–2364.
43. Chen S.-Y., Li Q., Wang H., *J. Org. Chem.* 2017, 82, 11173–11181.
44. Chen S.-Y., Han X.-L., Wu J.-Q., Li Q., Chen Y., Wang H., *Angew. Chem., Int. Ed.* 2017, 56, 9939–9943.
45. Wang C., Wang A., Rueping M., *Angew. Chem., Int. Ed.* 2017, 56, 9935–9938.
46. Lei C., Peng L., Ding K., *Adv. Synth. Catal.* 2018, 360, 2952–2958.
47. Ma, X.; Dang, Y. J. Org. Chem. 2019, 84, 1916–1924.
48. Mo, J.; Mueller, T.; Oliveira, J. C. A.; Ackermann, L. Angew. Chem., Int. Ed. 2018, 57, 7719–7723.
49. Yamauchi M., Morimoto M., Miura T., Murakami M., J. Am. Chem. Soc. 2010, 132, 54–55.
50. Miura T., Yamauchi M., Kosaka A., Murakami M., Angew. Chem., Int. Ed. 2010, 49, 4955–4957.
51. Nakanowatari S., Mueller T., Oliveira J. C. A., Ackermann L., Angew. Chem., Int. Ed. 2017, 56, 15891–15895.
52. Liu Y., Wang K., Ling B., Chen G., Li Y., Liu L., Bi S., Catal. Sci. Technol. 2020, DOI: 10.1039/d0cy00965b.
53. Liu Y., Bandini M., Chin. J. Chem. 2019, 37, 431–441.
54. Santhoshkumar R., Cheng C.-H., Asian J. Org. Chem. 2018, 7, 1151–1163.
55. Han X.-L., Lin P.-P., Li Q., Chin. Chem. Lett. 2019, 30, 1495–1502.
56. Boobalan R., Kuppusamy R., Santhoshkumar R., Gandeepan P., Cheng C.-H., ChemCatChem 2017, 9, 273–277.
57. Boobalan R., Santhoshkumar R., Cheng C.-H., Adv. Synth. Catal. 2019, 361, 1140–1145.
58. Kuppusamy R., Muralirajan K., Cheng C.-H., ACS Catal. 2016, 6, 3909–3913.
59. Thrimurtulu N., Dey A., Maiti D., Volla C. M. R., Angew. Chem., Int. Ed. 2016, 55, 12361–12365.
60. Li T. L., Zhang C., Tan Y., Pan W., Rao Y., Org. Chem. Front. 2017, 4, 204–209.
61. Zhai S., Qiu S., Chen X., Tao C., Li Y., Cheng B., Wang H., Zhai H.B., ACS Catal. 2018, 8, 6645–6649.
62. Meyer T. H., Oliveira J. C. A., Sau S. C., Ang N. W. J., Ackermann L., ACS Catal. 2018, 8, 9140–9147.
63. Mei R., Fang X., He L., Sun J., Zou L., Ma W., Ackermann L., Chem. Commun. 2020, 56, 1393–1396.
64. Xuan J., Xiao W.-J., Angew. Chem., Int. Ed. 2012, 51, 6828–6838.
65. Prier C. K., Rankic D. A., MacMillan D. W. C., Chem. Rev. 2013, 113, 5322–5363.
66. Romero N. A., Nicewicz D. A., Organic Photoredox Catalysis. Chem. Rev. 2016, 116, 10075–10166.
67. Chen J.-R., Hu X.-Q., Lu L.-Q., Xiao W.-J., Acc. Chem. Res. 2016, 49, 1911–1923.
68. Cheng Y.-Z., Zhang X., You S.-L., Visible-light-mediated photocatalysis as a new tool for catalytic asymmetric dearomatization (CADA) reactions. Sci. Bull. 2018, 63, 809–811.
69. Jiang H., Studer A., Chemistry with N-centered radicals generated by single-electron transfer-oxidation using photoredox catalysis. CCS Chem. 2019, 1, 38–49.
70. Barham J. P., Koenig B., Angew. Chem., Int. Ed. 2020, 59, 11732–11747.
71. Skubi K. L., Blum T. R., Yoon T. P., Chem. Rev. 2016, 116, 10035–10074.
72. Twilton J., Le C., Zhang P., Shaw M. H., Evans R. W., MacMillan D. W. C., Nat. Rev. Chem. 2017, 1, 0052.
73. Hopkinson M. N., Tlahuext-Aca A., Glorius F., Acc. Chem. Res. 2016, 49, 2261–2272.
74. Tellis J. C., Kelly C. B., Primer D. N., Jouffroy M., Patel N. R., Acc. Chem. Res. 2016, 49, 1429–1439.
75. Fabry D. C., Rueping M., Acc. Chem. Res. 2016, 49, 1969–1979.
76. Wang C.-S., Dixneuf P. H., Soule J.-F., *Chem. Rev.* 2018, 118, 7532–7585.
77. Kalsi D., Dutta S., Barsu N., Rueping M., Sundararaju B., *ACS Catal.* 2018, 8, 8115–8120.
78. Kalsi D., Barsu N., Chakrabarti S., Dahiya P., Rueping M., Sundararaju B., *Chem. Commun.* 2019, 55, 11626–11629.
79. Dhawa U., Tian C., Li W., Ackermann L., *ACS Catal.* 2020, 10, 6457–6462.
80. Gaster E., Kozuch S., Pappo D. *Angew. Chem., Int. Ed.* 2017, 56, 5912–5915.
81. Wu X., Wen X., Li J., *Dalton Trans.* 2018, 47, 13592–13601.
82. Ma P., Chen H., *ACS Catal.* 2019, 9, 1962–1972.
83. Grigorjeva L., Daugulis O., *Angew. Chem., Int. Ed.* 2014, 53, 10209–10212.
84. Zhang L.-B., Hao X.-Q., Liu Z.-J., Zheng X.-X., Zhang S.-K., Niu J.-L., Song M.-P. *Angew. Chem., Int. Ed.* 2015, 54, 10012–10015.
85. Zhang J., Chen H., Lin C., Liu Z.; Wang C., Zhang Y. *J. Am. Chem. Soc.* 2015, 137, 12990–12996.
86. Srivastavaa V., Singh P. P., *RSC Adv.* 2017, 7, 31377–31392.

**Figures**

![Reaction Scheme](image)

1b. Our design

1c. This work

Q = 8-quinolyl
Figure 1

Scheme 1: Catalytic Approaches for C–H Activation and Annulation Reactions with Allenes

\[
1a-1p + 2a \xrightarrow{\text{Co(acac)}_2 20 \text{ mol\%}} \xrightarrow{\text{Eosin Y 5 mol\%}} \xrightarrow{\text{TFCK 20 mol\%}} \xrightarrow{\text{O}_2 \text{ TFE, r.t., 24 h}} \xrightarrow{15\text{W CFL}} 3a-3p
\]

| Product | Conversion |
|---------|------------|
| 3a      | 87%        |
| 3b      | 85%        |
| 3c      | 83%        |
| 3d      | 89%        |
| 3e      | 73%        |
| 3f      | 88%        |
| 3g      | 91%        |
| 3h      | 88%        |
| 3i      | 90%        |
| 3j      | 93%        |
| 3k      | 93%        |
| 3l      | 81%        |
| 3m      | 70%        |
| 3n      | 77% (3:1)  |
| 3o      | 87%        |
| 3p      | 71%        |

Q = 8-quinolyl

Figure 2

Scheme 2: Scope of benzamides with benzyl buta-2,3-dienoate
Figure 3

Scheme 3: Scope of isoquinolinones from different allenes
Figure 4

Scheme 4: Synthesis of isoquinolinones with exo-double bonds
Figure 5

Scheme 5: Preliminary mechanistic investigation
Figure 6

Scheme 6: Proposed reaction mechanism

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Supportinginformation2.pdf
- Supportinginformation1.pdf