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ARTICLE

Bifunctional NHC Catalysis Enables Umpolung Photocarbonylation of Two Electrophiles: Access to Unsymmetric Diaryl 1,4-Diketones

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Unsymmetric diaryl 1,4-diketones are valuable structural motifs in organic synthesis. Direct controlled installation of two distinct aryl-substituted carbonyl groups is conceptually straightforward yet synthetically challenging. Herein we report an example of unsymmetric diaryl 1,4-diketones synthesis via *N*-heterocyclic carbene enabled umpolung photo-carbonylation. In this system, NHC catalysis induces umpolung reactivity while simultaneously generating Breslow intermediates *in situ* that participate in the photochemical single electron transfer process as intrinsic redox mediators. In cooperation with the photoactive aryl thianthrenium salts, this bifunctional catalytic design enables photocatalytic carbonylation under metal-free and external-photocatalyst-free conditions without the need for stoichiometric reductants. The process overcomes the polarity mismatch and enables regioselective carbonylation and acylation, providing a diverse array of unsymmetric diaryl 1,4-diketones with high precision. This strategy establishes a mechanistically distinct and sustainable platform for regioselective umpolung photocarbonylation.

Introduction

Umpolung carbonylation enabled by N-heterocyclic carbene (NHC) catalysis has fundamentally expanded the reactivity landscape of carbonyl chemistry. Formation of the Breslow intermediate converts electrophilic aldehydes into nucleophilic acyl anion equivalents, enabling diverse bond-forming processes in modern organocatalysis.[1–6] Beyond this classical two-electron reactivity mode, more recent mechanistic studies have demonstrated that Breslow-type intermediates also possess intrinsic redox activity and can engage in single-electron-transfer (SET) processes, giving rise to radical and radical–polar crossover reactivity. [1–6,55-64] In particular, it has been shown that the electron-rich nature of these intermediates enables SET processes rather than purely nucleophilic C-centered reactivity, consistent with their role as redox-active species in NHC catalysis. In parallel, visible-light photochemistry has emerged as a powerful platform for generating reactive radical intermediates under mild conditions, although achieving precise chemo- and regioselective control remains challenging. [12-16] Collectively, these advances suggest that Breslow-derived intermediates can participate as intrinsic redox-active species within photochemical manifolds, providing a conceptual basis for merging NHC catalysis with light-driven SET processes under photocatalyst-free conditions.

Carbon monoxide (CO) is an abundant and versatile C1 synthon in carbonylation chemistry.[17–20] Although numerous metal-catalyzed carbonylation reactions, metals are typically required to activate both CO and the coupling partners.[21–25] Cross-electrophile coupling has recently emerged as an attractive alternative that avoids preformed nucleophiles but generally relies on stoichiometric reductants such as Zn, Mg, or Mn.[26–27] Selective carbonylative coupling between two electrophiles while suppressing homocoupling therefore remains challenging. Cooperative metal catalysis, pioneered by Weix, partially addresses this issue by employing different metals to selectively activate each electrophile prior to transmetalation and reductive elimination.[28-31] Recent studies by Lian further expanded this concept through dual-metal-catalyzed cross-electrophile carbonylation using CO as the reductant.[32] More recently, Zheng and Xue reported an electrochemical nickel-/cobalt-catalyzed carbonylative cross-electrophile coupling reaction.[33] Despite these advances, radical carbonylation of electrophilic partners remains largely unexplored main due to the intrinsic polarity mismatch and the limitation of intermediates lifetime. (Figure. 1.1a–b).

Unsymmetric diaryl 1,4-diketones are valuable structural motifs widely found in pharmaceuticals and bioactive molecules and serve as versatile intermediates for the synthesis of value-added unsymmetric aryl-substituted furans, pyrroles, pyridazines, 1,4-diols and 1,4-enones.[34–39] However, efficient and selective access to these structures remains challenging, particularly for the regioselective incorporation of two distinct aryl groups. We envisioned that integrating NHC-enabled polarity inversion with photochemical radical control could

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enable a regioselective umpolung photocarbonylation of two electrophiles under a CO atmosphere, thereby providing a mechanistically distinct and sustainable strategy for the synthesis of unsymmetric diaryl 1,4-diketones while expanding the scope of radical carbonylation (Figure. 1.1b–c).

The proposed reaction design is illustrated in Figure 1.2. Condensation of aryl aldehydes with an *N*-heterocyclic carbene generates a Breslow intermediate that undergoes base-assisted deprotonation to form a nucleophilic enolate, there-by achieving aldehyde umpolung.[1–11] As shown in Figure 1.1c, this enolate functions as an intrinsically photoactive electron donor and engages in single electron transfer (SET) with electrophilic aryl thianthrenium salts[42–46] (Figure 1.1d) to generate aryl radicals. Subsequent CO capture furnishes aryl acyl radicals. To address the short lifetime and limited reactivity of these intermediates, styrenes are introduced as a "bridge" to promote productive carbonylation and enabling regioselective C–C bond formation to afford unsymmetric diaryl 1,4-diketones. This strategy overcomes key challenges in electrophiles-based multicomponent carbonylation, including polarity mismatch and redox compatibility, while proceeding with-out metals, external photocatalysts, or stoichiometric reductants. By merging aldehyde umpolung with intrinsic photochemical activation, this work establishes a mechanistically distinct platform for NHC-enabled photocarbonylation for the synthesis of unsymmetric diaryl 1,4-diketones.

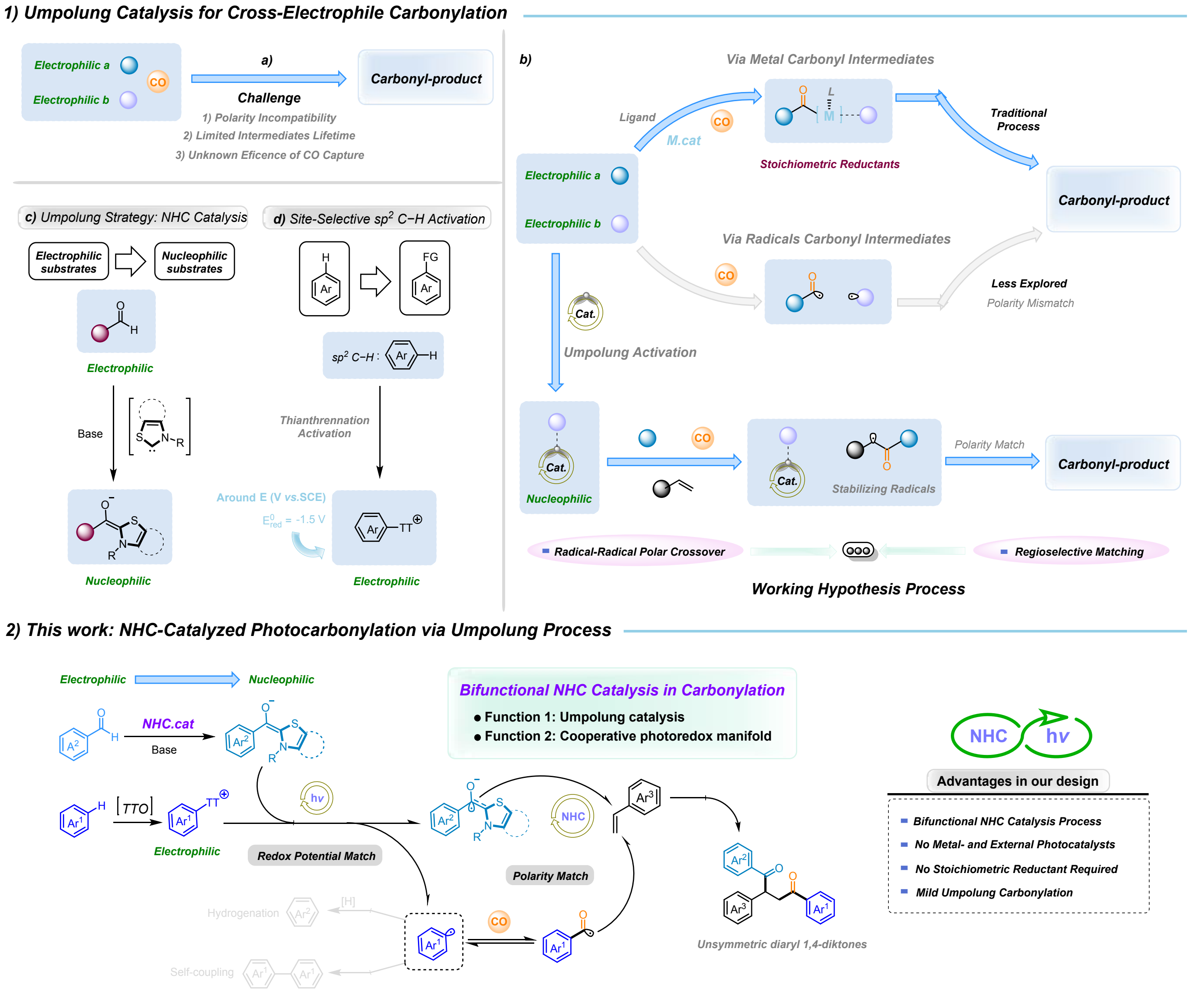

Figure 1. Background of NHC- and Photocatalyzed Umpolung Carbonylation.

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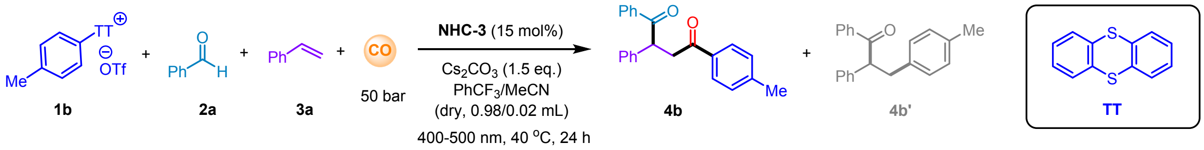

Entry	Deviation from standard conditions	Yield of **4b-4b'** (%)
1	none	66(60)-18
2	w/o **NHC-3** or Light	N.D.
3	w/o CO	N.D.-58
4	w/o base	N.D.
5	**NHC-1** instead of **NHC-3**	trace-trace
6	**NHC-2** instead of **NHC-3**	50-12
7	**NHC-4** instead of **NHC-3**	33-trace
8	**NHC-5** instead of **NHC-3**	40-trace
9	**NHC-6** instead of **NHC-3**	40-20
10	**NHC-7** instead of **NHC-3**	30-18
11	**NHC-8** instead of **NHC-3**	35-10
12	**NHC-9** instead of **NHC-3**	46-18
13	**NHC-(10-13)** instead of **NHC-3**	N.D.
14	**TT-1** instead of **TT-2**	36-25
15	**TT-3** instead of **TT-2**	42-16
16	**A-(2-4)** instead of **A-1**	N.D. for diketones
17	Single solvent $PhCF_3$	50-15
18	Single solvent MeCN	10-30
19	$PhCF_3$/MeCN = 0.5/0.5 mL	20-36
20	$PhCF_3$/MeCN = 0.7/0.3 mL	58-25
21	$PhCF_3$/MeCN = 0.02/0.98 mL	30-40
22	K_2CO_3 instead of Cs_2CO_3	48 for **4b**
23	K_3PO_4 instead of Cs_2CO_3	50 for **4b**
24	DBU instead of Cs_2CO_3	trace for **4b**
25	^{t}BuONa instead of Cs_2CO_3	trace for **4b**

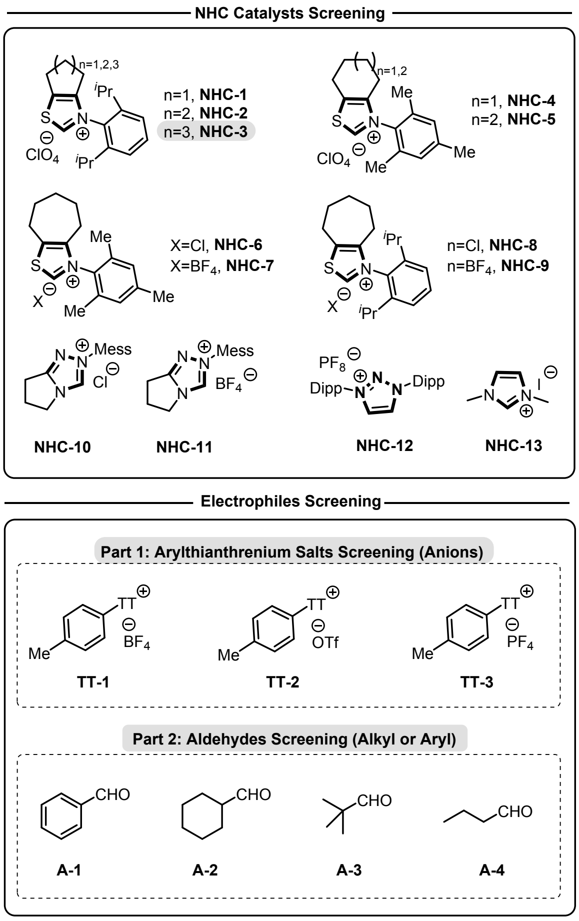

Figure 2. Optimization of the reaction. Reaction conditions: **1b** (0.1 mmol), **2a** (2.0 equiv.), **3a** (3.0 equiv.), **NHC-3** (15 mol%), Cs_2CO_3 (1.5 equiv.), $PhCF_3$ (dry, 0.98 mL), MeCN (dry, 0.02 mL), CO (50 bar), 400-500 nm, stirred at 40 ºC for 24 h, GC yield. Isolated yield in parentheses. Dipp = 2,6-diisopropylphenyl. Mess = 2,4,6-trimethylphenyl.

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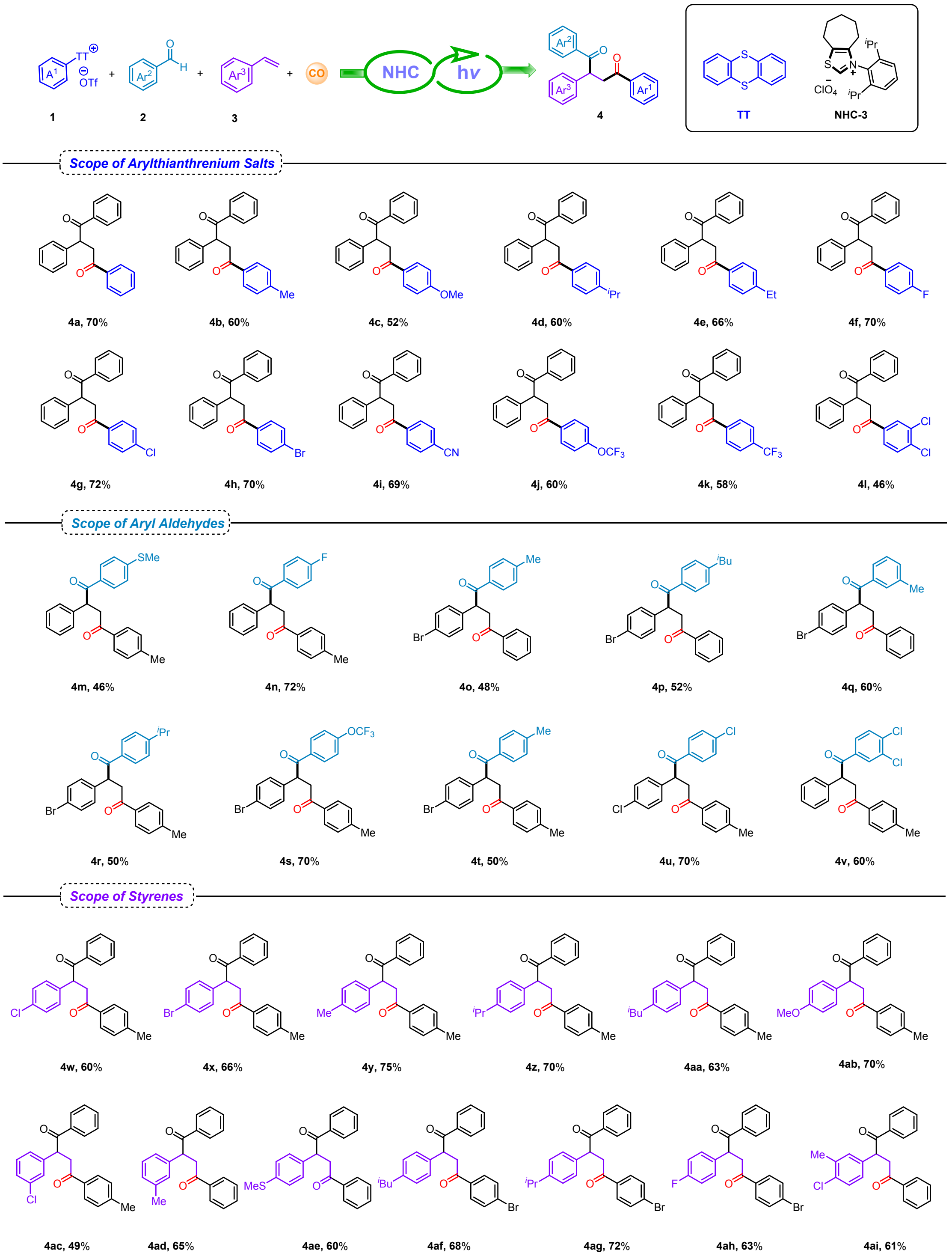

Figure 3. Evaluation of the NHC catalyzed umpolung photocarbonylation process. **1** (0.1 mmol), **2** (2.0 equiv.), **3** (3.0 equiv.), **NHC-3** (15 mol%), Cs_2CO_3 (1.5 equiv.), $PhCF_3$ (dry, 0.98 mL), MeCN (dry, 0.02 mL), CO (50 bar), 400-500 nm, stirred at 40 ºC for 24 h.

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Inspired by recent advances in NHC catalysis and thianthrenium salts in radical chemistry,[1-11, 40-46] we employed an NHC catalyst as a bifunctional mediator to realize this transformation. We initially employed aryl thianthrenium salts **1b**, benzaldehyde **2a** and styrene **3a**, as model substrate to find the ideal conditions, as shown in Figure 2, Table. Control experiments confirmed that light, the NHC catalyst, and the base are all essential for the reaction (Figure 2, Table, entries 1–4). To efficiently achieve the NHC-catalyzed umpolung photocarbonylation of two electrophiles with styrenes for the synthesis of unsymmetric diaryl 1,4-diketones, we first examined the effect of different NHC catalysts, as their steric and electronic properties significantly influenced the reactivity (Figure 2, Table, entries 5–13). We initially evaluated commonly used NHC precursor salts featuring N,S-containing backbones, dinitrogen backbones, and trinitrogen frameworks. Among them, the NHC precursor **NHC-3** bearing an N,S-based core, particularly incorporating a fused seven-membered ring, proved to be most effective for the desired transformation. Furthermore, N-aryl substituents bearing 2,6-diisopropylphenyl groups provided the optimal steric environment. Recent studies have revealed that Breslow-derived enolates can display substantially enhanced reducing power, enabling SET processes at potentials below –1.5 V vs SCE[40-41] and aryl thianthrenium salts ($E_{red} \approx -1.5$ V vs SCE),[42-46] which renders the photoinduced single-electron transfer thermodynamically feasible. Following SET activation, the weak C-S bond of the thianthrenium moiety undergoes rapid fragmentation, efficiently generating aryl radicals while maintaining compatibility with the NHC-catalyzed umpolung manifold. Next, the effects of the two electrophilic partners were investigated in carbonylation. First, aryl thianthrenium salts bearing different counter anions were examined under CO atmosphere in an autoclave (Figure 2, Table, entries 14–15), and the trifluoromethanesulfonate (OTf$^-$) salt was found to be optimal. We then evaluated the aldehyde component. Although aryl and alkyl aldehydes possess similar oxidation potentials for generating the corresponding N,S-based enolate intermediates, only aryl aldehydes afforded the desired products under the reaction conditions (Figure 2, Table, entry 16), likely due to the instability and short lifetime of the corresponding radical enolate derived from alkyl aldehydes. Solvent effects were subsequently examined and were found to play a crucial role in the carbonylation process (Figure 2, Table, entries 17–21). A mixed solvent system ($PhCF_3$/MeCN = 0.98/0.02 mL) proved essential for controlling the reaction pathway. The polar MeCN component facilitates photoinduced SET between the Breslow-derived enolate and aryl thianthrenium salts, whereas the predominantly nonpolar $PhCF_3$ environment enhances CO solubility and promotes rapid trapping of aryl radicals by CO.[53-54] This balance between efficient radical generation and effective CO capture selectively favors the carbonylation pathway. Finally, the choice of base significantly affected the reaction efficiency. Cs_2CO_3 was identified as the optimal base, whereas alternative inorganic bases or strong organic bases resulted in diminished reactivity (Figure 2, Table, entries 22–25). Under the optimized conditions, the desired product was obtained in the highest yield (Figure 2, Table, entry 1).

With the optimized NHC-catalyzed umpolung photocarbonylation conditions in hand, we next examined the substrate scope using aryl thianthrenium salts **1** and benzaldehydes **2** as the two electrophilic partners for the regioselective carbonylation and acylation of styrenes **3** (Figure 3). We first investigated the scope of aryl thianthrenium salts **1**. A series of para-substituted aryl thianthrenium salts were compatible with the reaction, affording the desired unsymmetric diaryl 1,4-diketones **4a–4l** in moderate to good yields (52–72%). Electron-withdrawing substituents generally exhibited higher reactivity, delivering products **4a** and **4f–4h** (*p*-H, F, Cl, Br) in good yields of 70–72%. Slightly lower yields were observed for strongly electron-withdrawing substituents such as *p*-CN (**4i**, 68%), *p*-OCF_3 (**4j**, 60%), and *p*-CF_3 (**4k**, 58%). In contrast, electron-donating substituents resulted in somewhat diminished reactivity, affording products **4b–4e** (*p*-Me, OMe, ^{i}Pr, Et) in 52–66% yields. Disubstituted aryl thianthrenium salts were also tolerated, giving product **4l** (3-Cl,4-Cl) in 46% yield. However, ortho- and meta-substituted substrates were less suitable, due to competing non-carbonylative pathways. Next, the scope of the aldehydes component **2** was explored. Both para- and meta-substituted benzaldehydes proved compatible with the reaction, furnishing the corresponding products **4m–4u** in moderate yields (44–72%). Substrates bearing substituents such as *p*-SMe, F, Me, ^{i}Bu, ^{i}Pr, OCF_3, and Cl, as well as *m*-Me, were successfully converted to the de-sired products. However, benzaldehydes bearing electron-donating substituents generally afforded lower yields, likely due to competing non-carbonylative pathways, as illustrated by *p*-SMe (**4m**, 44%), p-Me (**4o**, 48%), and *p*-iBu (**4p**, 52%). In addition, disubstituted benzaldehydes were also suitable substrates, delivering product **4v** (3-Cl,4-Cl) in 60% yield. Finally, the scope of styrenes **3** was examined. Para-substituted styrenes bearing both electron-withdrawing and electron-donating groups (Cl, Br, Me, ^{i}Pr, ^{t}Bu, OMe, SMe, F) were well tolerated, furnishing the corresponding products **4w–4ab** and **4ae–4ah** in 60–75% yields. Meta-substituted styrenes also participated smoothly in the transformation, affording **4ac** (m-Cl) and **4ad** (*m*-Me) in 49% and 65% yields, respectively. In addition, disubstituted styrenes were compatible with the reaction, providing product **4ai** (3-Me,4-Cl) in 61% yield. Overall, the broad substrate compatibility highlights the effectiveness of this NHC-catalyzed umpolung photocarbonylation in enabling regioselective carbonylative acylation of styrenes using two electrophilic partners. Notably, this strategy overcomes the inherent polarity mismatch between electrophilic components and enables controlled radical photocarbonylation under mild conditions without the need for metals, external photocatalysts, or stoichiometric reductants.

To further demonstrate the synthetic value of this umpolung photocarbonylation strategy, a series of downstream transformations of unsymmetric diaryl 1,4-diketone **4** were conducted (Figure 4).[34–39] As versatile intermediates, these 1,4-diketones can be readily converted into diverse heterocyclic frameworks and functionalized motifs. For example, acid-promoted condensation of 1,4-diketones **4** with *p*-toluenesulfonic acid (PTSA) in ethanol afforded the 2,3,5-trisubstituted furan **6a**. Reaction of **4** with aniline in toluene in the presence of PTSA delivered the 1,2,3,5-tetrasubstituted pyrrole **6b**. Treatment of **4** with ammonium acetate in acetic acid produced the 2,3,5-trisubstituted pyrrole **6c**. In addition, reaction with hydrazine hydrate at provided the 3,5,6-trisubstituted pyridazine **6d**. Then, reduction of **4** with BH_3·THF in THF furnished the corresponding 1,4-diol **6e**. Follow, treatment of **4** with amino acids in acetic acid produced the 2,3,5-trisubstituted antimycobacterial activity of 1,2,3,5-tetrasubstituted pyrrolyl-N-acetic acid derivatives **6f**. Finally, **4** can be catalyzed by Cs_2CO_3 in DMSO for the synthesis of unsymmetric diaryl 1,4-enones **6g**. These results highlight the synthetic versatility of the unsymmetric diaryl 1,4-diketones and further demonstrate the utility of the NHC-catalyzed radical-mediated umpolung photocarbonylation strategy for accessing structurally diverse and value-added molecular scaffolds.

To evaluate the atom economy of the reaction, the recovery of thianthrene was examined. Gratifyingly, thianthrene could be recovered in yields of up to 90%, highlighting the high atom economy of the process (Figure 5a). To gain insight into the reaction mechanism, a series of control experiments were performed (Figure 5b–g). First, radical trapping experiments were conducted to probe the involvement of radical intermediates. When 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) was introduced as a radical scavenger under the standard conditions, the formation of product **4b** was completely suppressed (Figure 5b). Instead, the Ar^1–TEMPO adduct **5a** was detected by GC–MS, supporting the generation of aryl radical intermediates. Similarly, when 1,1-diphenylethylene (1,1-DPE) was employed as a radical trap, the desired product **4b** was also fully inhibited (Figure 5c), while the aryl addition adduct **5b** and the aryl acyl addition adduct **5c** were detected by GC–MS. These results further support the involvement of aryl radical and aryl acyl radical species in the reaction pathway (**5d** and **5e**). Next, control experiments were performed to examine the role of NHC catalysis in the photocarbonylation process. Further control experiments were conducted to investigate the roles of the individual reaction components using 1,1-DPE as a radical acceptor (Figure 5d). In the absence of Cs_2CO_3, none of the products **4b**, **5b**, or **5c** were detected (Figure 5d.1), indicating that the base is essential for initiating the catalytic process. Likewise, omission of **NHC-3**, aldehyde **2a**, or styrene **3a** resulted in only trace amounts of the radical addition products **5b** and **5c** being observed (Figure 5d.2–5), suggesting that both the NHC catalytic cycle and the complete reaction system are indispensable for efficient radical generation. In addition, no formation of the 1,4-dicarbonyl product **4b** was detected in the absence of light (Figure 5d.6), highlighting the critical role of photoactivation in the transformation. Taken together with the thianthrene recovery experiment shown in Figure 5a, these observations support a cooperative photoredox activation pathway in which neither the Breslow-derived intermediate nor the aryl thianthrenium salt alone is sufficient to promote productive carbonylation. Instead, under photoirradiation, the *in situ* generated Breslow-derived intermediate and the photoactive aryl thianthrenium salt cooperatively participate in the SET process, enabling aryl radical formation and the subsequent carbonylation sequence. These results suggest that the interaction between the aldehyde and the NHC catalyst generates the key reactive species responsible for initiating the bifunctional catalytic process. Finally, light on/off experiments were conducted to examine the role of photoirradiation (Figure 5e). The yield of product **4b** increased only during periods of blue-light irradiation, whereas no further conversion was observed when the light source was turned off while stirring continued. These results confirm the necessity of light for sustaining the catalytic cycle. Combined with previous literature reports,[47–50] these observations support a mechanism in which *in situ*-generated Breslow intermediates participate in a photoinduced catalytic cycle.

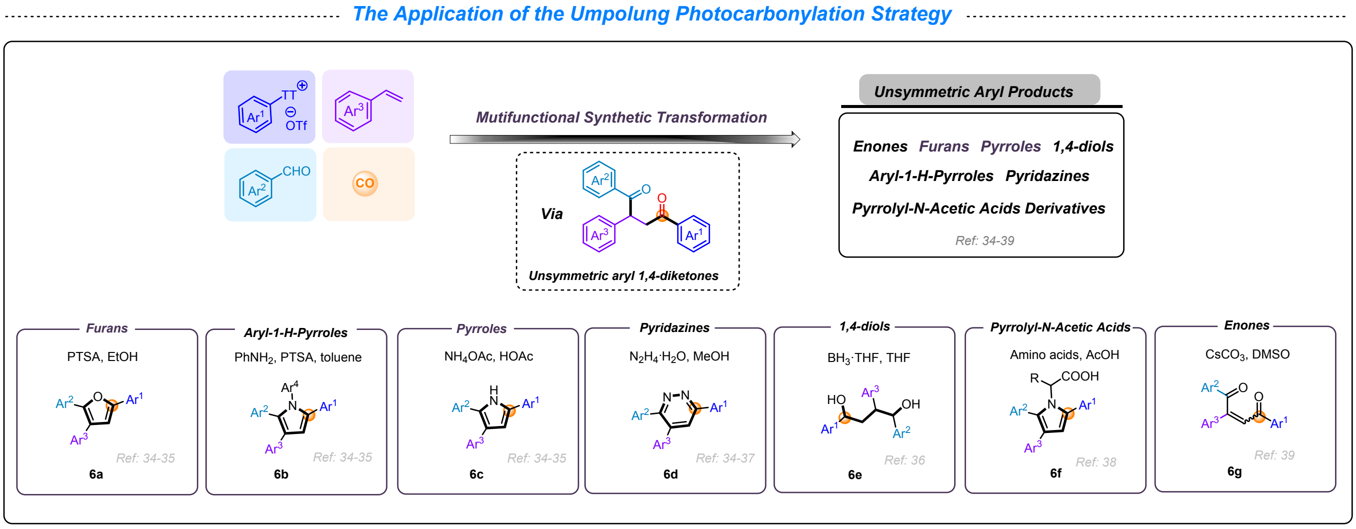

Figure 4. Synthetic applications of the NHC catalyzed umpolung photocarbonylation strategy.

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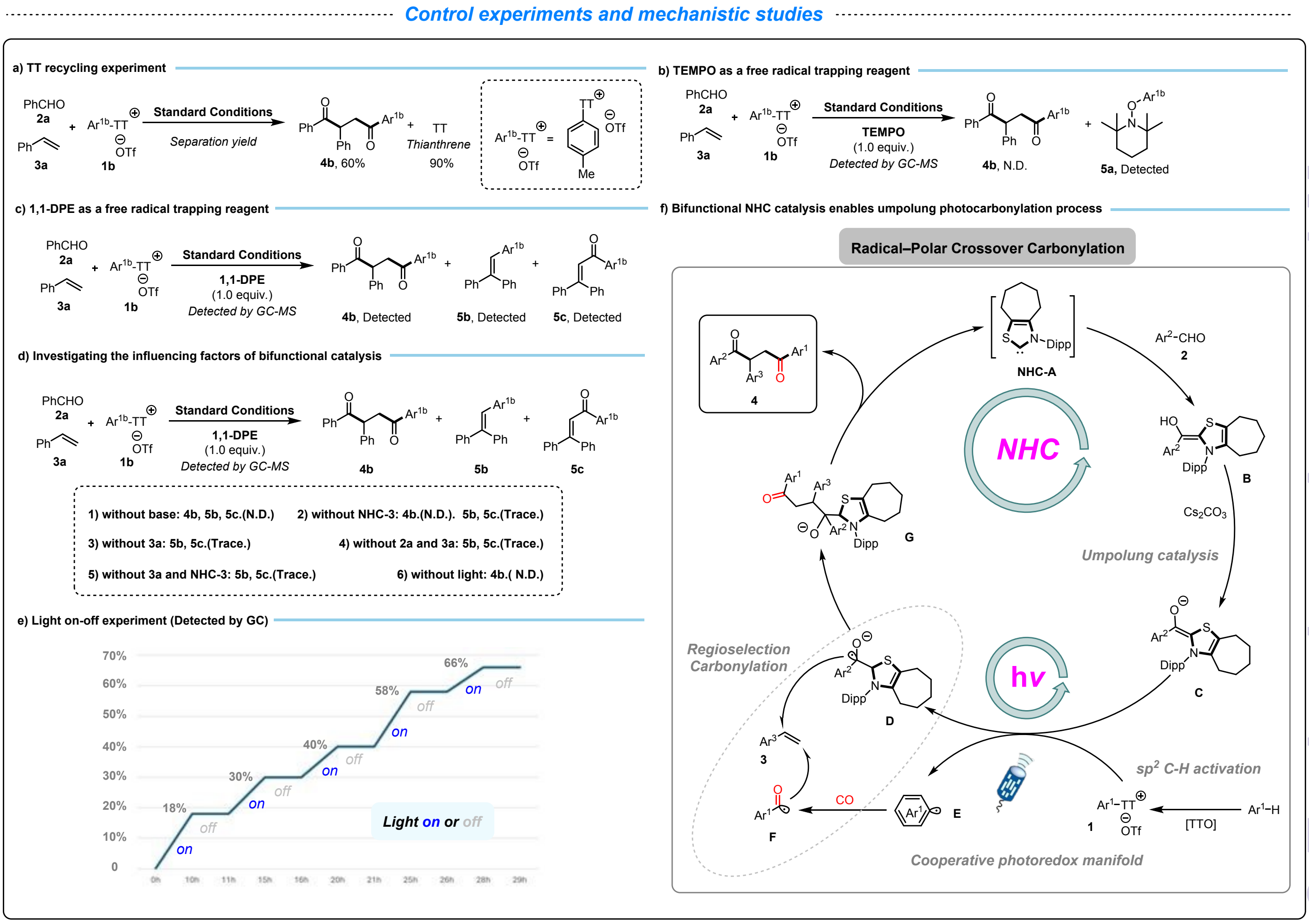

Figure 5. Mechanistic investigations and plausible reaction mechanism.

Based on our mechanistic investigations and related literature,[1-11, 40–64] a plausible catalytic cycle is proposed in Figure 5f. Initially, condensation of benzaldehyde **2** with the NHC catalyst (**NHC-A**), generated from **NHC-3**, forms the Breslow intermediate **B**. Subsequent deprotonation by Cs_2CO_3 affords the corresponding enolate species **C**, thereby accomplishing the umpolung activation of the aldehyde. Notably, the Breslow-derived enolate intermediate plays a dual functional role in the catalytic cycle. Beyond serving as the classical nucleophilic acyl anion equivalent, the in situ generated enolate C also participates in the photochemical SET process with aryl thianthrenium salt **1**. Upon blue light irradiation, a cooperative photoinduced electron transfer event between **C** and **1** lead to the formation of the oxidized Breslow intermediate **D** and the aryl radical **E**. The highly reactive aryl radical **E** rapidly traps carbon monoxide to generate the aryl acyl radical intermediate **F**. Subsequently, a regioselective radical carbonylative acylation process involving intermediates **D** and **F** with styrene **3** delivers intermediate **G**. Finally, intermediate **G** undergoes further transformation to furnish the desired unsymmetric diaryl 1,4-diketone product **4** while regenerating the free carbene catalyst **NHC-A**, thus completing the catalytic cycle.

Conclusions

In summary, we disclose a bifunctional NHC-catalyzed umpolung photocarbonylation manifold, without the need of metals, external photocatalysts, or stoichiometric reductants. In this catalytic design, NHC catalysis simultaneously induces polarity inversion of aldehydes and generates This cooperative catalytic manifold combines classical NHC-mediated umpolung reactivity with photoredox sensitization pathways to enable multicomponent carbonylation. This strategy straightforward overcomes the inherent polarity mismatch and enables regioselective photocarbonylation. Consequently, a diverse array of unsymmetric diaryl 1,4-diketones can be accessed with high precision and readily elaborated into value-added molecular architectures. More broadly, this work demonstrates that merging umpolung catalysis with intrinsic photochemical activation unlocks unconventional carbonylation reactivity and establishes a conceptual framework for NHC-enabled umpolung carbonylation strategies.

Author contributions

X.-F. W. conceived and directed the project. M.-L. Y. performed all the experiments, prepared the manuscript and the ESI.

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.

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Notes and references

1 L. Delfau, S. Nichilo, F. Molton, J. Broggi, E. Tomás-Mendivil and D. Martin, Critical Assessment of the Reducing Ability of Breslow-Type Derivatives and Implications for Carbene-Catalyzed Radical Reactions, *Angew. Chem. Int. Ed.*, 2021, **60**, 26783–26789.

2 Y.-C. Chang, R. Guo, T. Fessard, Q. Lefebvre, C. Salomé and M. K. Brown, Umpolung Activation of Bicyclobutanes via N-Heterocyclic Carbene Catalysis, *Angew. Chem. Int. Ed.*, 2025, **64**, e202513913.

3 M. H. Wang and K. A. Scheidt, Cooperative Catalysis and Activation with N-Heterocyclic Carbenes, *Angew. Chem. Int. Ed.*, 2016, **55**, 14912–14922.

4 S. Gehrke and O. Hollóczki, Are There Carbenes in N-Heterocyclic Carbene Organocatalysis?, *Angew. Chem. Int. Ed.*, 2017, **56**, 16395–16398.

5 X. Bugaut and F. Glorius, Organocatalytic Umpolung: N-Heterocyclic Carbenes and Beyond, *Chem. Soc. Rev.*, 2012, **41**, 3511–3522.

6 Z.-Z. Zhang, R. Zeng, Y.-Q. Liu and J.-L. Li, Cross-Coupling Reaction of Alkyl Halides with Aldehydes through NHC Catalysis, *ChemCatChem*, 2024, **16**, e202400063.

7 Q.-Z. Li, Y.-Q. Liu, X.-X. Kou, W.-L. Zou, T. Qi, P. Xiang, J.-D. Xing, X. Zhang and J.-L. Li, Oxidative Radical NHC Catalysis: Divergent Difunctionalization of Olefins through Intermolecular Hydrogen Atom Transfer, *Angew. Chem. Int. Ed.*, 2022, **61**, e202207824.

8 Q.-Z. Li, W.-L. Zou, Z.-Y. Yu, X.-X. Kou, Y.-Q. Liu, X. Zhang, Y. He and J.-L. Li, Remote Site-Selective Arene C–H Functionalization Enabled by N-Heterocyclic Carbene *Organocatalysis*, Nat. Catal., 2024, **7**, 900–911.

9 H. Huang, Z.-Y. Yu, L.-Y. Han, Y.-Q. Wu, L. Jiang, Q.-Z. Li, W. Huang, B. Han and J.-L. Li, N-Heterocyclic Carbene Catalytic 1,2-Boron Migrative Acylation Accelerated by Photocatalysis, *Sci. Adv.*, 2024, **10**, eadn8401.

10 T. Ishii, K. Nagao and H. Ohmiya, Recent Advances in N-Heterocyclic Carbene-Based Radical Catalysis, *Chem. Sci.*, 2020, **11**, 5630–5639.

11 K. Liu, M. Schwenzer and A. Studer, Radical NHC Catalysis, *ACS Catal*., 2022, **12**, 11984–11999.

12 X.-Y. Yu, J.-R. Chen and W.-J. Xiao, Visible Light-Driven Radical-Mediated C–C Bond Cleavage/Functionalization in Organic Synthesis, *Chem. Rev.*, 2021, **121**, 506–561.

13 P.-Z. Wang, B. Zhang, W.-J. Xiao and J.-R. Chen, Photocatalysis Meets Copper Catalysis: A New Opportunity for Asymmetric Multi-component Radical Cross-Coupling Reactions, *Acc. Chem. Res.*, 2024, **57**, 3433–3448.

14 H. Kisch, Semiconductor Photocatalysis for Chemoselective Radical Coupling Reactions, *Acc. Chem. Res.*, 2017, **50**, 1002–1010.

15 L. Song, L. Cai, E. V. Van der Eycken and L. Gong, Recent Advances in Copper-Catalyzed Multicomponent Reactions with Photoinduction, *Coord. Chem. Rev.*, 2025, **528**, 216428.

16 F.-D. Lu, G.-F. He, L.-Q. Lu and W.-J. Xiao, Metallaphotoredox Catalysis for Multicomponent Coupling Reactions, *Green Chem.*, 2021, **23**, 5379–5393.

17 J.-B. Peng, H.-Q. Geng and X.-F. Wu, The Chemistry of CO: Carbonylation, *Chem*, 2019, **5**, 526–552.

18 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, **126**, 500–605.

19 M.-L. Yang and X.-F. Wu, N-Heterocyclic carbene-/photoredox-catalyzed regioselective carbonylation of alkenes, *Green Chem.*, 2025, **27**, 5257–5264.

20 M. Yang, Y. Liu, P. Yang, Y. Zhao and X.-F. Wu, Visible-Light-Driven Four-Component Diacylation of Styrenes with Acyl Azolium Salts: Carbonylative Synthesis of 1,4-Diketones, *Sci. China Chem.*, 2025, **61**, 2485–2490.

21 X.-F. Wu, H. Neumann and M. Beller, Palladium-Catalyzed Carbonylative Coupling Reactions between Ar–X and Carbon Nucleophiles, *Chem. Soc. Rev.*, 2011, **40**, 4986–5009.

22 Y. Li, Y. Hu and X.-F. Wu, Non-Noble Metal-Catalysed Carbonylative Transformations, *Chem. Soc. Rev.*, 2018, **47**, 172–194.

23 M. Yang, Y. Liu, X. Qi, Y. Zhao and X.-F. Wu, Carbonylative Transformation of Aryl Halides and Strong Bonds via Cheap Metal Catalysts and Sustainable Technologies, *Green Synth. Catal.*, 2024, **5**, 211–269.

24 J.-B. Peng, F.-P. Wu and X.-F. Wu, First-Row Transition-Metal-Catalyzed Carbonylative Transformations of Carbon Electrophiles, *Chem. Rev.*, 2019, **119**, 2090–2127.

25 J.-B. Peng, F.-P. Wu and X.-F. Wu, Copper-Catalyzed Carbonylative Coupling of Alkyl Halides, *Acc. Chem. Res.*, 2021, **54**, 2261–2274.

26 K. E. Poremba, S. E. Dibrell and S. E. Reisman, Nickel-Catalyzed Enantioselective Reductive Cross-Coupling Reactions, *ACS Catal.*, 2020, **10**, 8237–8246.

27 D. J. Weix, Methods and Mechanisms for Cross-Electrophile Coupling of Csp^2 Halides with Alkyl Electrophiles, *Acc. Chem. Res.*, 2015, **48**, 1767–1775.

28 L. K. G. Ackerman, M. M. Lovell and D. J. Weix, Multimetallic Catalysed Cross-Coupling of Aryl Bromides with Aryl Triflates, *Nature*, 2015, **524**, 454–457.

29 L. Huang, L. K. G. Ackerman, K. Kang, A. M. Parsons and D. J. Weix, LiCl-Accelerated Multimetallic Cross-Coupling of Aryl Chlorides with Aryl Triflates, *J. Am. Chem. Soc.*, 2019, **141**, 10978–10983.

30 K. Kang, L. Huang and D. J. Weix, Sulfonate versus Sulfonate: Nickel and Palladium Multimetallic Cross-Electrophile Coupling of Aryl Triflates with Aryl Tosylates, *J. Am. Chem. Soc.*, 2020, **142**, 10634–10640.

31 A. M. Olivares and D. J. Weix, Multimetallic Ni- and Pd-Catalyzed Cross-Electrophile Coupling to Form Highly

View Article Online
DOI: 10.1039/D6CY00554C

Substituted 1,3-Dienes, *J. Am. Chem. Soc.*, 2018, **140**, 2446–2449.

32 G. Chen, R. Zhou, X. Zhang, X. Xiao, S. Kramer, G.-J. Cheng and Z. Lian, Carbonylative Cross-Electrophile Coupling between Aryl Bromides and Aryl Triflates Enabled by Palladium and Rhodium Co-operative Catalysis and CO as Reductant, *ACS Catal.*, 2022, **12**, 14582–14591.

33 S. Tao, Y. Yang, L. Chen, J. Xu, H. Fu, H. Chen, W. Jiang, R. Li, W. Xue and X. Zheng, Electrochemical Synergistic Ni/Co-Catalyzed Carbonylative Cross-Electrophile Coupling of Aryl and Alkyl Halides with CO, *JACS Au*, 2025, **5**, 1413–1420.

34 J. Liu, L.-Q. Lu, Y. Luo, W. Zhao, P.-C. Sun, W. Jin, X. Qi, Y. Cheng and W.-J. Xiao, Photoredox-Enabled Chromium-Catalyzed Alkene Diacylations, *ACS Catal.*, 2022, **12**, 1879–1885.

35 J. Tan, C. Xie, N. Yusuipujiang, M. Xu, L. Wang and D. Ma, An Efficient Semipinacol Rearrangement toward α,β-Unsaturated Ketones via Lewis Acid and Base Synergistic Catalysis, *J. Org. Chem.*, 2025, **90**, 8687–8692.

36 Y. Luo, Q. Wei, L. Yang, Y. Zhou, W. Cao, Z. Su, X. Liu and X. Feng, Enantioselective Radical Hydroacylation of α,β-Unsaturated Carbonyl Compounds with Aldehydes by Triplet-Excited Anthraquinone, *ACS Catal.*, 2022, **12**, 12984–12992.

37 Y. Ge, Q. Zhu, Y. Zhu and G. Dong, Core Diversification Using 1,2-Oxaborines as a Versatile Molecular Platform, *Nat. Chem.*, 2026, **18**, 128–134.

38 L. R. Pagadala, L. D. Mukkara, S. Singireddi, A. Singh, V. R. Thummaluru, P. S. Jagarlamudi, R. S. Guttala, Y. Perumal, S. Dharmarajan, S. M. Upadhyayula, R. Ummanni, V. S. R. Basireddy and N. Ravirala, Design, Synthesis and Anti-Mycobacterial Activity of 1,2,3,5-Tetrasubstituted Pyrrolyl-N-Acetic Acid Derivatives, *Eur. J. Med. Chem.*, 2014, **84**, 118–126.

39 Y. Shao, Y.-M. Zeng, J.-Y. Ji, X.-Q. Sun, H.-T. Yang and C.-B. Miao, The Cs_2CO_3-Catalyzed Reaction of 2-Oxindoles with Enones for the Preparation of Indolin-3-Ones and Their Further Transformation, *J. Org. Chem.*, 2016, **81**, 12443–12450.

40 I. Nakanishi, S. Itoh, T. Suenobu, H. Inoue and S. Fukuzumi, Redox Behavior of Active Aldehydes Derived from Thiamin Coenzyme Analogs, *Chem. Lett.*, 1997, **26**, 707–708.

41 I. Nakanishi, S. Itoh, T. Suenobu and S. Fukuzumi, Direct Observation of Radical Intermediates While Investigating the Redox Behavior of Thiamin Coenzyme Models, *Angew. Chem. Int. Ed.*, 1998, **37**, 153–156.

42 Y. Cai, S. Chatterjee and T. Ritter, Photoinduced Copper-Catalyzed Late-Stage Azidoarylation of Alkenes via Arylthianthrenium Salts, *J. Am. Chem. Soc.*, 2023, **145**, 13542–13548.

43 B. Lansbergen, P. Granatino and T. Ritter, Site-Selective C–H Alkylation of Complex Arenes by a Two-Step Aryl Thianthrenation–Reductive Alkylation Sequence, *J. Am. Chem. Soc.*, 2021, **143**, 7909–7914.

44 Y.-H. Zhao, L.-C. Wang and X.-F. Wu, Controllable Copper-Catalysed Photo-Induced Carbonylative Cyclization to Access Dihydroquinolines and Oxindoles, *Chem. Sci.*, 2026, **17**, 4632–4639.

45 J. Zhang, R.-H. A, C. Xu and X.-F. Wu, Photoinduced Copper-Catalyzed Carbonylation of Arylthianthrenium Salts with Aryl Boronates toward Ketones, *ACS Catal.*, 2026, **16**, 1958–1965.

46 Z. Bai and T. Ritter, Thianthrenium Salts in Photochemistry, *Acc. Chem. Res.*, 2026, **59**, 915–931.

47 A. V. Bay, K. P. Fitzpatrick, R. C. Betori and K. A. Scheidt, Combined Photoredox and Carbene Catalysis for the Synthesis of Ketones from Carboxylic Acids, *Angew. Chem. Int. Ed.*, 2020, **59**, 9143–9148.

48 Y. Sato, Y. Goto, K. Nakamura, Y. Miyamoto, Y. Sumida and H. Ohmiya, Light-Driven N-Heterocyclic Carbene Catalysis Using Alkylborates, *ACS Catal.*, 2021, **11**, 12886–12892.

49 Z.-L. Chen, S.-C. Ma, S.-Y. Tang, H.-Y. Yu, Y. Zhao and J. Xuan, Visible-Light-Driven Borylacylation of Alkenes by NHC/Photoredox Dual Catalysis: Accessing Boryl 1,4-Dicarbonyl Architectures, *ACS Catal.*, 2025, **15**, 7101–7111.

50 J. Liu, X.-N. Xing, J.-H. Huang, L.-Q. Lu and W.-J. Xiao, Light Opens a New Window for N-Heterocyclic Carbene Catalysis, *Chem. Sci.*, 2020, **11**, 10605.

51 X. Wang, S. Wu, R. Yang, H. Song, Y. Liu and Q. Wang, Recent advances in combining photo- and N-heterocyclic carbene catalysis, *Chem. Sci.*, 2023, **14**, 13367–13383.

52 H. Ohmiya, N-Heterocyclic Carbene-Based Catalysis Enabling Cross-Coupling Reactions, *ACS Catal.*, 2020, **10**, 6862–6869.

53 A. Isakova, J. Parker, C. J. Nwosu, J. R. Howse and K. Novakovic, Broadening the Scope of Pd-Catalyzed Oscillatory Carbonylation Reactions: Solvent, Substrate, Catalyst, *React. Kinet. Mech. Catal.*, 2019, **127**, 161–174.

54 X. Wu, J. Van Waeyenberg, D. Vangestel and B. Sels, The Overlooked Solvent Effects: A Reconsideration of the Paradigm in Semiconductor Photocatalysis, *Energy Environ. Sci.*, 2025, **18**, 1191–1204.

55 Y. Matsuki, N. Ohnishi, Y. Kakeno, S. Takemoto, T. Ishii and K. Nagao, Aryl radical-mediated N-heterocyclic carbene catalysis, *Nat. Commun.*, 2021, **12**, 3848.

56 W. Liu, A. Vianna, Z. Zhang, S. Huang, L. Huang, M. Melaimi, G. Bertrand and X. Yan, Mesoionic carbene-Breslow intermediates as super electron donors: Application to the metal-free arylacylation of alkenes, *Chem Catal*, 2021, **1**, 196–206.

57 F. Su, F. Lu, K. Tang, X. Lv, Z. Luo, F. Che, H. Long, X. Wu and Y. R. Chi, Organocatalytic C−H Functionalization of Simple Alkanes, *Angew. Chem. Int. Ed.,*2023, **62**, e202310072.

58 F. Su, J. Zou, X. Lv, F. Lu, Y. Long, K. Tang, B. Li, H. Chai, X. Wu and Y. R. Chi, Carbene-Catalyzed Intermolecular Dehydrogenative Coupling of Aldehydes with C(sp3)−H Bonds, *Angew. Chem. Int. Ed.*, 2023, **62**, e202303388.

59 N. Assani, L. Delfau, P. Smits, S. Redon, Y. Kabri, E. Tomás-Mendivil, P. Vanelle, D. Martin and J. Broggi, A simple N-heterocyclic carbene for the catalytic up-conversion of aldehydes into stoichiometric super electron donors, *Chem. Sci.*, 2024, **15**, 14699–14704.

60 R. Breslow, On the Mechanism of Thiamine Action. IV. Evidence from Studies on Model Systems, *J. Am. Chem. Soc.*, 1958, 80, 3719–3726.

61 M. Paul, J.-M. Neudörfl and A. Berkessel, Breslow Intermediates from a Thiazolin-2-ylidene and Fluorinated Aldehydes: XRD and Solution-Phase NMR Spectroscopic Characterization, *Angew. Chem. Int. Ed.*, 2019, 58, 10596–10600.

62 D. Enders, O. Niemeier and A. Henseler, Organocatalysis by N-Heterocyclic Carbenes, *Chem. Rev.*, 2007, 107, 5606–5655.

63 D. M. Flanigan, F. Romanov-Michailidis, N. A. White and T. Rovis, Organocatalytic Reactions Enabled by N-Heterocyclic Carbenes, *Chem. Rev.*, 2015, 115, 9307–9387.

64 V. Regnier, E. A. Romero, F. Molton, R. Jazzar, G. Bertrand and D. Martin, What Are the Radical Intermediates in Oxidative N-Heterocyclic Carbene Organocatalysis?, *J. Am. Chem. Soc.*, 2019, 141, 1109–1117.

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The data supporting this article have been included as part of the Supplementary Information.