

Visible-Light-Induced Radical Cascade Cross-Coupling via C(sp³)-H Activation and C-N/N-O Cleavage: Feasible Access to Methylenebisamide Derivatives

Jinglan Lei, Min Li,* Qingqing Zhang, Shuyang Liu, Haifang Li, Lei Shi, Wen-Feng Jiang, Chunying Duan, and Yunhe Jin*



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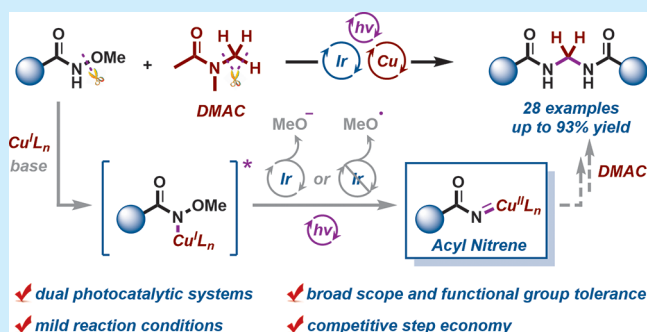


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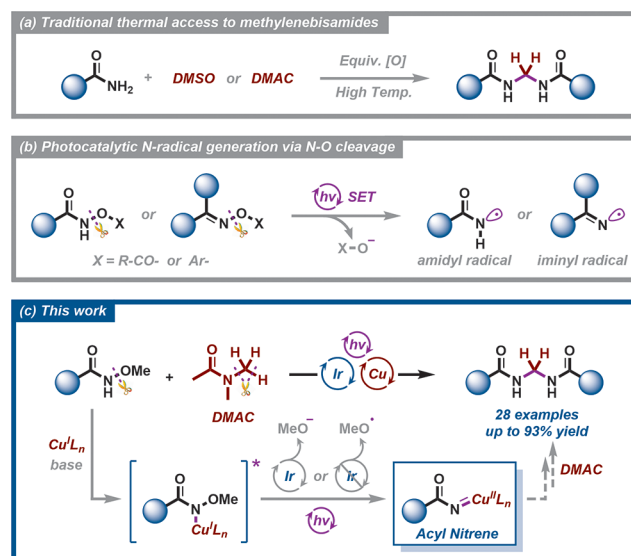
ABSTRACT: Here we report facile and manipulable access to methylenebisamide derivatives via visible-light-driven radical cascade processes incorporating C(sp³)-H activation and C-N/N-O cleavage. Mechanistic studies reveal that a traditional Ir-catalyzed photoredox pathway and a novel copper-induced complex-photolysis pathway are both involved, contributing to activating the inert *N*-methoxyamides and rendering the valuable bisamides. This approach exhibits many advantages, including mild reaction conditions, broad scope and functional group tolerance, and competitive step economy. Given the mechanistic plenitude and operational simplicity, we believe this package deal paves a promising way for the synthesis of valuable nitrogen-containing molecules.



The vicinal bisamide structural core is ubiquitous in natural products and pharmacologically active compounds.¹ Thereinto, methylenebisamides as one of the most important categories of this family find wide applications in the synthesis of peptidomimetic compounds and inhibitors against HIV-1 integrases.² Amides or nitriles were generally used in the traditional synthesis of methylenebisamides with formaldehyde as a methylene source.³ Following reports on other methylene precursors include dimethyl sulfoxide (DMSO)⁴ and *N,N*-dimethylacetamide (DMAC)⁵ as substitutes for formaldehyde (Scheme 1a). However, these approaches always suffer from high temperature and consumption of equivalent strong oxidants to our knowledge.^{4,5}

Recently, photocatalysis has been developed as an environmentally friendly, sustainable, and unique process for the construction of C-N bonds with an open-shell pathway.⁶ Photogenerated amidyl and iminyl radicals exhibit remarkable activities in providing nitrogen-containing compounds under mild conditions.⁷ With the development of the built-in oxidant strategy,⁸ *N*-hydroxyamide and ketoxime analogues have been proved to be efficient *N*-radical sources via N-OX cleavage.⁹ Among these kinds of substrates, strong electron-withdrawing X groups including acyl and electron-deficient aryl groups are always essential to facilitate the single electron transfer (SET) process between the substrate and photocatalyst (Scheme 1b). A similar SET becomes challenging with X = alkyl (especially for methyl) instead. In our design, introduction of a transition metal ion into the system may result in a photosensitive metal-

Scheme 1. Approaches for the Construction of Methylenebisamide Derivatives



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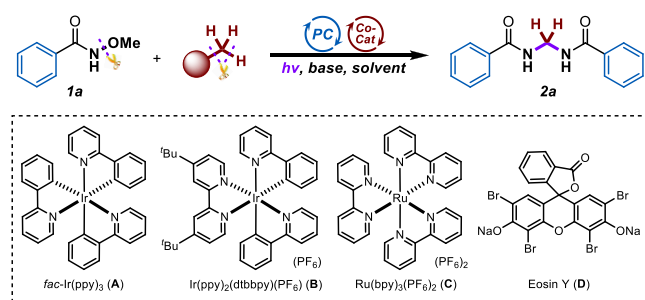
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substrate complex, accelerating the photolysis of *N*-methoxyamide in the presence or absence of photocatalysts. Meanwhile, the stable metal-nitrene produced from metal-induced photolysis effectively promotes the radical–radical coupling process that is a pivotal but always challenging step in photocatalytic cascade reactions.¹⁰ Depending on the above opinion and our previous experience on light-driven synthetic chemistry,¹¹ we herein envision to realize a photo/copper dual-catalyzed radical cascade synthesis of valuable methylenebisamide derivatives with inert *N*-methoxyamide as the amide source and DMAC as the methylene donor under moderate conditions (Scheme 1c).

We started our exploration with the model reaction from *N*-methoxybenzamide (**1a**) to *N,N'*-methylenebisbenzamide (**2a**) in the presence of DMAC under irradiation of 405 nm LEDs. As shown in Table 1, the target product **2a** was successfully

Table 1. Optimization of the Reaction Conditions^a



Entry	PC	Co-catalyst	Base	Solvent	Yield% ^b
1	A	FeCl ₃	KO ^t Bu	DMAC	59
2	A	FeCl ₃	Cs ₂ CO ₃	DMAC	76
3	A	FeCl ₃	K ₃ PO ₄	DMAC	trace
4	A	FeCl ₃	K ₂ CO ₃	DMAC	14
5	A	FeCl ₃	Pyridine	DMAC	trace
6	A	FeCl ₃	Cs ₂ CO ₃	DMF	69
7	A	FeCl ₃	Cs ₂ CO ₃	DMSO	7
8	A	FeCl ₃	Cs ₂ CO ₃	1,4-Dioxane ^c	47
9	A	FeCl ₃	Cs ₂ CO ₃	CH ₃ CN ^c	23
10	A	FeCl ₂	Cs ₂ CO ₃	DMAC	60
11	A	NiCl ₂	Cs ₂ CO ₃	DMAC	67
12	A	CuCl	Cs₂CO₃	DMAC	92
13	A	CuCl ₂	Cs ₂ CO ₃	DMAC	47
14	A	Cu(NO ₃) ₂	Cs ₂ CO ₃	DMAC	35
15	A	MnCl ₂	Cs ₂ CO ₃	DMAC	55
16	B	CuCl	Cs ₂ CO ₃	DMAC	68
17	C	CuCl	Cs ₂ CO ₃	DMAC	53
18	D	CuCl	Cs ₂ CO ₃	DMAC	51

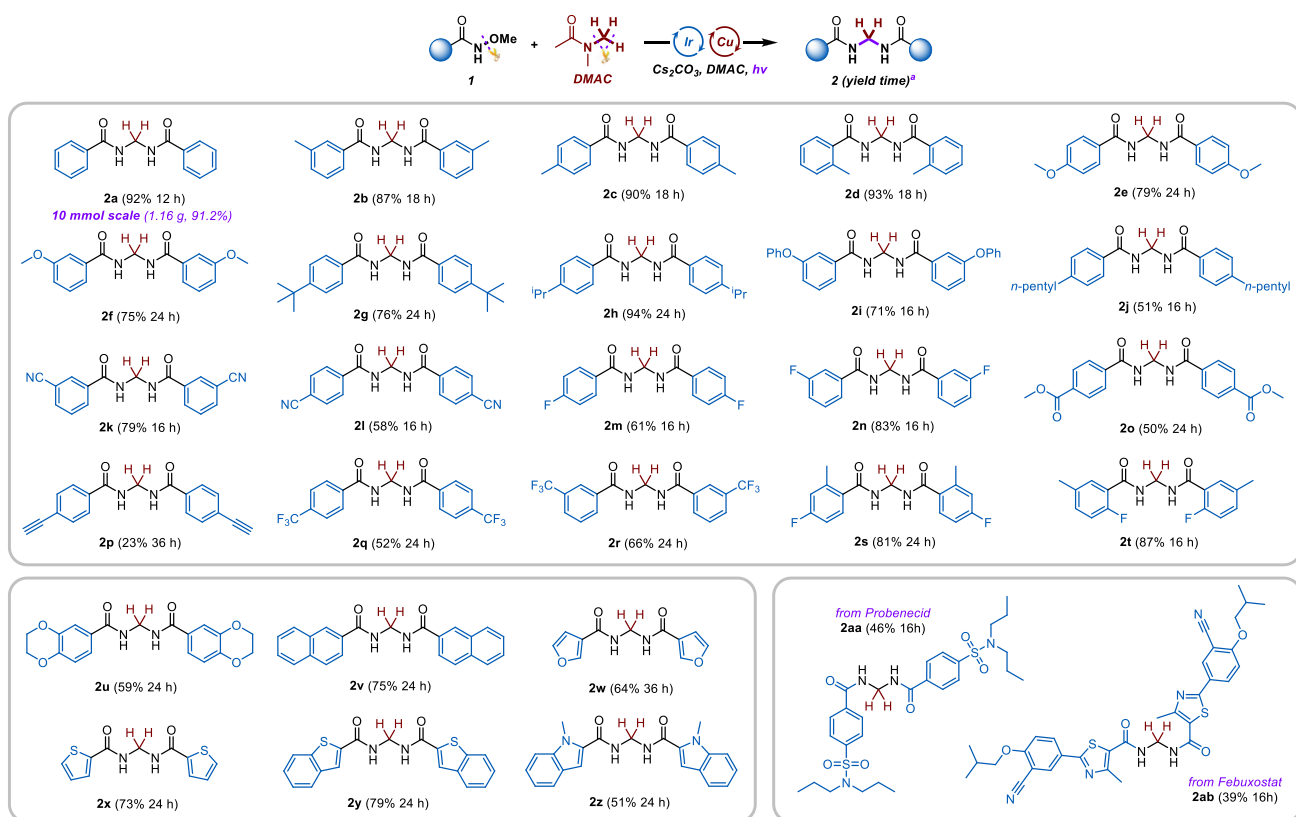
^aReaction conditions: **1a** (0.2 mmol), photocatalyst (PC) (2×10^{-5} equiv), cocatalyst (0.1 equiv), base (1.0 equiv), solvent (2.0 mL) under N₂ and 30 W 405 nm LEDs for 12 h. ^bIsolated yield. ^cDMAC (10 equiv) in 2 mL of solvent.

obtained in 59% yield with *fac*-Ir(ppy)₃ as the photocatalyst, FeCl₃ as the metal cocatalyst, and KO^tBu as the base (entry 1). Base screening exhibited that Cs₂CO₃ was the most suitable choice among various organic and inorganic bases (entries 1–5, for more details see Table S1). Next, testing of different methylene donors showed *N,N*-dimethylformamide (DMF) to be a comparable donor to DMAC and DMSO to be a bad one (entries 6 and 7). Other solvents with 10 equiv of DMAC as the methylene source were also tried, but no better outcomes were

given (entries 8–9, for more details see Table S2). The metal cocatalyst plays a vital role in activating the substrate to initiate the tandem reaction. To further improve the reaction efficiency, different kinds of transition metal salts were screened (entries 10–15, for more details see Table S3). To our delight, CuCl delivered a remarkable result in 92% yield (entry 12). Switching the photocatalyst to other ones led to lower yields (entries 16–18, for more details see Table S4). Moreover, increasing the catalyst loading scale did not mean a promoted performance in general but provided additional benzamides as byproducts on the contrary (Table S5).

With the optimized reaction conditions established, we then exploited the substrate scope of this dual-catalyzed bisamidation protocol (Scheme 2). Initially, various substituted *N*-methoxybenzamides were tested. Pleasingly, amides bearing electron-donating or electron-withdrawing functional groups at the *ortho*-, *meta*-, or *para*-positions were all applicatory substrates, affording the desired methylenebisamides in moderate to excellent yields (**2a–2t**). To be noted, incorporation of strong electron-withdrawing substituents including –CN (**2k**, **2l**), –COOMe (**2o**), and –CF₃ (**2q**, **2r**) seems to be detrimental to this transformation. Assembling this kind of group on the *meta*-position instead of the *ortho*-one can reduce the impact of the negative effect (compare **2k** and **2l** and **2q** and **2r**). Substrates carrying multiple substituents also reacted smoothly to deliver the corresponding products **2s** and **2t** in good yields. Furthermore, *N*-methoxyamides derived from polycyclic and heterocyclic aromatic acids, such as furan-3-carboxylic acid and benzo[*b*]thiophene-2-carboxylic acid, known as poisons to metal catalysts,¹² were also examined and displayed satisfying yields (**2u–2z**). The synthetic utilization of this protocol in late-stage functionalization was explored next through direct bisamidation of complex substrates derived from drug molecules, *Probenecid* and *Febuxostat*. To our satisfaction, the corresponding bisamide was successfully acquired in moderate yields (**2aa**, **2ab**). Moreover, a gram-scale synthesis was carried out with 10 mmol of **1a** to test the scalability of this protocol, and the final product **2a** was obtained in a comparable yield (91.2%, for more details see SI).

In attempt to gain more insights into this bisamidation transformation, a combination of experimental mechanistic studies were then conducted (Scheme 3). First, several control experiments were performed, unfolding the necessity of light, copper catalyst, and base (Scheme 3a). To our surprise, the reaction could still render **2a** in a moderate yield without a photocatalyst, which is always the vital component for absorbing and transforming optical energy in most photodriven systems. Addition of a radical scavenger, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), almost completely suppressed the formation of product **2a**, demonstrating a radical pathway involved in the system. The light on–off experiment with **1a** synchronously certified the requirement of constant irradiation and little radical-chain contribution (Figure S2). Different leaving groups were examined next (Scheme 3b). The preliminary results presented that benzamide (**3a**) and *N*-methylbenzamide (**3b**) were not effective substrates for this method. The reaction from *N*-ethoxybenzamide (**3c**) gained the desired **2a** in only 29% yield, while no valid outcome was achieved with *tert*-butoxy (**3d**) or phenoxy (**3e**) as the leaving group instead of methoxy. *N*-(Benzoyloxy)benzamide (**3f**) was found to be a competitive substrate with moderate reaction efficiency due to the good leaving ability of BzO. Further investigation on the photocatalyst-free catalytic cycle was conducted via UV/vis absorption

Scheme 2. Substrate Scope^b

^aIsolated yield. ^bReaction conditions: **1** (0.2 mmol), Ir(ppy)₃ (2 × 10⁻⁵ equiv), CuCl (0.1 equiv), Cs₂CO₃ (1.0 equiv), DMAC (2.0 mL) under N₂ and 30 W 405 nm LEDs.

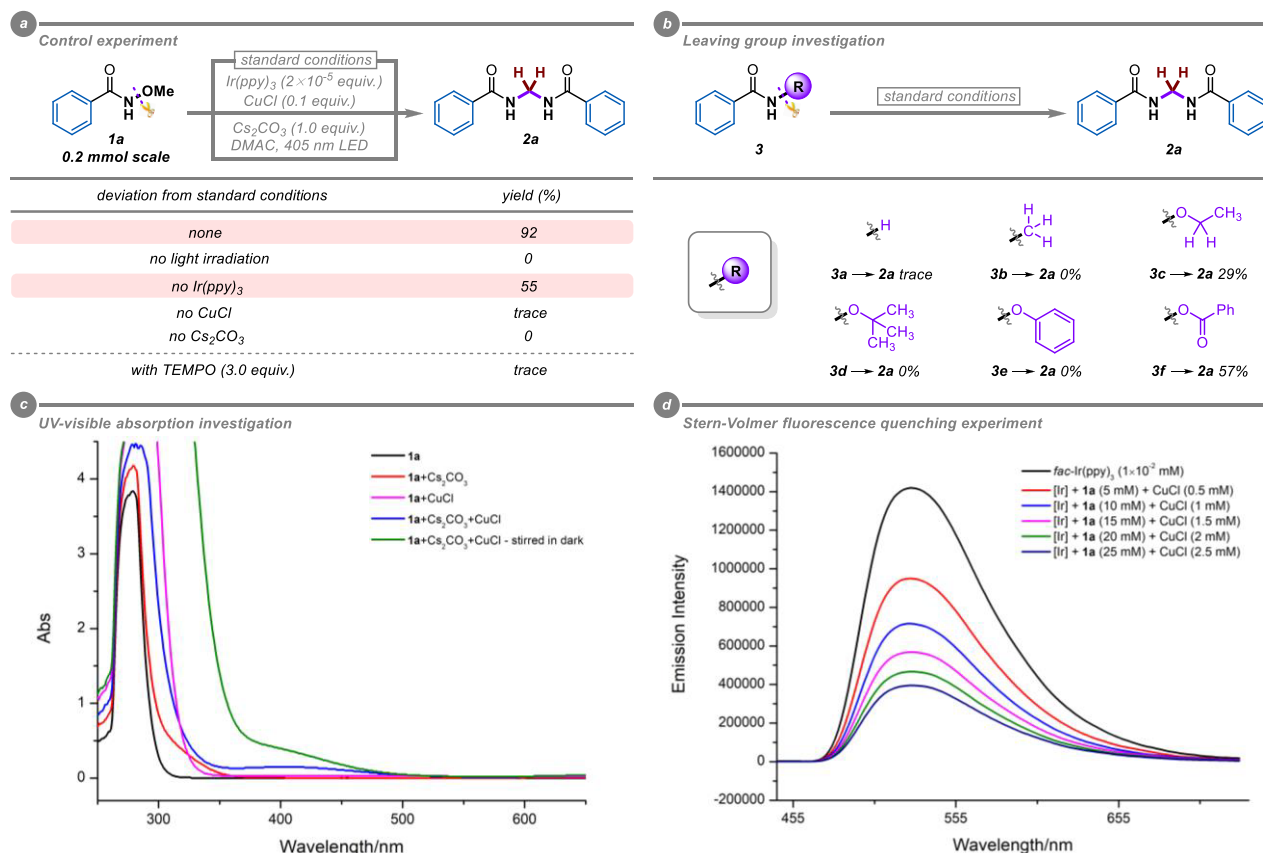
spectroscopy. As displayed in Scheme 3c, no obvious absorption in the visible range was observed for either **1a** or a simple mixture of **1a** and CuCl/base. Excitingly, a ternary mixture of **1a**, CuCl, and Cs₂CO₃ produced a visible-range absorption peak near 410 nm, and the absorption became stronger after stirring the mixture under dark. This phenomenon revealed that it seemed plausible to form a photosensitive complex between the copper catalyst and the anion of *N*-methoxybenzamide. Our following attention was focused on the initial SET procedure of the Ir-catalyzed cycle through Stern–Volmer fluorescence quenching experiments. After several attempts, we found that no single component included in the catalytic system, such as **1a**, CuCl, Cs₂CO₃, and DMAC, could efficaciously quench the luminescence of Ir(ppy)₃ excited at 375 nm under the reaction conditions (Figures S4–S7). Interestingly, the luminescence was rapidly and regularly quenched by simultaneous addition of **1a** and CuCl, suggesting a SET process between the excited Ir catalyst and copper-methoxyamide complex (Scheme 3d, for more details see Figure S8). The crossover experiment with a mixture of **1a** (0.1 mmol) and **1n** (0.1 mmol) as substrate gave a ternary mixture of methylenebisamides (**2a:2a + n:2n = 1.50:2.58:1**) in a total yield of 86% (Scheme 4a, for more details see Figure S9). The isotope labeling experiment with DMAC-*d*₉ as solvent provided the deuterated **2a** in 90% yield, demonstrating DMAC to be the methylene precursor in this system (Scheme 4b, for more details see Figure S10). To confirm our assumption for the existence of an acyl nitrene intermediate, the reaction with PPh₃ was exploited under standard conditions, and the expected corresponding product **4** was obtained in 52% yield (Scheme 4c).^{9b} Besides, the

methoxyamides derived from alkyl carboxylic acids were proved to be inapplicable substrates for this reaction (Scheme 4d).

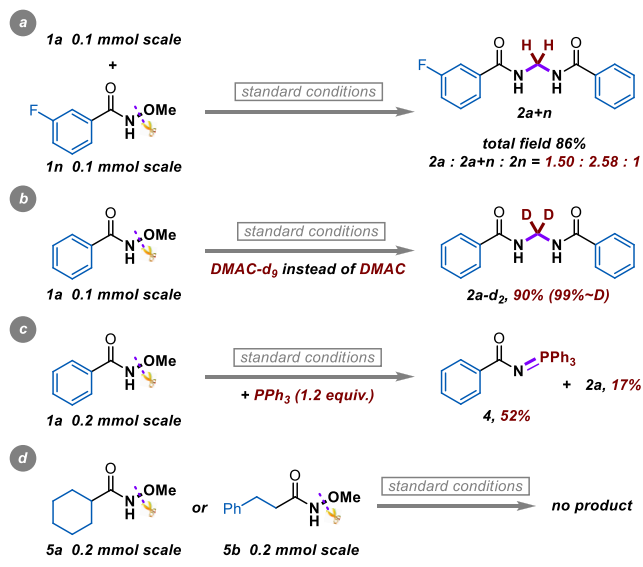
On the basis of these observations, the plausible reaction mechanism is depicted in Scheme 5. First, integrating anion **A** from alkalization of **1** with copper catalyst gives the important photosensitive complex **B** in the photocatalyst-free cycle (Path I). Direct photolysis of **B** generates copper nitrene **C** and a hydrogen atom transfer (HAT)-active methoxyl radical. A subsequent HAT from DMAC to a methoxyl radical delivers α -amino radical **D**, followed by the formation of another copper complex **E** via incorporating **C** and **D**. β -Elimination of **E** provides imine **F** and MeNHAc which is detected as a byproduct by GC-MS (Figure S11). Another HAT between **C** and DMAC results in amidyl complex **G**, and the following combination of **F** and **G** produces the methylenebisamidyl complex **H**.^{4a,c} Protonation of **H** furnishes the final product **2**. In the Ir-catalyzed cycle, the foremost SET from excited *Ir(III) to **A** under the existence of copper catalyst affords **C** and a methoxyl anion (Path II). Another SET finishing the iridium cycle from Ir(IV) to DMAC and a subsequent deprotonation also supply radical **D**. Therefore, the two cycles undergo the same intermediates **C** and **D**, while addition of iridium catalyst formally accelerates the photolysis of **B** and consequently promotes the reaction efficiency.

In conclusion, facile and manipulable access to methylenebisamide derivatives has been developed through visible-light-mediated radical cascade synthesis via C(sp³)–H activation and C–N/N–O cleavage. This approach is characterized by mild reaction conditions, broad scope and functional group tolerance, and competitive step economy. Mechanistic experimental

Scheme 3. Experimental Mechanistic Studies

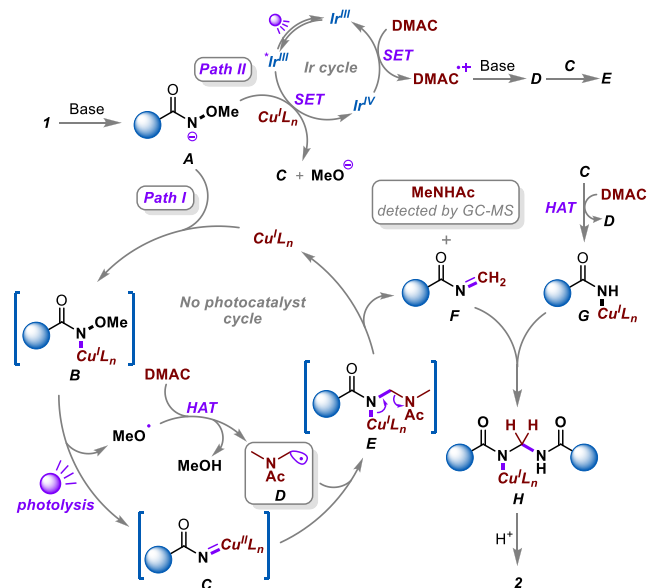


Scheme 4. Additional Control Experiments



investigations disclose that both a traditional Ir-catalyzed photoredox pathway and a novel copper-induced complex-photolysis pathway contribute to activating the inert *N*-methoxyamides and rendering the value-added bisamides. Given the mechanistic plenitude and operational simplicity of this method, we anticipate this work will bring rewarding inspiration for the synthesis of high-value-added nitrogen-containing molecules.

Scheme 5. Proposed Reaction Pathway



■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.3c00646>.

Mechanism investigations, synthetic procedures, characterization data, and ^1H and ^{13}C NMR spectra of these synthesized compounds (PDF)

AUTHOR INFORMATION

Corresponding Authors

Min Li – Experiment Center of Chemistry, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China; Email: nulilimin@dlut.edu.cn

Yunhe Jin – State Key Laboratory of Fine Chemicals, Zhang Dayu School of Chemistry, Dalian University of Technology, Dalian 116024, China; orcid.org/0000-0003-0626-4587; Email: jinyh18@dlut.edu.cn

Authors

Jinglan Lei – State Key Laboratory of Fine Chemicals, Zhang Dayu School of Chemistry and Experiment Center of Chemistry, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

Qingqing Zhang – State Key Laboratory of Fine Chemicals, Zhang Dayu School of Chemistry, Dalian University of Technology, Dalian 116024, China

Shuyang Liu – State Key Laboratory of Fine Chemicals, Zhang Dayu School of Chemistry, Dalian University of Technology, Dalian 116024, China

Haifang Li – MOE Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology, Department of Chemistry, Tsinghua University, Beijing 100084, China; orcid.org/0000-0002-0447-4655

Lei Shi – State Key Laboratory of Fine Chemicals, Zhang Dayu School of Chemistry, Dalian University of Technology, Dalian 116024, China; orcid.org/0000-0002-2644-1168

Wen-Feng Jiang – Experiment Center of Chemistry, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

Chunying Duan – State Key Laboratory of Fine Chemicals, Zhang Dayu School of Chemistry, Dalian University of Technology, Dalian 116024, China; orcid.org/0000-0003-1638-6633

Complete contact information is available at:

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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