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Construction of All-Carbon Quaternary Stereocenters via Sequential Photoactivation/Isothiourea Catalysis

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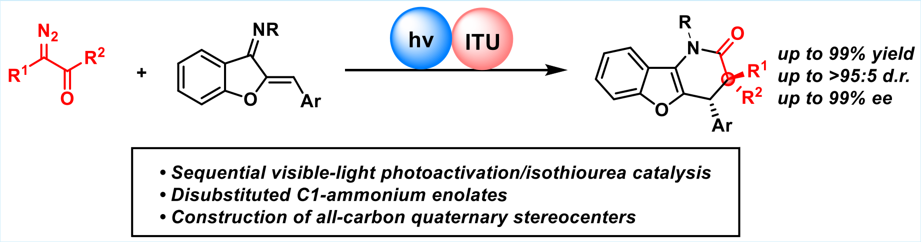
Supporting Information



- *Sequential visible-light photoactivation/isothiourea catalysis*
- *Disubstituted C1-ammonium enolates*
- *Construction of all-carbon quaternary stereocenters*

ABSTRACT: Highly enantioselective [4 + 2] cyclizations of azadienes with in situ generated ketenes were developed through sequential visible-light photoactivation/isothiourea catalysis, which offers a novel approach for the creation of all-carbon quaternary stereocenters through disubstituted C1-ammonium enolates. The visible-light-induced sustained release of reactive ketene species through Wolff rearrangement of α-diazoketones is crucial for achieving high levels of chemical efficiency and stereoinduction.

The chiral isothioureas (ITUs)[1] have emerged as one of the most powerful organocatalysts for the discovery of novel asymmetric synthetic transformations, allowing access to a wide array of heterocycles and bioactive compounds. Since the first demonstration in 2008,[2] numerous chiral isothiourea catalyzed enantioselective transformations that proceed via an ammonium enolate intermediate[3] have been developed[4] and have shown promising applications in the field of catalytic organic synthesis. A wide range of carboxylic acids, esters, anhydrides, and acyl imidazoles[5] can be activated with ITUs to form C1-ammonium enolates (R^2 = H, Scheme 1a, left side)[3b] and can then react with a broad chemical class of electrophilic species, especially with transition-metal-mediated electrophiles developed recently.[6] However, despite remarkable progress achieved in the past decade, many challenges remain. The generation of disubstituted C1-ammonium enolates ($R^2 \neq H$) from readily available starting materials for the enantioselective construction of all-carbon quaternary stereocenters[7] represents one of the most challenging tasks (Scheme 1a, right side).

Ketenes are a family of privileged C2-synthons for [2 + *n*] annulations in organic synthesis.[8] Within this area, disubstituted ketenes (isolated or generated *in situ*) have proven to be versatile building blocks for the construction of all-carbon quaternary stereocenters catalyzed by nucleophilic Lewis bases,[9] such as cinchona alkaloid derivatives,[10] planar-chiral ferrocene catalysts,[11] *N*-heterocyclic carbenes (NHCs),[12] and chiral phosphine catalysts.[13] Notably, photochemistry[14] has proved to be an efficient and green synthetic method for the generation of ketenes through Wolff rearrangement[15] of α-diazoketones, which opens up new opportunities for sequential annulation reactions (Scheme 1b). The pioneering work reported by the Lectka group introduced the sequential photoactivation and chiral amine catalysis in the mechanistic study of the asymmetric [2 + 2] annulation reaction of ketenes and imines.[16] Recently, the Xiao group successfully developed the photoinduced Wolff rearrangement/Pd-catalyzed [2 + *n*] cycloaddition sequence, which provides rapid access to a wide variety of functionalized heterocyclic compounds.[17] Intrigued by their work, and our research interests[18] in Lewis base catalysis, we developed a novel approach to efficient access of disubstituted C1-ammonium enolates from photogenerated ketenes and ITUs. With this purpose in mind, aurone-derived α,β-unsaturated imines[19] were carefully selected as suitable electrophilic partners owing to their driving force of aromatization (Scheme 1c). This class of compounds has been widely employed as a privileged four-atom synthon in asymmetric [4 + *n*] annulation reactions.[20] Here we report the sequential photoinduced Wolff rearrangement/chiral isothiourea-catalyzed transformation of α-diazoketones and azadienes for the construction of benzofuran-fused heterocyclic compounds bearing all-carbon quaternary stereocenters.

Initially, the model reaction of α-diazoketone **1a** and auronederived α,β-unsaturated imine **2a** was investigated via sequential visible-light photoactivation[17] and Lewis base catalysis (Table 1). Screening of Lewis base catalysts (**LB**) including NHC precatalysts **4**, benzoylquinine **5**, and ITU catalyst **6a** revealed the superiority of the ITU catalyst **6a** with regard to both catalytic activity and stereoinduction (Table 1, entries 1−3 vs 4). Encouraged by this, further optimization was done with a survey of the ITU catalysts **6** (entries 4−9), and

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Scheme 1. Construction of All-Carbon Quaternary Stereocenters via Disubstituted C1-Ammonium Enolate Catalysis

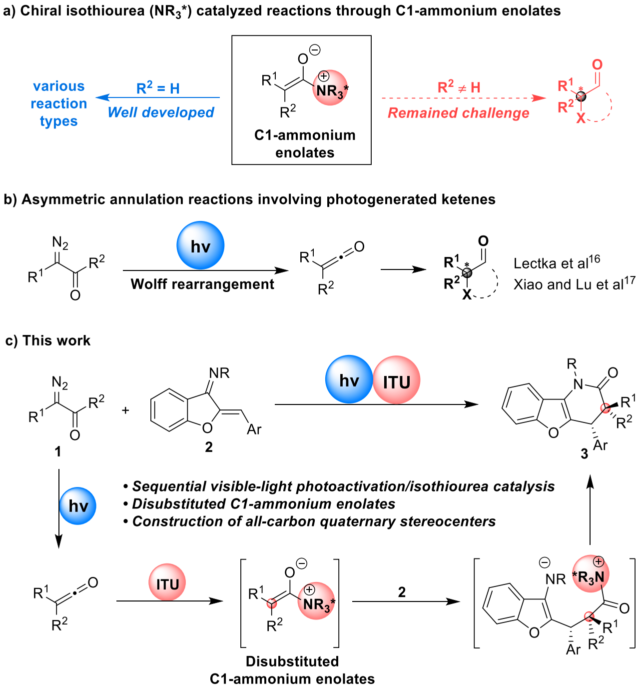
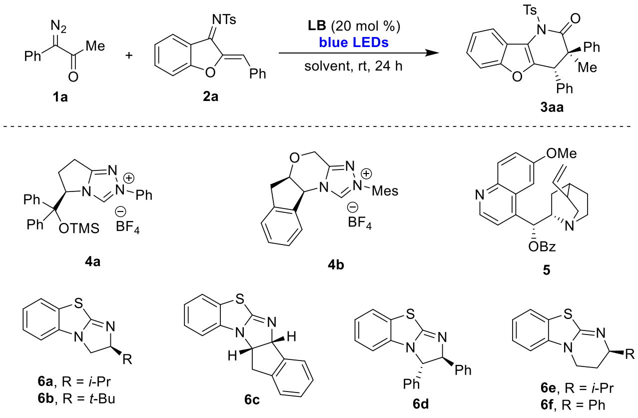


Table 1. Condition Optimization[a]



entry	LB	solvent	yield (%)[b]	d.r.[c]	ee (%)[d]
1[e]	**4a**	THF	53	62:38	11(2)
2[e]	**4b**	THF	33	67:33	2(2)
3	**5**	THF	35	55:45	8(5)
4	**6a**	THF	69	89:11	82
5	**6b**	THF	<5		
6	**6c**	THF	75	82:18	71[f]
7	**6d**	THF	69	>95:5	97
8	**6e**	THF	69	89:11	75
9	**6f**	THF	54	77:23	41
10	**6d**	$CDCl_3$	88	>95:5	97
11	**6d**	*i*-Pr_2O	96	>95:5	98
12[g]	**6d**	*i*-Pr_2O	96	>95:5	99
13[g]	–	*i*-Pr_2O	n.d.		
14[g,h]	**6d**	*i*-Pr_2O	n.d.		

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), and Lewis base catalyst (20 mol %) in solvent (1.0 mL) at rt under the irradiation of 5 W × 2 m blue LED strips for 24 h. [b]NMR yields. [c]The diastereomeric ratios were determined by ^1H NMR spectroscopic analysis. [d]The ee values were determined by HPLC. The ee of the minor diastereomer is shown in parentheses. [e]With Cs_2CO_3 (20 mol %). [f]The opposite enantiomer was obtained. [g]Diisopropyl ether (*i*-Pr_2O, 2.0 mL) was used. [h]In the dark. Ts: tosyl. n.d. = not detected.

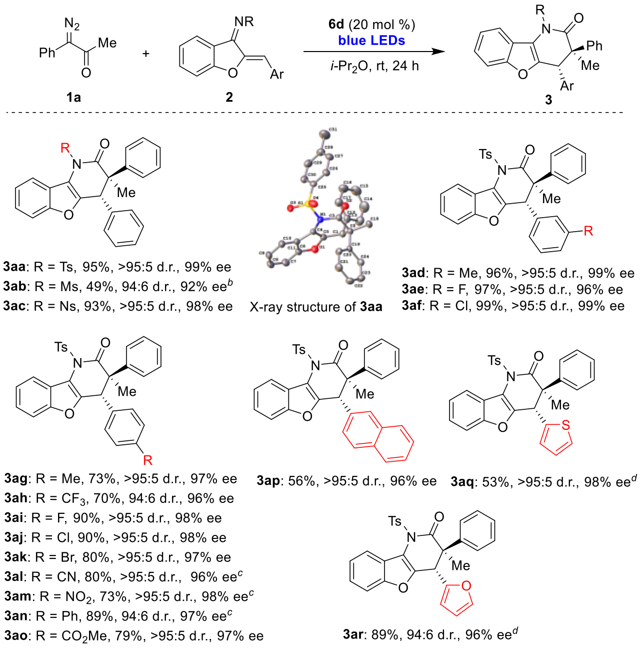
the newly designed catalyst **6d** was proven to be the optimal one (entry 7). The results of the solvent screen (entries 10 and 11; see Table S1 in Supporting Information for details) showed that the use of diisopropyl ether gave the best results (entry 11). The enantioselectivity was further improved at lower reactant concentrations (entry 12). In the absence of **6d** or light, no desired product was detected, thus indicating that the ITU catalyst and light irradiation were both crucial to promote the transformation (entries 13 and 14).

With the optimal conditions in hand, the generality of this protocol was evaluated initially by the reaction of α-diazoketone **1a** with various azadienes **2** (Scheme 2). A variety of *N*-substituents, including Ts, Ms, and Ns, were tolerated to give **3aa**–**3ac** in yields ranging from 49% to 95% with high levels of stereoselectivity (up to >95:5 d.r. and 99% ee). A range of aurone-derived α,β-unsaturated imines containing both electron-donating and electron-withdrawing substituents at the meta or para positions of the benzene ring were well-tolerated, and the desired benzofuran derivatives (**3ad**–**3ao**) were obtained in 70–99% yields with excellent stereoselectivities (94:6–>95:5 d.r., 96–99% ee). Similarly, azadienes with other aromatic ring substituents, such as 2-naphthalene, 2-thiophene, and 2-furan, delivered the corresponding products (**3ap**–**3ar**) with satisfactory results. The structure and stereochemistry of the corresponding products were confirmed unambiguously by single-crystal X-ray diffraction analysis of **3aa** (CCDC 1941477).

We next turned our attention to the scope of the α-diazoketone component of the reaction. As indicated in Scheme 3, a diverse set of α-diazoketones **1** underwent the sequential Wolff rearrangement/ITU-catalyzed [4 + 2] annulation reaction smoothly, affording target benzofuran-fused dihydropyridinone derivatives **3** in high yields (up to 99%) with excellent stereocontrol (up to >95:5 d.r., up to 99% ee). When aryl-substituted 1-diazopropan-2-ones bear electron-donating or electron-withdrawing substituents at the para or meta positions on the benzene ring, the reaction led to the corresponding products (**3ba**–**3ka**) in good yields (87–99%) with excellent stereoselectivities (93:7–>95:5 d.r., 93–99% ee). In addition, aryl-substituted 1-diazopropan-2-ones bearing naphthyl and heteroaryl moieties were also good partners for this transformation and delivered products (**3la** and **3ma**) smoothly. Moreover, replacement of the methyl group of α-diazoketone **1a** with other linear alkyl groups, such as ethyl and *n*-butyl groups, afforded the desired products (**3na**, **3oa**, **3nf**, and **3pa**) in satisfactory results, albeit a prolonged reaction time and increased catalyst usage were necessary. However, simple monosubstituted α-diazoketones and aliphatic α-diazoketones were unreactive substrates for this reaction.

Further investigations were performed to gain a deeper mechanistic understanding of the sequential Wolff rearrangement/ITU-catalyzed [4 + 2] annulation reaction (Figure 1; see the Supporting Information for details). Initially, a one-pot two-step reaction was performed, involving the *in situ* formation of ketene **1a′** under the irradiation of blue light, followed by the addition of azadiene **2a** and chiral isothiourea catalyst **6d** (Figure 1a). Significant decreases in the activity and product selectivity were obtained (**3aa**, 23% yield, 91:9 d.r.,

Scheme 2. Substrate Scope for Azadienes[a]



3aa: R = Ts, 95%, >95:5 d.r., 99% ee
3ab: R = Ms, 49%, 94:6 d.r., 92% ee[b]
3ac: R = Ns, 93%, >95:5 d.r., 98% ee

X-ray structure of **3aa**

3ad: R = Me, 96%, >95:5 d.r., 99% ee
3ae: R = F, 97%, >95:5 d.r., 96% ee
3af: R = Cl, 99%, >95:5 d.r., 99% ee

3ag: R = Me, 73%, >95:5 d.r., 97% ee
3ah: R = CF$_3$, 70%, 94:6 d.r., 96% ee
3ai: R = F, 90%, >95:5 d.r., 98% ee
3aj: R = Cl, 90%, >95:5 d.r., 98% ee
3ak: R = Br, 80%, >95:5 d.r., 97% ee
3al: R = CN, 80%, >95:5 d.r., 96% ee[c]
3am: R = NO$_2$, 73%, >95:5 d.r., 98% ee[c]
3an: R = Ph, 89%, 94:6 d.r., 97% ee[c]
3ao: R = CO$_2$Me, 79%, >95:5 d.r., 97% ee

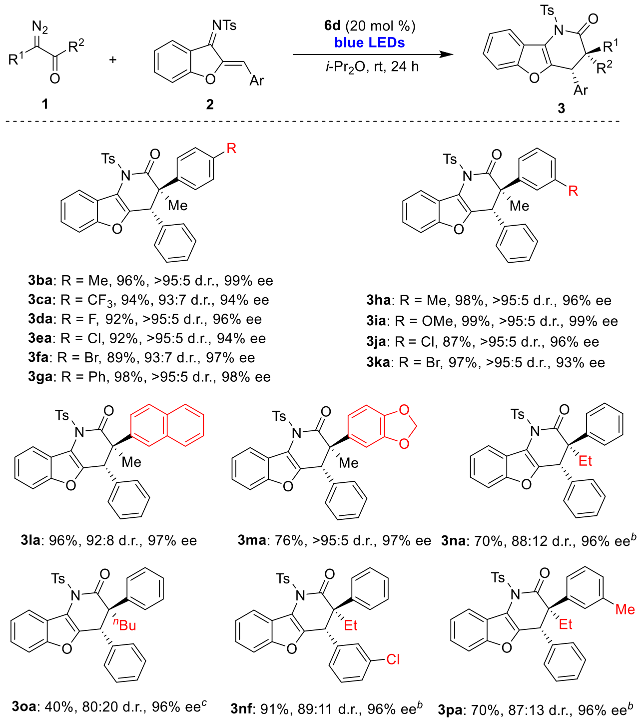
3ap: 56%, >95:5 d.r., 96% ee

3aq: 53%, >95:5 d.r., 98% ee[d]

3ar: 89%, 94:6 d.r., 96% ee[d]

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.1 mmol), and chiral isothiourea catalyst **6d** (20 mol %) in diisopropyl ether (2.0 mL) at rt under the irradiation of 5 W × 2 m blue LED strips for 24 h. Yields of isolated products **3**. The diastereomeric ratios were determined by ^{1}H NMR spectroscopic analysis. The ee values were determined by HPLC. [b] For 120 h. [c] For 72 h. [d] For 48 h.

Scheme 3. Substrate Scope for α-Diazoketones[a]



3ba: R = Me, 96%, >95:5 d.r., 99% ee
3ca: R = CF$_3$, 94%, 93:7 d.r., 94% ee
3da: R = F, 92%, >95:5 d.r., 96% ee
3ea: R = Cl, 92%, >95:5 d.r., 94% ee
3fa: R = Br, 89%, 93:7 d.r., 97% ee
3ga: R = Ph, 98%, >95:5 d.r., 98% ee

3ha: R = Me, 98%, >95:5 d.r., 96% ee
3ia: R = OMe, 99%, >95:5 d.r., 99% ee
3ja: R = Cl, 87%, >95:5 d.r., 96% ee
3ka: R = Br, 97%, >95:5 d.r., 93% ee

3la: 96%, 92:8 d.r., 97% ee

3ma: 76%, >95:5 d.r., 97% ee

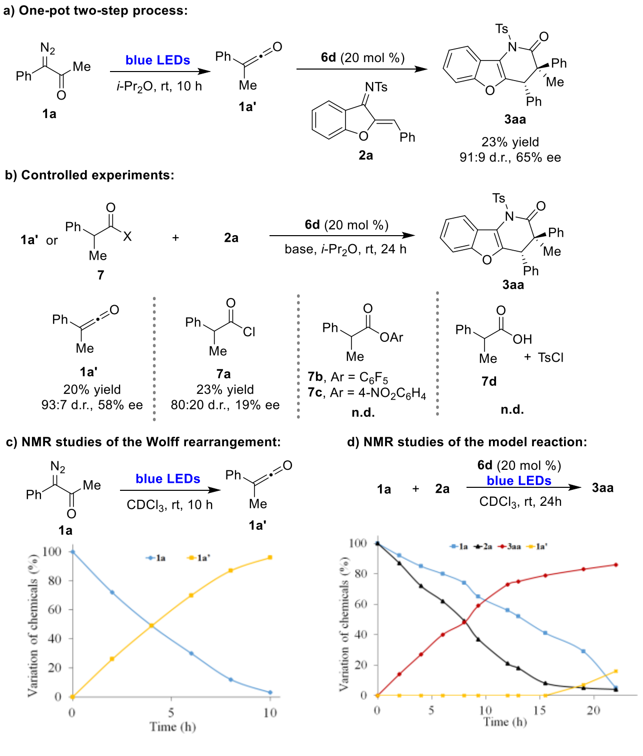
3na: 70%, 88:12 d.r., 96% ee[b]

3oa: 40%, 80:20 d.r., 96% ee[c]

3nf: 91%, 89:11 d.r., 96% ee[b]

3pa: 70%, 87:13 d.r., 96% ee[b]

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.1 mmol), and chiral isothiourea catalyst **6d** (20 mol %) in diisopropyl ether (2.0 mL) at rt under the irradiation of 5 W × 2 m blue LED strips for 24 h. Yields of isolated product **3**. The diastereomeric ratios were determined by ^{1}H NMR spectroscopic analysis. The ee values were determined by HPLC. [b] 30 mol % of **6d**, 96 h. [c] 40 mol % of **6d**, 120 h.


a) One-pot two-step process:

b) Controlled experiments:

c) NMR studies of the Wolff rearrangement:

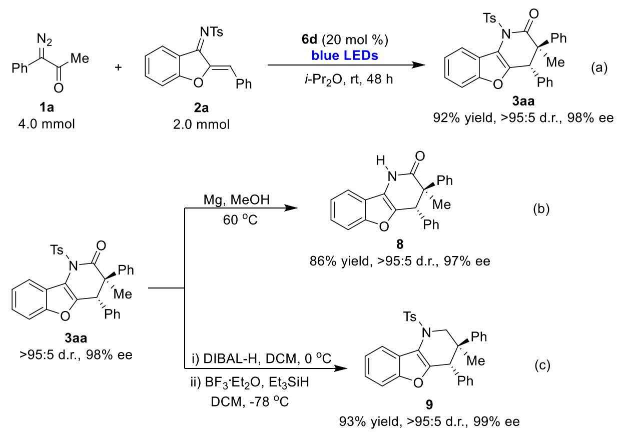
d) NMR studies of the model reaction:

Figure 1. Further investigations on the reaction mechanism.

and 65% ee). Next, we conducted several controlled experiments (Figure 1b). Use of an isolated ketene **1a′** or ketene precursor **7a** as a substrate would lead to the formation of **3aa** in low yield with poor stereocontrol. Carboxylic esters (**7b** and **7c**) and carboxylic acids **7d** (with TsCl as activator) were found to be unsuccessful reactants. Comparing these results (obtained in Figure 1a and 1b) with those achieved under standard conditions (Table 1, entry 12, **3aa** obtained in 95% yield, >95:5 d.r., and 99% ee), it is found that the *in situ* generation of ketenes through photoactivation offers many advantages and benefits over the previous situation. Finally, the reaction profile for the photoactivated Wolff rearrangement of **1a** was monitored by analyzing the ^{1}H NMR spectra of the reaction mixture, and almost quantitative conversion was completed after 10 h (Figure 1c). The diagram in Figure 1d shows the reaction profile for the model reaction. The ketene intermediate **1a′** was not detected until the sequential reaction was nearly complete. These results implied that the ITU-catalyzed [4 + 2] annulation reaction of ketene **1a′** is relatively faster than the photogeneration of **1a′**. All these results suggested the visible-light-induced sustained release of ketenes is identified as a vital factor for achieving high levels of reaction efficiency and stereocontrol in the sequential photoactivation/isothiourea catalysis.

The reaction of α-diazoketone **1a** with azadiene **2a** can be scaled-up to a 2.0 mmol scale successfully (Scheme 4, reaction a). The resulting dihydropyridinones are structurally interesting and ready for further chemical transformations. The *N*-tosyl group can be removed with magnesium powder in methanol (MeOH) at 60 °C to give the unprotected dihydropyridinone **8** in 86% yield, with >95:5 d.r., and 97% ee (Scheme 4, reaction b). The reduction of **3aa** using diisobutylaluminum hydride (DIBAL-H) and Et$_3$SiH/BF$_3$·Et$_2$O provided the chiral benzofuran-fused tetrahydropyridine

Scheme 4. Preparation of 3aa in 2.0 mmol Scale and Further Derivatizations



9 in 93% yield, with >95:5 d.r. and 99% ee (Scheme 4, reaction c).

In conclusion, we have disclosed an efficient method for the enantio- and diastereoselective construction of benzofuran-fused dihydropyridinone derivatives from α-diazoketones and azadienes through the sequential Wolff rearrangement/ITU-catalyzed [4 + 2] annulation reaction. A new general concept for the stereocontrolled creation of all-carbon quaternary centers has been developed via disubstituted C1-ammonium enolates by merging visible-light chemistry with isothiourea catalysis. Mechanistic studies identified that the visible-light induced sustained release of reactive ketene species through Wolff rearrangement is crucial to the success of this reaction.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02892.

Experimental procedures and spectroscopic data (PDF)

Accession Codes

CCDC 1941477 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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