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C–H Amination

Synthesis of Carbazoles and Related Heterocycles from Sulfilimines by Intramolecular C–H Aminations

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In memory of Rolf Huisgen

Abstract: *While direct nitrene insertions into C–H bonds have become an important tool for building C–N bonds in modern organic chemistry, the generation of nitrene intermediates always requires transition metals, high temperatures, ultraviolet or laser light. We report a mild synthesis of carbazoles and related building blocks through a visible light-induced intramolecular C–H amination reaction. A striking advantage of this new method is the use of more reactive aryl sulfilimines instead of the corresponding hazardous azides. Different catalysts and divergent light sources were tested. The reaction scope is broad and the product yield is generally high. An efficient gram-scale synthesis of Clausine C demonstrates the applicability and scalability of this new method.*

The ubiquity of C–N bonds decorating organic molecules existing in widespread areas makes the construction of C–N bonds one of the most attractive topics. Nitrene chemistry has a long history, possessing a distinct advantage in forging C–N bonds.[1] In the last decade, gold-catalyzed transformations involving nitrene transfer[2] from nitrene equivalents to C≡C triple bonds, forming highly reactive α-imino gold carbenes, have shown extraordinary advantages for the synthesis of heterocycles, as demonstrated by the representative work of Ye,[2f,g] Hashmi,[2a,e] Liu,[2b–d] and Gagosz.[2h,j] Nitrenes can also insert into C–H bonds to give disubstituted amines through C–N bond formations.[3] This reactivity is similar to the C–H insertions of the related carbenes, placing nitrenes among the most promising synthons for the construction of nitrogen-containing molecules. Despite indisputable advances in the field of nitrene chemistry, the generation of these intermediates from reagents such as azides,[4] iminoiodanes,[5] 2*H*-azirines[6] and dioxazolone derivatives[7] always requires transition metal catalysts with expensive ligands, high temperatures or strong UV-light irradiation, compromising principles of green chemistry. Reagents that can generate nitrenes using mild and green energy sources under transition-metal-free reaction conditions are still sparse.

Carbazoles and related heterocycles are widely found in a large number of natural products, such as Carprofen, Furostifoline, Atanisatin, Glycoborine, Siamenol, and the Clausine family (Figure 1).[8] The efficacy of the carbazole core to improve the druglikeness of pharmaceutically active molecules has also been the subject of extensive studies.[9] Moreover, the special properties of polymers based on carbazoles have enabled them to be versatile photosensitizers for photoreactions[10] and promising candidates for organic photovoltaic devices.[11]

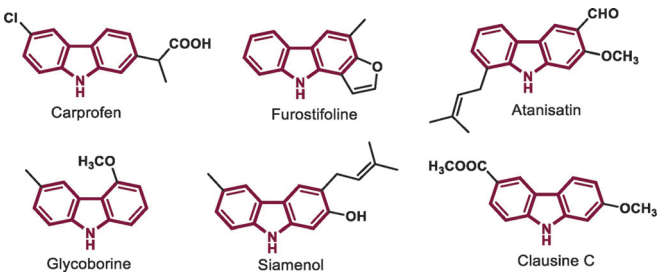

Figure 1. Representative carbazole-based natural products.

Consequently, the development of concise synthetic approaches to these privileged heterocyclic scaffolds has received considerable attention from the synthetic community. Main synthetic strategies include construction of a benzene ring by intermolecular[12] or intramolecular[13] cycloadditions of complex unsaturated systems through transition-metal catalysis or at high temperature, Pd-catalyzed intermolecular cross-coupling reactions,[14] transition-metal catalyzed intramolecular oxidative C–H amination reactions of *N*-substituted 2-amidobiphenyls[15] and intramolecular aryl nitrene C–H insertions.[16] Among these methods, those involving direct nitrene C–H insertions for the synthesis of unprotected carbazoles are particularly attractive. 2-Azido biaryls are commonly employed as nitrene precusors, primarily promoted by ultraviolet light,[16g] laser light[16f] or high temperature (180 °C).[16f] Recently, complex Fe catalysts[16b,c] or rhodium-dimer catalysts with complex ligands[4h,16d–f] were employed to decompose azides for the generation of metal

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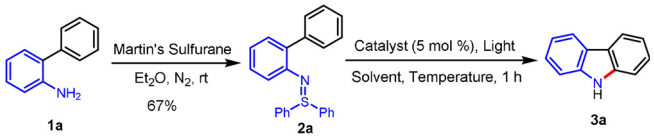
nitrene complexes, which subsequently inserted into aryl or alkenyl C–H bonds to afford carbazoles or indoles. Nitrogen as leaving group, however, may cause the danger of explosive decomposition in large scale reactions, which diminishes the synthetic applicability of these methods. For the synthesis of carbazoles, an elaborately designed aryl nitrene precursor which can overcome the above challenging issues, including security concerns and production costs, is highly desirable.

We herein report a new intramolecular C–H amination reaction towards unprotected carbazoles and related compounds by using novel *ortho*-substituted aryl sulfilimines[17] as substrates. The required sulfilimines can be readily prepared by a simple treatment of the corresponding anilines with Martin's sulfurane (Table 1).[18] With substrate **2a**, our study commenced preliminary with transition metal catalysis (Table 1). The generated metal nitrene intermediate inserts into the *ortho* C–H bond to give carbazole **3a**. At 70 °C, gold(I) catalysts, such as IPrAuCl, JohnPhosAuCl and JohnPhosAuSbF$_6$, afforded the target compound in poor yield (Table 1, entries 1–3). Gold(III) catalysts did not improve the reaction (Table 1, entries 4–5). Other metal salts, including Pd^{II}, Zn^{II}, Cu^{II}, gave no measurable boost in product yield (Table 1, entries 6–8). As mentioned above, the generation of rhodium nitrenes from azides always requires rhodium-dimer catalysts, in sharp contrast to this, herein a mononuclear rhodium catalyst, $Rh(OAc)_3$, successfully decomposed sulfilimine **2a** to afford carbazole **3a** in 90% yield (Table 1, entry 9). Light can also promote the decomposition of sulfilimine **2a**. UVA-irradiation efficiently afforded the target product in different solvents and performed best in THF (Table 1, entries 10–14). Milder light sources were also examined. Although white light worked less efficiently (Table 1, entry 16), blue LEDs led to a quantitative yield of **3a** (Table 1, entry 15). Without any catalyst and light source, no desired product was observed (Table 1, entry 17).

Table 1: Optimization of the reaction conditions.[a,b]



Entry	Catalyst[e]	Light Source	Temperature	Solvent	Yield of **3a** from **2a**
1	IPrAuCl	–	70 °C	DCE[d]	9%
2	JohnPhosAuCl	–	70 °C	DCE	10%
3	JohnPhosAuSbF$_6$	–	70 °C	DCE	14%
4	$AuBr_3$	–	70 °C	DCE	5%
5	$NaAuCl_4{\cdot}2H_2O$	–	70 °C	DCE	5%
6	$Pd(OAc)_2$	–	70 °C	DCE	13%
7	$Zn(OTf)_2$	–	70 °C	DCE	14%
8	$CuCl_2{\cdot}2H_2O$	–	70 °C	DCE	trace
9	**$Rh(OAc)_3$**	**–**	**70 °C**	**DCE**	**90%**
10	–	UVA	RT[c]	DCE	79%
11	–	UVA	RT	CH_3CN	76%
12	–	UVA	RT	CH_3OH	86%
13	–	UVA	RT	toluene	89%
14	–	UVA	RT	THF	90%
15	**–**	**Blue LEDs**	**RT**	**THF**	**99%**
16	–	CFL[g]	RT	THF	76%
17	–	–	RT or 70 °C	THF	n.d.[f]

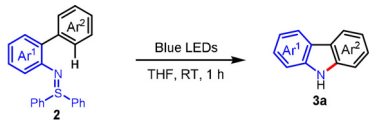
[a] Reaction conditions: for entries 1–9: **2a** (0.1 mmol), catalyst (0.005 mmol), DCE (1.0 mL, 0.1 M), 70 °C; for entries 10–16: **2a** (0.1 mmol), light source, solvent, room temperature; [b] the yield of **3a** was determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxyl benzene as the internal standard; [c] RT: room temperature; [d] DCE: 1,2-dichloroethane; [e] IPr: 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene; JohnPhos: (2-Biphenyl)di-tert-butylphosphine; [f] n.d.: not detected; [g] CFL: compact fluorescent lamp.

Under the optimized reaction conditions (Table 1, entry 15), we investigated the substrate scope (Table 2). First, substrates with different *ortho* aryls (Ar^2 shown in Table 2) were tested. Non-substituted carbazole **3a** was isolated in 95% yield. Substrates **2b–e** with chloro, methyl, *tert*-butyl and phenyl groups in *para* position underwent C–H aminations to form the expected products **3b–e** in excellent yield. As a comparison, the product yields by using $Rh(OAc)_3$ were shown in parentheses, clearly demonstrating that blue light is a better promoter for this transformation. Sulfilimine **2f** offered product **3f** (47%) and product **3f′** (52%) in 99% combined yield. 3-Methoxyl-substituted substrate **2g** presented a different selectivity, products **3g** and **3g′** were obtained in 52% and 43% yield. The 2-Chloro substituent was well tolerated under standard conditions, albeit in 89% yield (**3h**). With 2-Naphthalenyl group, C–H amination at 1-position to yield 11*H*-benzo[*a*]carbazole framework (**3i**) is preferred. Even π-conjugated pentacyclic frameworks **3j–k** were elegantly constructed in quantitative yields from the corresponding phenanthrene- and dibenzo[*b*,*d*]furan-containing ylides **2j–k**. Sulfilimines featuring a range of functional groups at Ar^1 (shown in Table 2) were also subjected to the standard conditions. *tert*-Butyl, fluoro, chloro, dichloro and trifluoromethoxy remained untouched in this reaction (**3l–o**). Substrate **2p** bearing a trifluoromethyl group and a bromo substituent was also readily cyclized to give the desired product. Notably, this reaction is compatible with functionalized sulfilimines, containing F, Cl, Br substituents. The obtained product **3q** would be an excellent substrate for further cross-coupling strategies. The products are not only confined to carbazole derivatives, other tricyclic compounds were also prepared. With *ortho* thiophen-3-yl group, the nitrene intermediate regioselectively inserted into the C–H bond at the 2-position to form a 8*H*-thieno[2,3-*b*]indole product (**3r**, 63%). γ-Carboline **3s** was obtained in 96% yield when *N*-pyridin-4-yl sulfilimine **2s** was irradiated.

To explore this C–H amination process further, we turned our attention to *ortho*-alkenyl aryl sulfilimines (Scheme 1). With sulfilimines **2t–v** in hand, we assessed their ability to undergo N–S bond cleavages and subsequent alkenyl C–H bond aminations. To our delight, the desired reaction proceeded smoothly and the indole products were obtained in moderate to good yield.

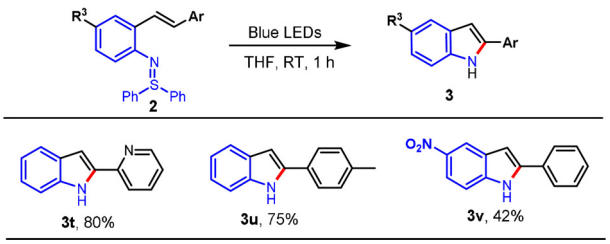
This reaction is efficiently scalable. Taking substrate **2w** as an example, the 1 mmol scale reaction afforded Clausine C in 94% yield (Scheme 2). A reaction on larger scale (2.6 mmol scale) was performed with a similar product yield. Especially, a gram-scale reaction delivered the desired product in 86% yield and the purification step only required simple filtration

Table 2: Scope for the synthesis of carbazole derivatives.[a,b]

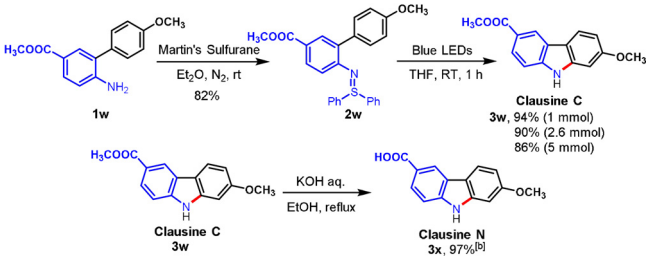


Substrate 2	Product 3	Substrate 2	Product 3
2a	3a, 95% (86%)[c]	2j	3j, 95% (57%)[c]
2b	3b, 95% (83%)[c]	2k	3k, 99%
2c	3c, 98% (90%)[c]	2l	3l, 80%
2d	3d, 99% (35%)[c]	2m	3m, 65%
2e	3e, 99% (87%)[c]	2n	3n, 92% (trace)[c]
2f	3f, 47% 3f', 52%	2o	3o, 83% (99%)[c]
2g	3g, 52% 3g', 43%	2p	3p, 96%
2h	3h, 89%	2q	3q, 96%
2i	3i, 78%	2r	3r, 63%
		2s	3s, 96%

[a] Reaction conditions: **2** (0.2 mmol), THF (2 mL, 0.1 M), blue LEDs, room temperature; [b] Yield of isolated product **3**; [c] Yield by using $Rh(OAc)_3$ (2.8 mg, 5 mol%, Table 1, entry 9) are shown in parentheses.



Scheme 1. Synthesis of indoles. Reaction conditions: **2** (0.2 mmol), THF (2 mL, 0.1 M), blue LEDs; Yield of isolated product **3**.



Scheme 2. Synthesis of Clausine C and a subsequent preparation of Clausine N.[a] [a] Yield of isolated product; [b] 0.5 mmol scale.

and wash without column chromatography. A KOH-mediated ester hydrolysis of Clausine C gave another natural product, Clausine N, in 97% yield.

We conducted two independent reactions for the synthesis of carbazole **3a** by using biphenyl azide **4a** and biphenyl sulfilimine **2a** to understand the difference between these two reagents (Figure 2). The line charts clearly illustrate that azide

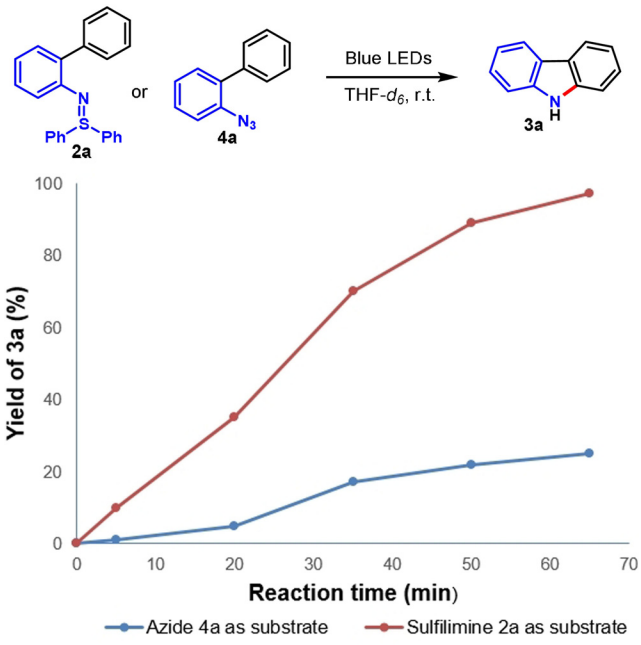
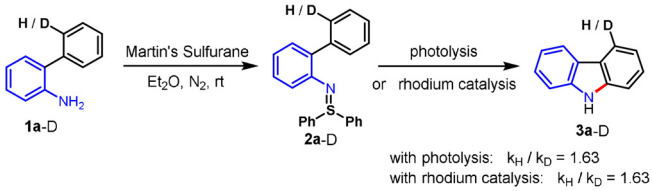


Figure 2. The difference between azide **4a** and sulfilimine **2a** in photolysis reactions. Yield of **3a** was determined by ^1H NMR spectroscopy with CH_2Br_2 as the internal standard.

4a afforded carbazole **3a** slowly with the prolongation of reaction time, while sulfilimine **2a** led to a much faster generation of the desired product. After a reaction time of approximate 65 minutes, sulfilimine **2a** gave a quantitative yield of carbazole **3a**, however, azide **4a** only delivered **3a** in lower than 30% yield with a low conversion, demonstrating that sulfilimine **2a** is more reactive than azide **4a**.

With monodeuterated substrate **1a**-D, two isotope experiments were conducted to understand the kinetic isotope effects of both the photoreaction and the rhodium-catalyzed transformation (Scheme 3). Same primary isotope effects of 1.63:1 were observed,[19] indicating that these two processes have a similar rate-determining step, for example, C–H insertion or hydrogen-atom migration.



Scheme 3. Isotope experiments.

In conclusion, we have described aryl sulfilimines as a new generation of nitrene precursors for the synthesis of carbazoles and related heterocycles by means of either visible-light irradiation or rhodium catalysis. A straightforward comparison with the commonly employed azides indicated that sulfilimines are more reactive substrates, rendering its synthetic use under milder reaction conditions. Furthermore, sulfide as a safe and readily removable leaving group makes this method a promising alternative for carbazole synthesis. The gram-scale synthesis of Clausine C was efficiently performed with a simple purification step, demonstrating the distinct applicability and scalability of the new methodology.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbazoles · C–H aminations · C–H insertions · nitrenes · sulfilimines

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[19] For details, see the Supporting Information.

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