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Sc(OTf)$_3$-Catalyzed Formal [3 + 3] Cycloaddition Reaction of Diaziridines and Quinones for the Synthesis of Benzo[*e*][1,3,4]oxadiazines

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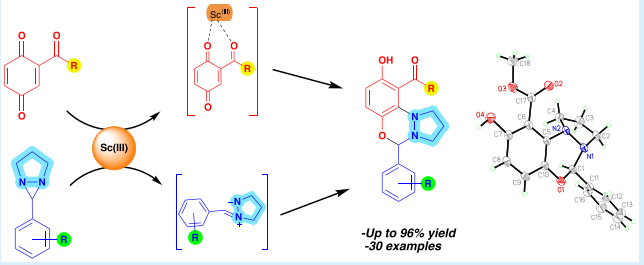
ABSTRACT: A formal [3 + 3] cyclization reaction of diaziridines and quinones has been developed offering 1,3,4-oxadiazinanes in generally high yields (up to 96%). The reaction was catalyzed by Sc(OTf)$_3$ with a large substrate scope for both diaziridines and quinones. The synergistic activation of 1,3-dipolar diaziridines and the dipolar quinones was found to be essential to enable this reaction.



Heterocycles are important structural scaffolds present in biologically active substances, natural products, and pharmaceuticals. Heterocycles play a central role in drug design.[1] Roughly 75% of low-molecular-weight drugs contain heterocycles. Heterocycles are also becoming an attractive design factor in organic materials science. Significant efforts have been devoted to developing new reactions to construct five- and six-membered heterocycles containing one heteroatom such as oxygen or nitrogen.[2] In contrast, much less has been done for heterocycles containing two or more heteroatoms due to the limited availability of appropriate substances to provide two or more heteroatoms in one operation.[3] The synthesis of oxadiazinanes has only been sporadically reported.[4] In particular, a catalytic methods to access 1,3,4-oxadiazinanes remains elusive to our knowledge. Nevertheless, the core 1,3,4-oxadiazinane structure has been found in a number of bioactive compounds.[4a−c] (See Figure S2 in the SI.) A concise method to directly access 1,3,4-oxadiazinane is desirable.

[3 + *n*] Annulation via 1,3-dipoles is a powerful tool to construct various ring systems. In particular, [3 + 3] cycloadditions can serve as a complementary strategy to prepare six-membered heterocycles that are not accessible through traditional [4 + 2] cycloadditions.[5] Currently, [3 + 3] annulation is still in its infancy. Three-membered-ring 1,3-dipoles such as cyclopropanes, oxiranes, and aziridines have been effectively utilized in developing [3 + *n*] annulation reactions.[6] Diaziridines have attracted increasing attention as a new class of three-membered-ring 1,3-dipoles in recent years.[7] The C−N bond of diaziridines can be cleaved heterolytically through thermolysis or in the presence of Lewis acid to give azomethine imine, which could serve as a 1,3-dipole in cycloaddition reactions.[7c,d,i] Through C−N bond cleavage, Punniyamurthy and coworkers have developed an FeCl$_3$-catalyzed [3 + 3]-annulation of *N*-alkyl aziridines with bicyclic diaziridines to give triazines (Scheme 1a).[7f] Ivanova and Trushkov have also developed a formal [3 + 3]-annulation of diaziridine with D−A cyclopropanes to afford perhydropyridazines (Scheme 1b).[7a] [3 + 2] Cycloadditions of diaziridines have been achieved with an activated double bond.[7b−e,h,i] In 2020, the Feng group reported the first asymmetric reaction of diaziridines with chalcones through [3 + 2] cyclization (Scheme 1c).[7b] Very recently, Doyle and coworkers demonstrated the feasibility of the selective cleavage of a N−N bond through a formal [3 + 3] cycloaddition of diaziridines with metalloenolcarbenes.[7g]

Despite these impressive achievements, the versatility of diaziridines as 1,3-dipoles remains largely unexplored. We are interested in developing new methods to construct ring systems that contain two or more heteroatoms because these heterocyclic rings are much less accessible. Taking advantage of the unique feature of diaziridine that offers two nitrogen atoms simultaneously, we decided to explore the possibility of diaziridines with quinones. Quinones have displayed high activity and multifunctionality in a number of organic transformations.[8] A [3 + 3] cycloaddition reaction of diaziridines with quinones represents a new reaction pattern for both diaziridines and quinones. Herein we report a metal Lewis-acid-catalyzed formal [3 + 3] cycloaddition of

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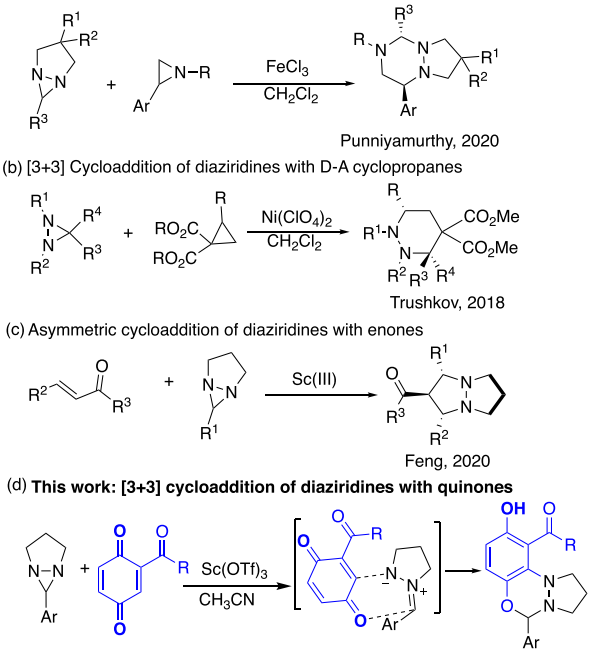
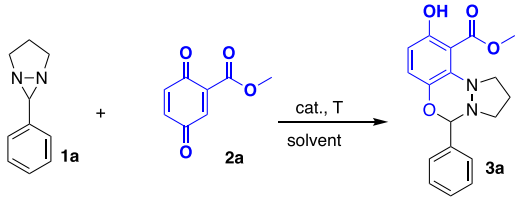
Scheme 1. Reaction of Diaziridines through C−N Bond Cleavage



diaziridines and quinones to afford tricyclic 1,3,4-oxadiazinanes in high yields with large substrate scopes.

We started our investigation using diaziridine **1a** and quinone ester **2a** (Table 1). When diaziridine **1a** was mixed with quinone ester **2a** in the presence of $Sc(OTf)_3$ at −30 °C in dichloromethane (DCM), a formal [3 + 3] reaction occurred to generate tricyclic 1,3,4-oxadiazinane **3a** in 57% yield (entry 1). In sharp contrast, another rare-earth metal Lewis acid $Y(OTf)_3$ was able to yield only a trace amount of product (entry 2). The use of a transition metal $Cu(OTf)_2$ decreased the yield significantly (entry 3). It appears that both the acid strength and the coordination sphere of the metal Lewis acid played a role in determining the reactivity of this reaction. We then decided to use $Sc(OTf)_3$ as the catalyst to screen solvents. The reaction carried out in THF gave a moderate yield of 46% (entry 4). The nonpolar solvent toluene increased the yield to 70% (entry 5). Switching back to the polar solvent MeCN further enhanced the yield to 77% (entry 6). The influence of temperature was also investigated. Lowering the temperature to −44 °C decreased the yield to 54% (entry 7). On the contrary, increasing the temperature to −25 °C significantly increased the yield to 91% (entry 9). However, when temperature was further elevated to −10 °C, the yield of the reaction declined again. We speculate that the sensitivity of this reaction to temperature likely arises from the susceptibility of quinone ester to decomposition in the presence of a metal Lewis acid at higher temperature. The structure of **3a** was revealed by ^1H and ^{13}C NMR spectroscopy along with COSY and NOESY 2D NMR spectroscopy. The X-ray crystal structure of **3a** was also resolved, further confirming its structure (Scheme 2, CCDC 2060287).

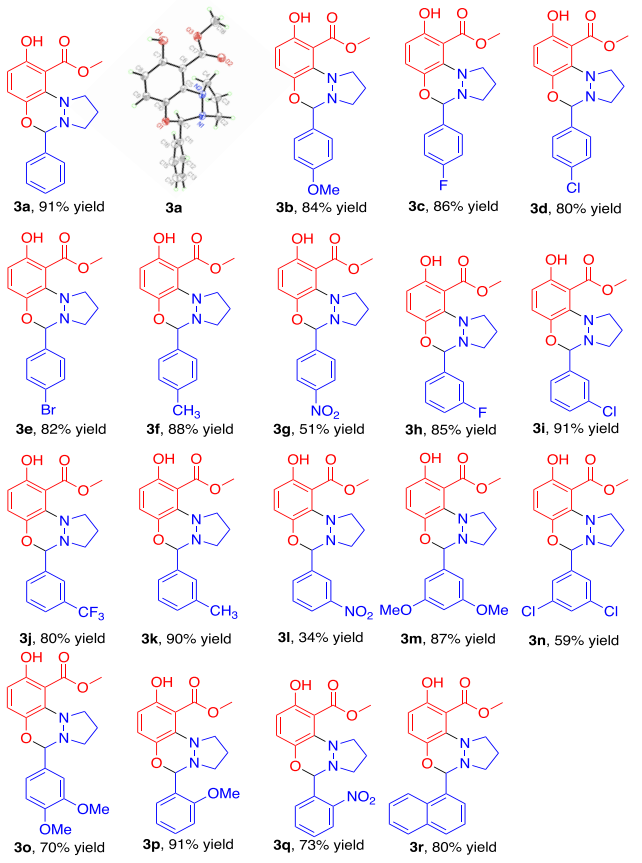
Table 1. Optimization of the Reaction Conditions[a]



entry	cat.	solvent	T (°C)	yield (%)[b]
1	$Sc(OTf)_3$	DCM	−30	57
2	$Y(OTf)_3$	DCM	−30	trace
3	$Cu(OTf)_2$	DCM	−30	25
4	$Sc(OTf)_3$	THF	−30	46[c]
5	$Sc(OTf)_3$	toluene	−30	70[c]
6	$Sc(OTf)_3$	MeCN	−30	77
7	$Sc(OTf)_3$	MeCN	−44	54[c]
9[d]	$Sc(OTf)_3$	MeCN	−25	91
10	$Sc(OTf)_3$	MeCN	−10	81

[a]Unless otherwise noted, the reactions were carried out with **1a** (0.10 mmol) and **2a** (0.10 mmol) with 10 mol % of catalyst in DCM (1.25 mL) for 24 h. [b]Yield of isolated **3a**, unless otherwise stated. [c]NMR yield. [d]Stirred for 19 h.

Scheme 2. Substrate Scope of Diaziridines[a,b]



[a]Standard reaction conditions: **1** (0.1 mmol), **2a** (0.1 mmol), $Sc(OTf)_3$ (10 mol %) at −25 °C in MeCN (1.25 mL). [b]Isolated yield.

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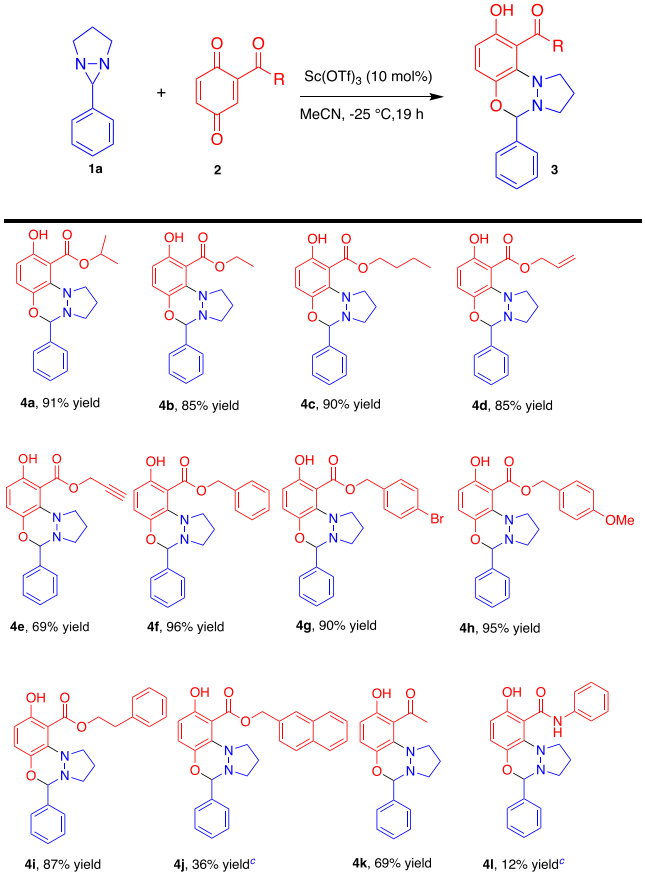
Using the optimized conditions (Table 1, entry 9), we examined the substrate scope of diaziridine with quinone ester **2a** (Scheme 2). Diaziridine **1** displayed a large substrate scope with a variety of substituents on the phenyl ring. Both electron-withdrawing groups including F, Cl, and Br and electron-donating groups (OMe, CH_3) at the para position gave the desired benzo[*e*][1,3,4]oxadiazines in very good yields (**3b**−**3f**, 80−88%). A strongly electron-withdrawing nitro group at the para position reduced the yield to 51% (**3g**). Substituents at the meta position also showed high yields in generating benzo[*e*][1,3,4]oxadiazines (**3h** and **3i**, 80−93%), except for **3m** bearing a nitro group at the meta position (34%). Whereas meta-disubstituted diaziridine with a electron-donating methoxy group produced **3n** in 87% yield, meta-disubstituted diaziridine with a slightly electron-withdrawing Cl led to a decreased yield of 59% (**3o**). 3,4-Dimethoxy substituted diaziridine gave benzo[*e*][1,3,4]oxadiazine **3p** in moderate yield (70%). Ortho-substituted diaziridine with a strongly electron-donating methoxy group produced the desired benzo[*e*][1,3,4]oxadiazine **3q** in high yield (91%). On the contrary, ortho-substituted diaziridine with a strongly electron-withdrawing nitro group generated **3q** in 73% yield. Naphthyl-substituted diaziridine also produced benzo[*e*][1,3,4]-oxadiazine **3r** in good yield (80%).

We also investigated the scope of quinones with diaziridine **1a** (Scheme 3). Quinone esters with a variety of different alkoxy groups successfully generated the desired benzo[*e*]-[1,3,4]oxadiazines in very good to excellent yields (85−96%, **4a**−**4d** and **4f**−**i**), except for **4e** (69%) and **4j** (36%) bearing a prop-2-yn-1-yloxy group and a naphthalen-2-ylmethoxy, respectively. Quinone ketone also displayed good activity toward diaziridine **1a**, offering **4k** in good yield (69%). On the contrary, quinone amide showed only low activity toward this reaction, giving **4i** in 12% yield. We also attempted this reaction with unsubstituted quinone and chloroquinone; unfortunately, no product was obtained. Quinone has been known for a narrow substrate scope in the majority of the previous works done on quinone esters. The achievement of the [3 + 3] reaction with quinone ketone and quinone amide demonstrated the broader scope of this reaction. A reaction of **1a** and **2a** on the 3.1 mmol scale was conducted to give **3a** in 85% yield (see the SI), which confirmed the utility of this reaction on a large scale.

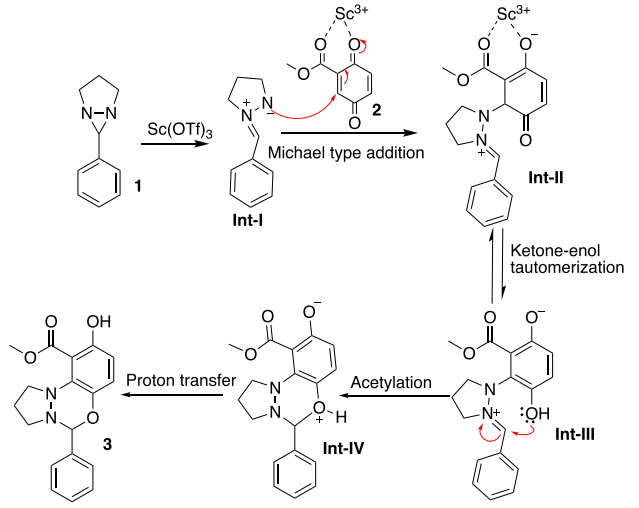
On the basis of the reaction results, a mechanism has been proposed for this formal [3 + 3] reaction (Scheme 4).

Scheme 3. Substrate Scope of Quinones[a,b]



[a]Standard reaction conditions: **1a** (0.1 mmol), **2** (0.1 mmol), $Sc(OTf)_3$ (10 mol %) at −25 °C in MeCN (1.25 mL). [b]Isolated yield. [c]Reactions were carried out in 1.25 mL of DCM.

Scheme 4. Proposed Mechanism



Diaziridine **1** undergoes ring opening in the presence of $Sc(OTf)_3$ to give azomethine imine (**Int-I**). 1,3-Dipolar azomethine imine **Int-I** then attacks quinone **2** through Michael-type addition to give **Int-II**. Our data indicate that the activation of quinone **2** through chelation to the metal Lewis acid is critical for the success of this reaction, as quinones without a chelating site were not reactive toward this reaction. We speculate that the coordination to Sc^{3+} illustrated in **Int-II** helps stabilize **Int-II**, facilitating the tautomerization of **Int-II** to the enol form **Int-III**. The intramolecular nucleophilic addition of the hydroxy group to the iminium bond led to the ring-closure product **Int-IV** followed by proton transfer to give the final benzo[*e*][1,3,4]oxadiazine.

In summary, we have developed a formal [3 + 3] reaction of diaziridine and quinones through the C−N bond cleavage of diaziridine, introducing a new reaction type for diaziridines. Our study indicates that the synergistic activation of both the dipolar substrate (diaziridine) and the dipolarophile (quinone) with a metal Lewis acid catalyst, that is, $Sc(OTf)_3$, is essential to enable this reaction, revealing a new set of reactivities of both diaziridines and quinone. This reaction displayed a large substrate scope for both diaziridines and quinones. The synthetic method developed in this work provides a new

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synthetic route to access heterocycles containing three heteroatoms, which is currently in high demand.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00818.

Experimental procedures, ^{1}H and ^{13}C NMR and other characterization data, and single-crystal X-ray analysis (PDF)

Accession Codes

CCDC 2060287 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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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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