


 Cite this: *RSC Adv.*, 2021, 11, 20118

Received 30th April 2021

Accepted 24th May 2021

DOI: 10.1039/d1ra03387e

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# Construction of cyclopentane-fused coumarins via DBU-catalyzed [3+2] cycloaddition of 3-homoacyl coumarins with cyclic 1-azadienes†

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The metal-free DBU catalyzed [3+2] cycloaddition of 3-homoacyl coumarins with cyclic 1-azadienes proceeded smoothly to furnish the corresponding highly functionalized cyclopentane-fused coumarins with excellent diastereoselectivity and complete chemoselectivity and in good yields under mild conditions.

Coumarins<sup>1</sup> and cyclopentane scaffolds<sup>2</sup> are widely distributed in natural products and display a wide range of biological and pharmacological activities. When combining coumarin skeletons with cyclopentane moieties, the cyclopentane-fused coumarins show interesting biological activities. For example, aflatoxins, which occur naturally, exhibit acute toxicity, teratogenicity, mutagenicity and carcinogenicity (Fig. 1).<sup>3</sup> Herbertenolide, which belongs to the family of sesquiterpenoids, was first isolated from the leafy liverwort *Herberta adunca*, the extract of which showed significant inhibition against the growth of certain plant pathogenic fungi (Fig. 1).<sup>4</sup> Not surprisingly, the strategies for synthesis of cyclopentane-fused coumarins have attracted much attention.<sup>5</sup>

Recently, the group of Lin developed a 1,3-dipolar precursor 3-homoacyl coumarin, which is an efficient synthon for the

construction of cyclopentane-fused coumarins under the catalysis of bases (Scheme 1a and b).<sup>6</sup> However, the partners reacted with 3-homoacyl coumarins were focus on  $\alpha,\beta$ -unsaturated carbonyl compounds and conjugated dienes. The other dipolarophiles, such as aza-dienes, might also be potential candidates for the [3+ $n$ ] cycloadditions with 3-homoacyl coumarins but never been developed.

The cyclic 1-azadienes are extensive used dipolarophiles and have been widely involved in a series of cyclization reactions as two-,<sup>7</sup> three-<sup>8</sup> or four-<sup>9</sup> member synthons. While the



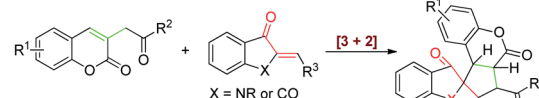
Fig. 1 Bioactive molecule bearing cyclopentane-fused coumarin.

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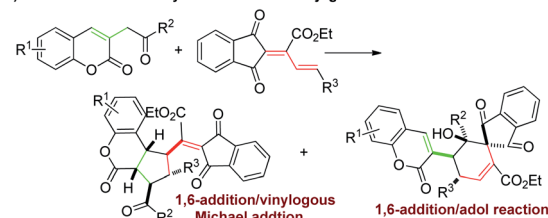
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† Electronic supplementary information (ESI) available: Experimental conditions and spectroscopic data of all new compounds. CCDC 2073841. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1ra03387e

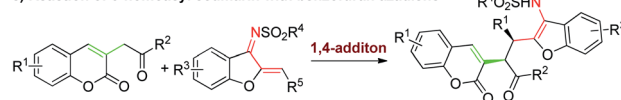
### a) Reactions of 3-homoacyl coumarins with $\alpha,\beta$ -unsaturated carbonyl compounds



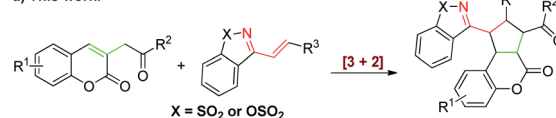
### b) Reaction of 3-homoacyl coumarin with conjugated diene



### c) Reaction of 3-homoacyl coumarin with benzofuran azadiene



### d) This work:



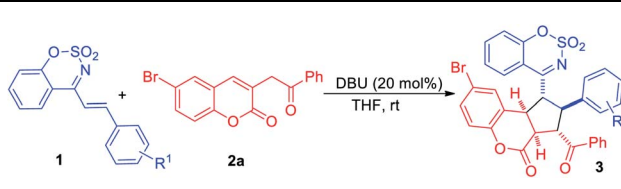
Scheme 1 The reaction of 3-homoacyl coumarins with dipolarophiles catalyzed by Brønsted base.



organocatalytic [3+2] cycloaddition of cyclic 1-azadiene as two synthons has rarely been investigated.<sup>7b,c</sup> In 2016, Chen's<sup>7b</sup> and Guo's<sup>7c</sup> group respectively developed an asymmetric [3+2] annulation reaction of Morita-Baylis-Hillman carbonates with cyclic 1-azadienes catalyzed by Lewis base. Encouraged by these works above and as our continuing efforts on cycloadditions,<sup>10</sup> herein we expected to achieve the first [3+2] cycloaddition reaction of 3-homoacyl coumarins with cyclic 1-azadienes catalyzed by Brønsted base for synthesis of various functionalized cyclopentane-fused coumarins derivatives efficiently (Scheme 1d). However, Huang's group reported an enantioselective 1,4-addition reaction of benzofuran azadiene with 3-homoacyl coumarin, instead of cycloaddition (Scheme 1c).<sup>11</sup> To achieve our assumption in high chemoselectivity would be a challenging work.

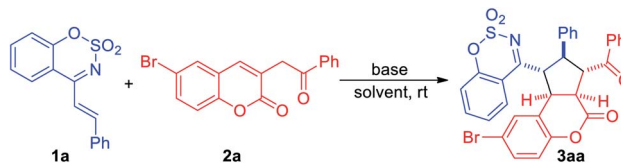
In an initial experiment, cyclic 1-azadiene **1a** and 6-bromo-3-(2-oxo-2-phenylethyl)-2*H*-chromen-2-one **2a** were employed as the model substrates to carry out the reaction in CH<sub>2</sub>Cl<sub>2</sub> at room temperature in the presence of DABCO. To our delight, the desired [3+2] cycloadduct **3aa** was obtained in 56% yield (Table 1, entry 1). Subsequently, several bases were screened and when the use of stronger base (Table 1, entries 2–4), DBU, the reaction gave a higher yield in 12 h, and no 1,4-addition product was observed (Table 1, entry 3). Further screening of several representative solvents, such as THF, toluene, DCE and CH<sub>3</sub>CN, revealed that the reaction proceeded better in THF with 86% yield (Table 1, entry 5). Therefore, the best reaction conditions were determined as below: DBU, THF and room temperature (Table 1, entry 5).

Under optimal reaction conditions, the substrate scope of the cyclic 1-azadienes **1** was investigated and the results were summarized in Table 2. As expected, the desired [3+2] cycloadducts **3ba–3qa** were obtained in moderate to good

Table 2 Substrate scope of cyclic 1-azadienes **1**<sup>a</sup>


Entry	R <sup>1</sup> in <b>1</b>	<b>3</b>	Yield <sup>b</sup> (%)	dr <sup>c</sup>
1	2-FC <sub>6</sub> H <sub>4</sub> ( <b>1b</b> )	<b>3ba</b>	85	>20 : 1
2	3-FC <sub>6</sub> H <sub>4</sub> ( <b>1c</b> )	<b>3ca</b>	90	>20 : 1
3	4-FC <sub>6</sub> H <sub>4</sub> ( <b>1d</b> )	<b>3da</b>	85	>20 : 1
4	3-ClC <sub>6</sub> H <sub>4</sub> ( <b>1e</b> )	<b>3ea</b>	86	>20 : 1
5	4-ClC <sub>6</sub> H <sub>4</sub> ( <b>1f</b> )	<b>3fa</b>	80	>20 : 1
6	3-BrC <sub>6</sub> H <sub>4</sub> ( <b>1g</b> )	<b>3ga</b>	79	>20 : 1
7	4-BrC <sub>6</sub> H <sub>4</sub> ( <b>1h</b> )	<b>3ha</b>	80	>20 : 1
8	4-CNC <sub>6</sub> H <sub>4</sub> ( <b>1i</b> )	<b>3ia</b>	75	>20 : 1
9	2-MeC <sub>6</sub> H <sub>4</sub> ( <b>1j</b> )	<b>3ja</b>	79	>20 : 1
10	3-MeC <sub>6</sub> H <sub>4</sub> ( <b>1k</b> )	<b>3ka</b>	76	>20 : 1
11	4-MeC <sub>6</sub> H <sub>4</sub> ( <b>1l</b> )	<b>3la</b>	73	>20 : 1
12	2-OMeC <sub>6</sub> H <sub>4</sub> ( <b>1m</b> )	<b>3ma</b>	67	>20 : 1
13	3-OMeC <sub>6</sub> H <sub>4</sub> ( <b>1n</b> )	<b>3na</b>	75	>20 : 1
14	4-OMeC <sub>6</sub> H <sub>4</sub> ( <b>1o</b> )	<b>3oa</b>	77	>20 : 1
15	2-Naphthyl ( <b>1p</b> )	<b>3pa</b>	72	>20 : 1
16	2-Thienyl ( <b>1q</b> )	<b>3qa</b>	74	>20 : 1

<sup>a</sup> Reactions were carried out with **1** (0.1 mmol), **2a** (0.12 mmol), and DBU (20 mol%) in 2 mL of THF at rt for 12–48 h. <sup>b</sup> Isolated yields. <sup>c</sup> Determined by <sup>1</sup>H NMR.

Table 1 Screening of the reaction conditions<sup>a</sup>


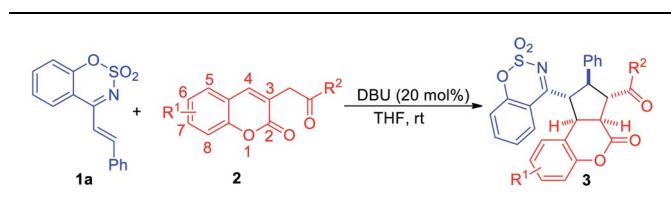
Entry	Base	Solvent	Time (h)	Yield <sup>b</sup> (%)	dr <sup>c</sup>
1	DABCO	CH <sub>2</sub> Cl <sub>2</sub>	24	56	>20 : 1
2	DMAP	CH <sub>2</sub> Cl <sub>2</sub>	24	60	>20 : 1
3	DBU	CH <sub>2</sub> Cl <sub>2</sub>	12	78	>20 : 1
4	Et <sub>3</sub> N	CH <sub>2</sub> Cl <sub>2</sub>	24	67	>20 : 1
5	DBU	THF	12	86	>20 : 1
6	DBU	Toluene	12	31	>20 : 1
7	DBU	DCE	12	76	>20 : 1
8	DBU	CH <sub>3</sub> CN	12	73	>20 : 1

<sup>a</sup> Reactions were carried out with **1a** (0.1 mmol), **2a** (0.12 mmol), and base (20 mol%) in 2 mL of solvent at rt. <sup>b</sup> Isolated yields. <sup>c</sup> Determined by <sup>1</sup>H NMR.

yields. Both electron-withdrawing (entries 1–8) and electron-donating substituents (entries 9–14) on the benzene ring were tolerated and the yields of the former were slightly higher than the latter. And either *para*-, *meta*- or *ortho*-substituted phenyl cyclic 1-azadienes **1** could serve as suitable reaction partners, while **1m** bearing *ortho*-methoxyphenyl gave moderate yield (67% yield) due to the steric hindrance (entry 12). Moreover, 2-naphthyl and 2-thienyl substituted substrates **1p** and **1q** exhibited good reactivities, delivering the desired products **3pa** in 72% yield and **3qa** in 74% yield, respectively (entries 15–16).

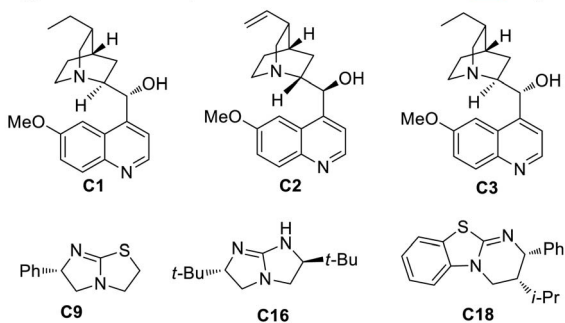
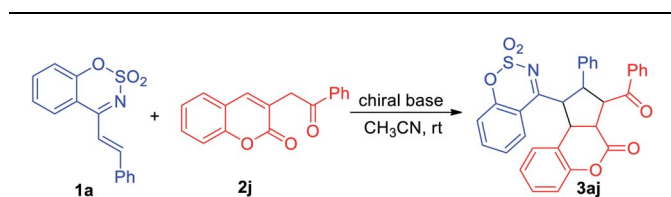
Subsequently, we performed the application of cyclic 1-azadiene **1a** in DBU-catalyzed [3+2] cycloaddition with a variety of 3-homoacyl coumarins **2** under the optimal conditions (Table 3). And substrates **2** with electron-withdrawing (F, Cl, Br, Table 2, entries 1–5) or electron-donating (Me, MeO, entries 6–9) substituents at 6 or 7 position were all suitable for the cycloaddition, affording the cycloadducts **3aa–3ai** in good to excellent yields of 78–94%. Replacing the R<sup>1</sup> group with H, the desired product **3aj** was obtained in 85% yield (entry 10). Notably, when the R<sup>2</sup> were *para*-substituted phenyl groups, the cycloaddition reactions underwent smoothly to deliver the products **3ak–3am** in up to 92% yield, and *para*-methyl substituted **2m** gave a lower yield compared to *para*-electron-withdrawing substituted **2k** and **2l** (entries 11–13). The structure of product **3aj** was confirmed by its X-ray crystallographic data.<sup>12</sup>



Table 3 Substrate scope of 3-homoacyl coumarins 2<sup>a</sup>

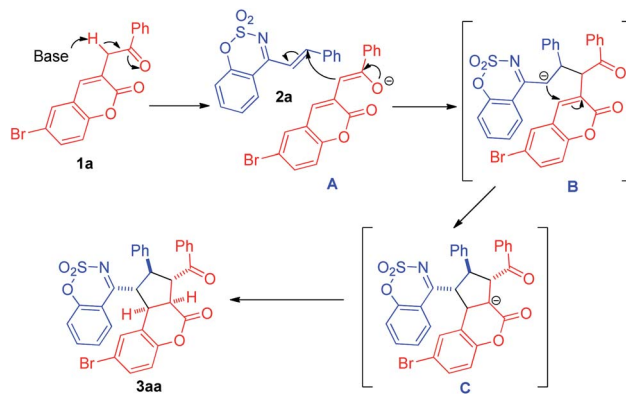
Entry	R <sup>1</sup> /R <sup>2</sup>	3	Yield <sup>b</sup> (%)	dr <sup>c</sup>
1	6-Br/C <sub>6</sub> H <sub>5</sub> (2a)	3aa	86	>20 : 1
2	6-F/C <sub>6</sub> H <sub>5</sub> (2b)	3ab	88	>20 : 1
3	6-Cl/C <sub>6</sub> H <sub>5</sub> (2c)	3ac	78	>20 : 1
4	7-Cl/C <sub>6</sub> H <sub>5</sub> (2d)	3ad	84	>20 : 1
5	7-Br/C <sub>6</sub> H <sub>5</sub> (2e)	3ae	86	>20 : 1
6	6-Me/C <sub>6</sub> H <sub>5</sub> (2f)	3af	87	>20 : 1
7	6-OMe/C <sub>6</sub> H <sub>5</sub> (2g)	3ag	94	>20 : 1
8	7-Me/C <sub>6</sub> H <sub>5</sub> (2h)	3ah	86	>20 : 1
9	7-OMe/C <sub>6</sub> H <sub>5</sub> (2i)	3ai	83	>20 : 1
10	H/C <sub>6</sub> H <sub>5</sub> (2j)	3aj	83	>20 : 1
11	H/4-FC <sub>6</sub> H <sub>4</sub> (2k)	3ak	90	>20 : 1
12	H/4-BrC <sub>6</sub> H <sub>4</sub> (2l)	3al	92	>20 : 1
13	H/4-MeC <sub>6</sub> H <sub>4</sub> (2m)	3am	80	>20 : 1

<sup>a</sup> Reactions were carried out with **1a** (0.1 mmol), **2** (0.12 mmol), and DBU (20 mol%) in 2 mL of THF at rt for 12–48 h. <sup>b</sup> Isolated yields. <sup>c</sup> Determined by <sup>1</sup>H NMR.

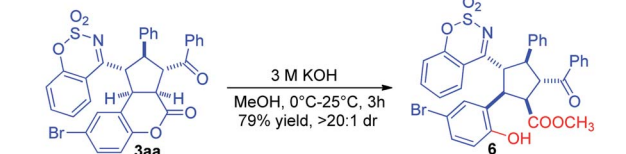
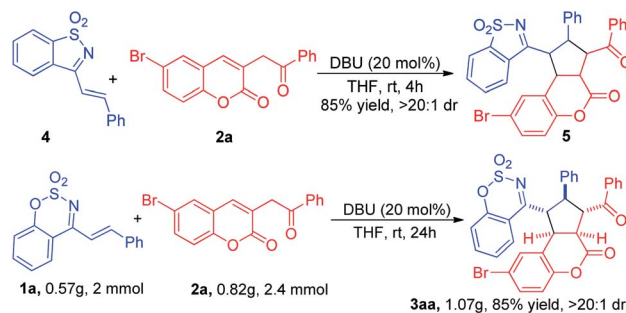
Table 4 Screening of enantioselective reaction conditions<sup>a</sup>

Entry	Catalyst	Time (h)	Yield <sup>b</sup> (%)	dr <sup>c</sup>	ee <sup>d</sup> (%)
1	C1	120	46	>20 : 1	27.3
2	C2	120	52.4	>20 : 1	9.5
3	C3	120	60	>20 : 1	8
4	C9	120	31	>20 : 1	4.5
5	C16	120	73	>20 : 1	11
6	C18	120	36	>20 : 1	11

<sup>a</sup> Reactions were carried out with **1a** (0.1 mmol), **2j** (0.12 mmol), and 20 mol% catalyst in 2 mL of CH<sub>3</sub>CN at rt. <sup>b</sup> Isolated yields. <sup>c</sup> Determined by <sup>1</sup>H NMR. <sup>d</sup> Determined by HPLC analysis.



Scheme 2 Plausible reaction mechanism.

Scheme 3 [3+2] cycloaddition of **4** and **2a**, gram-scale reaction and further transformation.

To explore the asymmetric variant of this [3+2] cycloaddition reaction of **1a** and **2j**, a series of commercially available chiral amines were screened, and unfortunately, this reaction did not proceed in CH<sub>2</sub>Cl<sub>2</sub> and THF. However, when CH<sub>3</sub>CN was employed as a solvent, this reaction could be catalysed by a few of chiral amines, giving poor enantioselectivities and low to moderate yields (see ESI Table S1†). As shown in Table 3, cinchona catalyst **C1** catalyzed the reaction to afford the **3aj** in 46% yield with the highest 27.3% ee, and the reaction could be catalyzed by diimidazole catalyst **C16** to give the highest 73% yield but poor 11% ee. The subsequent attempts to find the optimal asymmetric reaction conditions failed (Table 4).

On the basis of the results and previous literature,<sup>6</sup> herein we proposed a plausible mechanism for the [3+2] cycloaddition reaction (Scheme 2), which proceeded *via* stepwise mechanism with zwitterion.<sup>13</sup> Firstly, **1a** is deprotonated to deliver the dienolate intermediate **A** under basic conditions. Subsequently, the  $\alpha$ -carbanion of **A** attacks the olefinic bond of **2a** to form the anion **B**. Then through cyclization and protonation, the final [3+2] cycloaddition product **3aa** is given.



As shown in Scheme 3, the saccharin-derived cyclic 1-azadiene **4** was tested under the optimized reaction conditions. Delightfully, the [3+2] cycloadduct **5** could also be easily prepared in 85% yield and >20 : 1 dr. To explore the synthetic utility of this cycloaddition, a gram scale reaction was carried out to obtain the desired cycloadduct **3aa** without any loss of yield and diastereoselectivity. The lactone of **3aa** was opened under basic condition to give the multisubstituted cyclopentane **6** in 79% yield and >20 : 1 dr (Scheme 3).

## Conclusions

In summary, we have successfully developed a DBU catalyzed [3+2] cycloaddition reaction of 3-homoacyl coumarins with cyclic 1-azadienes. The present protocol offers an efficient methodology to synthesize cyclopentane-fused coumarin derivatives with complete chemoselectivity and excellent diastereoselectivity in good yields. Efforts on further investigations of this protocol are underway in our group.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21801180), the Natural Science Foundation of Shandong Province (ZR2018LB010, ZR2019BB054), Doctoral Scientific Research Foundation of Shandong First Medical University, the Innovative Research Programs of Higher Education of Shandong Province (2019KJC009), Academic promotion programme of Shandong First Medical University (2019QL008).

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