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# A formal [3 + 3] cycloaddition of allenyl imide and activated ketones for the synthesis of tetrasubstituted 2-pyrones†

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CsOH·H<sub>2</sub>O-catalyzed formal [3 + 3] cycloadditions of allenyl imide with β-ketoesters, 1,3-diketones or β-ketonitriles for the synthesis of tetrasubstituted 2-pyrone derivatives have been demonstrated. The allenyl imide was utilized as a C3-synthon, and a ketenyl intermediate was proposed *via* the process of 1,4-addition of carbon anion to allene followed by elimination of the 2-oxazolidinyl group.

The 2-pyrone (or α-pyrone) moiety<sup>1</sup> is widely found in natural products,<sup>2</sup> and bioactive compounds exhibiting anti-HIV, anti-bacterial, anti-infective, and anti-cancer activities (Fig. 1).<sup>3</sup>

In addition, 2-pyrones have found broad application as synthetic handles in cross-coupling reactions,<sup>4</sup> Diels–Alder reactions<sup>5</sup> and conjugate additions<sup>6</sup> by virtue of their aromatic, diene and enone structural characteristics. Significantly, 2-pyrones have been utilized as diene components in [4 + 2] cycloadditions for the total syntheses of natural products.<sup>7</sup> Therefore, the development of efficient approaches to synthesize 2-pyrones has drawn much attention.<sup>8</sup> Thus far, organo-metallic catalysts, base or acid-enabled the generation of 2-pyrone structures in an intermolecular or intramolecular manner have been established. Whilst partially substituted 2-pyrones can be readily synthesized, the synthetic methods to prepare tetrasubstituted 2-pyrones remains scarce.<sup>9</sup> For instance, in 2007, Ryu and coworkers achieved tetrasubstituted 2-pyrones through the [3 + 2 + 1] cycloaddition using silylacetlenes, α,β-unsaturated ketones and CO as starting materials.<sup>10</sup> In 2019, Yasuda and coworkers installed tetrasubstituted metalated 2-pyrones *via* the oxyindation of carbonyl-ene-yne compounds with indium trihalides, which could be applied into the synthesis of tetrasubstituted 2-pyrones through cross-coupling and halogenation reactions.<sup>11</sup> In the same year, Mei and coworkers communicated the iridium-catalyst enabling C–H/O–H functionalization for alkyne annulation to install tetrasubstituted 2-pyrones.<sup>12</sup> Furthermore, as exemplified in Fig. 1, some natural products possess tetrasubstituents in the 2-pyrone skeleton. In this context, the discovery of novel strategy to build

tetrasubstituted 2-pyrones under mild conditions should be highly demanding and rewarding. To the purpose, we launched this project and documented the preliminary results.

In our previous work, we discovered that allenyl imides could be transformed into 1,4-(bis)electrophilic α,β-unsaturated ketenyl phosphonium species under nucleophilic catalysis condition, which was further utilized as C4-synthons in the [4 + 1] cycloaddition of methyl ketimines, enamines, and a primary amine (Scheme 1a).<sup>13</sup> The 2-oxazolidinyl imide group acts as a good leaving group. Encouraged by these results, we envisaged that allenyl imide **1** should be applied into the cycloaddition of other (bis)nucleophilic partners, such as activated ketones, and thus novel types of heterocycles would be assembled; if [3 + 3] cycloaddition reaction occurs, 2-pyrone derivatives will be available (Scheme 1b).

β-Ketoester is one type of activated ketones, and known as 1C,3O-bisnucleophile in cycloaddition reactions. Ethyl benzoylacetate **2a** and allenyl imide **1** were used as two substrates in the model reaction (Table 1). Under the previous [4 + 1] cycloaddition conditions by using PBu<sub>3</sub> as a nucleophilic catalyst,<sup>13</sup>

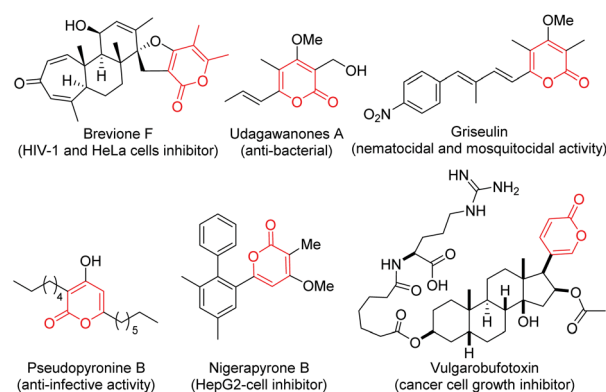


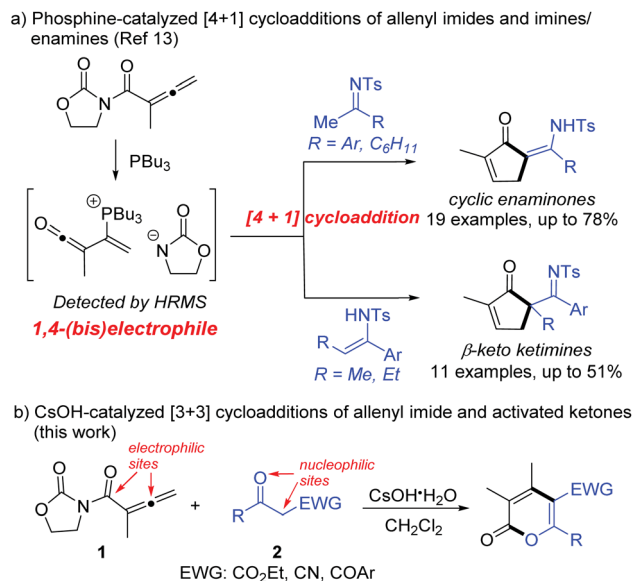
Fig. 1 2-Pyrone-derived bioactive molecules.

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Scheme 1 Cycloaddition with allenyl imide.

Table 1 Optimization of reaction conditions<sup>a</sup>

Entry	Base/equiv.	Solvent	Time/h	Yield <sup>b</sup> (%)
1	PBu <sub>3</sub> /0.5	CH <sub>2</sub> Cl <sub>2</sub>	48	Trace
2	DABCO/0.5	CH <sub>2</sub> Cl <sub>2</sub>	48	Trace
3	Et <sub>3</sub> N/0.5	CH <sub>2</sub> Cl <sub>2</sub>	24	Trace
4	Cs <sub>2</sub> CO <sub>3</sub> /0.5	CH <sub>2</sub> Cl <sub>2</sub>	6	77
5	Cs <sub>2</sub> CO <sub>3</sub> /0.5	Et <sub>2</sub> O	6	61
6	Cs <sub>2</sub> CO <sub>3</sub> /0.5	ClCH <sub>2</sub> CH <sub>2</sub> Cl	20	63
7	Cs <sub>2</sub> CO <sub>3</sub> /0.5	Toluene	20	72
8	Cs <sub>2</sub> CO <sub>3</sub> /0.5	MeCN	6	73
9	Cs <sub>2</sub> CO <sub>3</sub> /0.5	1,4-Dioxane	6	64
10	Cs <sub>2</sub> CO <sub>3</sub> /0.5	EtOAc	4	76
11	CsOH·H <sub>2</sub> O/0.5	CH <sub>2</sub> Cl <sub>2</sub>	6	85
12 <sup>c</sup>	CsOH·H <sub>2</sub> O/0.1	CH <sub>2</sub> Cl <sub>2</sub>	24	40
13 <sup>c</sup>	CsOH·H <sub>2</sub> O/0.2	CH <sub>2</sub> Cl <sub>2</sub>	12	75
14 <sup>c</sup>	CsOH·H <sub>2</sub> O/0.3	CH <sub>2</sub> Cl <sub>2</sub>	6	90

<sup>a</sup> Reaction conditions: **1** (0.1 mmol), **2a** (0.12 mmol), and solvent (1.0 mL) were stirred at 30 °C. <sup>b</sup> Isolated yield. <sup>c</sup> 0.5 mL of solvent was used.

trace amount of [3 + 3] cycloadduct 2-pyrone **3a** instead of [4 + 1] cycloadduct was detected (entry 1). Then screening other base catalysts including DABCO, NEt<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> solvent (1.0 mL) at 30 °C revealed that only Cs<sub>2</sub>CO<sub>3</sub> could trigger an effective [3 + 3] cycloaddition reaction;<sup>14</sup> compound **3a** was delivered in 77% yield within 6 h (entry 4), where allenyl imide **1** displays dual electrophilic reactivity at βC and amide carbonyl positions. The structural assignment of **3a** was spectroscopically determined and later confirmed by analogy to the X-ray crystallography of product **3e** (see Table 2 below).<sup>15</sup> The

solvent effect further showed that CH<sub>2</sub>Cl<sub>2</sub> was more suitable than other solvents. When we changed the base from Cs<sub>2</sub>CO<sub>3</sub> to CsOH·H<sub>2</sub>O, the yield was improved to 85% (entry 11). Since CsOH·H<sub>2</sub>O is a strong base, which may better facilitate the deprotonation of β-ketoester than other bases. After investigating the lower loading of CsOH·H<sub>2</sub>O catalyst in less amount of CH<sub>2</sub>Cl<sub>2</sub> solvent, the optimal reaction conditions for the access to product **3a** (90%) were found: 0.3 equiv. of CsOH·H<sub>2</sub>O and 0.5 mL of CH<sub>2</sub>Cl<sub>2</sub> at 30 °C (entry 14).

After establishing the optimized conditions, the scope of β-ketoesters was carried out to synthesize various tetrasubstituted 2-pyrone derivatives (**3**) bearing an ester group at the 5-position, and the results were summarized in Table 2. Initially, the scale-up (4.0 mmol of **1**) synthesis was carried out to provide an identical level of yield (87%, entry 1). Then the effects of steric hindrance and electronic structure properties of substituents on the phenyl ring were checked. The incorporation of electron-donating groups (Me- and MeO-) at the *para*-position provided slightly lower level of yields (82–85%, entries 3 and 4). 4-Br

Table 2 Scope of β-ketoesters<sup>a</sup>

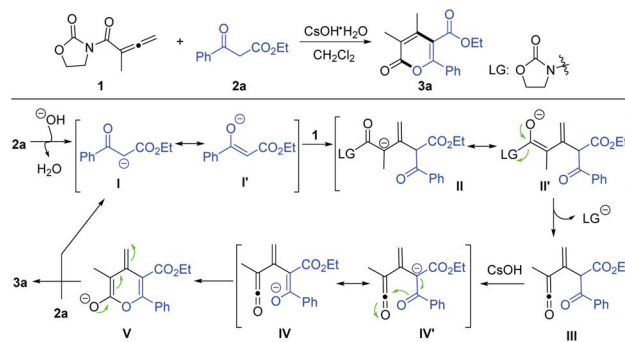
Entry	R	R'	Product	t/h	Yield <sup>b</sup> /%
1	C <sub>6</sub> H <sub>5</sub>	Et	<b>3a</b>	6	90 (87) <sup>c</sup>
2	C <sub>6</sub> H <sub>5</sub>	Me	<b>3b</b>	6	87
3	4-Me-C <sub>6</sub> H <sub>4</sub>	Et	<b>3c</b>	16	85
4	4-OMe-C <sub>6</sub> H <sub>4</sub>	Me	<b>3d</b>	6	82
5	4-Br-C <sub>6</sub> H <sub>4</sub>	Et	<b>3e</b>	6	95
 (ORTEP of <b>3e</b> , CCDC 2031826)					
6	4-I-C <sub>6</sub> H <sub>4</sub>	Et	<b>3f</b>	24	85
7	4-CN-C <sub>6</sub> H <sub>4</sub>	Et	<b>3g</b>	6	87
8	4-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	Et	<b>3h</b>	36	60
9	3,4-(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	Et	<b>3i</b>	24	85
10	3-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	Me	<b>3j</b>	24	84
11	3-OMe-C <sub>6</sub> H <sub>4</sub>	Et	<b>3k</b>	6	95
12	3-F-C <sub>6</sub> H <sub>4</sub>	Et	<b>3l</b>	24	95
13	3-Cl-C <sub>6</sub> H <sub>4</sub>	Et	<b>3m</b>	6	95
14	3-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	Et	<b>3n</b>	12	90
15	2-OMe-C <sub>6</sub> H <sub>4</sub>	Et	<b>3o</b>	20	80
16	2-F-C <sub>6</sub> H <sub>4</sub>	Et	<b>3p</b>	24	87
17	2-Cl-C <sub>6</sub> H <sub>4</sub>	Me	<b>3q</b>	12	80
18	2-Br-C <sub>6</sub> H <sub>4</sub>	Me	<b>3r</b>	24	93
19	1-Naphthyl	Et	<b>3s</b>	5	94
20	2-Naphthyl	Et	<b>3t</b>	12	85
21	2-Thienyl	Et	<b>3u</b>	8	92
22	2-Furyl	Et	<b>3v</b>	6	94
23	Cyclohexyl	Et	<b>3w</b>	20	80
24	Me	Et	<b>3x</b>	12	85

<sup>a</sup> Reaction condition: **1** (0.1 mmol), **2** (0.12 mmol), CsOH·H<sub>2</sub>O (30 mol%), and CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) were stirred at 30 °C. <sup>b</sup> Isolated yield based on **1**. <sup>c</sup> The data in brackets was obtained by using 4.0 mmol of **1**.



substituent provided a higher yield than the 4-I variant (95% vs. 85%, entries 5 and 6). Based on the single crystal X-ray analysis of compound **3e**, the pyrone structure was determined.<sup>15</sup> Similar reactivity and yield were observed by comparing CN-substituent (entry 7) with MeO- and Me-substituents (entries 3 and 4), however, the strong electron-withdrawing group ( $-\text{CF}_3$ ) was not beneficial to the yield (60%, entry 8). The use of *meta,para*-disubstituted  $\beta$ -arylketooester was found to be compatible with the reaction conditions, and 84% yield of product **3i** was observed. In the case of *meta*-substituted substrates, good to excellent yields were obtained (entries 10–14). The incorporation of  $-\text{OMe}$  and  $-\text{CF}_3$  groups at *meta*-position exhibited much higher yields than those at *para*-position. When  $-\text{OMe}$  or halide (F, Cl and Br) groups were introduced at the *ortho*-position of phenyl group in  $\beta$ -ketoesters, up to 93% yield was obtained. Both 1-naphthyl and 2-naphthyl substitutions were tolerated, albeit much higher yield was received for the former case (94% vs. 85%). Likewise, heterocyclic  $\beta$ -ketoesters including 2-thienyl and 2-furyl groups underwent the [3 + 3] cycloaddition, leading to products **3u–v** in excellent yields (entries 21 and 22). Except aromatic  $\beta$ -ketoesters, aliphatic  $\beta$ -ketoesters having cyclohexyl or methyl groups were also applied in the [3 + 3] cycloaddition, providing compounds **3w** and **3x** in 80% and 85% yields, respectively.

In order to alter the substituent at the 5-position of 2-pyrone product,  $\beta$ -ketonitriles and 1,3-diketones were utilized as 1C,3O-bisnucleophiles in the [3 + 3] cycloaddition of allene **1** (Table 3). Under the above-mentioned standard conditions, 9 examples of  $\beta$ -ketonitriles with different substituents at the phenyl group were studied. As expected, 2-pyrone **4a** was successfully synthesized in 90% yield (entry 1). The use of *para*-Br-substituted arylketonitrile gave the corresponding product **4b** in 80% yield (entry



Scheme 2 Proposed reaction pathway.

2). More than 90% yield was obtained for three *meta*-substituted substrates (Me-, MeO- and F-; entries 3–5), albeit 84–88% yields for other two *meta*-substituted cases (Cl- and  $\text{CF}_3$ -, entries 6 and 7). Similarly, *ortho*-substituted products **4h** ( $-\text{OMe}$ ) and **4i** ( $-\text{I}$ ) were obtained in 85% and 80% yields, respectively (entries 8 and 9). Furthermore, 2-benzoylacetophenone reacted with **1** to give the corresponding product **4j** in 83% yield (entry 10). Another three symmetric 1,3-diketones also performed well in this [3 + 3] cycloaddition (entries 11–13).

As shown in Scheme 2, based on our previous work,<sup>13</sup> the proposed mechanism of this [3 + 3] annulation is presented. Firstly,  $\beta$ -ketoester **2a** is deprotonated by the CsOH base to form nucleophilic species **I**, which undergoes a Michael-type addition to the Csp atom of allene **1** to give intermediate **II**. After eliminating the 2-oxazolidinyl anion, intermediate **III** containing an electrophilic ketene group is formed, which is again deprotonated at the tertiary carbon by the CsOH base to provide intermediate **IV**. Next, the O-containing six-member ring (**V**) is generated through the nucleophilic addition of oxygen anion into the ketene group. Finally, the isomerization and interception of a proton from new substrate **2a** occur to produce **3a** and intermediate **I** to initiate another catalytic cycle.

In summary, we have established a novel CsOH·H<sub>2</sub>O-catalyzed [3 + 3] cycloaddition to access various tetrasubstituted 2-pyrones (37 examples, up to 95% yield), which used activated ketones as 1C,3O-bisnucleophiles and expanded the synthetic potential of allenyl imide as a C3-synthon in cycloadditions. A wide arrange of  $\beta$ -ketoesters,  $\beta$ -ketonitriles and 1,3-diketones were applied, and good to excellent yields were observed. The proposed reaction pathway including Michael addition/elimination and intramolecular nucleophilic cyclization was demonstrated. Further study of allenyl imides in other types of annulations are underway in our lab.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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Table 3 Scope of  $\beta$ -ketonitriles and 1,3-diketones<sup>a</sup>

Entry	R	R'	Product	Time/h	Yield <sup>b</sup> /%
1	C <sub>6</sub> H <sub>5</sub>	CN	<b>4a</b>	24	90
2	4-Br-C <sub>6</sub> H <sub>4</sub>	CN	<b>4b</b>	12	80
3	3-Me-C <sub>6</sub> H <sub>4</sub>	CN	<b>4c</b>	12	92
4	3-OMe-C <sub>6</sub> H <sub>4</sub>	CN	<b>4d</b>	12	90
5	3-F-C <sub>6</sub> H <sub>4</sub>	CN	<b>4e</b>	12	95
6	3-Cl-C <sub>6</sub> H <sub>4</sub>	CN	<b>4f</b>	12	88
7	3-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	CN	<b>4g</b>	12	84
8	2-OMe-C <sub>6</sub> H <sub>4</sub>	CN	<b>4h</b>	12	85
9	2-I-C <sub>6</sub> H <sub>4</sub>	CN	<b>4i</b>	12	80
10	C <sub>6</sub> H <sub>5</sub>	C(O)-C <sub>6</sub> H <sub>5</sub>	<b>4j</b>	6	83
11	3-Me-C <sub>6</sub> H <sub>4</sub>	C(O)-(3-Me-C <sub>6</sub> H <sub>4</sub> )	<b>4k</b>	6	88
12	3-OMe-C <sub>6</sub> H <sub>4</sub>	C(O)-(3-OMe-C <sub>6</sub> H <sub>4</sub> )	<b>4l</b>	6	80
13	3-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	C(O)-(3-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> )	<b>4m</b>	16	78

<sup>a</sup> Reaction conditions: **1** (0.1 mmol), **2** (0.12 mmol), CsOH·H<sub>2</sub>O (30 mol%), and CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) were stirred at 30 °C. <sup>b</sup> Isolated yield based on **1**.



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- CCDC 2031826 (compound **3e**) contains the ESI crystallographic data for this paper.†

