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This work reports the first efficient enantioselective intramolecular Buchner reaction of diazoacetamides. The Ru(II)-Pheox catalyst was shown to be highly efficient in this transformation in terms of both the regio- and enantioselectivity (up to 99% ee) giving the desired products in quantitative yield.

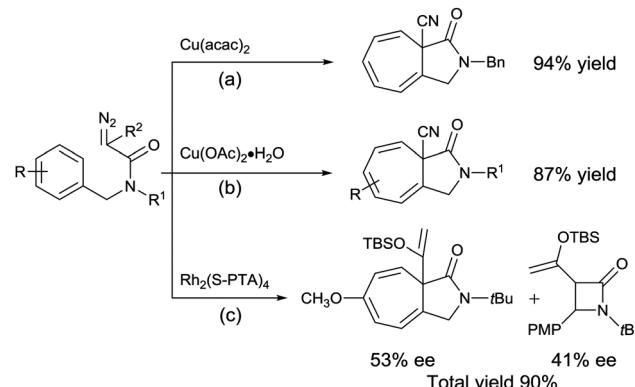
Medium ring-containing organic molecules, such as seven-membered rings, are the cornerstone of many bioactive natural compounds such as guaiane sesquiterpenes, guaianolide sesquiterpene lactones, and diterpene tiglianes.<sup>1</sup> However, there are few reports on their synthesis. Unlike five- and six-membered rings, the synthesis of seven-membered rings is more challenging and generally limited to multi-step processes rather than direct intramolecular reactions.<sup>2</sup> Thus, development of an efficient method to prepare these scaffolds has attracted a significant amount of research attention.

Over the past few decades, the transition metal-catalyzed intramolecular Buchner reaction<sup>3</sup> has been reported by several research groups.<sup>4</sup> This unique strategy toward seven-membered carbocycles has been utilized in natural product synthesis.<sup>5</sup> However, the catalytic intramolecular reaction of diazoacetamides, diazoketones and diazoesters usually leads to competition between the Buchner and C-H insertion reactions.<sup>6</sup> Therefore, many reports deal with controlling the regioselectivity of the reaction, which not only depends on the type of starting material used, but also the nature of the reaction solvent.

Moreover, when compared to the intramolecular C-H insertion reaction of diazoacetamides, there are fewer reports on the Buchner reaction (Scheme 1a and b).<sup>7</sup> In particular, very few examples have addressed the stereoselectivity of the Buchner product from the corresponding diazoacetamide.<sup>8</sup> To date, only one research study by Doyle and co-workers (2015) has reported

## Highly stereoselective intramolecular Buchner reaction of diazoacetamides catalyzed by a Ru(II)-Pheox complex†

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Scheme 1 Transition metal catalytic carbene transfer reaction of diazoacetamides.

the asymmetric intramolecular Buchner reaction of diazoacetamides, whereby *N*-*tert*-butyl-*N*-(*p*-methoxybenzyl)enoldiazoacetamide resulted in a mixture of the C-H insertion product and Buchner product in a total yield of 90% with moderate enantioselectivities of 41 and 53% ee, respectively (Scheme 1c).<sup>8</sup>

Recently, we have developed a Ru(II)-Pheox<sup>9a</sup> complex, which is efficient in carbene transfer reactions, in particular, asymmetric cyclopropanation and Si-H insertion reactions.<sup>9</sup>

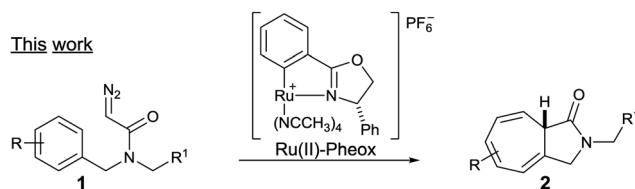
Driven by our interests in the catalytic intramolecular Buchner reaction of diazoacetamide, the efficiency displayed by the Ru(II)-Pheox catalyst, and the importance of the seven-membered ring scaffold in natural product synthesis,<sup>5</sup> we started to study the enantioselective reaction, which is much more challenging (Scheme 2).

Herein, we report the development of an intramolecular Buchner reaction of a variety of *N*-benzyl diazoamide derivatives in the presence of a chiral Ru(II)-Pheox catalyst. The aromatic rings are converted into the corresponding  $\gamma$ -lactam ring fused seven-membered ring system with high regio- and stereoselectivity.

At the outset of this investigation, *N,N*-bis(4-methoxybenzyl)-2-diazoacetamide **1b** was chosen as the substrate using 1 mol% of catalyst to optimize the reaction conditions. Initially, well-known

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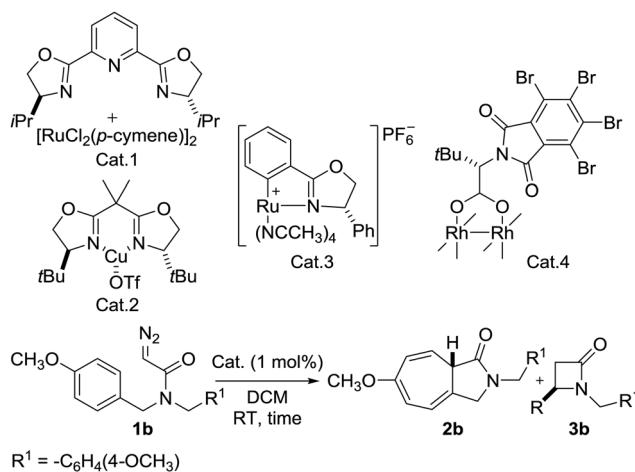
Scheme 2 Asymmetric intramolecular reaction of diazoacetamides catalyzed by the Ru(II)-Pheox complex.

carbene transfer catalysts were screened and the results summarized in Table 1.

Extensive studies on the reaction conditions indicated that after 48 h, product **2b** was obtained in 52% yield with no chirality using Ru(II)-Pybox<sup>10</sup> (Table 1, entry 1). When Cu(II)-Box<sup>11</sup> was used, product **2b** was formed in 87% yield and 15% ee (Table 1, entry 2). In the case of the Rh<sub>2</sub>(S-TBPTT)<sub>4</sub><sup>12</sup> complex, the yield of **2b** increased dramatically to 95%. However, the enantioselectivity was relatively low (21% ee) (Table 1, entry 4). Screening the various Ru(II)-Pheox catalyst derivatives developed by our group showed that the chiral Ru(II)-Pheox complex (Cat. 3) was the most effective catalyst (Table 1, entry 3 and Table S1, ESI<sup>†</sup>).<sup>9</sup> The reaction proceeds rapidly to give **2b** in excellent yield (99%) with almost perfect enantioselectivity (99% ee). For more details on the catalyst screening process, see the ESI<sup>†</sup>.

We next focused on the efficiency of the Ru(II)-Pheox catalyst and the results shown in Table 2. We found that decreasing the catalyst loading from 1 to 0.002 mol% showed no change in the enantioselectivity (99% ee) of product **2b**, while the TON and TOF values increased (Table 2). Using a very small amount of

Table 1 Catalyst screening experiments



Entry	Cat.	Time [min]	<b>2b</b> : <b>3b</b> <sup>a</sup>	Yield <sup>b</sup> [%]	<b>2b</b> ee [%]
1	Cat. 1	48 h	100:0	52	0
2 <sup>d</sup>	Cat. 2	60	100:0	87	15
3	Cat. 3	2	100:0	99	99
4	Cat. 4	2	100:0	95	21

<sup>a</sup> The ratio of **2b**:**3b** was determined using <sup>1</sup>H NMR spectroscopy.

<sup>b</sup> Isolated yield. <sup>c</sup> Determined using chiral HPLC analysis. <sup>d</sup> The reaction temperature was 40 °C.

Table 2 Efficiency of the Ru(II)-Pheox catalyst

Entry	X [%]	Time [min]	TON <sup>a</sup>	TOF <sup>b</sup> [min <sup>-1</sup> ]	Yield <sup>c</sup> [%]	<b>2b</b> ee <sup>d</sup> [%]
1	1	2	99	49.5	99	99
2	0.1	2	990	495	99	99
3	0.01	2	9900	4950	99	99
4	0.005	2	19 800	9900	99	99
5	0.003	30	33 000	1100	99	99
6	0.002	60	10 000	167	20	99

<sup>a</sup> TON = moles of desired product (**2b**)/moles of catalyst (Ru(II)-Pheox).

<sup>b</sup> TOF = TON/reaction time (min). <sup>c</sup> Isolated yield. <sup>d</sup> Determined using chiral HPLC analysis.

the Ru(II)-Pheox catalyst (0.005 mol%) gave product **2b** within 2 min in 99% yield with excellent TOF (9900 min<sup>-1</sup>) (Table 2, entry 4). When 0.003 mol% of catalyst was used, the TON increased dramatically to 33 000 (Table 2, entry 5).

In Table 2, we found that decreasing catalyst loading from 1 to 0.005 mol% Ru(II)-Pheox, the reaction kept proceeding rapidly with excellent regio- and stereoselectivities. Therefore the Ru(II)-Pheox catalyst is extremely efficient for synthesis product **2b** from the corresponding diazoacetamide **1b**. However, to avoid substrate dependency for various diazoamides, we decided to use 1 mol% Ru(II)-Pheox as the standard condition for screening solvent and substrate scope of the reaction.

In addition, the influence of various solvents on the decomposition of diazoacetamides was examined and the results shown in Table S2 (ESI<sup>†</sup>). DCM was found to be the best solvent for the Ru(II)-Pheox catalyzed reaction. For more details on the optimization of the reaction conditions, see the ESI<sup>†</sup>.

Using the optimized reaction conditions, we decided to explore the substrate scope of the reaction (Table 3). Various diazoacetamides of *N,N*-bis(aryl)-2-diazo-acetamides were examined (Table 3, entries 1–7). Substrates bearing either electron-withdrawing or electron-donating groups (R = H, F, Cl, Br, CH<sub>3</sub>, and OCH<sub>3</sub>) on the *N*-benzyl ring were tolerated in the reaction, giving the desired products (**2a–g**) in 69–99% yield and 74–99% ee.

Substitution with an electron-donating group (e.g., 4-OCH<sub>3</sub>, 3-OCH<sub>3</sub>, and 4-CH<sub>3</sub>) on the *N*-benzyl ring moiety has a strong impact on the reaction (Table 3, entries 2, 3 and 7). The corresponding Buchner reaction products were obtained in excellent yield (up to 99%) and enantioselectivity (up to 99% ee). In the case of substrates bearing an electron-withdrawing group (namely 4-Cl, 4-Br and 4-F), the rate of the Buchner reaction slightly decreased and formation of the C–H insertion product was observed (Table 3, entries 4–6). Nevertheless, the yield and enantioselectivity of the products (**2d–f**) remained excellent (70–91% yield and 90–96% ee). In addition, the bicyclic product **2d** was prepared with the purpose of growing crystals suitable for analysis. The structure of **2d** was confirmed and the absolute configuration was determined to be the *S* configuration using single-crystal X-ray diffraction (Fig. 1 and Fig. S1, ESI<sup>†</sup>).

**Table 3** Ru(II)-Pheox-catalyzed intramolecular Buchner reactions of diazoacetamides

Entry	1	R	R <sup>1</sup>	Time [min]	2 Yield <sup>b</sup> [%]		2 ee <sup>c</sup> [%]
					2:3 <sup>a</sup>	3 [%]	
1	<b>1a</b>	H	C <sub>6</sub> H <sub>5</sub>	2	75:25	69	78
2	<b>1b</b>	4-OCH <sub>3</sub>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	2	100:0	99	99
3	<b>1c</b>	4-CH <sub>3</sub>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2	97:3	96	97
4	<b>1d</b>	4-Cl	4-ClC <sub>6</sub> H <sub>4</sub>	2	83:17	80	96
5	<b>1e</b>	4-Br	4-BrC <sub>6</sub> H <sub>4</sub>	2	80:20	70	95
6	<b>1f</b>	4-F	4-FC <sub>6</sub> H <sub>4</sub>	2	92:8	91	90
7	<b>1g</b>	3-OCH <sub>3</sub>	3-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	2	100:0	87	74
8	<b>1i</b>	H	H	4 h	45:55	40	71
9	<b>1j</b>	4-OCH <sub>3</sub>	H	2	100:0	76	99
10	<b>1k</b>	4-CH <sub>3</sub>	H	2	90:10	48	99
11	<b>1k</b>	4-CH <sub>3</sub>	H	4 h	93:7	67	99
12	<b>1l</b>	4-Cl	H	4 h	83:17	61	92
13	<b>1m</b>	4-Br	H	4 h	80:20	43	96
14	<b>1n</b>	4-F	H	4 h	79:21	55	92
15	<b>1o</b>	4-NO <sub>2</sub>	H	4 h	—	n.o.	—

<sup>a</sup> The ratio was determined using <sup>1</sup>H NMR spectroscopy of the reaction mixture. <sup>b</sup> Isolated yield. <sup>c</sup> Determined using chiral HPLC analysis.

In short, entries 1–7 in Table 3 present an overview of the decomposition of a series of *N,N*-bis(aryl)-2-diazo-acetamides used to prepare the target seven-membered ring products (**2a–g**) with excellent stereo- and regioselectivity.

Besides, a diazoamide bearing both electron-withdrawing and electron-donating groups (**1h**) was also investigated as a substrate, affording the desired Buchner reaction product (**2h**) in high yield (84%) and excellent enantioselectivity (99% ee) (Scheme 3).

Subsequently, a series of *N*-aryl-2-diazo-*N*-methylacetamides was also investigated under the same reaction conditions (Table 3, entries 8–15). Substrates with both electron-withdrawing and electron-donating groups work well in the reaction and afford their Buchner reaction products (**2i–n**) in moderate to good yield (40–76%) and enantioselectivity (71–99% ee).

The reaction afforded the intramolecular Buchner product **2j** ( $R = 4\text{-OCH}_3$ ) in 76% yield with high enantioselectivity (99% ee) (Table 3, entry 9). Switching the substrate to **1k** ( $R = 4\text{-CH}_3$ )



**Scheme 3** Asymmetric intramolecular reaction of diazoacetamide **1h** catalyzed by Ru(II)-Pheox.

dramatically changed the reaction, affording the corresponding seven-membered ring product (**2k**) in 48% yield in 2 min (Table 3, entry 10). Surprisingly, we found that the reaction could afford product **2k** in 67% yield over a longer reaction time (4 h) (Table 3, entry 11). The dimerization reaction was prevented and the reaction yield was improved upon slow addition of a solution of the diazoacetamide to a stirred mixture of the Ru(II)-Pheox catalyst in DCM over 4 h (Table 3, entries 8 and 11–15).

Furthermore, there is intense competition between the reactive sites of the *N*-aryl-2-diazo-*N*-methylacetamide (Table 3, entries 8 and 12–14). Therefore, bicyclic products **2i** and **2l–2n** could be obtained in moderate yield (40–61%). In the case of diazo compound **1o**, the corresponding product **2o** was not obtained.

As a plausible explanation, the substituent changes the electronic properties of the benzene ring and affects the regioselectivity. Nucleophilic substituents, such as 4-CH<sub>3</sub> and 4-OCH<sub>3</sub>, are regarded as electronic donating groups, which increase the electropositivity of the aryl group and improve the reactivity in the aromatic addition reaction. Electrophilic substituents, such as -Cl, -Br, -F, and -H, are regarded as electron-withdrawing groups, which decrease the electropositivity of the aryl group and favor the C–H insertion reaction.

In summary, we have presented a highly stereoselective intramolecular Buchner reaction of diazoacetamides using a Ru(II)-Pheox catalyst. Specifically, a variety of  $\gamma$ -lactam fused 5,7-bicyclic-heptatriene derivatives have been prepared from diazoacetamides in up to 99% yield with high enantioselectivity (up to 99% ee) using a chiral Ru(II)-Pheox catalyst under mild reaction conditions. The product containing diene can be used for further transformation *via* the Diels–Alder cycloaddition reaction.<sup>7a,13</sup>

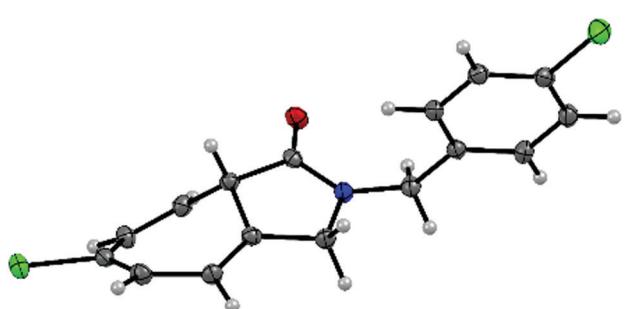
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## Conflicts of interest

There are no conflicts to declare.

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**Fig. 1** X-ray analysis of (S)-6-chloro-2-(4-chlorobenzyl)-3,8a-dihydrocyclohept[c]pyrrol-1(2H)-one (**2d**).

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