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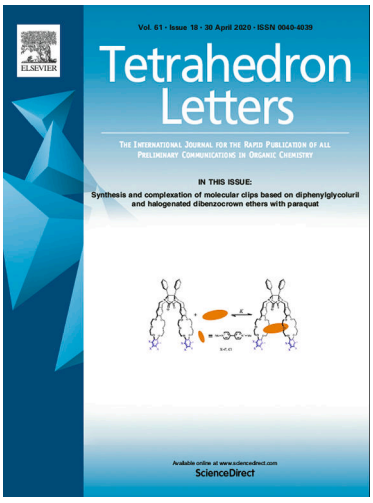

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Hideaki Matsuo, Jun-Chul Choi, Tadahiro Fujitani, Ken-ichi Fujita

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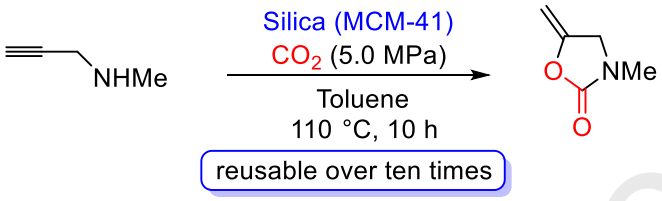

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Silica-catalyzed carboxylative cyclization of propargylic amines with CO_2

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ABSTRACT

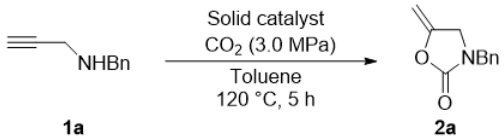
By employing only silica as a catalyst, the carboxylative cyclization of a propargylic amine with CO_2 proceeded to afford the corresponding 2-oxazolidinone. MCM-41, which was a mesoporous silica, was found to be the most effective silica for this purpose. Moreover, after the reaction, the MCM-41 catalyst was recovered by filtration and could be reused over ten times without deactivation.

Strategies for the capture and transformation of carbon dioxide (CO_2) into value-added chemicals have gained tremendous attention, because CO_2 can be used as a nontoxic, non-flammable, abundant, and renewable resource.[1] Moreover, CO_2 is one of the most attractive C_1 building blocks to displace toxic reagents such as phosgene and carbon monoxide.[2] Although CO_2, as the most oxidized carbon derivative, is much less reactive, its application to organic synthesis has been considered one of the most challenging research topics. In particular, the cyclization of unsaturated organic molecules with CO_2 is an atom-economical approach to produce cyclic carbonates and oxazolidinones, which are the essential building blocks for plastics and antibiotics, respectively.[3]

One of the promising approaches for transforming CO_2 is through the carboxylative cyclization of propargylic amines with CO_2 to provide 2-oxazolidinones.[4] Recently, various investigations of the carboxylative cyclization of propargylic amines with CO_2 catalyzed by metal nanoclusters[5] and by organometallic complexes of transition metals such as ruthenium,[6] silver,[7] and gold[8] have been conducted. It is also reported that a number of metal-free catalysts, such as superbases,[9] N-heterocyclic carbenes,[10] triethanolamine,[11] and ammonium fluoride,[12] have been developed for this reaction. In addition, in order to easily recover a catalyst by filtration after the reaction, the use of silica (SiO_2)-bound catalytic active species, such as a ruthenium complex and organic bases, has been reported.[13] We report herein that silica can be used alone to catalyze the carboxylative cyclization of propargylic amines with CO_2 to provide 2-oxazolidinones.[14] In a screening of various silicas as catalysts, MCM-41 was found to be the most effective catalyst for the carboxylative cyclization of propargylic amines with CO_2. Further, it was found that the MCM-41 catalyst could be recovered by filtration and reused without deactivation.

We have examined the carboxylative cyclization of a propargylic amine **1a** with CO_2 to provide a 2-oxazolidinone **2a** through the use of various solid catalysts, as shown in Table 1.[15] First, when a toluene solution of propargylic amine **1a** (0.4 mmol) was stirred at 120 ºC for 5 h in a sealed autoclave under 3.0 MPa of CO_2 using Q-6 (80 mg), an amorphous silica, as a catalyst, the corresponding 2-oxazolidinone **2a** was obtained in a 58% chemical yield (Table 1, entry 1). Next, by employing mesoporous silicas, such as SBA-15 and MCM-41, as catalysts, it was found that MCM-41 afforded the highest chemical yield of **2a** (77%; Table 1, entry 3).[16] In contrast, neither basic alumina nor acidic alumina exhibited catalytic activities (Table 1, entries 4 and 5). When hydrotalcite was used as a catalyst, **2a** was obtained in a low chemical yield (24%; Table 1, entry 6). When no catalyst was used, **2a** was not obtained (Table 1, entry 7). These results indicate that the carboxylative cyclization of **1a** with CO_2 in entries 1–3 in Table 1 could be catalyzed by silica.

Table 1. Carboxylative cyclization of the propargylic amine **1a** with CO_2 using various solid catalysts.[a]



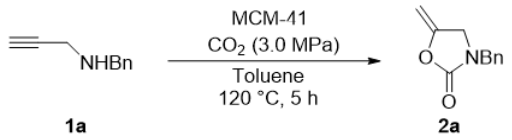
1a **2a**

Entry	Solid catalyst	Yield (%)[b]
1	Silica (Q-6)	58
2	Silica (SBA-15)	66
3	Silica (MCM-41)	77
4	Basic alumina	1
5	Acidic alumina	0
6	Hydrotalcite	24
7	none	0

[a] R... d in 0.4 M based on **1a**), carried out in a sealed autoclave at 120 °C for 5 h under pressurized CO_2 (3.0 MPa).
[b] Determined by the integration of ^{1}H NMR absorptions with reference to an internal standard.

Encouraged by these results, we subsequently optimized the amount of catalyst, as shown in Table 2. By employing various amounts of MCM-41 as a catalyst, the carboxylative cyclization of a propargylic amine **1a** with CO_2 was carried out under the same reaction conditions and scale as shown in Table 1. As a result, when 40 mg of MCM-41 was used as a catalyst, the corresponding 2-oxazolidinone **2a** was obtained in the highest chemical yield (84%; Table 2, entry 2).

Table 2. Optimization of the amount of the MCM-41 catalyst in carboxylative cyclization of the propargylic amine **1a** with CO_2.[a]



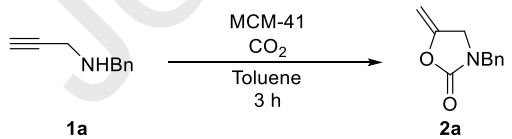
1a **2a**

Entry	MCM-41	Yield (%)[b]
1	80 mg	77
2	40 mg	84
3	20 mg	77

[a] The reaction conditions and scale were identical to those in Table 1.
[b] Determined by the integration of ^{1}H NMR absorptions with reference to an internal standard.

Next, by employing the optimized amount of the MCM-41 catalyst, we examined two of the reaction conditions—namely, the CO_2 pressure and reaction temperature—as shown in Table 3. We first performed the carboxylative cyclization of the propargylic amine **1a** in toluene at 120 ºC for 3 h under various CO_2 pressures (1.0–5.0 MPa). When the reaction was carried out under CO_2 pressure of 5.0 MPa, the 2-oxazolidinone **2a** was obtained in the highest chemical yield (70%; Table 3, entry 4). We then examined the reaction temperature under CO_2 pressure of 5.0 MPa. When the reaction was carried out at 100 ºC, the chemical yield of **2a** was very low (4%; Table 3, entry 5). On the other hand, even when the reaction was carried out at 140 ºC, the chemical yield of **2a** was almost the same as that at 120 ºC (71%; Table 3, entry 6).

Table 3. Carboxylative cyclization of the propargylic amine **1a** with CO_2 under various reaction conditions.[a]



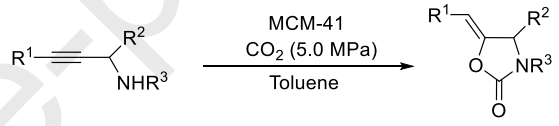
1a **2a**

Entry	CO_2 (MPa)	Temp. (ºC)	Yield (%)[b]
1	1.0	120	42
2	3.0	120	55
3	4.0	120	64
4	5.0	120	70
5	5.0	100	4
6	5.0	140	71

[a] Reaction conditions: **1a** (0.4 mmol), MCM-41 (40 mg), toluene (1 mL; 0.4 M based on **1a**), carried out in a sealed autoclave for 3 h under the indicated reaction conditions.
[b] Determined by the integration of ^{1}H NMR absorptions with reference to an internal standard.

We then performed the MCM-41-catalyzed carboxylative cyclization of various propargylic amines **1** under CO_2 pressure in Table 4. By carrying out the carboxylative cyclization of **1a** at 120 ºC for 10 h, the 2-oxazolidinone **2a** was obtained in an 84% chemical yield (Table 4, entry 1). In the case of the cyclization of *N*-methyl propargylic amine **1b**, which has a low boiling point, we used a sealed autoclave containing the reaction mixture pressurized with CO_2 of 5.0 MPa at room temperature before heating to 110 ºC.[17] As a result, the carboxylative cyclization of **1b** with CO_2 proceeded at 110 ºC to provide the corresponding 2-oxazolidinone **2b** in a 57% chemical yield (Table 4, entry 2). Even by the introduction of a methyl group at R^2 in **1**, the carboxylative cyclization of the propargylic amine **1c** proceeded to provide the corresponding 2-oxazolidinone **2c** in a 93% chemical yield by carrying out the reaction at 140 ºC for 20 h (Table 4, entry 3). In contrast, by the introduction of a phenyl group at R^1 in **1**, the carboxylative cyclization of **1d** gave a poor chemical yield (10%; Table 4, entry 4).[18] On the other hand, when a trifluoromethyl or a cyano group was introduced at the phenyl group in R^1, the chemical yields of the corresponding 2-oxazolidinones **2e** and **2f** slightly increased due to the high reactivity of the carbon–carbon triple bond owing to the introduction of electron-withdrawing groups[10a,12a] (46% and 33%;

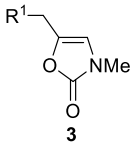
Table 4. Carboxylative cyclization of various propargylic amines **1** for the synthesis of **2**.[a]



1a-g **2a-g**

Entry	Substrate		Temp. (ºC)	Time (h)	Yield (%)[b]
1	NHBn	**1a**	120	10	84 (84)[c]
2[d]	NHMe	**1b**	110	10	57 (56)[c]
3	Me, NHBn	**1c**	140	20	93 (91)[c]
4	Ph, NHMe	**1d**	120	4	10
5	4-$CF_3C_6H_4$, NHMe	**1e**	120	10	46
6	4-CNC_6H_4, NHMe	**1f**	100	5	33
7	Me, NHBn	**1g**	140	20	6
8[d]	NH_2	**1h**	140	20	0

[a] Reaction conditions: **1** (0.4 mmol), MCM-41 (40 mg), toluene (1 mL; 0.4 M based on **1**), carried out in a sealed autoclave under the conditions indicated in the table.
[b] Determined by the integration of ^{1}H NMR absorptions with reference to an internal standard.
[c] Isolated yield. Purified with silica gel column chromatography (hexane–ethyl acetate as eluents).
[d] Pressurized with CO_2 of 5.0 MPa at room temperature before heating to the indicated temperature.

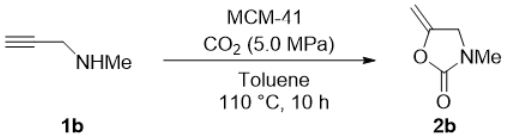


3

R^1: 4-$CF_3C_6H_4$ **3e** 4%
4-CNC_6H_4 **3f** 2%

Figure 1. Structure of 2-oxazolones **3e** and **3f**.

Table 5. Catalyst recycling in carboxylative cyclization of the propargylic amine **1b** with CO_2.[a,b]



No. of run	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Yield (%)[c]	68	74	78	79	81	80	81	81	79	80	81	80	78	77	76

[a] Reaction conditions: **1b** (4 mmol), MCM-41 (400 mg), toluene (5 mL; 0.8 M based on **1b**), carried out at 110 ºC in a sealed autoclave for 10 h under pressurized CO_2.
[b] Pressurized with CO_2 of 5.0 MPa at room temperature before heating to 110 ºC.
[c] Determined by the integration of ^{1}H NMR absorptions with reference to an internal standard.

Table 4, entries 5 and 6, respectively). Only in these cases, the corresponding 2-oxazolones **3e** and **3f** were also obtained in slight chemical yields, respectively (Figure 1; **3e**: 4%, **3f**: 2%). 2-Oxazolones **3e** and **3f** appeared to be obtained by the tautomerization of the generated 2-oxazolidinones **2e** and **2f**, respectively.[10a,19] When we introduced the methyl group in R^1, the corresponding 2-oxazolidinone **2g** was obtained in a low chemical yield (6%, Table 4, entry 7).[20] When a primary amine **1h** was used as a substrate, the corresponding 2-oxazolidinone **2h** was not obtained (Table 4, entry 8).

Finally, the reusability of the MCM-41 catalyst was examined by use of the *N*-methyl propargylic amine **1b**, as shown in Table 5.[21] In this experiment, it was found that the MCM-41 catalyst was recovered by filtration of the reaction mixture, and could be reused over ten times without deactivation to afford the corresponding 2-oxazolidinone **2b** in a fair chemical yield.

Figure 2 shows a proposed mechanism for the silica-catalyzed carboxylative cyclization of the propargylic amine **1**. First, the propargylic amine **1** reacts with CO_2 to form the corresponding carbamic acid **4** in situ.[8g,12b] It is considered that the thus-obtained carbamic acid **4** was activated by silica-surface OH–π interaction with the carbon–carbon triple bond, as shown in **5**.[22] Then, the corresponding 2-oxazolidinone **2** was provided with the regeneration of silica.

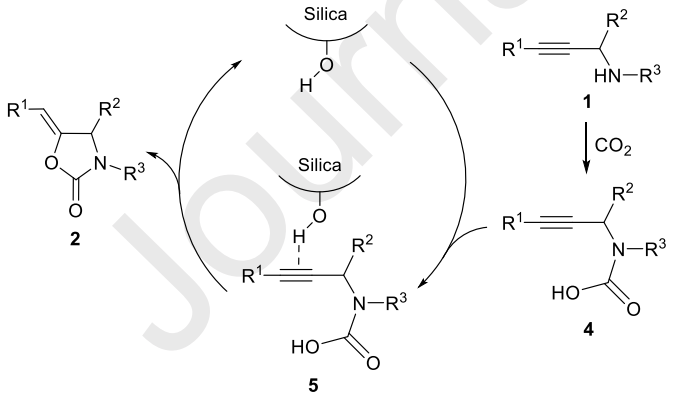


Figure 2. Proposed mechanism of the silica-catalyzed carboxylative cyclization of the propargylic amine **1**.

In summary, by employing only silica as a catalyst, the carboxylative cyclization of propargylic amines with CO_2 proceeded to afford the corresponding 2-oxazolidinones. MCM-41, which was a mesoporous silica, was the most effective catalyst for the reaction, providing a 2-oxazolidinone derivative in a maximum chemical yield of 93%. Moreover, after the reaction, the MCM-41 catalyst was recovered by filtration and could be reused over ten times without deactivation. We are currently trying to apply a silica catalyst to other chemical transformations of CO_2. The results will be reported in due course.

Acknowledgment

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Supplementary Data

Supplementary data associated with this article can be found, in the online version , at http:// .

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15. *Carboxylative cyclization of a propargylic amine **1a** with CO_2: General Procedure.* To a toluene solution (1 mL) of propargylic amine **1a** (0.4 mmol) in a stainless steel autoclave was added a solid catalyst (80 mg) under an argon atmosphere. The autoclave was sealed, heated to 120 ºC and then pressurized with CO_2 of 3.0 MPa. The resulting mixture was magnetically stirred at 120 ºC for 5 h. After the autoclave was cooled in an ice bath and depressurized, a solid catalyst was separated by filtration under a vacuum, followed by washing with dichloromethane. The chemical yield of the 2-oxazolidinone **2a** was determined by the integration of ^{1}H NMR absorption with reference to an internal standard (2-benzyloxynaphthalene), which was added to the filtrated dichloromethane solution.
16. By measuring the nitrogen adsorption-desorption isotherm of silicas, it was found that MCM-41 has the largest BET specific surface area, which is shown in the supplementary data.
17. The pressure of CO_2 at 110 ºC was raised to 6.0 MPa.
18. Recovery of the propargylic amine **1d** could not be detected. By prolonging the reaction time, the chemical yield of a 2-oxazolidinone **2d** decreased, probably due to the thermal decomposition of **2d**.
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20. In Figure 2, by the introduction of the methyl group in R^1, it is assumed that the nucleophilic ring-closure process from **5** to **2** is probably retarded due to the electron-donating methyl group.
21. *Catalyst recycling in the carboxylative cyclization of **1b** with CO_2:* To a toluene solution (5 mL) of the propargylic amine **1b** (277 mg, 4.01 mmol) in a stainless steel autoclave was added MCM-41 (402 mg) under an argon atmosphere. The autoclave was sealed, pressurized with CO_2 of 5.0 MPa at room temperature, and then heated to 110 ºC (CO_2: 6.6 MPa). The resulting mixture was magnetically stirred at 110 ºC for 10 h. The autoclave was cooled in an ice bath and depressurized. MCM-41 was separated by filtration under a vacuum, followed by washing with 2-propanol and dichloromethane successively, under an argon atmosphere. After drying MCM-41 under reduced pressure, it was reused according to the above reaction procedure. The chemical yield of the 2-oxazolidinone **2b** was determined according to the method, which was similar to that of Table 1.[15]
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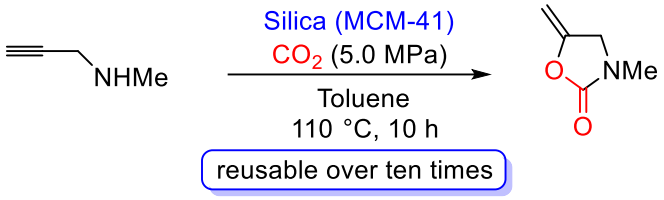
Silica-catalyzed carboxylative cyclization of propargylic amines with CO_2

Hideaki Matsuo, Jun-Chul Choi, Tadahiro Fujitani, Ken-ichi Fujita*



Authors: Hideaki Matsuo, Jun-Chul Choi, Tadahiro Fujitani, Ken-ichi Fujita*

Title: Silica-catalyzed carboxylative cyclization of propargylic amines with CO_2

Highlights

- Silica catalyzed the carboxylative cyclization of a propargylic amine with CO_2.
- MCM-41 was the most effective silica catalyst for the reaction.
- The MCM-41catalyst was recovered by filtration and could be reused over ten times.