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Cu-MOF-Catalyzed Carboxylation of Alkynes and Epoxides

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Abstract—The catalytic activity of copper-containing heterogeneous catalysts, in particular metal–organic frameworks, zeolites, and alumina-supported nanoparticles, in the carboxylation of terminal alkynes and oxiranes has been evaluated. Temperature dependences of these reactions have been studied.

Keywords: metal–organic frameworks, catalysis, copper, carboxylation, alkynes, epoxides.

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Carbon dioxide is one of the greenhouse gases, and its utilization is an important environmental problem. On the other hand, nontoxic carbon dioxide is very promising for organic synthesis since it can be regarded as a convenient and safe substitute for isocyanates and phosgene. Carbon dioxide can be chemically captured via reactions with alkenes, alkynes, dienes, enynes, and aromatic or heteroaromatic compounds [1–3]. Among the reactions of carbon dioxide leading to the formation of useful organic compounds, of exceptional importance is carboxylation of epoxides to produce cyclic carbonates [4] that are used as electrolytes in lithium ion batteries, aprotic polar solvents, and synthetic intermediates [5–7]. Another important reaction is carboxylation of acetylenes, which leads to the formation of propiolic acid derivatives [8–11] widely used in organic synthesis.

It should be noted that carbon dioxide molecule is characterized by high kinetic and thermodynamic stabilities; therefore, carboxylation reactions require the use of either active substrates such as organometallic compounds [12] or active catalysts [13]. The catalyst should be efficient, available, stable, and recyclable. These properties are intrinsic to heterogeneous catalysts based on transition metals, such as metal–organic frameworks, metal-containing zeolite structures, and metal nanoparticles immobilized on various polymeric or inorganic supports.

Metal–organic frameworks (MOFs) are a new class of highly porous hybrid materials that are cage structures formed by metal ions and organic bridging ligands (linkers) [14]. Metal–organic frameworks are advantageous due to the possibility of changing their catalytic properties by variation of the metal nature, functionality and size of the linker, position of functional groups, and/or pore size and shape, which allows the selectivity of catalysis to be controlled [15–17]. In addition, MOFs are efficiently used for adsorption and storage of gases, including carbon dioxide, as well as for separation of gas mixtures [18]. This makes them promising as carboxylation catalysts.

There are published data on the synthesis of cyclic carbonates and polycarbonates by cycloaddition of carbon dioxide to oxiranes in the presence of MOFs based on zinc [19, 20], cobalt [21], zirconium [22], manganese [23], chromium [24], iron [24], indium [22], and hafnium [25]. A few examples of carboxylation catalyzed by copper-based MOFs have also been reported. In particular, copper MOF obtained from aminoterphenyltetracarboxylic acid efficiently catalyzed cycloaddition of carbon dioxide to epoxides under mild conditions (room temperature, CO_2 pressure 1 atm) [26]. A MOF based on copper 2,5-ditriazolylterephthalate provided a higher substrate conversion than did copper benzene-1,3,5-tricarboxylate HKUST-1 (86 and 67%, respectively). However, in the latter case, an N_2/CO_2 gas mixture was used, so that the lower yield of cyclic carbonates could be caused by the lower concentration of CO_2 in the reactor [27]. Catalysts for the carboxylation of propylene oxide and epichlorohydrin were obtained by encapsulation of copper, aluminum, cobalt, and nickel phthalocyanines in faujasite type zeolite (zeolite-Y) [28].

We previously studied carboxylation of epoxides catalyzed by zinc chloride immobilized on various inorganic supports in the presence of tetrabutylammo-

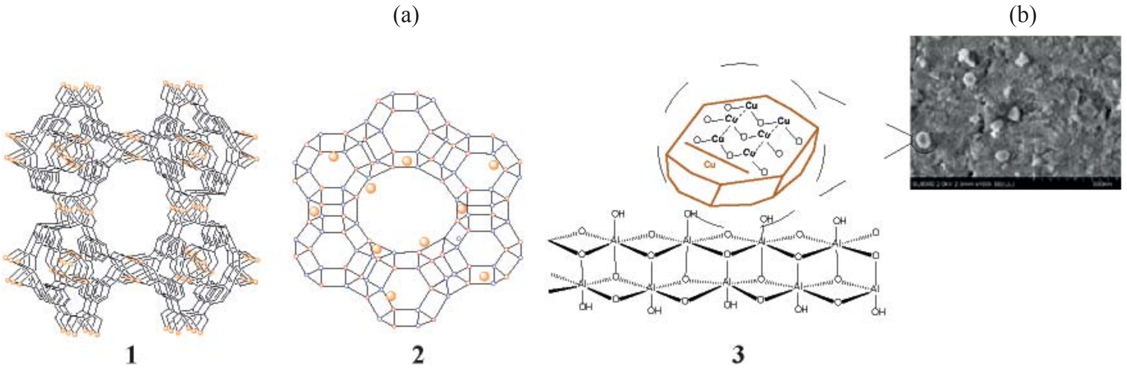


Fig. 1. (a) Copper-containing heterogeneous catalysts HKUST-1 (**1**), CuCa-LSF (**2**), and Cu/Al_2O_3 (**3**); (b) SEM image of catalyst **3**.

nium halide (Bu_4NX) as a nucleophilic additive. Among the catalysts used, $ZnCl_2/Al_2O_3$ turned out to be the most efficient and selective [29]. We also studied carboxylation of alkynes catalyzed by oxide-supported copper nanoparticles, where Cu/Al_2O_3 showed the highest activity [30]. These findings, as well as published data on the use of Cu-MOFs and zeolites as catalysts [27, 28], prompted us to compare the catalytic activities of copper benzene-1,3,5-tricarboxylate (HKUST-1, **1**) [27] and copper-containing bimetallic zeolite based on low-silicon faujasite (CuCa-LSF, **2**) [31] with the activity of alumina-supported copper nanoparticles (40–70 nm; Cu/Al_2O_3, **3**) (Fig. 1) [30] in the above reactions. The morphology and particle size of these catalysts were studied previously [30–32], but no comparative analysis of their catalytic activity was performed.

The carboxylation of styrene oxide **4a** with CO_2 (2 atm) in the presence of 1.5 mol % of tetrabutylammonium bromide (TBAB) was used as a model reaction. The reactions were carried out under solvent-free conditions at various temperatures (Scheme 1, Fig. 2). In the presence of Cu-MOF **1** and copper zeolite **2**, the complete conversion of **4a** was achieved in 15 h at 100°C, whereas the conversions at 80°C were 78 and 83%, and at 50°C, 47 and 53%, respectively. The reactions at room temperature were very slow, and the yield of **5a** did not exceed 20% after 15 h and 30% after 48 h. It should be noted that in the reaction catalyzed by Cu/Al_2O_3, raising the temperature to 80–100°C dramatically reduced the yield (by 15–20%), which may be due to lower solubility of carbon dioxide at elevated temperature. In contrast, catalysts **1** and **2** that effectively adsorb and retain CO_2 provided higher yields as the temperature rose.

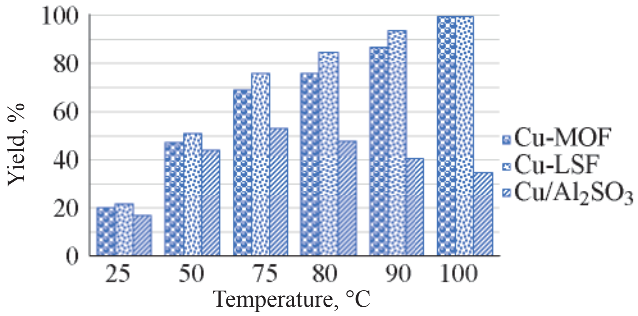


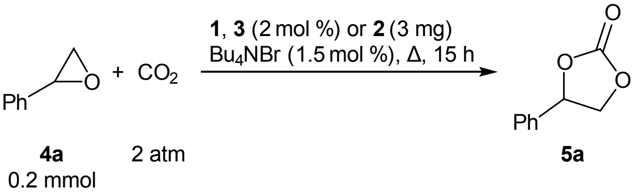
Fig. 2. Temperature effect on the carboxylation of 2-phenyloxirane (**4a**) in the presence of catalysts **1**–**3**.

Thus, a high yield of **5a** can be achieved at 80°C (76 and 83% in 15 h or 86 and 92% in 20 h for catalysts **1** and **2**, respectively). The yield significantly decreased when a lower amount of Cu-MOF was used (61% for 1 mol % of **1** and 33% for 0.2 mol % of **1**).

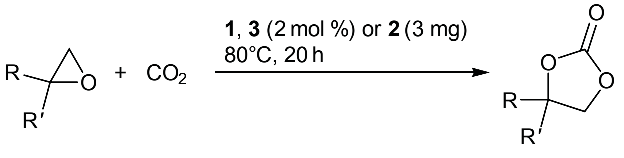
Rise in the carbon dioxide pressure had a positive but insignificant effect on the yield of **5a** which increased by 4–7% for every 2-atm increment in the CO_2 pressure. Therefore, a CO_2 pressure of 2 atm was assumed to be optimal.

Variation of the nucleophilic additive showed that tetrabutylammonium iodide (TBAI) provided the best results. However, the difference in the yields between TBAI and TBAB was insignificant, so that more available TBAB was used in further experiments. No reaction occurred in the absence of a nucleophilic additive. As a rule, the reaction requires no solvent, since both initial oxirane and the resulting cyclic carbonate act as a reaction medium.

Scheme 1.



Scheme 2.



4a–4g
0.2 mmol

2 atm

5a–5g

Compound no.	R, R′	Yield of **5**, %		
		Catalyst **1**	Catalyst **2**	Catalyst **3**
5a	Ph, H	86	92	51
5b	4-ClC_6H_4, H	77	89	–
5c	Me, H	100	100	82
5d	$ClCH_2$, H	98	96	–
5e	$CH_2=CHCH_2CH_2$, H	93	98	73
5f	$PhOCH_2$, H	85	97	59
5g	Me, Me	52	49	17

Under the optimized conditions, we examined carboxylation of a series of alkyl- and aryloxiranes **4a**–**4g** in the presence of copper-containing catalysts **1**–**3** (Scheme 2). Catalysts **1** and **2** provided high to excellent yields of **5a**–**5f** (77–100%) from monosubstituted oxiranes **4a**–**4f**, whereas in the reactions catalyzed by Cu/Al_2O_3 (**3**) the yields of alkyl derivatives were somewhat higher (**5c**, 82%; **5e**, 73%) than the yield of phenyldioxolane **5a** (51%). 2,2-Dimethyloxirane (**4g**) reacted with CO_2 more poorly in the presence of all tested catalysts (yield of **5g** 52, 49%, and 17% for catalysts **1**–**3**, respectively); however, the half-conversion was achieved during the same period using porous catalysts **1** and **2** (HKUST-1 and CuCa-LSF).

We also found that in the reactions catalyzed by CuCa-LSF and HKUST-1 the addition of a new portion of substrate **4a** after the reaction was complete (fresh start) gives rise to a new cycle either without loss of yield (**1**) or with an insignificantly reduced yield (**2**). In contrast, the catalytic activity of **3** considerably decreased even in the second cycle (Fig. 3). Thus, though the Cu-MOF catalyst was somewhat inferior to zeolite-based one in terms of yield, it was superior in terms of reusability.

Published data on the carboxylation of styrene oxide over heterogeneous copper catalysts [22, 24, 26–28, 32] are given in Table 1. Under the conditions proposed by us, the catalytic activities of HKUST-1 and CuCa-LSF were comparable to or exceeded the activity of other copper-based MOFs.

Catalysts **1**–**3** were also evaluated in the carboxylation of terminal alkynes. This reaction is usually carried out in the presence of copper(I) [33–36] or silver salts and complexes [37–39]. However, in the past decade extensive studies were aimed at searching for heterogeneous catalytic systems for carboxylation

Table 1. Carboxylation of 2-phenyloxirane (**4a**) in the presence of copper-containing heterogeneous catalysts

Catalyst	Amount, mol %	Temperature, °C	Reaction time, h	$P(CO_2)$, atm	Yield of **5a**, %	Reference
HKUST-1	0.32	80	16	1	42	[22]
HKUST-1	1.1	25	48	8	10	[24]
Cu(II)-MOF	0.2	25	8	1	89	[26]
Cu(II)-MOF	0.2	25	24	Air	45	[26]
HKUST-1	0.48	80	24	0.85 (+N_2)	67	[27]
FJI-H14	0.48	80	24	0.85 (+N_2)	86	[27]
CuPc-Y-zeolyte	0.4	120	4	6.8	65	[28]
HKUST-1	2.8	100	4	7	34	[32]
HKUST-1	2	80	15	2	86	This work
LSF	2	80	15	2	94	This work
Cu/Al_2O_3	2	80	15	2	51	This work

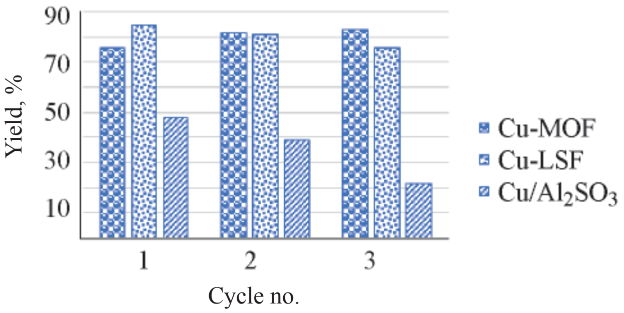


Fig. 3. Fresh-start carboxylation of 2-phenyloxirane (**4a**) in the presence of catalysts **1**–**3**.

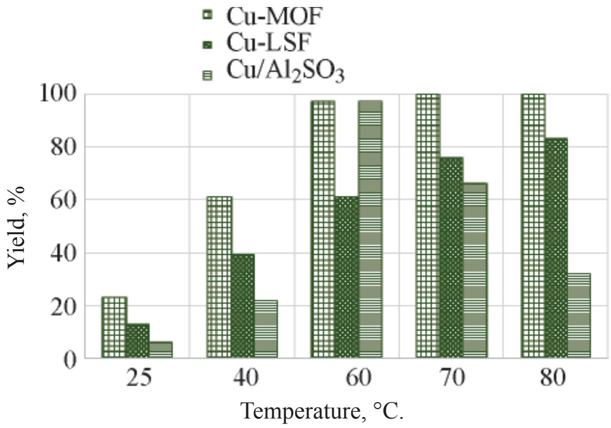


Fig. 4. Temperature effect on the carboxylation of 4-methoxyphenylacetylene (**6a**) in the presence of catalysts **1**–**3**.

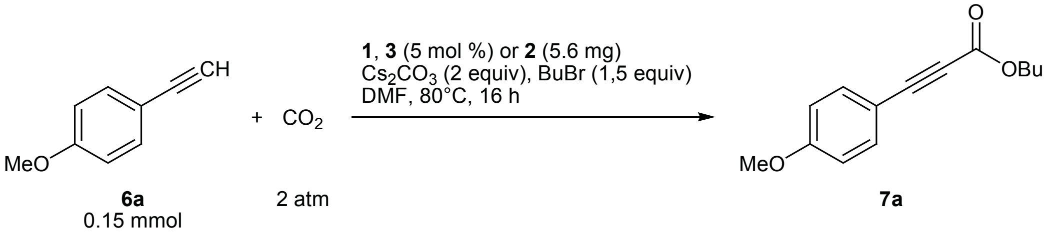
of alkynes. In particular, NHC (N-heterocyclic carbene) polymeric systems based on copper(I) chloride (CuCl-polyNHC) [35] and silver nanoparticles [9], activated carbon-supported copper bromide [40], and silver-containing MOFs based on chromium (MIL-101) [41], cobalt [42], and zirconium (core–shell nanostructures; UiO-66@UiO-67-BPY-Ag) [43] have been proposed. As we already noted, Al_2O_3-supported copper catalyst also efficiently catalyzed this reaction [30].

In this work, the carboxylation of terminal alkynes was carried out using 5 mol % of catalyst **1**–**3**, dimethylformamide as a solvent, and cesium carbonate (2 equiv) as a base. Butyl bromide (1.5 equiv) was also added to simplify the isolation procedure and analysis of the product which was formed as butyl ester, as well as to shift the carboxylation–decarboxylation equilibrium toward product formation. The catalytic activities of **1**–**3** were compared in the carboxylation of 4-methoxyphenylacetylene **6a** (Scheme 3, Fig. 4). The yield of ester **7a** was determined by ^{1}H NMR.

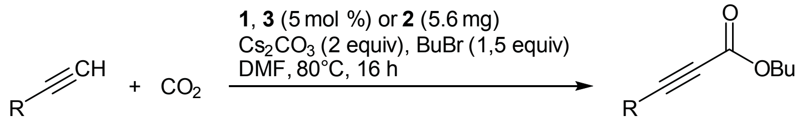
The complete conversion of **6a** under catalysis by HKUST-1 was achieved at 70–80°C in 16 h. The yield of **7a** was also high (97%) at 60°C, whereas it decreased to 61% at 40°C. In the reaction catalyzed by CuCa-LSF, the yield linearly increased with temperature, but the conversion was not complete even at 80°C (yield 83%). The conversion of **6a** was almost complete in the presence of Cu/Al_2O_3 at 60°C, but the yield of **7a** abruptly decreased as the temperature rose (66% at 70°C and 32% at 80°C). A similar pattern was observed for carbon-supported catalyst [40] and was explained by increase of the rate of decarboxylation at elevated temperature [30]. However, highly porous catalysts such as **1** and **2** are free from this drawback due to efficient adsorption of CO_2, which provides easy access to carbon dioxide by the substrate and shift of the equilibrium toward product formation. In all cases, the reaction at room temperature was slow, and the yield of **7a** did not exceed 20%. Thus, the optimal reaction temperature for porous catalysts **1** and **2** is 80°C, whereas Cu/Al_2O_3 (**3**) is more efficient at 60°C, and the activity of the latter exceeds that of the homogeneous CuI–phenanthroline system (yield 97 and 76%, respectively).

A series of terminal alkynes **6a**–**6e** were subjected to carboxylation under the optimal conditions (2 equiv of Cs_2CO_3, 5 mol % of catalyst **1**–**3**, 1.5 equiv of BuBr, CO_2 pressure 2 atm, solvent DMF, temperature 80 or 60°C; Scheme 4). Unsubstituted phenylacetylene (**6b**) and its analogs **6a** and **6c** with electron-donating substituents in the benzene ring were converted to the corresponding butyl propiolates **7a**–**7c** in nearly quantitative yields in the presence of HKUST-1 (**7a**–**7c**, 100%) and Cu/Al_2O_3 (**7a**, **7c**, 97%; **7b**, 100%; 60°C) and in high yields in the presence of CuCa-LSF (**7a**,

Scheme 3.



Scheme 4.



6a–6e 0.15 mmol

2 atm

7a–7e

Compound no.	R	Yield of **7**, %		
		Catalyst **1**	Catalyst **2**	Catalyst **3**, 60°C
7a	4-MeOC$_6$H$_4$	100	83	97
7b	Ph	100	88	100
7c	4-*t*-BuC$_6$H$_4$	100	79	97
7d	4-FC$_6$H$_4$	82	64	67
7e	C$_5$H$_{11}$	71	58	52

83%; **7b**, 88%; **7c**, 79%). The yields of **7d** containing an electron-withdrawing fluorine atom in the benzene ring and **7e** (aliphatic alkyne) were lower (82, 64, and 67% and 71, 58, and 52% for catalysts **1**–**3**, respectively). We succeeded in performing several further cycles of carboxylation of **6a** at 60°C (fresh-start) without significant loss of catalytic activity (Fig. 5); the best results were obtained using Cu-MOF **1**.

Published data on the carboxylation of phenylacetylene [9, 35, 41] are presented in Table 2. It is seen that under the given conditions, the catalytic activities of HKUST-1 and Cu/Al$_2$O$_3$ are comparable to or exceed those found for other copper- and silver-based heterogeneous catalytic systems.

As follows from Figs. 2 and 4, both carboxylation reactions showed similar temperature dependences for copper catalysts. The activity of porous catalysts **1** and **2** increased with temperature. In contrast, the catalytic efficiency of alumina-supported copper nanoparticles (catalyst **3**) decreased as the temperature rose above 60–75°C due to weaker adsorption of CO$_2$ at elevated temperature. The catalytic activity of **3** in the carboxylation of alkynes dropped to a greater extent because of a larger contribution of the decarboxylation process. The amount of the catalyst in the reaction with alkynes was higher than in the cycloaddition of CO$_2$ to oxiranes (5 and 2 mol %, respectively). The effects of substituents in the substrates were also different for oxiranes and alkynes. Monoalkyl-substituted oxiranes reacted slightly more readily than their aryl-substituted analog and significantly better than 2,2-disubstituted oxirane. Contrastingly, aliphatic alkynes were considerably less reactive than arylacetylenes, especially those with electron-donating substituents. Furthermore, zeolite catalyst **2** was much less efficient than Cu-MOF in the carboxylation of alkynes, whereas their efficiencies in the carboxylation of epoxides were fairly similar. A probable reason is that copper(II) predominates in CuCa-LSF, whereas HKUST-1 and Cu/Al$_2$O$_3$ contain large amounts of copper(I) [30, 44] which catalyzes the carboxylation process.

In summary, copper-containing heterogeneous catalysts are efficient in the carboxylation of alkynes and epoxides. The copper-containing catalyst based on a porous metal–organic coordination polymer persistently showed a high activity in both reactions,

Table 2. Carboxylation of phenylacetylene (**6b**) in the presence of copper- and silver-containing heterogeneous catalysts

Metal	Catalyst, mol %	P(CO$_2$), atm	Temperature, °C	Reaction time, h	Yield of **7b**, %	Reference
Cu	P(NHC)$_{0.5}$(NHC-Cu)$_{0.5}$	1	25	16–24	95	[35]
Cu	P(NHC)$_{0.5}$(NHC-Cu)$_{0.5}$	1	25	24	90	[35]
Ag	AgNPs MIL-101 zeolite-type MOF, 2.7	1	50	15	99	[41]
Ag	Poly-NHC	1	25		98	[9]
Cu	HKUST-1, 5	2	60/80	16	97/100	This work
Cu	CuCa-LSF	2	80	16	88	This work
Cu	Cu/Al$_2$O$_3$, 5	2	60/80	16	97/100	This work

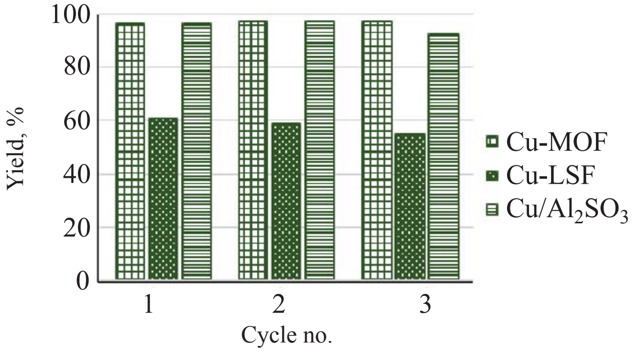


Fig. 5. Fresh-start carboxylation of 4-methoxyphenylacetylene (**6a**) in the presence of catalysts **1**–**3**.

whereas the catalytic system based on low-silicon faujasite worked better in the carboxylation of epoxides. In the carboxylation of alkynes, the cheaper catalyst based on alumina-supported copper nanoparticles is a worthy alternative to MOFs, since it provides comparable results even at lower temperature.

EXPERIMENTAL

Preparation of MOF HKUST-1. An authentic sample of **1** was synthesized as described in [45]. Benzene-1,3,5-tricarboxylic acid (5.0 g), was dissolved in 250 mL of EtOH–DMF (volume ratio 1 : 1) on stirring with a magnetic stirrer. Copper(II) nitrate trihydrate (10.387 g) was dissolved in 85 mL of deionized water on stirring with a magnetic stirrer (10 min, 25°C), and the copper(II) nitrate solution was added to the solution of benzene-1,3,5-tricarboxylic acid. The mixture was stirred for 24 h at 65°C. The blue crystals of HKUST-1 were separated using a laboratory centrifuge and washed first with DMF and then with methylene chloride (3 × 12 mL) to remove DMF from pores of the MOF. The light turquoise crystalline solid was dried at 180°C for 4 h and activated by heating for 16 h under reduced pressure ($\sim 10^{-2}$ mm Hg) while gradually raising the temperature from 25 to 150°C. As a result, the product became dark violet.

General procedure for the carboxylation of oxiranes 4a–4g. An RLP15ML 15-mL glass low-pressure reactor equipped with a gas inlet system, pressure gage, and magnetic stirrer was charged with 0.2 mmol of oxirane **4a**–**4g**, 0.004 mmol of catalyst **1** or **3** or 3.0 mg of CuCa-LSF (**2**), and 0.003 mmol of TBAB. The reactor was filled thrice with CO_2, the gas pressure was adjusted to 2 atm, and the mixture was stirred for 15 h at 80°C. The mixture was then cooled to room temperature, the liquid part was separated by centrifugation, and the product was isolated by silica gel column chromatography using petroleum ether as eluent and dried under reduced pressure. The spectral characteristics of compounds **5a**–**5g** were in agreement with published data [29, 46].

General procedure for the carboxylation of terminal alkynes 6a–6e. An RLP25ML 25-mL glass low-pressure reactor equipped with a gas inlet system, pressure gage, and magnetic stirrer was charged with 0.15 mmol of alkyne **6a**–**6e**, 0.30 mmol of Cs_2CO_3, 0.0075 mmol of catalyst **1** or **3** or 5.6 mg of CuCa-LSF (**2**), 0.225 mmol of butyl bromide, and 2 mL of DMF. The reactor was filled thrice with CO_2, the gas pressure was adjusted to 2 atm, and the mixture was stirred for 16 h at 80°C (or at 60°C in the case of Cu/Al_2O_3). The mixture was then cooled to room temperature, and the liquid part was separated by centrifugation, concentrated under reduced pressure, and analyzed by GLC or ^1H NMR (using DMSO-d_6 or $CDCl_3$ as solvent). The product was isolated by silica gel column chromatography using petroleum ether–ethyl acetate (20 : 1) as eluent and dried under reduced pressure. The spectral characteristics of compounds **7a**–**7e** were in agreement with published data [30, 34].

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CONFLICT OF INTERESTS

The authors declare the absence of conflict of interests.

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