Supporting Information

Cu(I)-containing MOF as efficient catalyst for the reactions of carbon dioxide and propargylic alcohols to carbonates at room temperature

Yifan Li, Zhenwei Wei, Jiayin Hu,* Tianlong Deng*

Tianjin Key Laboratory of Brine Chemical Engineering and Resource Eco-utilization, College of Chemical Engineering and Materials Science, Tianjin University of Science and Technology, Tianjin, China

E-mail: hujiayin@tust.edu.cn; tldeng@tust.edu.cn.

Content

| 1. NMR data of products | 2 |
|-------------------------|----|
| 2. Figure S1 | .3 |
| 3. Table S1 | 3 |

1. NMR data of products



4,4-Dimethyl-5-methylene-[1,3]dioxolan-2-one.

¹H NMR (400 MHz, Chloroform-*d*) δ 4.76 (s, 1H), 4.30 (s, 1H), 1.61 (s, 6H).¹³C NMR (101 MHz, Chloroform-*d*) δ 158.75, 151.29, 85.31, 84.64, 27.59.



4-Ethyl-4-methyl-5-methylene-[1,3]dioxolan-2-one.

¹H NMR (400 MHz, Chloroform-*d*) δ 4.78 (d, *J* = 3.9 Hz, 1H), 4.25 (d, *J* = 3.9 Hz, 1H), 1.88 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.73 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.55 (s, 3H), 0.95 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 157.38, 151.56, 87.63, 85.61, 33.36, 25.94, 7.31.



4-Isobutyl-4-methyl-5-methylene-[1,3]dioxolan-2-one.

¹H NMR (400 MHz, Chloroform-*d*) δ 4.75 (d, *J* = 4.0 Hz, 1H), 4.25 (d, *J* = 3.9 Hz, 1H), 1.87–1.73 (m, 2H), 1.68–1.57 (m, 1H), 1.54 (s, 3H), 0.93 (dd, *J* = 6.5, 2.6 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.26, 151.46, 87.36, 85.60, 48.46, 26.96, 24.27, 23.94, 23.64.



4-Methylene-1,3-dioxa-spiro[4.5]decan-2-one.

¹H NMR (400 MHz, Chloroform-*d*) δ 4.76 (d, *J* = 3.9 Hz, 1H), 4.33 (d, *J* = 3.9 Hz, 1H), 2.07–1.95 (m, 2H), 1.75–1.61 (m, 7H), 1.42–1.18 (m, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.63, 151.45, 86.42, 85.51, 36.40, 24.25, 21.57.



4-Methyl-5-methylidene-4-phenyl-[1,3]dioxolan-2-one.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.10–6.94 (m, 5H), 4.50 (d, *J* = 4.1 Hz, 1H), 4.06 (d, *J* = 4.1 Hz, 1H), 1.52 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 157.41, 151.25, 139.34, 129.23, 128.98, 124.73, 88.29, 87.25, 27.38.





Figure S1 The XRD spectrum of [Cu^I]-Cu-BTC before and after the catalytic reaction.

3. Table S1

| Table S1 A compa | rison of the cataly | tic activity [C | Cu ¹]-Cu-BTC in this v | vork and reported Cu(I)-MOFs. |
|------------------|---------------------|-----------------|------------------------------------|-------------------------------|
| 1 | | | - | I (7) |

| Entry | Cu(I)-MOFs/co-catalyst | P (MPa) | T (°C) | <i>t</i> (h) | Solvent | Yield (%) | Ref. |
|-------|---|---------|--------|--------------|--------------------|-----------|--------------|
| 1 | BPDPrCuCl/CsF | 2.0 | r.t. | 24 | CH ₃ CN | 92 | 1 |
| 2 | Cu(I)-CN-BPY/TEA | 0.5 | 50 | 24 | CH ₃ CN | 96 | 2 |
| 3 | $[Cu^I(bib)]_4\{V^V{}_4O_{12}\}/DBU$ | 0.4 | r.t. | 12 | CH ₃ CN | 99 | 3 |
| 4 | {(NH ₂ C ₂ H ₆) _{0.75} [Cu ₄ I ₄ ·(L) ₃ · (In) _{0.75}]·DMF·H ₂ O}/TEA | 0.5 | 50 | 10 | | 99 | 4 |
| 5 | [Cu ^I]-Cu-BTC/[Emim][OAc] | 1.0 | r.t. | 12 | | 91 | This work |

References

[1] A. C. Reyes, K. Farshadfar, M. Rudolph, F. Rominger, T. Schaub, A. Ariafard, A. Stephen, K. Hashmi, *Green Chem.*, 2021, **23**, 889.

[2] Z. L. Shi, J. C. Jiao, Q. X Han, Y. Xiao, L. K. Huang, M. X. Li, *Molecular Catalysis*, 2020, **496**, 111190.

[3] H. -R. Tian, Z. Zhang, S. -M. Liu, T. -Y. Dang, Z. Li, Y. Lu, S. -X. Liu, *Green Chem.*, 2020, 22, 7513.

[4] S. -L. Hou, J. Dong, X. -L. Jiang, Z. -H. Jiao, B. Zhao, Angewandte Chemie., 2018, 58, 577.