

Supporting Information

Zinc(II)-Catalyzed Reactions of Carbon Dioxide and Propargylic Alcohols to Carbonates at Room Temperature

Jiayin Hu, Jun Ma*, Qinggong Zhu, Qingli Qian, Hongling Han, Qingqing Mei, Buxing Han*

Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China; Tel: (+) 86-10-62562821; E-mail: majun@iccas.ac.cn; hanbx@iccas.ac.cn.

Contents

1. General	
2. Experimental results	
2.1. Figures S1-S3	2
2.2. Products	4
3. NMR Spectra	6

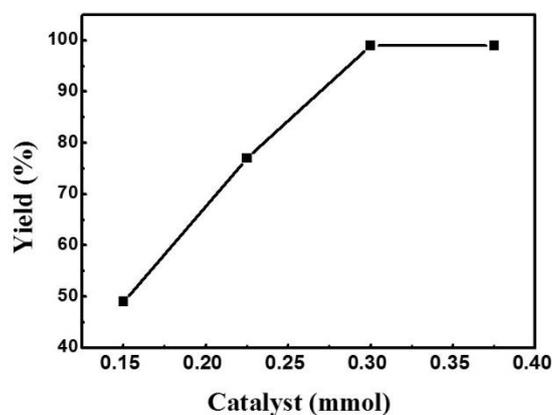
1. General

CO₂ was supplied by Beijing Analytical Instrument Factory with a purity of 99.99%. Zinc Iodide was supplied by Aladdin and was dried at 70 °C under vacuum for 24 h before used. Other solvents and substances were obtained commercially and were used as received. Standard column chromatography was performed on 200-300 mesh silica gel. NMR spectra were recorded on a Bruker Avance III HD 300 MHz NMR spectrometer (300 MHz for ¹H and 75 MHz for ¹³C). Deuterated solvents chloroform-D (D, 99.8% +3% v/v TMS), dimethyl sulfoxide-d₆ (D, 99.9%) were purchased from Cambridge Isotope Laboratories, Inc., and were used without further purification.

2. Experimental Results

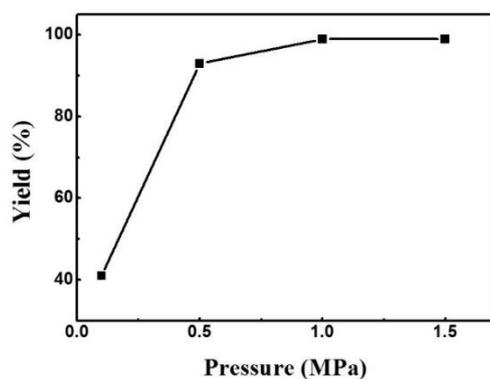
2.1 Figures S1-S3

Fig. S1 Optimization of catalyst amount.^a



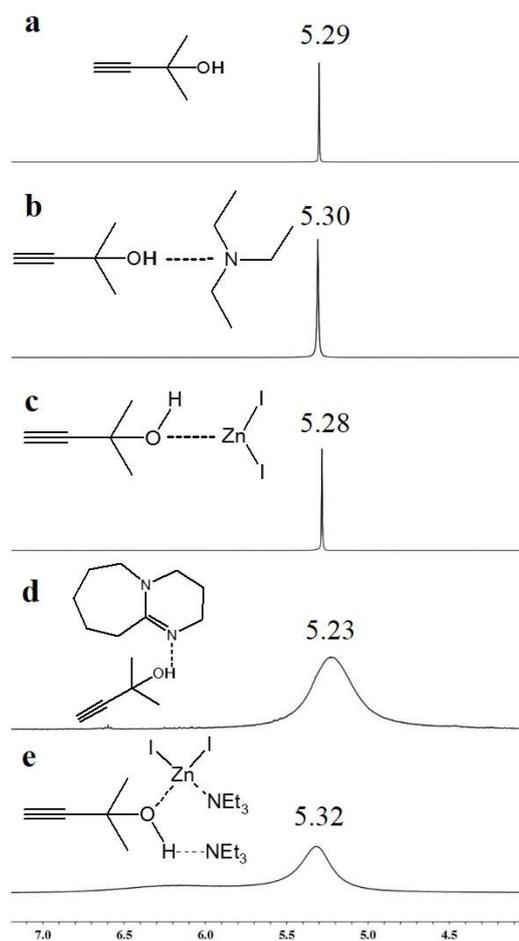
Typical reaction conditions were as follows: 1.5 mmol of **1a**, 1.5 mmol of triethylamine, different dosages of ZnI₂, 30 °C, 1 MPa CO₂, 14 h. ^aYields were determined by ¹H NMR spectroscopy using 1,3,5-trioxane as an internal standard.

Fig. S2 Optimization of reaction pressure.^a



Typical reaction conditions were as follows: 1.5 mmol of **1a**, 1.5 mmol of triethylamine, 0.3 mmol of ZnI₂, different reaction pressure, 30 °C, 14h. ^aYields were determined by ¹H NMR spectroscopy using 1,3,5-trioxane as an internal standard.

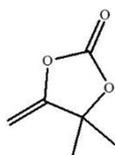
Fig. S3 ¹H NMR spectra of **1a**, **1a**/NEt₃, **1a**/ZnI₂, **1a**/DBU, **1a**/ZnI₂/NEt₃. ([D₆]DMSO, 298 K).



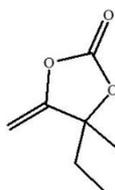
2.2. Products

Typical procedure for the synthesis of α -alkylidene cyclic carbonates. As an example, the procedure using **1a** as the substrate was described, and those for other substrates were similar. **1a** (1.5 mmol), triethylamine (1.5 mmol), ZnI₂ (0.3 mmol) were loaded into a 22 mL stainless-steel batch reactor equipped with a magnetic stirrer. The air in the reactor was removed by blowing CO₂ into the reactor. Then the pressure of CO₂ was kept at 1 MPa. The reactor was placed in a constant temperature water bath and the reaction mixture was stirred for desired time. After the reaction, the reactor was placed in ice water for 20 minutes and CO₂ was vented slowly. Then dichloromethane (5 mL) was added in the reaction mixture. After removing precipitate by centrifuging, the reaction mixture was washed with water, dried over Na₂SO₄ and filtered. The solvent was removed under vacuum to afford the product. The product **2e** was obtained by silica gel column chromatography (ethyl acetate:petroleum ether = 1:30).

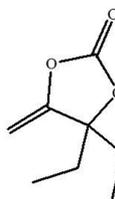
data:



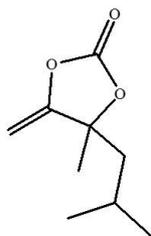
4,4-Dimethyl-5-methylene-[1,3]dioxolan-2-one (2a). colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 4.73 (d, J = 4.0 Hz, 1H), 4.30 (d, J = 4.0 Hz, 1H), 1.59 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 158.75, 151.22, 85.25, 84.63, 27.51.



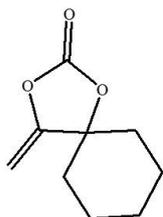
4-Ethyl-4-methyl-5-methylene-[1,3]dioxolan-2-one (2b). light yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 4.78 (d, J = 3.9 Hz, 1H), 4.25 (d, J = 3.9 Hz, 1H), 1.89 (dq, J = 14.7, 7.4 Hz, 1H), 1.73 (dq, J = 14.6, 7.4 Hz, 1H), 1.55 (s, 3H), 0.95 (t, J = 7.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 157.42, 151.53, 87.60, 85.56, 33.36, 25.92, 7.30.



4,4-Diethyl-5-methylene-[1,3]dioxolan-2-one (2c). light yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 4.85 (d, J = 3.8 Hz, 1H), 4.22 (d, J = 3.8 Hz, 1H), 1.92 (dq, J = 14.6, 7.3 Hz, 2H), 1.70 (dq, J = 14.7, 7.4 Hz, 2H), 0.96 (t, J = 7.4 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 155.79, 151.85, 90.85, 85.80, 31.89, 7.09.



4-Isobutyl-4-methyl-5-methylene-[1,3]dioxolan-2-one (2d). light yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 4.77 (d, $J = 3.9$ Hz, 1H), 4.26 (d, $J = 3.9$ Hz, 1H), 1.88-1.73 (m, 2H), 1.68-1.60 (m, 1H), 1.56 (s, 3H), 1.01-0.89 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 158.32, 151.45, 87.33, 85.56, 48.51, 26.99, 24.28, 23.96, 23.66.



4-Methylene-1,3-dioxaspiro[4.5]decan-2-one (2e). colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 4.74 (d, $J = 3.8$ Hz, 1H), 4.28 (d, $J = 3.8$ Hz, 1H), 2.08-1.91 (m, 2H), 1.85-1.51 (m, 7H), 1.40-1.17 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 158.75, 151.48, 86.40, 85.49, 36.50, 24.34, 21.62.

3. NMR Spectra

