JOC The Journal of Organic Chemistry

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Organocatalytic Strategy for the Fixation of CO_2 via Carboxylation of Terminal Alkynes

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Cite This: J. Org. Chem. 2021, 86, 1850−1860 Read Online

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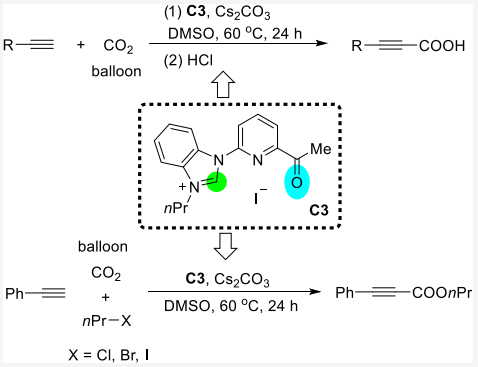
ABSTRACT: An organocatalytic strategy for the direct carboxylation of terminal alkynes with CO_2 has been developed. The combined use of a bifunctional organocatalyst and Cs_2CO_3 resulted in a robust catalytic system for the preparation of a range of propiolic acid derivatives in high yields with broad substrate scope using CO_2 at atmospheric pressure under mild temperatures (60 °C). This work has demonstrated that this organocatalytic method offers a competitive alternative to metal catalysis for the carboxylation of terminal alkynes and CO_2. In addition, this protocol was suitable for the three-component carboxylation of terminal alkynes, alkyl halides, and CO_2.

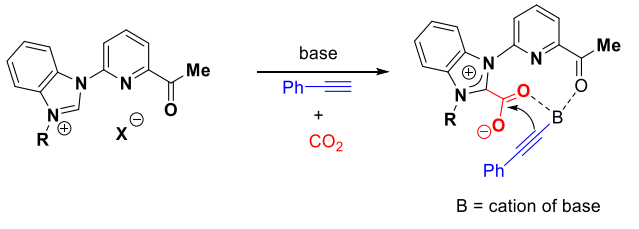


INTRODUCTION

Carbon dioxide (CO_2), as a greenhouse gas, has caused a climate change worldwide. The use of CO_2 as a raw material for preparing chemicals can not only facilitate the change from fossil energy to renewable resources, but also provide a strategy to solve the climate problems caused by CO_2. Hence, CO_2, as a cheap, nontoxic, and abundant C1 building block in organic synthesis, has attracted wide attention in recent years.[1] The design and synthesis of efficient catalysts for the direct carboxylation of terminal alkynes with CO_2 have attracted increasing attention due to their high atom-economy.[2] The carboxylation of terminal alkynes with CO_2 has experienced impressive development over the past few years,[3] with the field being clearly dominated by metal-catalyzed approaches such as Ag,[4] Au,[5] Cu,[6] Ni,[7] Mg,[8] Mo,[9] and rare-earth metals.[10] Recently, metal-free base-promoted approaches[11] have been presented as alternatives for metal-catalyzed carboxylation of terminal alkynes with CO_2, but these methods require a high reaction temperature or the terminal alkynes require preactivation or *in situ* activation. The organocatalytic strategy for carboxylation of terminal alkynes with CO_2 represents an attractive approach because organocatalysts are typically inexpensive, readily available, and free of transition-metal contaminants. Recently, an *N*-heterocyclic carbene (NHC) catalytic method[12] was developed for the synthesis of propiolic acid esters by three-component carboxylation of terminal alkynes with organochlorides in the presence of CO_2 (14.8 atm). To the best of our knowledge, only one example of an organocatalytic method for the carboxylation of terminal alkynes with CO_2 has been reported. However, the use of a high CO_2 pressure (14.8 atm) in the reported organocatalytic system[12] is still a drawback that needs to be overcome. Thus, the development of organocatalysts that can perform with high efficiency under a CO_2 atmosphere (1 atm) remains a challenge.

Inspired by the NHC catalysis for CO_2[1e,12,13] and our previous catalyst design,[14] we synthesized a type of bifunctional organocatalyst possessing two active sites including a carbonyl group and an NHC precursor situated at the ortho-position of the nitrogen of the pyridine ring, thus offering two active sites to activate terminal alkynes by a carbonyl group and simultaneously activate CO_2 through NHC (Scheme 1). In this work, we will demonstrate that this first example of an organocatalytic method has been developed for the carbox-

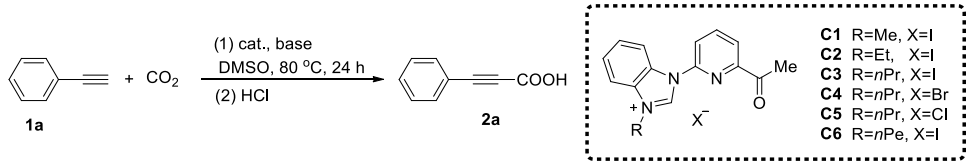
Scheme 1. Proposed Cooperative Activation Concept for CO_2 and Terminal Alkynes



Received: November 9, 2020
Published: December 24, 2020

https://dx.doi.org/10.1021/acs.joc.0c02673
J. Org. Chem. 2021, 86, 1850−1860

Table 1. Optimization of Carboxylation of Phenylacetylene with CO_2[a]



entry	catalyst (mol %)	base (mmol)	T (°C)	solvent	yield (%)[b]
1	**C1** (5)	Cs_2CO_3 (1.2)	40	DMF	11
2	**C2** (5)	Cs_2CO_3 (1.2)	40	DMF	13
3	**C3** (5)	Cs_2CO_3 (1.2)	40	DMF	47
4	**C4** (5)	Cs_2CO_3 (1.2)	40	DMF	13
5	**C5** (5)	Cs_2CO_3 (1.2)	40	DMF	0
6	**C6** (5)	Cs_2CO_3 (1.2)	40	DMF	13
7	**C3** (5)	K_2CO_3 (1.2)	40	DMF	trace
8	**C3** (5)	Na_2CO_3 (1.2)	40	DMF	trace
9	**C3** (5)	KO*t*Bu (1.2)	40	DMF	24
10	**C3** (5)	NaO*t*Bu (1.2)	40	DMF	trace
11	**C3** (5)	NaOH (1.2)	40	DMF	0
12	**C3** (5)	KOH (1.2)	40	DMF	0
13	**C3** (5)	DBU (1.2)	40	DMF	23
14	**C3** (2.5)	Cs_2CO_3 (1.2)	40	DMF	21
15	**C3** (5)	Cs_2CO_3 (1.0)	40	DMF	18
16	**C3** (5)	Cs_2CO_3 (1.2)	40	MeCN	9
17	**C3** (5)	Cs_2CO_3 (1.2)	40	THF	0
18	**C3** (5)	Cs_2CO_3 (1.2)	40	MeOH	0
19	**C3** (5)	Cs_2CO_3 (1.2)	40	toluene	21
20	**C3** (5)	Cs_2CO_3 (1.2)	40	DMSO	72
21	**C3** (5)	Cs_2CO_3 (1.2)	60	DMSO	94
22	**C1** (5)	Cs_2CO_3 (1.2)	60	DMSO	65
23	**C2** (5)	Cs_2CO_3 (1.2)	60	DMSO	83
24	**C6** (5)	Cs_2CO_3 (1.2)	60	DMSO	63
25	**C3** (5)	Cs_2CO_3 (0)	60	DMSO	0
26	**C3** (0)	Cs_2CO_3 (1.2)	60	DMSO	43
27	**C3** (0)	Cs_2CO_3 (2.5)	120	DMSO	84

[a][a]Reaction conditions: phenylacetylene (**1a**, 1.0 mmol), base (1.2 mmol), cat. (as indicated in Table 1), solvent (2 mL), CO_2 (balloon), 24 h. [b]Isolated yield.

ylation of terminal alkynes with atmospheric CO_2. In addition, we will illustrate that organocatalysis can offer a competitive alternative to metal catalysis for this transformation.

RESULTS AND DISCUSSION

Four pyridine-bridged bifunctional organocatalysts were prepared in our previously reported method.[14a,b] First, the catalytic activity and performance of the bifunctional organocatalysts **C1**−**6** were evaluated using the carboxylation of phenylacetylene with CO_2 as a benchmark reaction (Table 1, entries 1−6). The effect of *N*-substituents and counter anions was investigated for the carboxylation of phenylacetylene with CO_2, respectively. The results indicated that organocatalyst **C3** with a moderate chain length of the *n*-propyl group exhibits higher catalytic activity than **C1**, **C2**, and **C6** with different alkyl chains, such as methyl, ethyl, and *n*-pentyl groups (Table 1, entry 3 vs entries 1, 2, and 6). Organocatalyst **C3** containing iodine anion exhibits better catalytic performance than **C4** and **C5** with bromide and chlorine anions (Table 1, entry 3 vs entries 4 and 5). The NHC precursor can be converted to NHC by the release of HX molecules (X = Cl, Br, I). It is well known that iodide anions more easily combine with hydrogen molecules from C2−H to release HI than the bromide and chloride anions. Therefore, the leaving ability of HX may be responsible for the catalytic performance. Next, the carboxylation of phenylacetylene with CO_2 was chosen to optimize the reaction conditions using **C3** as a catalyst (Table 1). A wide range of bases, including Cs_2CO_3, K_2CO_3, Na_2CO_3, KO*t*Bu, NaO*t*Bu, NaOH, KOH, and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), were investigated (Table 1, entries 3 and 7−13), and most of these bases had a low activity or were ineffective for this transformation (Table 1, entries 7−13), with only Cs_2CO_3 exhibiting a high activity (Table 1, entry 3). The influence of the loading amount of catalyst **C3** and Cs_2CO_3 was explored (Table 1, entries 3, 14, and 15), and our results indicated that 5 mol % of **C3** along with 1.2 equiv of Cs_2CO_3 was appropriate for the reaction (Table 1, entry 3). In addition to *N*,*N*-dimethylformamide (DMF), other solvents such as MeCN, tetrahydrofuran (THF), MeOH, toluene, and dimethyl sulfoxide (DMSO), were explored under the same reaction conditions, and DMSO exhibited the best performance (Table 1, entry 20), compared to most of the solvents (Table 1, entries 3 and 16−20). We inferred that there are three reasons for the superior performance of DMSO. First, inorganic bases combined with dipolar aprotic solvents, such as DMSO, to form a superbasic media.[15] The extraordinary basicity of Cs_2CO_3/DMSO may accelerate the deprotonation of terminal alkynes. Second, CO_2 is highly soluble in DMSO

https://dx.doi.org/10.1021/acs.joc.0c02673
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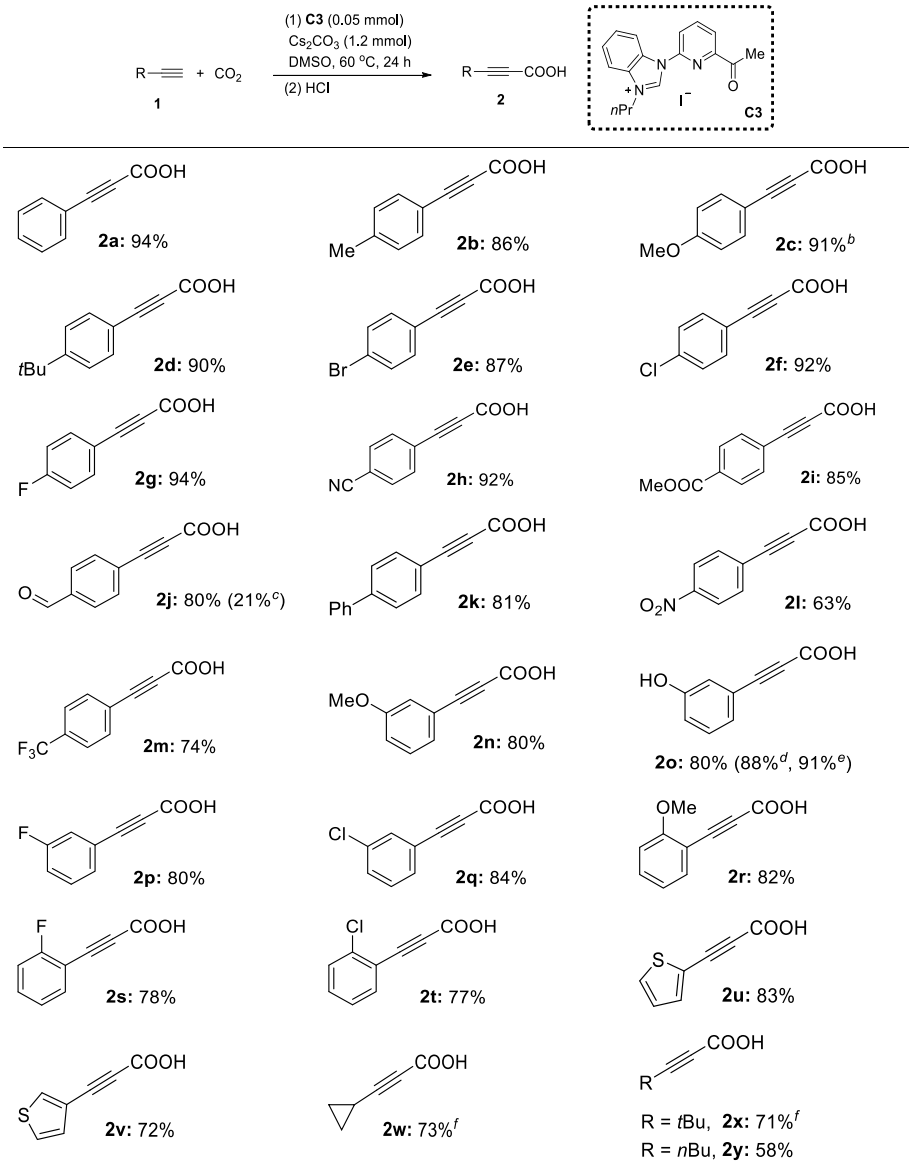
Table 2. Scope of Terminal Alkynes[a]



[a]Reaction conditions: terminal alkynes (1.0 mmol), **C3** (5 mol %), Cs_2CO_3 (1.2 mmol), CO_2 (balloon), DMSO (2 mL), 60 °C, 24 h, isolated yield. [b]**C3** (10 mol %). [c]**C7** (5 mol %). [d]Cs_2CO_3 (1.5 mmol). [e]Cs_2CO_3 (2.0 mmol). [f]CO_2 (5 bar, in 25 mL stainless steel reactor).

compared to other solvents.[16] Third, DMSO may promote the dissolution of Cs_2CO_3 in the reaction system.[4h,10] The reaction temperature also had a significant influence on the reaction rate when the reaction temperature was increased to 60 °C, resulting in a 94% product yield (Table 1, entry 21). In addition, different chain length influences of different *N*-alkyl substitutions were explored in the best solvent DMSO (Table 1, entries 21−24). A similar trend was obtained with the use of DMF as the solvent (Table 1, entries 1−3 and 6). We inferred that the steric effect of *N*-alkyl substitutions was responsible for these results. The bulkiness of *N*-alkyl substitutions forced the halide anion away from the cation, which promoted the leaving of hydrogen halide from benzimidazole salts to generate NHC active species. However, excessive steric hindrance, such as *n*-pentyl group, might prevent the attack of CO_2 on NHC to form NHC−CO_2 adducts. These results suggest that moderate steric hindrance is beneficial to the reaction working well. The control experiments in the absence of the catalyst **C3** and Cs_2CO_3 indicated that the two partners were necessary for a high product yield because the absence of any one of the two resulted in a significant decline in the product yield (Table 1, entries 25 and 26). To confirm the importance of our organocatalysts in the catalysis, we performed a control experiment in the absence of organocatalyst **C3**, and more details can be found in the Supporting Information. To achieve a catalytic efficiency similar to that of organocatalyst **C3**, the loading amount of Cs_2CO_3 was increased to 2.5 mol, and the reaction temperature was increased to 120 °C, affording an 84% yield (Table 1, entry 21 vs 27). The results suggest that our developed organocatalysts were extremely important for improving the catalytic performance.

Under the optimized reaction conditions (60 °C, 1 atm CO_2, and 5 mol % **C3**), the scope of terminal alkynes was investigated to evaluate the catalytic performance of the organocatalytic system (Table 2). First, we evaluated the electronic influence of substituents bearing terminal alkynes at

https://dx.doi.org/10.1021/acs.joc.0c02673
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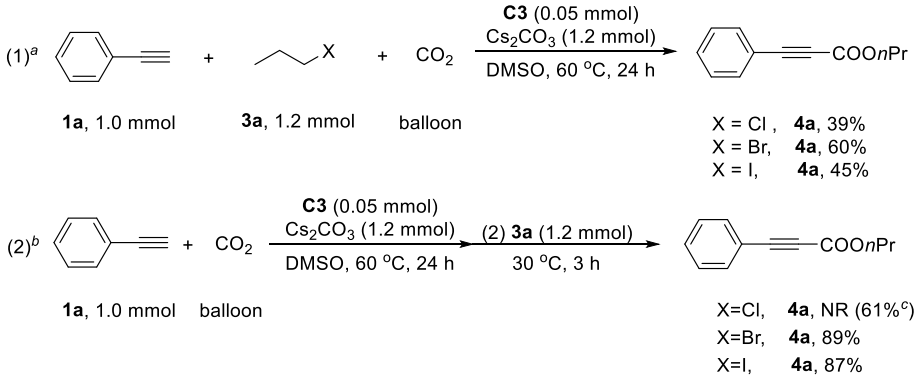
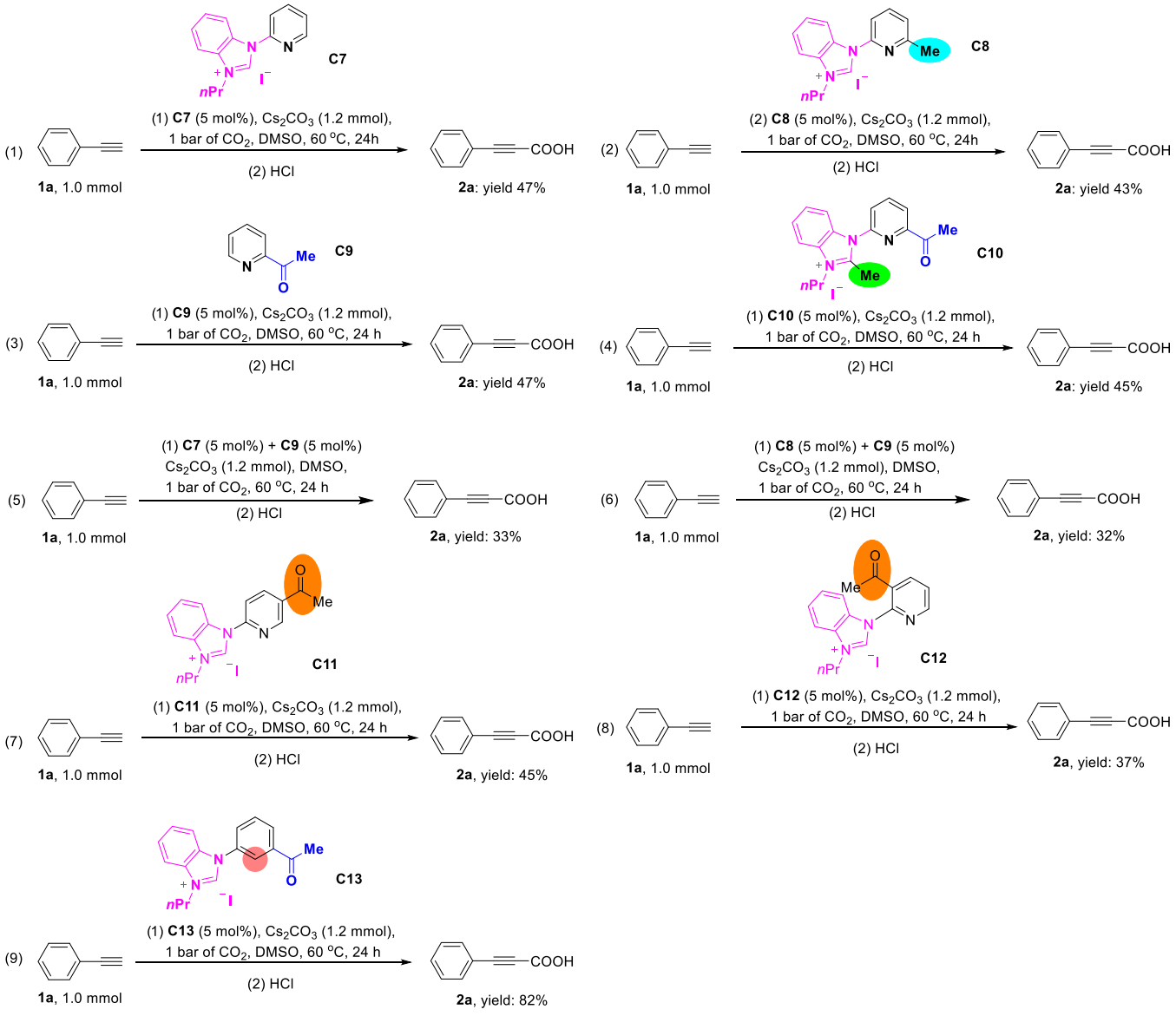
Scheme 2. Coupling of Three Components of Terminal Alkynes, Halides, and CO_2[c]



[a]Reaction conditions: **1a** (102 mg, 1.0 mmol), halide (**3a**, 1.2 mmol), Cs_2CO_3 (1.2 mmol), **C3** (5 mol %), CO_2 (1.0 bar), DMSO (2 mL), 60 °C, 24 h. [b](1) **1a** (102 mg, 1.0 mmol), Cs_2CO_3 (1.2 mmol), **C3** (5 mol %), CO_2 (1.0 bar), DMSO (2 mL), 60 °C, 24 h; (2) halide (**3a**, 1.2 mmol), 30 °C, 3 h. [c](2) halide (**3a**, 1.2 mmol), 60 °C, 3 h.

Scheme 3. Control Experiments to Investigate the Reaction Mechanism



the para-position of the benzene ring. The phenylacetylene could smoothly react with CO_2 to achieve a 94% yield (Table 2, **2a**). The substrates bearing the electron-donating group at the para-position of the benzene ring, such as the methyl group

https://dx.doi.org/10.1021/acs.joc.0c02673
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and *tert*-butyl group, were suitable for the organocatalytic system, producing 86 and 90% yields (Table 2, **2b** and **2d**). The *para*-methoxy phenylacetylene displayed low reactivity. However, a 91% product yield was also obtained when the amount of organocatalyst **C3** was increased to 10 mol % (Table 2, **2c**). The substrates bearing weak and moderate electron-withdrawing groups, such as chloride, bromide, fluoro, cyano, ester, aldehyde, and phenyl groups, exhibit good reactivity to give 80−94% product yields (Table 2, **2e**−**k**). Because substrate **1j** contained an aldehyde group, we inferred whether the reaction worked well using a catalyst without a carbonyl group. Therefore, we designed and synthesized a catalyst (**C7**) to investigate its feasibility. However, only a 21% yield of **2j** was obtained. The terminal alkynes bearing strong electron-withdrawing substituents, such as nitro group (Table 2, **2l**) and trifluoromethyl group (Table 2, **2m**), exhibit a remarkable decrease in the reactivity, affording relatively low yields of 63 and 74%. The electronic effect of substituents at the *meta*-positions (Table 2, **2n**−**q**) and ortho-positions (Table 2, **2r**−**t**) of terminal alkynes was not obvious in the reactivity. Various meta- and ortho-substituted terminal alkynes exhibited high reactivity, affording the desired products in yields of 77−84% (Table 2, **2n**−**t**). The acidity of the hydroxyl group on substrate **1o** may consume a portion of Cs_2CO_3, and hence an increasing amount of Cs_2CO_3. Therefore, the effect of increasing the amount of Cs_2CO_3 was evaluated in this case. The results indicated that the yields of **2o** increased slightly with an increase in the Cs_2CO_3 amounts. In addition, the heteroaryl terminal alkynes were examined in the organocatalytic system. For example, the coupling of 2-thienylacetylene and 3-thienylacetylene with CO_2 proceeded well, affording product yields of 83% for **2u** and 72% for **2v**, respectively. Encouraged by the outstanding performance of **C3** in the carboxylation of terminal alkynes with CO_2, three challenging aliphatic terminal alkynes (i.e., cyclopropyl, *tert*-butyl, and *n*-butyl acetylene) were investigated using our developed organocatalytic system. Under the same reaction conditions, *n*-butyl acetylene reacts with CO_2 to afford a 58% yield of **2y**. The carboxylation of cyclopropyl and *tert*-butyl acetylene with CO_2 also worked well when a high CO_2 pressure of 5 bar was used (Table 2, **2w** and **2x**).

The transition metal-catalyzed carboxylation of terminal alkynes with alkyl halides and CO_2 has been studied.[2c,4,6c,d] Due to the importance of propiolic acid ester derivatives, our developed organocatalytic system was applied to the synthesis of propiolic acid esters using terminal alkynes, alkyl halides, and CO_2 as starting materials. Under the optimized reaction conditions, alkyl halides with different halogens for three-component carboxylative coupling were explored. The carboxylative coupling reaction of chloropropane, bromopropane, and iodopropane with phenylacetylene and CO_2 proceeded smoothly to afford the desired propyl 3-phenylpropiolate **4a** in low to moderate yields of 39, 60, and 45% (Scheme 2, eq 1), respectively. The literature studies[4,6c] indicate that the reaction pathway involves (1) propiolic acid formation and (2) ester formation from propiolic acid and alkyl halides. We inferred that the one-pot two-step method was beneficial to the formation of propiolic acid esters. As expected, bromopropane and iodopropane smoothly reacted with phenylacetylene and CO_2 to afford the desired products in 89 and 87% yields (Scheme 2, eq 2), respectively. However, the reaction of chloropropane and propiolic acid did not produce the desired product, which may be due to the high bond energy of the C−Cl bond. As shown in Scheme 2, 61% yield of the desired ester **4a** was obtained when the reaction temperature was increased to 60 °C in the second step (Scheme 2, eq 2).

To confirm the effect of carbonyl groups on this reaction, two catalysts, **C7** and **C8**, were designed and synthesized by removing carbonyl groups or replacing them with methyl groups from organocatalyst **C3**. In the absence of carbonyl groups, 47 and 43% yields were obtained (Scheme 3, eqs 1 and 2), respectively, which is equivalent to the result of the blank experiment (Table 1, entry 21). The results suggested that the existence of carbonyl groups is essential for high catalytic performance. The effects of the NHC precursor (benzimidazolium salts) were also investigated. When the designed catalyst **C9**, where the NHC precursor was removed from **C3**, was used, this reaction only resulted in a 47% yield (Scheme 3, eq 3). To determine whether CO_2 preferentially binds to the C2 position of the benzimidazolium ring, a catalyst was designed by introducing a methyl group to the C2 position of the benzimidazolium ring (Scheme 3, eq 4). The obtained results from catalyst **C10** in this reaction indicated that alkylation of the C2 position leads to a significant decline in the catalytic performance. These results suggest that NHC plays an important role in the activation of CO_2.

To determine whether the cooperative catalytic action between the imidazolium and carbonyl group moieties occurs via intramolecular interactions or intermolecular interactions, two control experiments were performed using a binary catalyst system combining **C7** with **C9** or **C8** with **C9** (Scheme 3, eqs 5 and 6). In addition, the NHC−CO_2 adduct **C14**/benzaldehyde and NHC−CO_2 adduct **C14**/acetophenone binary system were also evaluated in the carboxylation (see Scheme S1 in the Supporting Information for details). However, the low yields of the product in these cases indicated that the two-component catalytic systems had difficulty promoting this reaction. To explore the influence of the position structure relationship between NHC and the carbonyl group on the catalytic activity, we synthesized *para*- and *ortho*-carbonyl catalysts **C11** and **C12** at the position of the pyridine ring. However, the use of catalyst **C11** or **C12** resulted in low product yields (Scheme 3, eqs 7 and 8). The results above indicated that the unique pincer-type structures between the NHC and the carbonyl group in catalyst **C3** were essential for high performance, which enabled intramolecular interactions between CO_2 and the terminal alkynes.

To clarify whether the pyridine nitrogen is essential for catalysis, a benzene ring-bridged bifunctional catalyst **C13** was designed and synthesized for use in this reaction (Scheme 3, eq 9). The results indicated that the catalytic performance of catalysts **C13** and **C3** were not significantly different (82 vs 94%). The results suggest that the pyridine nitrogen may not be necessary for the catalytic process.

We carried out several control experiments using Fourier transform infrared (FT-IR) method to investigate the interaction between catalyst **C3** and substrate **1a** or CO_2 (Figure 1). We recorded the FT-IR spectra of catalyst **C3** alone and mixed with substrate **1a** and/or Cs_2CO_3 and/or CO_2. The absorption peak at 1699 cm^{-1} can be assigned to the stretching vibration peak of the carbonyl group bearing catalyst **C3** (Figure 1, black curve). The absorption peak for the carbonyl group at 1699 cm^{-1} had no change during the addition of Cs_2CO_3 to catalyst **C3** (Figure 1, red curve). However, when 20 equiv (1.0 mmol) of substrate **1a** was

https://dx.doi.org/10.1021/acs.joc.0c02673
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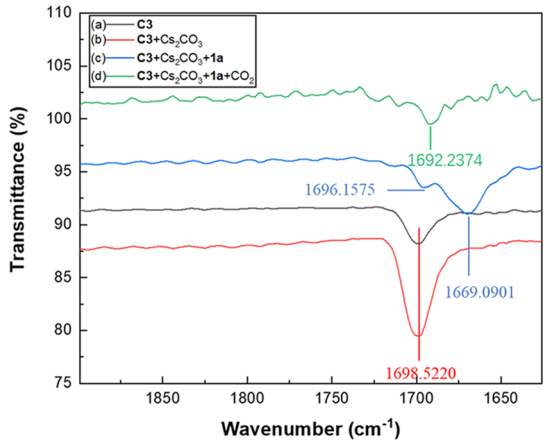


Figure 1. FT-IR experiments. Reaction conditions: (a) **C3** (0.05 mmol) in MeCN (2 mL). (b) **C3** (0.05 mmol), Cs_2CO_3 (0.2 mmol) in MeCN (2 mL). (c) **1a** (1.0 mmol), **C3** (0.05 mmol), Cs_2CO_3 (1.2 mmol) in MeCN (2 mL), 60 °C, 24 h. (d) **1a** (1.0 mmol), **C3** (0.05 mmol), Cs_2CO_3 (1.2 mmol) in MeCN (2 mL) under CO_2 (1 bar), 60 °C, 24 h.

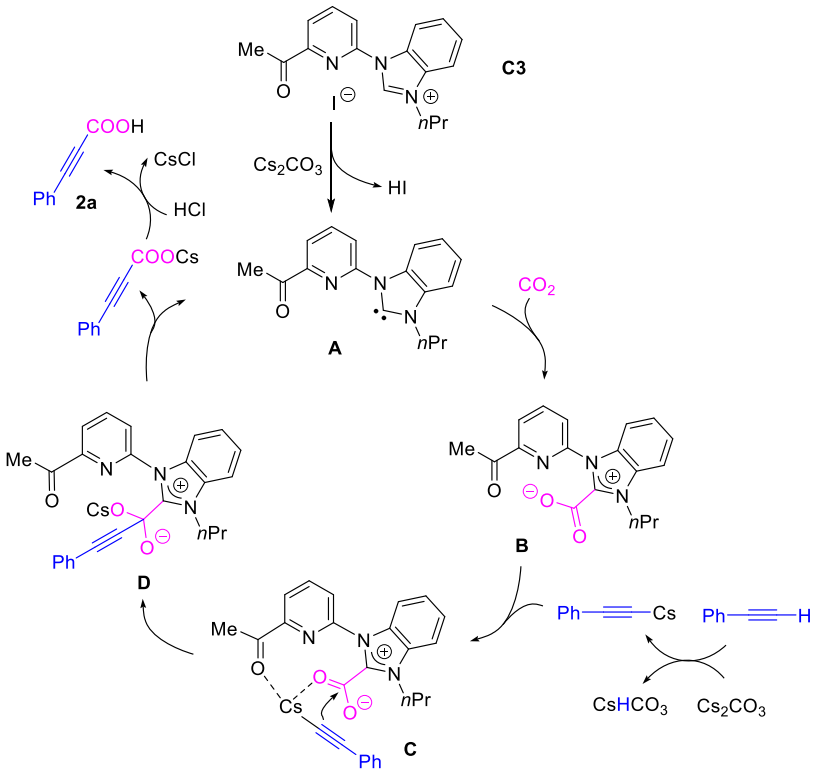
added to the mixture of catalyst **C3** and Cs_2CO_3, the absorption peak of the carbonyl group shifted from 1699 to 1669 cm^{-1} (Figure 1, blue curve). This result indicated that an interaction exists between the carbonyl group of catalyst **C3** and substrate **1a**. When CO_2 was introduced into the reaction mixtures containing catalyst **C3**, substrate **1a**, and Cs_2CO_3, the absorption peak of the carbonyl group reappeared, which means that the reaction completed and catalyst **C3** was regenerated (Figure 1, green curve). The complete IR spectra from Figure 1 is shown in Figure S1 in the Supporting Information.

The control experiments suggest that **C3** acts as a bifunctional organocatalyst. As shown in Scheme 4, the *N*-heterocyclic carbene (NHC) precursor is converted to NHC catalyst **A** by the release of HI molecule in the presence of Cs_2CO_3. Second, the NHC−CO_2 adduct **B** is formed through nucleophilic attack of the NHC catalyst **A** to the carbon atom of CO_2.[13,17] The phenylacetylene undergoes a deprotonation process in the presence of Cs_2CO_3 to generate an alkynyl cesium. Thereafter, the oxygen atoms of the carbonyl group on **B** interact with the alkynyl cesium to form intermediate **C**. Then, an intramolecular nucleophilic substitution of intermediate **C** occurs to generate intermediate **D**. Finally, the dissociation of the NHC catalyst **A** takes place to yield product **2a**.

CONCLUSIONS

In Summary, this work provides an efficient organocatalytic protocol utilizing **C3** as a catalyst in combination with Cs_2CO_3 as an additive for the direct carboxylation of terminal alkynes and CO_2. This organocatalytic system allows for a broad application to terminal alkynes, tolerating different functional groups, to afford a wide range of propiolic acid derivatives in good to excellent yields under atmospheric pressure using CO_2 at 60 °C. In addition, this protocol has been applied to the three-component carboxylation of terminal alkynes, alkyl halides, and CO_2. Control experiments suggest that the reaction proceeded by cooperative activation of the carbene as a catalyst for the activation of CO_2 where the carbonyl group activates terminal alkynes. This work has demonstrated that the organocatalysts can offer a competitive alternative to metal catalysts for the carboxylation of terminal alkynes and CO_2.

Scheme 4. Proposed Cycles for Organocatalytic Carboxylation of Terminal Alkynes with CO_2



https://dx.doi.org/10.1021/acs.joc.0c02673
J. Org. Chem. 2021, 86, 1850−1860

EXPERIMENTAL SECTION

General Information. Unless otherwise stated, all solvents and starting materials **1** and **3** were purchased from commercial suppliers and used without further purification. The starting materials **1** and **3** are all known compounds in the Experimental Section.

Analytical Methods. The NMR spectra were recorded using a Bruker Avance III HD 400 spectrometer using TMS as an internal standard (400 or 600 MHz for ^{1}H NMR and 101 or 151 MHz for ^{13}C NMR). High-resolution mass spectrometry (HRMS) data were collected on a Bruker solanX 70 FT-MS and Agilent 6224 TOF mass spectrometer.

Direct Carboxylation of Terminal Alkynes with CO_2. A mixture containing a terminal alkyne (1.0 mmol), **C3** (20 mg, 0.05 mmol), Cs_2CO_3 (390 mg, 1.2 mmol), and 1 mL of DMSO was added to a 25 mL glass tube. The reaction mixture was heated to 60 °C in a heating mantle for 24 h under a CO_2 atmosphere (1 atm, using a balloon). After the reaction was completed, the reaction tube was cooled to room temperature, and saturated brine (25 mL) and an aqueous solution of HCl (1 M, 6 mL) were added to the reaction mixture. The acidified mixture was extracted with dichloromethane (3 × 15 mL), and the solvent was removed under reduced pressure. Finally, the desired products were isolated by flash chromatography.

Three-Component Carboxylation of Terminal Alkynes, Alkyl Halide, and CO_2. A mixture containing a terminal alkyne (1.0 mmol), **C3** (20 mg, 0.05 mmol), Cs_2CO_3 (390 mg, 1.2 mmol), halide (1.2 mmol), and 1 mL of DMSO was added to a 25 mL glass tube. The reaction mixture was heated to 60 °C in a heating mantle for 24 h under a CO_2 atmosphere (1 atm, using a balloon). Once the reaction was completed, the reaction tube was cooled to room temperature, and saturated brine (25 mL) and an aqueous solution of HCl (1 M, 6 mL) were added to the reaction mixture. The acidified mixture was extracted with dichloromethane (3 × 15 mL), and the solvent was removed under reduced pressure. Finally, the desired products were isolated by flash chromatography.

*3-Phenylpropiolic Acid (**2a**).*[11a] Purification by flash chromatography (EtOAc) gave a white solid (137.2 mg, 94%). MP = 137.1−138.0 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.63 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 154.3, 132.6, 130.9, 129.1, 119.0, 84.4, 81.8 ppm.

*3-(p-Tolyl)propiolic Acid (**2b**).*[11e] Purification by flash chromatography (EtOAc) gave a white solid (137.7 mg, 86%). MP = 149.5−150.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 6.4 Hz, 2H), 7.21(d, J = 6.4 Hz, 2H), 2.39 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.6, 141.9, 133.3, 129.5, 116.0, 89.7, 79.8, 21.8 ppm.

*3-(4-Methoxyphenyl)propiolic Acid (**2c**).*[6a] Purification by flash chromatography (EtOAc) gave a white solid (160.3 mg, 91%). MP = 151.2−151.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.0, 158.1, 135.5, 114.5, 111.1, 89.8, 79.8, 55.6 ppm.

*3-(4-(tert-Butyl)phenyl)propiolic Acid (**2d**).*[18] Purification by flash chromatography (EtOAc) gave a white solid (182.0 mg, 90%). MP = 152.8−153.6 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.55 (d, J = 24.6 Hz, 4H), 1.27 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 154.5, 153.9, 132.5, 125.9, 116.1, 84.6, 81.6, 34.8, 30.8 ppm.

*3-(4-Bromophenyl)propiolic Acid (**2e**).*[18] Purification by flash chromatography (EtOAc) gave a white solid (195.7 mg, 87%). MP = 165.4−166.7 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.68 (d, J = 7.8 Hz, 2H), 7.58 (d, J = 7.8 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 154.2, 134.5, 132.2, 124.7, 118.2, 83.2, 82.7 ppm.

*3-(4-Chlorophenyl)propiolic Acid (**2f**).*[11e] Purification by flash chromatography (EtOAc) gave a white solid (166.1 mg, 92%). MP = 167.7−168.4 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.66 (d, J = 11.4 Hz, 2H), 7.55 (d, J = 11.4 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 154.2, 135.8, 134.4, 129.3, 117.9, 83.0, 82.7 ppm.

*3-(4-Fluorophenyl)propiolic Acid (**2g**).*[18] Purification by flash chromatography (EtOAc) gave a white solid (154.3 mg, 94%). MP = 142.2−143.3 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.71−7.70 (m, 2 H), 7.34 (t, J = 9.0 Hz, 2 H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 163.3 (d, C-F, $^1J_{C\text{-}F}$ = 249.0 Hz), 154.3, 135.4 (d, C-F, $^3J_{C\text{-}F}$ = 9.2 Hz), 116.5 (d, C-F, $^2J_{C\text{-}F}$ = 22.4 Hz), 115.5 (d, C-F, $^3J_{C\text{-}F}$ = 9.9 Hz), 83.4, 81.7. ^{19}F NMR (376 MHz, DMSO-d_6) δ −109.0 ppm.

*3-(4-Cyanophenyl)propiolic Acid (**2h**).*[11a] Purification by flash chromatography (EtOAc) gave a white solid (157.5 mg, 92%). MP = 185.8−186.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 153.9, 133.2, 132.8, 123.8, 118.1, 113.0, 84.5, 82.2 ppm.

*3-(4-(Methoxycarbonyl)phenyl)propiolic Acid (**2i**).*[11e] Purification by flash chromatography (EtOAc) gave a white solid (173.5 mg, 85%). MP = 161.8−162.5 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.00 (s, 2H), 7.76 (s, 2H), 3.87 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 165.4, 154.0, 132.9, 131.2, 129.5, 123.6, 83.8, 82.9, 52.5 ppm.

*3-(4-Formylphenyl)propiolic Acid (**2j**).*[11a] Purification by flash chromatography (EtOAc) gave a yellow solid (139.3 mg, 80%). MP = 183.4−184.0 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.06 (s, 1H), 7.99 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 192.6, 154.0, 137.0, 133.2, 129.7, 124.6, 84.2, 83.0 ppm.

*3-([1,1′-Biphenyl]-4-yl)propiolic Acid (**2k**).*[11e] Purification by flash chromatography (EtOAc) gave a white solid (180.0 mg, 81%). MP = 137.9−138.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71(d, J = 8.8 Hz, 2H), 7.64−7.60 (m, 4H), 7.47 (d, J = 7.4 Hz, 2H), 7.40 (d, J = 7.2 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.1, 144.1, 139.8, 133.9, 129.1, 128.4, 127.5, 127.3, 117.9, 89.3, 80.7 ppm.

*3-(4-Nitrophenyl)propiolic Acid (**2l**).*[11a] Purification by flash chromatography (EtOAc) gave a brown solid (120.4 mg, 63%). MP = 169.1−170.0 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.28 (d, J = 8.8 Hz, 2H), 7.91 (d, J = 8.8 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 153.8, 148.2, 133.8, 125.6, 124.0, 85.1, 81.7 ppm.

*4-Trifluoromethylphenylpropiolic Acid (**2m**).*[18] Purification by flash chromatography (EtOAc) gave a white solid (158.4 mg, 74%). MP = 137.8−138.6 °C. ^{1}H NMR (400 MHz, CD_3OD) δ 7.69−7.63 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, CD_3OD) δ 156.0, 134.4, 133.0 (q, C-F, $^2J_{C\text{-}F}$ = 32.5 Hz), 126.8 (q, C-F, $^4J_{C\text{-}F}$ = 3.7 Hz), 126.5, 124.5 (d, C-F, $^1J_{C\text{-}F}$ = 139.9 Hz), 84.0, 83.7. ^{19}F NMR (376 MHz, CD_3OD) δ −63.7 ppm.

*3-(3-Methoxyphenyl)propiolic Acid (**2n**).*[6a] Purification by flash chromatography (EtOAc) gave a white solid (140.9 mg, 80%). MP = 109.1−109.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, J = 8.0 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.12−7.11 (m, 1H), 7.05−7.02 (m, 1H), 3.82 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.5, 158.6, 129.9, 126.0, 120.0, 118.2, 117.7, 89.0, 79.9, 55.5 ppm.

*3-(3-Hydroxyphenyl)propiolic Acid (**2o**).*[11a] Purification by flash chromatography (EtOAc) gave a white solid (129.7 mg, 80%). MP = 177.5−178.0 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.28 (t, J = 8.8 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 6.95−6.93 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 157.5, 154.3, 130.3, 123.4, 119.7, 118.7, 118.5, 84.6, 81.2 ppm.

*3-(3-Fluorophenyl)propiolic Acid (**2p**).*[11e] Purification by flash chromatography (EtOAc) gave a white solid (131.3 mg, 80%). MP = 89.6−90.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.35 (m, 2H), 7.32−7.29 (m, 1H), 7.22−7.17 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.3 (d, C-F, $^1J_{C\text{-}F}$ = 197.6 Hz), 158.1, 130.6 (d, C-F, $^3J_{C\text{-}F}$ = 6.7 Hz), 129.3 (d, C-F, $^4J_{C\text{-}F}$ = 2.6 Hz), 121.0 (d, C-F, $^3J_{C\text{-}F}$ = 7.5 Hz), 120.0 (d, C-F, $^2J_{C\text{-}F}$ = 18.6 Hz), 118.8 (d, C-F, $^2J_{C\text{-}F}$ = 16.8 Hz), 87.4 (d, C-F, $^4J_{C\text{-}F}$ = 2.7 Hz), 80.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.4 ppm.

*3-(3-Chlorophenyl)propiolic Acid (**2q**).*[4d] Purification by flash chromatography (EtOAc) gave a white solid (151.6 mg, 84%). MP = 142.7−143.8 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.72 (t, J = 1.8 Hz, 1H), 7.62−7.59 (m, 2H), 7.51 (t, J = 8.1 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 154.1, 133.6, 131.9, 131.3, 131.0, 130.9, 121.0, 82.6, 82.5 ppm.

*3-(2-Methoxyphenyl)propiolic Acid (**2r**).*[6a] Purification by flash chromatography (EtOAc) gave a white solid (144.4 mg, 82%). MP = 128.3−129.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.4 Hz, 1H), 7.48 (t, J = 7.0 Hz, 1H), 6.97−6.91 (m, 2H), 3.91 (s, 3H).

https://dx.doi.org/10.1021/acs.joc.0c02673
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$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.0, 158.5, 135.4, 133.0, 120.7, 111.0, 108.5, 86.2, 84.1, 56.0 ppm.

*3-(2-Fluorophenyl)propiolic Acid (**2s**).*[18] Purification by flash chromatography (EtOAc) gave a grey solid (128.0 mg, 78%). MP = 115.7−116.2 °C. ^1H NMR (600 MHz, DMSO-d_6) δ 7.71 (t, J = 7.5 Hz, 1H), 7.63−7.59 (m, 1H), 7.40 (t, J = 9.0 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ 163.3 (d, C-F, $^1J_{C\text{-}F}$ = 251.0 Hz), 154.5, 135.0, 133.9 (d, C-F, $^3J_{C\text{-}F}$ = 8.4 Hz), 125.6 (d, C-F, $^4J_{C\text{-}F}$ = 3.6 Hz), 116.5 (d, C-F, $^2J_{C\text{-}F}$ = 20.0 Hz), 108.0 (d, C-F, $^2J_{C\text{-}F}$ = 15.0 Hz), 86.8, 76.1 ^{19}F NMR (376 MHz, DMSO-d_6) δ −107.0 ppm.

*3-(2-Chlorophenyl)propiolic Acid (**2t**).*[6a] Purification by flash chromatography (EtOAc) gave a white solid (139.0 mg, 77%). MP = 136.4−136.8 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 6.0 Hz, 1H), 7.47 (d, J = 6.4 Hz, 1H), 7.42 (t, J = 6.2 Hz, 1H), 7.31 (t, J = 6.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.1, 137.8, 135.1, 132.2, 129.8, 126.9, 119.6, 85.2, 84.3 ppm.

*3-(Thiophen-2-yl)propiolic Acid (**2u**).*[18] Purification by flash chromatography (EtOAc) gave a gray solid (126.3 mg, 83%). MP = 138.3−140.5 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 7.89 (d, J = 5.2 Hz, 1H), 7.68 (d, J = 3.6 Hz, 1H), 7.21 (t, J = 4.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 154.1, 137.0, 132.8, 128.3, 118.2, 85.8, 78.5 ppm.

*3-(Thiophen-3-yl)propiolic Acid (**2v**).*[11a] Purification by flash chromatography (EtOAc) gave a white solid (109.5 mg, 72%). MP = 155.2−156.9 °C. ^1H NMR (600 MHz, DMSO-d_6) δ 8.19 (dd, J = 1.2, 3.0 Hz, 1H), 7.70 (dd, J = 3.0, 4.8 Hz, 1H), 7.33 (dd, J = 1.2, 5.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ 154.4, 134.9, 130.0, 127.8, 117.9, 81.6, 80.4 ppm.

*3-Cyclopropylpropiolic Acid (**2w**).*[4d] Purification by flash chromatography (EtOAc) gave a white solid (80.3 mg, 73%). MP = 62.6−63.9 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 1.54−1.47 (m, 1H), 0.96−0.91 (m, 2H), 0.81−0.77 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 154.2, 92.1, 69.5, 8.9, 1.2 ppm.

*4,4-Dimethyl-2-pentynoic Acid (**2x**).*[6a] Purification by flash chromatography (EtOAc) gave a dark green liquid (89.4 mg, 71%). ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 154.6, 94.9, 72.9, 29.8, 27.2 ppm.

*Hept-6-en-2-ynoic Acid (**2y**).*[6a] Purification by flash chromatography (EtOAc) gave a dark green liquid (73.2 mg, 58%). ^1H NMR (400 MHz, $CDCl_3$) δ 2.36 (t, J = 6.8 Hz, 2H), 1.50−1.43 (m, 2H), 1.40−1.31 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 192.0, 126.1, 111.9, 66.9, 59.1, 55.0, 51.0 ppm.

*Propyl 3-Phenylpropiolate (**4a**).* Purification by flash chromatography (PE/EA, 10:1) gave a colorless liquid (114.2 mg, 60%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.60−7.58 (m, 2H), 7.47−7.43 (m, 1H), 7.39−7.35 (m, 2H), 4.20 (t, J = 6.8 Hz, 2H), 1.75 (q, J = 14.0 Hz, 2H), 0.99 (t, J = 7.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 154.4, 133.1, 130.7, 128.7 119.8, 86.2, 80.8, 67.8, 22.0, 10.5 ppm. HRMS (EI-TOF) calcd for $C_{10}H_{12}O_2$ $[M]^+$ 188.0837, found 188.0833.

*1-(6-(1H-Benzo[d]imidazol-1-yl)pyridin-2-yl)ethan-1-one (**L2**).* The ligand was synthesized following a previously reported method.[19] Purification by flash chromatography (PE/EA, 2:1) gave a white solid (902.6 mg, 76%). MP = 119.4−120.6 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.14 (d, J = 7.2 Hz, 1H), 8.02−8.09 (m, 2H), 7.90 (d, J = 7.2 Hz, 1H), 7.78 (m, 1H), 7.45−7.37 (m, 2H), 2.80 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.9, 153.0, 149.3, 144.9, 141.2, 140.2, 132.1, 124.7, 123.8, 121.0, 119.5, 117.5, 112.8, 26.2 ppm. HRMS (ESI-TOF) m/z: $C_{14}H_{12}N_3O$ $[M + H]^+$ calcd for 238.0975, found 238.0976.

*1-(6-(1H-Benzo[d]imidazol-1-yl)pyridin-3-yl)ethan-1-one (**L3**).* The ligand was synthesized following a previously reported method.[19] Purification by flash chromatography (PE/EA, 2:1) gave a white solid (925.4 mg, 78%). MP = 175.3−176.7 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, J = 1.6 Hz, 1H), 8.67 (s, 1 H), 8.45−8.43 (m, 1H), 8.19−8.17 (m, 1H), 7.89−7.86 (m, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.45−7.37 (m, 2H), 2.69 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.3, 152.7, 150.4, 145.1, 141.3, 138.9, 132.0, 130.3, 124.9, 124.1, 121.1, 113.5, 113.2, 26.8 ppm. HRMS (ESI-TOF) m/z: $C_{14}H_{12}N_3O$ $[M + H]^+$ calcd for 238.0975, found 238.0979.

*1-(2-(1H-Benzo[d]imidazol-1-yl)pyridin-3-yl)ethan-1-one (**L4**).* The ligand was synthesized following a previously reported method.[19] Purification by flash chromatography (PE/EA, 2:1) gave a white solid (290.1 mg, 24%). MP = 216.2−217.4 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.36−8.35 (m, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.92−7.90 (m, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.41−7.37 (m, 1H), 7.33−7.29 (m, 1H), 7.18−7.14 (m, 1H), 6.56 (s,1H), 1.98 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.7, 148.7, 134.6, 132.6, 124.7, 123.9, 120.4, 120.1, 112.8, 71.8, 25.8 ppm. HRMS (ESI-TOF) m/z: $C_{14}H_{12}N_3O$ $[M + H]^+$ calcd for 238.0975, found 238.0978.

*1-(3-(1H-Benzo[d]imidazol-1-yl)phenyl)ethan-1-one (**L5**).* The ligand was synthesized following a previously reported method.[19] Purification by flash chromatography (PE/EA, 2:1) gave a white solid (960.9 mg, 81%). MP = 78.4−79.5 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.10 (t, J = 1.6 Hz, 1H), 8.03−8.01 (m, 1H), 7.89−7.87 (m, 1H), 7.74−7.66 (m, 2H), 7.53−7.51 (m, 1H), 7.36−7.32 (m, 2H), 2.66 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.8, 144.2, 142.1, 139.0, 137.0, 133.5, 130.6, 128.3, 127.9, 124.1, 123.5, 123.2, 120.9, 110.3, 26.8. HRMS (ESI-TOF) m/z: $C_{15}H_{13}N_2O$ $[M + H]^+$ calcd for 237.1022, found 237.1022.

*1-(6-Acetylpyridin-2-yl)-3-methyl-1H-benzo[d]imidazol-3-ium Iodide (**C1**).* Organocatalyst **C1** was synthesized following a previously reported method.[14a−c] Purification by flash chromatography (DCM/MeOH, 10:1) gave a white solid (276.8 mg, 73%). MP = 238.1−238.4 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 10.63 (s, 1H), 8.63−8.61 (m, 1H), 8.49 (t, J = 8.0 Hz, 1H), 8.29 (d, J = 8.0 Hz, 1H), 8.21−8.17 (m, 2H), 7.86−7.80 (m, 2H), 4.23 (s, 3H), 2.78 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 197.8, 152.1, 146.7, 143.2, 142.1, 132.3, 129.3, 128.0, 127.3, 122.0, 120.6, 115.8, 114.1, 33.9, 26.2 ppm. HRMS (ESI-TOF) m/z: $C_{15}H_{14}IN_3O$ $[M - I]^+$ calcd for 252.1131, found 252.1136.

*1-(6-Acetylpyridin-2-yl)-3-ethyl-1H-benzo[d]imidazol-3-ium Iodide (**C2**).* Organocatalyst **C2** was synthesized following a previously reported method.[14a−c] Purification by flash chromatography (DCM/MeOH, 10:1) gave a white solid (314.6 mg, 80%). MP = 218.2−219.1 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 10.59 (s, 1H), 8.65−8.62 (m, 1H), 8.49 (t, J = 8.0 Hz, 1H), 8.34 (d, J = 8.0 Hz, 1H), 8.26−8.19 (m, 2H), 7.85−7.79 (m, 2H), 4.66 (q, J = 14.8 Hz, 2H), 2.77 (s, 3H), 1.65 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 197.9, 152.0, 146.8, 142.5, 142.0, 131.4, 129.5, 128.0, 127.3, 121.9, 120.8, 116.1, 114.1, 42.9, 26.2, 14.0 ppm. HRMS (ESI-TOF) m/z: $C_{16}H_{16}IN_3O$ $[M - I]^+$ calcd for 266.1288, found 266.1282.

*1-(6-Acetylpyridin-2-yl)-3-propyl-1H-benzo[d]imidazol-3-ium Iodide (**C3**).* Organocatalyst **C3** was synthesized following a previously reported method.[14a−c] Purification by flash chromatography (DCM/MeOH, 10:1) gave a white solid (309.5 mg, 76%). MP = 213.3−214.7 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 10.66 (s, 1H), 8.65−8.63 (m, 1H), 8.49 (t, J = 8.0 Hz, 1H), 8.35 (d, J = 8.0 Hz, 1H), 8.29−8.27 (m, 1H), 8.20 (d, J = 7.6 Hz, 1H), 7.86−7.79 (m, 2 H), 4.61 (t, J = 8.0 Hz, 2H), 2.78 (s, 3H), 2.07 (q, J = 14.8 Hz, 2H), 1.03 (t, J = 7.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 197.8, 152.0, 146.8, 142.7, 141.9, 131.7, 129.5, 128.0, 127.3, 121.9, 120.8, 116.0, 114.2, 48.8, 26.2, 22.0, 10.8 ppm. HRMS (ESI-TOF) m/z: $C_{17}H_{18}IN_3O$ calcd for $[M - I]^+$ 280.1444, found 280.1448.

*1-(6-Acetylpyridin-2-yl)-3-propyl-1H-benzo[d]imidazol-3-ium Bromide (**C4**).* Organocatalyst **C4** was synthesized following a previously reported method.[14a−c] Purification by flash chromatography (DCM/MeOH, 10:1) gave a white solid (259.2 mg, 72%). MP = 238.5−238.7 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 10.82 (s, 1H), 8.66−8.64 (m, 1H), 8.49 (t, J = 8.0 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.30−8.28 (m, 1H), 8.19 (d, J = 7.6 Hz, 1H), 7.85−7.78 (m, 2H), 4.63 (t, J = 7.2 Hz, 2H), 2.78 (s, 3H), 2.07 (q, J = 14.8 Hz, 2H), 1.02 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 235.5, 189.6, 184.5, 180.5, 179.6, 169.4, 167.1, 165.6, 164.9, 159.5, 158.5, 153.5 151.9, 86.4, 63.9, 59.7, 48.5 ppm. HRMS (ESI-TOF) m/z: $C_{17}H_{18}BrN_3O$ $[M\text{-}Br]^+$ calcd for 280.1444, found 280.1449.

*1-(6-Acetylpyridin-2-yl)-3-propyl-1H-benzo[d]imidazol-3-ium Chloride (**C5**).* Organocatalyst **C5** was synthesized following a

https://dx.doi.org/10.1021/acs.joc.0c02673
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previously reported method.[14a−c] Purification by flash chromatography (DCM/MeOH, 10:1) gave a white solid (116.1mg, 51%). MP = 216.4−217.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.55 (s, 1H), 8.63−8.61 (m, 1H), 8.48 (t, J = 8.0 Hz, 1H), 8.31 (d, J = 7.2 Hz, 1H), 8.26−8.24 (m, 1H), 8.19 (d, J = 7.2 Hz, 1H), 7.85−7.78 (m, 2H), 4.60 (t, J = 7.2 Hz, 2H), 2.77 (s, 3H), 2.09−2.03 (m, 2H), 1.02 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 197.9, 152.1, 146.8, 142.6, 142.1, 131.7, 129.6, 128.1, 127.4, 122.0, 120.9, 116.1, 114.2, 48.9, 26.2, 22.1, 10.9 ppm. HRMS (ESI-TOF) m/z: $C_{17}H_{18}ClN_3O$ [M-Cl]$^+$ calcd for 280.1444, found 280.1450.

*1-(6-Acetylpyridin-2-yl)-3-pentyl-1H-benzo[d]imidazol-3-ium Iodide (**C6**).* Organocatalyst **C6** was synthesized following a previously reported method.[14a−c] Purification by flash chromatography (DCM/MeOH, 10:1) gave a white solid (273.2 mg, 63%). MP = 130.5−131.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.69 (s, 1H), 8.65−8.63 (m, 1H), 8.50 (t, J = 8.0 Hz, 1H), 8.44−8.38 (m, 1H), 8.29−8.27 (m, 1H), 8.18 (d, J = 7.6 Hz, 1H), 7.86−7.79 (m, 2H), 4.65 (t, J = 7.6 Hz, 2H), 2.78 (s, 3H), 2.08−2.04 (m, 2H), 1.45−1.36 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 197.7, 151.9, 146.7, 142.5, 141.9, 131.6, 129.4, 127.9, 127.2, 121.8, 120.8, 116.0, 114.1, 47.4, 28.1, 27.9, 26.2, 21.6, 13.8 ppm. HRMS (ESI-TOF) m/z: $C_{19}H_{22}IN_3O$ [M − I]$^+$ calcd for 308.1757, found 308.1762.

*3-Propyl-1-(pyridin-2-yl)-1H-benzo[d]imidazol-3-ium Iodide (**C7**).*[14a] Organocatalyst **C7** was synthesized following a previously reported method.[14a−c] Purification by flash chromatography (DCM/MeOH, 10:1) gave a yellow solid (277.6 mg, 76%). MP = 189.6−190.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.61 (s, 1H), 8.77−8.75 (m, 1H), 8.46−8.43 (m, 1H), 8.32−8.24 (m, 2H), 8.15 (d, J = 7.2 Hz, 1H), 7.76−7.69 (m, 3H), 4.62 (t, J = 6.4 Hz, 2H), 2.10−2.00 (m, 2H), 0.99 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 149.2, 147.3, 141.9, 140.4, 131.5, 129.3, 127.6, 127.0, 124.9, 116.9, 115.9, 114.0, 48.7, 21.9, 10.7 ppm.

*1-(6-Methylpyridin-2-yl)-2-methyl-3-propyl-1H-benzo[d]-imidazol-3-ium Iodide (**C8**).* Organocatalyst **C8** was synthesized following a previously reported method.[14a−c] Purification by flash chromatography (DCM/MeOH, 10:1) gave a white solid (341.2 mg, 81%). MP = 178.7−179.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.51 (s, 1H), 8.53−8.51 (m, 1H), 8.25−8.23 (m, 1H), 8.17 (t, J = 7.6 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.80−7.75 (m, 2H), 7.58 (d, J = 7.6 Hz, 1H), 4.59 (t, J = 7.2 Hz, 2H), 2.66 (s, 3H), 2.07−2.01 (m, 2H), 1.00 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 158.6, 146.7, 142.0, 140.6, 131.6, 129.5, 127.6, 127.0, 124.3, 116.1, 114.0, 113.9, 48.7, 23.7, 22.0, 10.8 ppm. HRMS (ESI-TOF) m/z: $C_{16}H_{18}IN_3$ calcd for [M − I]$^+$ 252.1495, found 252.1498.

*1-(Pyridin-2-yl)ethan-1-one (**C9**).*[20] The reagent was purchased from Adamas Reagent Company. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60−8.58 (m, 1H), 7.96−7.93 (m, 1H), 7.76−7.72 (m, 1H), 7.40−7.36 (m, 1H), 2.64 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.0, 153.5, 148.9, 136.8, 127.0, 121.5, 25.7 ppm.

*1-(6-Acetylpyridin-2-yl)-2-methyl-3-propyl-1H-benzo[d]-imidazol-3-ium Iodide (**C10**).* Organocatalyst **C10** was synthesized following a previously reported method.[14a−c] Purification by flash chromatography (DCM/MeOH, 10:1) gave a white solid (341.2 mg, 81%). MP = 206.9−207.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.50 (t, J = 7.6 Hz, 1H), 8.30−8.28 (m, 1H), 8.22 (t, J = 7.6 Hz, 2H), 7.89 (d, J = 8.0 Hz, 1H), 7.77−7.66 (m, 2H), 4.60 (t, J = 7.6 Hz, 2H), 2.98 (s, 3H), 2.66 (s, 3H), 1.97−1.92 (m, 2H), 1.06 (t, J = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 197.9, 153.0, 152.1, 145.0, 142.1, 130.9, 130.6, 127.1, 126.8, 125.6, 122.9, 113.5, 46.9, 25.8, 21.9, 11.99, 11.97, 10.9 ppm. HRMS (ESI-TOF) m/z: $C_{18}H_{20}IN_3O$ calcd for [M − I]$^+$ 294.1601, found 294.1596.

*1-(5-Acetylpyridin-2-yl)-3-propyl-1H-benzo[d]imidazol-3-ium Iodide (**C11**).* Organocatalyst **C11** was synthesized following a previously reported method.[14a−c] Purification by flash chromatography (DCM/MeOH, 10:1) gave a white solid (297.3 mg, 73%). MP = 201.5−202.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.63 (s, 1H), 9.29 (d, J = 1.6 Hz, 1H), 8.76−8.73 (m, 1H), 8.63−8.60 (m, 1H), 8.27−8.21 (m, 2H), 7.84−7.79 (m, 2H), 4.59 (t, J = 7.2 Hz, 2H), 2.74 (s, 3H), 2.08−2.02 (m, 2H), 1.02 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 196.3, 150.0, 149.5, 142.8, 139.9, 132.3 131.7, 129.5, 128.0, 127.3, 116.5, 116.4, 114.2, 48.8, 27.3, 22.0, 10.8 ppm. HRMS (ESI-TOF) m/z: $C_{17}H_{18}IN_3O$ calcd for [M − I]$^+$ 280.1444, found 280.1446.

*1-(3-Acetylpyridin-2-yl)-3-propyl-1H-benzo[d]imidazol-3-ium Iodide (**C12**).* Organocatalyst **C12** was synthesized following a previously reported method.[14a−c] Purification by flash chromatography (DCM/MeOH, 10:1) gave a white solid (225.4 mg, 53%). MP = 195.1−196.1 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.63−8.61 (m, 1H), 8.38−8.36 (m, 1H), 8.33−8.30 (m, 2H), 7.88−7.82 (m, 2H), 7.63−7.60 (m, 1 H), 7.13 (s, 1H), 4.71 (t, J = 4.0 Hz, 2H), 2.09 (s, 3H), 2.07−2.00 (m, 2H), 1.05 (t, J = 8.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 158.9, 149.5, 149.3, 135.6, 134.1, 128.4, 127.4, 125.3, 123.6, 115.2, 114.2, 74.2, 47.4, 22.8, 22.4, 10.8 ppm. HRMS (ESI-TOF) m/z: $C_{17}H_{18}IN_3O$ calcd for [M − I]$^+$ 280.1444, found 280.1446.

*1-(3-Acetylphenyl)-3-propyl-1H-benzo[d]imidazol-3-ium Iodide (**C13**).* Organocatalyst **C13** was synthesized following apreviously reported method.[14a−c] Purification by flash chromatography (DCM/MeOH, 10:1) gave a white solid (321.0 mg, 79%). MP = 134.3−135.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.27 (s, 1H), 8.40 (s, 1H), 8.27 (t, J = 8.0 Hz, 2H), 8.14 (d, J = 7.6 Hz, 1H), 7.95−7.87 (m, 2H), 7.81−7.72 (m, 2H), 4.75 (t, J = 7.2 Hz, 2H), 2.70 (s, 3H), 2.07−2.02 (m, 2H), 1.02 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 196.9, 142.8, 138.4, 133.6, 131.3, 131.2, 130.9, 130.0, 129.7, 127.5, 127.0, 125.0, 114.1, 113.5, 48.5, 27.0, 22.0, 10.8 ppm. HRMS (ESI-TOF) m/z: $C_{18}H_{19}IN_2O$ calcd for [M − I]$^+$ 279.1492, found 279.1495.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02673.

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra of all ligands, organocatalysts, and products; synthetic procedures for organocatalysts; control experiments and IR spectra for reaction mechanism (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank support from the National Natural Science Foundation of China (21868033), Xinjiang Bingtuan Young and Middle-Aged Leading Scientists Program (2020CB027), Shihezi Young and Middle-Aged Leading Scientists Program (2019RC01), International Partnership Program of Shihezi University (GJHZ201908), and Double First-Class Program of Shihezi University (SHYL-ZD201801).

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