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CNN 型双核 Cu(I)配合物室温催化固定 CO_2 的直接羧基化反应

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摘要 将一类 CNN 型双核 Cu(I)配合物成功地应用于端炔和 CO_2 的直接羧基化反应, 该反应在室温、常压 CO_2 和较低催化剂用量条件下即可顺利进行. 该催化体系在端炔的直接羧基化反应中显示出较广的底物普适性, 以 83%～97%的收率得到了一系列丙炔酸类产物. 该方法还可用于杂芳烃的连续羧基化反应及酯化反应. 控制实验和文献研究表明, Cs_2CO_3 促进了端炔氢的脱除, 同时 Cu(I)配合物通过 Cu(I)中心与炔基配位作用对端炔活化起到了重要作用.
关键词 二氧化碳; 端炔; 铜催化; 羧基化反应; C—H 键活化

CNN-Type Binuclear Cu(I) Complexes Catalyzed Direct Carboxylation via the Fixation of CO_2 at Room Temperature

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Abstract A type of CNN-type binuclear Cu(I) complexes was used in the direct carboxylation of the terminal alkynes under room temperature and atmospheric CO_2 with a low catalyst loading. A broad range of the terminal alkynes were tolerated, leading to the desired propiolic acids in 83%～97% yields. The method was successfully applied to continuous carboxylation and esterification of hetero arenes. The control experimental results and literature suggest that Cs_2CO_3 promotes the removal of terminal alkyne hydrogen atoms, and Cu(I) complexes play an important role in the activation of terminal alkyne by the interaction between Cu(I) center and alkynyl group.
Keywords carbon dioxide; terminal alkyne; copper catalysis; carboxylation; C—H activation

1 Introduction

Carbon dioxide (CO_2) is an important greenhouse gas, of which the concentrations in the atmosphere have an evident impact on global climate. Therefore, there is an urgent need to develop a range of utilization and conversion method of CO_2.[1] The transform of CO_2 through chemical reactions with simple partners into high value-added chemicals is one of the most important strategies for CO_2 utilization.[2] Among these reactions, the direct carboxylation of terminal alkynes with CO_2 constitutes a promising method due to high atomic economy.[3] A wide range of Ag catalytic systems for the direct carboxylation of terminal alkynes with CO_2 have been developed, including ligands-free systems,[4] ligands-promoted systems[5] and heterogeneous catalytic systems.[6] Besides Ag catalytic systems, other transition metal catalysts, such as Ni,[7] Mo,[8] and rare-earth metal,[9] and organocatalysts,[10] were used in the direct carboxylation of terminal alkynes with CO_2. Inoue and co-workers[11] had successfully realized Cu(I) catalyzed the direct carboxylation of terminal alkynes with CO_2 in 1994. In the last decades, a wide range of Cu catalysts with different ligands, including PEt_3,[12] 1,10-phenanthroline,[13] P,P-bidentate ligand,[14] N-heterocyclic carbene (NHC) ligand,[15] and poly-NHC ligand,[16] have been described. In addition, the ligand-free system,[17] supercritical CO_2 system[18] and heterogeneous CuBr@C[19] have been developed. Recently, we reported a kind of CNN-type

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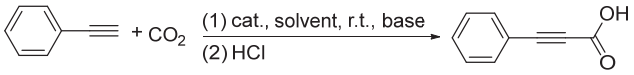
binuclear Cu(I) complexes (Figure 1),[20] which were used as catalysts for the synthesis of oxazolidinones from propargylic amines and CO_2. Inspired by the success of Cu(I) catalysts in the synthesis of oxazolidinones, the previously reported Cu(I) complexes (Figure 1)[20] were employed to investigate their catalytic performance in the direct carboxylation of terminal alkynes with CO_2 in this work. As expected, the Cu(I) complexes exhibited high activity for the direct carboxylation of terminal alkynes under room temperature and atmospheric CO_2 with a low catalyst loading (1 mol%).

2 Results and discussion

The reaction conditions, including the catalytic performance of Cu(I) complexes (Table 1, Entries 1～4), loading amount of **C1** (Table 1, Entries 1 and 5～7), bases (Table 1, Entries 1 and 8～14), loading amount of bases (Table 1, Entries 1, 22 and 23), solvents (Table 1, Entries 1 and 15～18) and reaction time (Table 1, Entries 1 and 19～21), were screened using the coupling of phenylacetylene with CO_2 as benchmark reaction (Table 1). A Cu(I) catalyst **C1** (1 mol%) combined with Cs_2CO_3 (1.2 equiv.) in *N*,*N*-dimethylformamide (DMF) under room temperature and atmospheric CO_2 for 24 h was found to be efficient for the direct carboxylation of terminal alkynes with CO_2, and afforded a 92% yield of **2a** (Table 1, Entry 1). Control experiments were performed in the absence of **C1** or Cs_2CO_3, and the use of **C1** or Cs_2CO_3 alone was difficult to trigger the reaction (Table 1, Entries 24 and 25). The results indicated that the cooperative effect between **C1** and Cs_2CO_3 is essential for the direct carboxylation. In order to explore whether the carboxyl group of propargylic acid from either CO_2 or Cs_2CO_3, a control experiment in the absence of CO_2 was performed, and no desired products was obtained (Table 1, Entry 26). The result indicated that CO_2 is indeed involved in the reaction.

The substrates scope of aryl terminal alkynes was investigated(Table 2). The terminal alkynes bearing electron-neutral group (**1a**), electron-donating group (**1b**～**1d**), and electron-withdrawing group (**1e**～**1j**) at the *para*-position of aryl ring, reacted smoothly with CO_2 to give high to excellent yields (Table 2, **2a**～**2j**). It was noted that substrates bearing strong electron-withdrawing group, such as cyano group, nitro group and aldehyde group, still gave 85%～92% yields through increasing reaction temperature to 40 ℃ and/or prolonging reaction time to 36 h (Table 2, **2k**～**2m**). The substrates with different substituents at the *meta*- and *ortho*-position of aryl ring were successfully transformed, providing the targeted products **2n**～**2t** in excellent yields. The selectivity of 1,4-diethynylbenzene

Table 1 Condition optimization of carboxylation of phenylacetylene with CO_2[a]



1a 2a

Entry	Catalyst (mol%)	Base (equiv.)	Time/h	Solvent	Yield/%
1	**C1** (1.0)	Cs_2CO_3 (1.2)	24	DMF	92
2	**C2** (1.0)	Cs_2CO_3 (1.2)	24	DMF	60
3	**C3** (1.0)	Cs_2CO_3 (1.2)	24	DMF	70
4	**C4** (1.0)	Cs_2CO_3 (1.2)	24	DMF	50
5	**C1** (0.75)	Cs_2CO_3 (1.2)	24	DMF	73
6	**C1** (0.50)	Cs_2CO_3 (1.2)	24	DMF	55
7	**C1** (0.25)	Cs_2CO_3 (1.2)	24	DMF	36
8	**C1** (1.0)	K_2CO_3 (1.2)	24	DMF	8
9	**C1** (1.0)	Na_2CO_3 (1.2)	24	DMF	0
10	**C1** (1.0)	DBU (1.2)	24	DMF	16
11	**C1** (1.0)	Et_3N (1.2)	24	DMF	3
12	**C1** (1.0)	K_3PO_4 (1.2)	24	DMF	5
13	**C1** (1.0)	NaOH (1.2)	24	DMF	0
14	**C1** (1.0)	Na^{t}OBu (1.2)	24	DMF	4
15	**C1** (1.0)	Cs_2CO_3 (1.2)	24	DMA	57
16	**C1** (1.0)	Cs_2CO_3 (1.2)	24	THF	14
17	**C1** (1.0)	Cs_2CO_3 (1.2)	24	MeCN	23
18	**C1** (1.0)	Cs_2CO_3 (1.2)	24	DMSO	60
19	**C1** (1.0)	Cs_2CO_3 (1.2)	12	DMF	48
20	**C1** (1.0)	Cs_2CO_3 (1.2)	18	DMF	72
21	**C1** (1.0)	Cs_2CO_3 (1.2)	30	DMF	94
22	**C1** (1.0)	Cs_2CO_3 (1.0)	24	DMF	62
23	**C1** (1.0)	Cs_2CO_3 (2.0)	24	DMF	98
24	**C1** (1.0)	None	24	DMF	0
25	None	Cs_2CO_3 (1.2)	24	DMF	Trace
26[b]	**C1** (1.0)	Cs_2CO_3 (1.2)	24	DMF	0

[a] Reaction conditions: (1) phenylacetylene (1.0 mmol, 105 mg), Cu(I) complexes **C1**～**C4**, base (indicated as Table 1), room temperature (r.t.), CO_2 (balloon), solvent (indicated as Table 1, 3 mL). [b] In the absence of CO_2; (2) 1 mol/L HCl, isolated yields. DMA = *N*,*N*-dimethylacetamide, THF = tetrahydrofuran, DMSO=dimethyl sulfoxide.

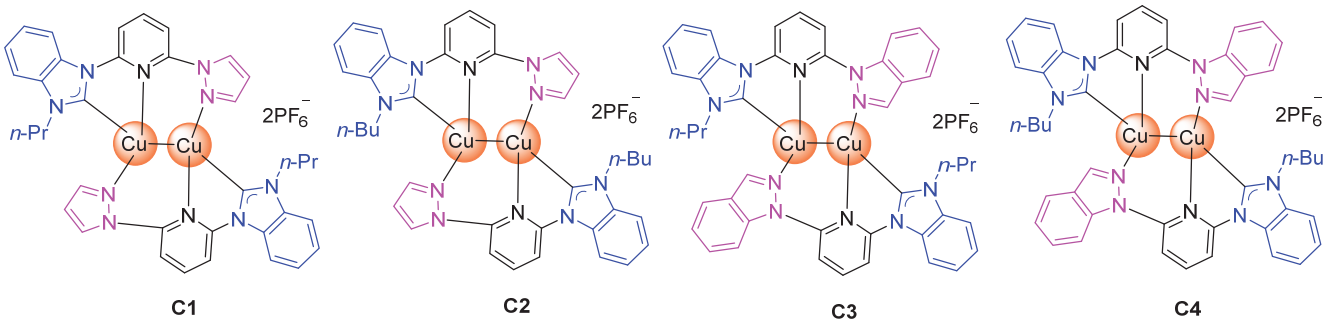
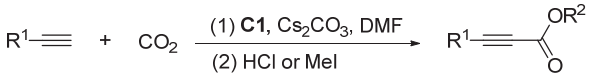
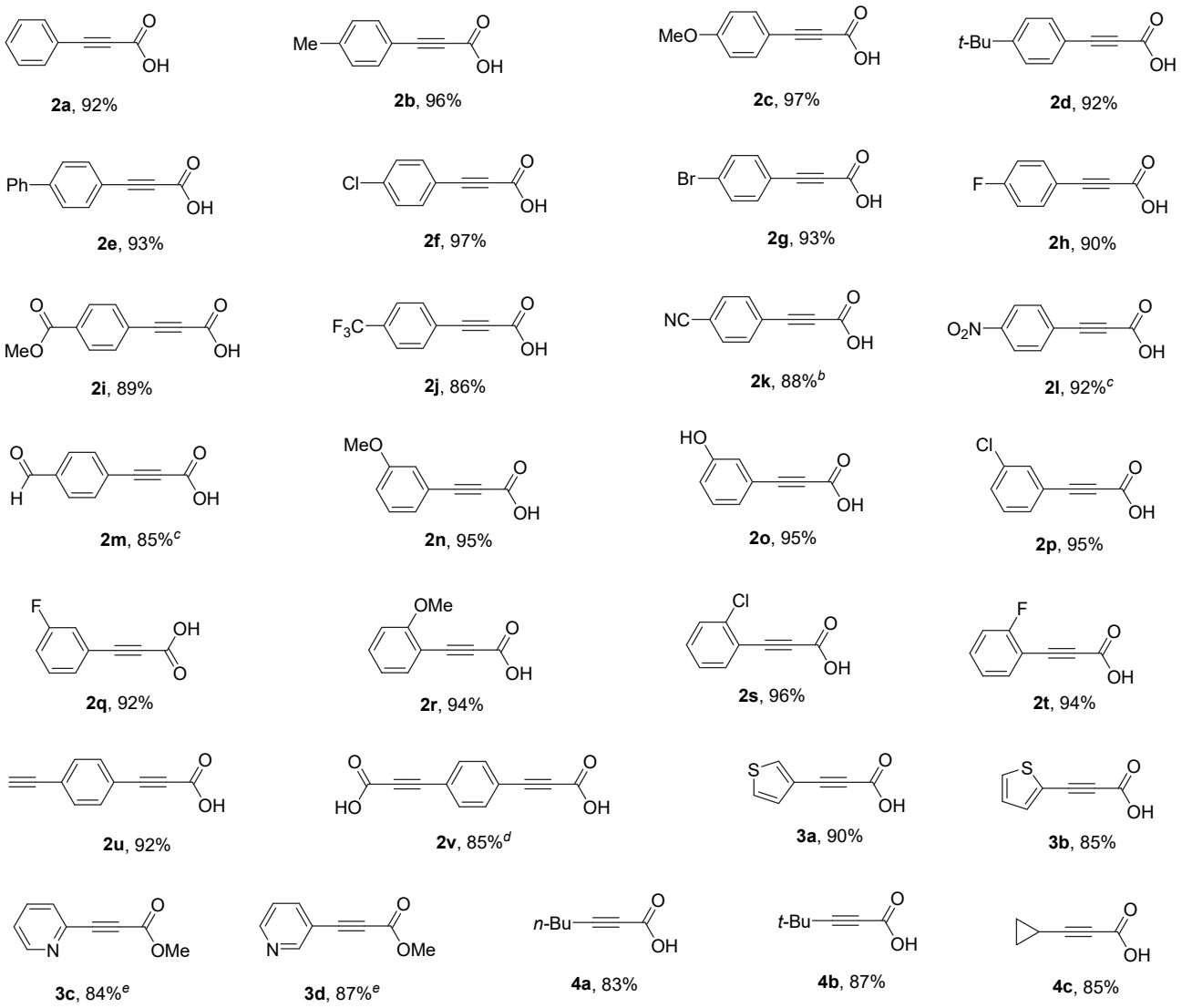


Figure 1 Cu(I) complexes used in this work

Table 2 Synthesis of propiolic acid derivatives from CO_2 and terminal alkynes[a]





[a] Reaction conditions: (1) terminal alkynes (1 mmol), Cu(I) complex **C1** (0.01 mmol, 1 mol%, 10.2 mg), Cs_2CO_3 (1.2 mmol, 395 mg), r.t., 24 h, CO_2 (balloon), DMF (3 mL). [b] 40 ℃, 24 h. [c] 40 ℃, 36 h. [d] Cs_2CO_3 (2.4 mmol, 790 mg), 50 ℃, 24 h; (2) 1 mol/L HCl, isolated yields. [e] (1) terminal alkynes (1 mmol), Cu(I) complex **C1** (0.01 mmol, 1 mol%, 10.2 mg), Cs_2CO_3 (1.2 mmol, 395 mg), r.t., 24 h, CO_2 (balloon), DMF (3 mL); (2) MeI (2 equiv., 289.6 mg), 50 ℃, 2 h.

could be controlled by tuning the reaction temperature. When the reaction was carried out under room temperature, mono-substituted product was obtained in 92% yield (Table 2, **2u**), however, di-substituted product was formed in 85% yield under 50 ℃ (Table 2, **2v**). To demonstrate the universality of this method, heteroaryl terminal alkynes were investigated (Table 2). The different heteroaryl terminal alkynes, such as thiophene substituted terminal alkynes and pyridine substituted terminal alkynes, could smoothly reacted to afford the desired products in 84%～90% yields (Table 2, **3a**～**3d**). In addition, the catalytic system was tolerable to alkyl substituted terminal alkynes under standard conditions (Table 2, **4a**～**4c**).

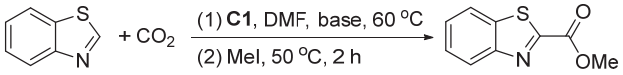
The C—H carboxylation of aromatic heterocycles represents atom- and step-economical method for efficient construction of valuable synthons.[21] We evaluated challenging aromatic heterocycles in our developed Cu(I) catalytic system. As shown in Table 3, the reaction conditions, including catalytic performance of Cu(I) complexes **C1**～**C4** (Table 3, Entries 1～4), the amount of Cu(I) catalyst (Table 3, Entries 1, 5 and 6), bases (Table 3, Entries 5, 9 and 10), reaction time (Table 3, Entries 5, 7 and 8), reaction temperature (Table 3, Entries 5, 11 and 12) and solvents (Table 3, Entries 5, 13～16), were optimized with our developed Cu(I) catalytic system. No significant effect of catalytic performance of **C1**～**C4** on carboxylation of benzothiazole with CO_2 (Table 3, Entries 1～4) was observed compared with the effect on of carboxylation of

phenylacetylene with CO_2 (Table 1, Entries 1～4). The C—H carboxylation of benzothiazole with CO_2 could proceed smoothly using **C1** (3 mol%) as catalyst and Cs_2CO_3 (1.5 equiv.) as bases at 60 ℃ for 18 h in DMF (Table 3, Entry 5). It was noted that the combination used of **C1** and base was necessary to accomplish the transformation, and the coupling did not proceed in the absence of **C1** or Cs_2CO_3 (Table 3, Entries 17 and 18). A similar result was obtained when a control experiment in the absence of CO_2 was performed (Table 3, Entry 19).

To demonstrate the scope of our developed Cu(I) catalytic system, a wide range of benzothiazoles and benzoxazoles were investigated. It was found that the benzothiazoles and benzoxazoles bearing different substituents, such as bromo, chloro, methoxy, methyl and phenyl groups, were successfully coupled with CO_2, affording the desired products in high to excellent yields (Table 4, **6a**～**6l**).

To understand the role of catalyst and base in the reaction process, a range of control experiments were performed. As shown in Table 5, phenylacetylene reacted firstly with CO_2 using Cs_2CO_3 as base under room temperature for 4 h in the absence of Cu(I) complex **C1**, and subsequently 1 mol% of **C1** was added to the reaction mixtures. After 4 h, 10% yield of desired product was obtained (Table 5, Entry 1). The product yield was not obviously improved when reaction time t_1 of the first step was prolonged from 4 h to 8 h (Table 5, Entries 1 vs 2 and 3). In contrast, the yields increased from 10% to 46% when the reaction time t_2 was prolonged to 8 h (Table 5, Entries 1 vs 4). The results indicated that Cu(I) complex **C1** played a more important role in comparison with Cs_2CO_3 (Table 5, Entries 2 vs 4). In order to explore whether the deprotonation of terminal alkynes with Cs_2CO_3 or the activation of terminal alkynes by copper catalyst first occurred, two control experiments were performed (Table 5, Entries 4, 5). The results showed that pre-deprotonation of terminal alkyne with Cs_2CO_3 (Table 5, Entry 4) was beneficial to improve the yield of product. In addition, deprotonation process of terminal alkyne with Cs_2CO_3 was studied by ^{1}H NMR method. The proton content of terminal alkyne decreased gradually with the addition of Cs_2CO_3, suggesting the proton of terminal alkyne occurred in the presence of Cs_2CO_3. Based on the results above, we inferred that the dehydrogenation of terminal alkynes by Cs_2CO_3 first occurred, and Cu(I) complexes then activated the terminal

Table 3 Condition optimization of the carboxylation of benzothiazole with CO_2[a]

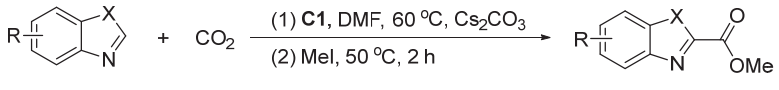


5a 6a

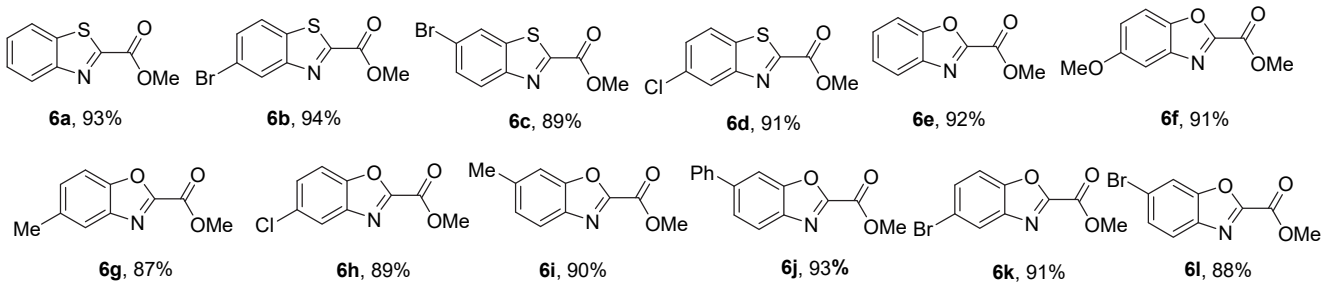
Entry	Catalyst (mol%)	Base	Solvent	Time/h	T/℃	Yield/%
1	**C1** (1.5)	Cs_2CO_3	DMF	18	60	55
2	**C2** (1.5)	Cs_2CO_3	DMF	18	60	50
3	**C3** (1.5)	Cs_2CO_3	DMF	18	60	49
4	**C4** (1.5)	Cs_2CO_3	DMF	18	60	41
5	**C1** (3.0)	Cs_2CO_3	DMF	18	60	93
6	**C1** (4.5)	Cs_2CO_3	DMF	18	60	91
7	**C1** (3.0)	Cs_2CO_3	DMF	12	60	79
8	**C1** (3.0)	Cs_2CO_3	DMF	24	60	92
9	**C1** (3.0)	K^{t}OBu	DMF	18	60	72
10	**C1** (3.0)	Li^{t}OBu	DMF	18	60	92
11	**C1** (3.0)	Cs_2CO_3	DMF	18	50	64
12	**C1** (3.0)	Cs_2CO_3	DMF	18	70	93
13	**C1** (3.0)	Cs_2CO_3	DMA	18	60	48
14	**C1** (3.0)	Cs_2CO_3	DMSO	18	60	54
15	**C1** (3.0)	Cs_2CO_3	THF	18	60	0
16	**C1** (3.0)	Cs_2CO_3	CH_3CN	18	60	Trace
17	**C1** (3.0)	None	DMF	18	60	0
18	None	Cs_2CO_3	DMF	18	60	0
19[b]	**C1** (3.0)	Cs_2CO_3	DMF	18	60	0

[a] Reaction conditions: (1) benzothiazole (1.0 mmol, 137.8 mg), Cu(I) complexes **C1**～**C4**, base (1.5 mmol, 1.5 equiv.), 60 ℃, CO_2 (balloon), solvent (3 mL). (2) MeI (2 equiv., 289.6 mg), 50 ℃, 2 h, isolated yields. [b] In the absence of CO_2.

Table 4 Carboxylation of hetero arenes catalyzed by binuclear copper **C1**[a]



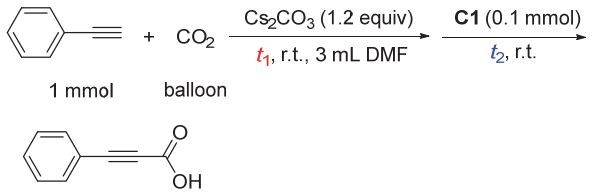
X = O, S (5) X = O, S (6)



[a] Reaction conditions: (1) hetero arenes (1 mmol), Cu(I) complex **C1** (0.03 mmol, 3 mol%, 30.6 mg), Cs_2CO_3 (1.5 mmol, 493.7 mg), 60 ℃, 18 h, CO_2 (balloon), DMF (3 mL); (2) MeI (2 equiv., 289.6 mg), 50 ℃, 2 h, isolated yields.

alkynes via the coordination interaction between Cu(I) center and alkynes.

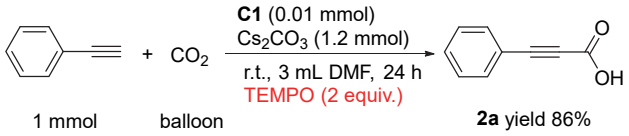
Table 5 Control experiments for reaction mechanism[a]



Entry	t_1/h	t_2/h	Isolated yield/%
1	4	4	10
2	8	4	9
3	12	4	14
4	4	8	46
5[b]			29

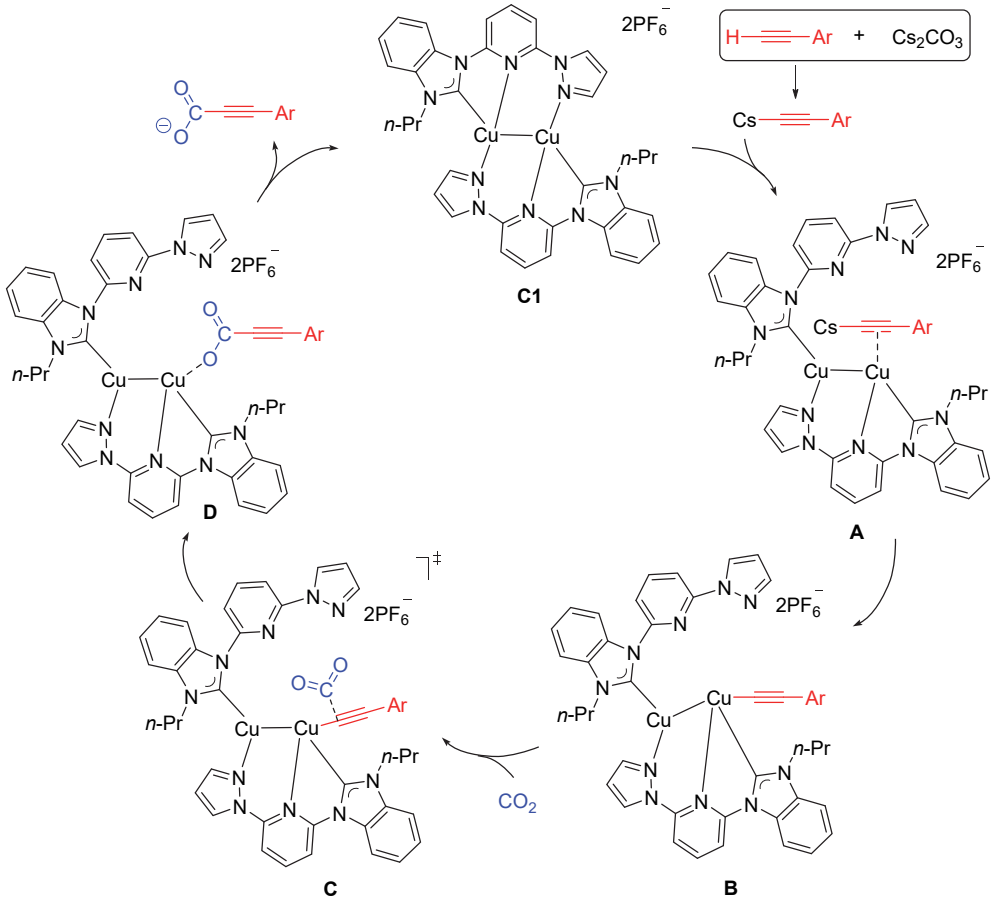
[a] One pot two-step method: (1) first step: phenylacetylene (1.0 mmol, 105 mg) and Cs_2CO_3 (1.2 mmol, 395 mg) reacted under CO_2 (balloon) and room temperature in 3 mL DMF for t_1 h. Subsequently, Cu(I) complexes **C1** (0.01 mmol, 1 mol%, 10.2 mg) was added to reaction mixtures under room temperature for t_2 h. [b] One-step method (**C1** was added together with Cs_2CO_3): phenylacetylene (1.0 mmol, 105 mg), Cu complexes **C1** (0.01 mmol, 1 mol%, 10.2 mg), Cs_2CO_3 (1.2 mmol, 395 mg), room temperature, CO_2 (balloon), DMF (3 mL), 8 h.

A free radical capture experiment was carried out to explore the reaction mechanism (Scheme 1). A yield of 86% for desired product **2a** was obtained when 2 equiv. of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was added in the reaction system. This result is not significant difference with that obtained in Table 1 (Entry 1). Therefore, we inferred that radical mechanism might be not involved in this catalytic cycle.



Scheme 1 Experiment for free radical trapping using TEMPO

The possible mechanism was proposed from our experimental results and previous literatures. As shown in Scheme 2, terminal alkynes are first deprotonated by Cs_2CO_3 to form alkynyl cesium. The activation of substrates by transition metal complexes usually requires transition metal complexes to dissociate one- or multi-coordination sites to provide access for the interaction between metal center and substrates.[22] The catalytic behavior of copper complex **C1** in carboxylation of terminal alkynes was studied by NMR method. The results showed that a new copper complex could be formed when terminal alkynes was added to **C1**. However, only the chemical shift of the new complex and the original complex was obs-



Scheme 2 Cu complex **C1** catalyzed carboxylation of terminal alkynes with CO_2

erved, indicating that the ligand was not completely removed, but individual coordination sites temporarily left from the Cu center. Therefore, a binuclear copper species may be involved in the catalytic cycle. Obvious changes in the chemical shift of pyridine ring and pyrazole ring were observed in the analysis of ^{13}C NMR spectra, so we infer that the pyridine ring and pyrazole ring may have left temporarily from Cu center. In our previous work, we have explored and elaborated the catalytic mode of this binuclear tridentate copper complexes in the carboxylative cyclization of propargylic amines with CO_2.[20] Once the pyridine and pyrazole ligands dissociate from Cu center, the real catalytic species is generated to allow the π-coordination between alkyne with Cu catalysts. To prove the interaction between alkyne with Cu catalysts, a control experiment was performed by NMR titration method. The shifts in the resonances of two alkynyl terminal carbon from δ 83.45 to δ 83.16, as well as from δ 80.74 to δ 80.38, were detected when Cu(I) complex **C1** was added to solution of phenylacetylene. [23] The copper-acetylide attacks CO_2 to form the transition state **C** through the interaction between the terminal carbon atom of alkynes and CO_2.[24] The nucleophilic attack of the copper-acetylide on carbon dioxide is considered generally to be the rate-determining step of the reaction.[24] Following C—C bond forming of terminal alkynes with CO_2, CO_2 is transferred from the terminal carbon atom of alkynes to the Cu center through the interaction of oxygen atom of CO_2, which produces the copper-propiolate **D**. Finally, the Cu catalyst **C1** is recovered by releasing the desired products

3 Conclusions

In conclusion, an efficient Cu(I) catalyzed the direct carboxylation of the terminal alkynes with CO_2 was developed. The Cu(I) catalytic system showed high catalytic activity and good tolerance toward a wide range of functional groups for the terminal alkynes or hetero arenes under relatively mild reaction conditions. The Cu(I) catalyst plays an important role in the activation of substrate, and base promotes the removal of terminal alkyne hydrogen atoms. We anticipate that the experimental results obtained through this work provides some knowledge for the synthesis of high catalytic active transition-metal catalysts.

4 Experimental section

4.1 General information

Unless otherwise stated, all solvents and starting materials were purchased from commercial suppliers and used without further purification. Cu complexes **C1**～**C4** were synthesized by our previously reported method.[20]

4.2 Analytical methods

NMR spectra were recorded on Bruker Avance III HD 400 or Bruker Avance NEO 600 spectrometer using TMS as an internal standard (400 MHz or 600 MHz for ^1H NMR and 100 MHz or 150 MHz for ^{13}C NMR).

4.3 Preparation procedure for the direct carboxylation of terminal alkynes with CO_2

The terminal alkynes (1.0 mmol), Cu(I) complex **C1** (0.01 mmol, 1 mol%, 10.2 mg), Cs_2CO_3 (1.2 mmol, 395 mg) and 3 mL of DMF were successively added to a 25 mL Schlenk tube. The reaction mixture reacted at room temperature for 24 h under CO_2 atmosphere (101 kPa, using a balloon). After the reaction was completed, saturated brine (25 mL) and an aqueous solution of HCl (1 mol/L, 6 mL) were successively added to the reaction mixture. The acidified mixture was extracted with ethyl acetate (15 mL×3), and the solvent was removed under reduced pressure. Finally, the desired products were isolated by flash chromatography.

4.4 Preparation procedure for three-component carboxylation of hetero arenes, CO_2 and MeI

Hetero arenes (1.0 mmol), Cu(I) complex **C1** (0.03 mmol, 3 mol%, 30.6 mg), Cs_2CO_3 (1.5 mmol, 493.7 mg) and 3 mL of DMF were successively added to a 25 mL Schlenk tube. The reaction mixture reacted at 60 ℃ for 18 h under CO_2 atmosphere (101 kPa, using a balloon). Next, MeI (2 mmol, 289.6 mg) was added to the reaction mixtures, and the reaction was continued for 2 h at 50 ℃. After the reaction was completed, saturated brine (25 mL) was successively added to the reaction mixture. The acidified mixture was extracted with ethyl acetate (15 mL×3), and the solvent was removed under reduced pressure. Finally, the desired products were isolated by flash chromatography.

3-Phenylpropiolic Acid (**2a**):[25] Purification by flash chromatography (EtOAc) gave a white solid (134.3 mg, 92%). m.p. 137.1～139.0 ℃; ^1H NMR (400 MHz, DMSO-d_6) δ: 13.89 (br, 1H), 7.66 (d, J=7.2 Hz, 2H), 7.59 (t, J=7.6 Hz, 1H), 7.51 (d, J=7.6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 154.8, 133.1, 131.4, 129.5, 119.4, 84.9, 82.3.

3-(*p*-Tolyl)propiolic Acid (**2b**):[25] Purification by flash chromatography (EtOAc) gave a white solid (153.6 mg, 96%). m.p. 149.6～150.8 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.51 (d, J=6.4 Hz, 2H), 7.20 (d, J=6.4 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.7, 142.0, 133.4, 129.6, 116.1, 89.8, 79.9, 21.9.

3-(4-Methoxyphenyl)propiolic Acid (**2c**):[4b] Purification by flash chromatography (EtOAc) gave a white solid (170.7 mg, 97%). m.p. 151.2～152.0 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, J=8.8 Hz, 2H), 6.90 (d, J=8.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.9, 158.5, 135.4, 114.4, 110.9, 90.0, 79.7, 55.5.

3-(4-(*tert*-Butyl)phenyl)propiolic Acid (**2d**):[26] Purification by flash chromatography (EtOAc) gave a white solid (185.8 mg, 92%). m.p. 152.6～153.9 ℃; ^1H NMR (600 MHz, DMSO-d_6) δ: 7.54 (d, J=36.6 Hz, 4H), 1.26 (s, 9H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 154.6, 154.0, 132.6, 126.0, 116.2, 84.7, 81.7, 34.9, 30.9.

3-([1,1'-Biphenyl]-4-yl)propiolic acid (**2e**):[27] Purification by flash chromatography (EtOAc) gave a white solid

(206.5 mg, 93%). m.p. 137.4～138.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, J=8.4 Hz, 2H), 7.67～7.63 (m, 4H), 7.52 (t, J=7.2 Hz, 2H), 7.45 (t, J=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.0, 144.0, 139.7, 133.8, 129.0, 128.3, 127.4, 127.2, 117.8, 89.2, 80.6.

3-(4-Chlorophenyl)propiolic acid (**2f**):[25] Purification by flash chromatography (EtOAc) gave a white solid (175.1 mg, 97%). m.p. 167.7～168.9 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.69 (d, J=8.8 Hz, 2H), 7.57 (d, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 154.6, 136.2, 134.8, 129.7, 118.3, 83.4, 83.1.

3-(4-Bromophenyl)propiolic acid (**2g**):[26] Purification by flash chromatography (EtOAc) gave a white solid (209.2 mg, 93%). m.p. 164.4～165.9 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 14.00 (br, 1H), 7.691 (d, J=7.8 Hz, 2H), 7.59 (d, J=7.8 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 154.6, 134.9, 132.6, 125.1, 118.6, 83.6, 83.1.

3-(4-Fluorophenyl)propiolic Acid (**2h**):[26] Purification by flash chromatography (EtOAc) gave a white solid (147.6 mg, 90%). m.p. 142.6～144.3 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 7.74～7.72 (m, 2H), 7.34 (t, J=9.0 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 164.5 (d, J=249 Hz), 154.7, 135.8 (d, J=9.2 Hz), 117.0 (d, J=22.4 Hz), 115.9 (d, J=3.3 Hz), 83.8, 82.1.

3-(4-(Methoxycarbonyl)phenyl)propiolic acid (**2i**):[27] Purification by flash chromatography (EtOAc) gave a white solid (181.6 mg, 89%). m.p. 161.8～162.7 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.04 (d, J=8.0 Hz, 2H), 7.80 (d, J=8.0 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.9, 154.5, 133.3, 131.5, 129.9, 124.2, 84.6, 83.0, 52.9.

3-(4-(Trifluoromethyl)phenyl)propiolic acid (**2j**):[28] Purification by flash chromatography (EtOAc) gave a white solid (184 mg, 86%). m.p. 137.8～138.8 ℃; ^{1}H NMR (400 MHz, CD_3OD) δ: 7.69～7.63 (m, 4H); ^{13}C NMR (100 MHz, CD_3OD) δ: 156.0, 134.4, 131.6 (q, $J_{C\text{-}F}$=32.6 Hz), 125.3 (q, $J_{C\text{-}F}$=3.7 Hz), 123.8, 123.7 (q, $J_{C\text{-}F}$=270 Hz), 84.0, 83.7.

3-(4-Cyanophenyl)propiolic Acid (**2k**):[27] Purification by flash chromatography (EtOAc) gave a white solid (150.5 mg, 88%). m.p. 185.9～186.8 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.95 (d, J=8.8 Hz, 2H), 7.83 (d, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 154.3, 133.7, 133.2, 124.3, 118.5, 113.5, 84.9, 82.6.

3-(4-Nitrophenyl)propiolic acid (**2l**):[25] Purification by flash chromatography (EtOAc) gave a brown solid (175.7 mg, 92%). m.p. 169.1～170.3 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.28 (d, J=8.8 Hz, 2H), 7.89 (d, J=8.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 154.3, 148.7, 134.3, 126.1, 124.5, 85.6, 82.2.

3-(4-Formylphenyl)propiolic acid (**2m**):[25] Purification by flash chromatography (EtOAc) gave a yellow solid (147.9 mg, 85%). m.p. 183.4～184.5 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 14.10 (br, 1H), 10.09 (s, 1H), 8.01 (d, J=6.0 Hz, 2H), 7.88 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 193.1, 154.4, 137.4, 133.7, 130.2, 125.1, 84.6, 83.4.

3-(3-Methoxyphenyl)propiolic acid (**2n**):[16] Purification by flash chromatography (EtOAc) gave a white solid (167.2 mg, 95%). m.p. 109.1～110.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (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 NMR (100 MHz, $CDCl_3$) δ: 159.4, 158.5, 129.8, 125.9, 120.0, 118.1, 117.6, 88.9, 79.8, 55.4.

3-(3-Hydroxyphenyl)propiolic Acid (**2o**):[25] Purification by flash chromatography (EtOAc) gave a white solid (153.9 mg, 95%). m.p. 177.5～178.0 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 13.74 (br, 1H), 9.90 (br, 1H), 7.29 (t, J=8.4 Hz, 1H), 7.05 (d, J=7.6 Hz, 1H), 6.95～6.93 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 157.9, 154.8, 130.8, 123.9, 120.2, 119.1, 118.9, 85.1, 81.6.

3-(3-Chlorophenyl)propiolic Acid (**2p**): Purification by flash chromatography (EtOAc) gave a white solid (171.5 mg, 95%). m.p. 141.7～143.8 ℃ (lit.[4d] 146.2 ℃); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 14.01 (s, 1H), 7.73 (t, J=1.2 Hz, 1H), 7.63～7.60 (m, 2H), 7.51 (t, J=5.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 154.5, 134.0, 132.3, 131.7, 131.4, 131.3, 121.4, 83.0, 82.9.

3-(3-Fluorophenyl)propiolic acid (**2q**):[27] Purification by flash chromatography (EtOAc) gave a white solid (150.9 mg, 92%). m.p. 89.6～91.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44～7.37 (m, 2H), 7.34～7.31 (m, 1H), 7.24～7.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.5 (d, J=197.6 Hz), 158.2, 130.7 (d, J=6.7 Hz), 129.4 (d, J=2.6 Hz), 121.1 (d, J=7.5 Hz), 120.3 (d, J=18.6 Hz), 119.0 (d, J=16.8 Hz), 87.5 (d, J=2.7 Hz), 80.6.

3-(2-Methoxyphenyl)propiolic acid (**2r**):[16] Purification by flash chromatography (EtOAc) gave a white solid (165.5 mg, 94%). m.p. 128.3～129.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49～7.46 (m, 1H), 7.39～7.35 (m, 1H), 6.90～6.84 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.9, 158.4, 135.2, 132.9, 120.6, 110.9, 108.4, 86.1, 84.1, 55.9.

3-(2-Chlorophenyl)propiolic Acid (**2s**):[16] Purification by flash chromatography (EtOAc) gave a white solid (173.3 mg, 96%). m.p. 136.4～137.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68～7.66 (m, 1H), 7.51～7.42 (m, 2H), 7.51～7.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.9, 136.7, 133.9, 131.0, 128.7, 125.7, 118.4, 84.0, 83.2.

3-(2-Fluorophenyl)propiolic Acid (**2t**):[26] Purification by flash chromatography (EtOAc) gave a white solid (154.2 mg, 94%). m.p. 116.7～117.5 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 14.04 (br, 1H), 7.72～7.70 (m, 1H), 7.63～7.60 (m, 1H), 7.40 (t, J=6.0 Hz, 1H), 7.33 (t, J=4.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.1, 162.4, 154.5, 135.0, 133.9, 133.9, 125.6, 125.6, 116.6, 116.4, 108.0, 107.9, 86.8, 78.1.

3-(4-Ethynylphenyl)propiolic acid (**2u**):[8] Purification by flash chromatography (EtOAc) gave a white solid (156.4 mg, 92%). m.p. 148.4～149.7 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.64 (d, J=8.4 Hz, 2H), 7.56 (d, J=8.4 Hz, 2H), 4.46 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 154.1, 132.8, 132.2, 124.0, 119.3, 83.9, 83.3, 83.3, 82.6.

3,3'-(1,4-Phenylene)dipropiolic acid (**2v**):[5d] Purification

by flash chromatography (EtOAc) gave a white solid (181.9 mg, 85%). m.p. 172.5～173.9 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.72 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 154.0, 133.0, 121.2, 83.9, 83.0.

3-(Thiophen-3-yl)propiolic Acid (**3a**):[25] Purification by flash chromatography (EtOAc) gave a white solid (136.9 mg, 90%). m.p. 155.2～157.0 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 13.70 (br, 1H), 8.19 (q, J=0.8, 2.0 Hz, 1H), 7.70 (q, J=2.0, 3.2 Hz, 1H), 7.33 (q, J=0.8, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 154.8, 135.3, 130.4, 128.2, 118.4, 82.0, 80.8.

3-(Thiophen-2-yl)propiolic acid (**3b**):[26] Purification by flash chromatography (EtOAc) gave a grey solid (129.2 mg, 85%). m.p. 139.3～140.6 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 13.84 (br, 1H), 7.89 (d, J=5.2 Hz, 1H), 7.67 (d, J=3.6 Hz, 1H), 7.21 (t, J=4.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 154.6, 137.5, 133.2, 128.8, 118.7, 86.3, 79.0.

Methyl 3-(pyridin-2-yl)propiolate (**3c**):[27] Purification by flash chromatography (petroleum ether/EtOAc, V∶V=5∶1) gave a white solid (135.2 mg, 84%). m.p. 87.0～88.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63～8.61 (m, 1H), 7.72～7.68 (m, 1H), 7.57～7.55 (m, 1H), 7.34～7.31 (m, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.9, 150.6, 140.5, 136.4, 128.6, 124.7, 84.2, 78.8, 53.0.

Methyl 3-(pyridin-3-yl)propiolate (**3d**):[27] Purification by flash chromatography (petroleum ether/EtOAc, V∶V=5∶1) gave a white solid (140.1 mg, 87%). m.p. 49.0～50.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.74 (s, 1H), 8.60 (d, J=3.6 Hz, 1H), 7.82～7.79 (m, 1H), 7.28～7.25 (m, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.9, 152.3, 149.8, 138.8, 122.2, 115.9, 82.2, 81.7, 52.0.

Hept-2-ynoic acid (**4a**):[25] Purification by flash chromatography (EtOAc) gave a colorless oil (104.6 mg, 83%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.37 (t, J=6.8 Hz, 2H), 1.49～1.42 (m, 2H), 1.40～1.30 (m, 2H), 0.89 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 154.7, 88.8, 74.6, 29.6, 21.8, 17.8, 13.8.

4,4-Dimethylpent-2-ynoic Acid (**4b**):[25] Purification by flash chromatography (EtOAc) gave a colorless oil (109.6 mg, 87%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.22 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 154.8, 95.2, 73.2, 30.1, 27.4.

3-Cyclopropylpropiolic acid (**4c**): Purification by flash chromatography (EtOAc) gave a white solid (93.5 mg, 85%). m.p. 58.9～60.0 ℃(lit.[4d] 56.7 ℃); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 13.26 (br, 1H), 1.54～1.48 (m, 1H), 0.97～0.92 (m, 2H), 0.82～0.78 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 155.0, 92.8, 70.2, 9.7, −0.5.

Methyl benzo[d]thiazole-2-carboxylate (**6a**):[8] Purification by flash chromatography (petroleum ether/EtOAc, V∶V=15∶1) gave a white solid (179.6 mg, 93%). m.p. 87.0～88.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (d, J=7.6 Hz, 1H), 7.97 (d, J=7.2 Hz, 1H), 7.61～7.52 (m, 2H), 4.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.2, 158.2, 153.3, 136.9, 127.8, 127.3, 125.7, 122.2, 53.8.

Methyl 5-bromobenzo[d]thiazole-2-carboxylate (**6b**):[8] Purification by flash chromatography (petroleum ether/EtOAc, V∶V=15∶1) gave a white solid (255.7 mg, 94%). m.p. 77.0～78.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.38 (d, J=1.6 Hz, 1H), 7.86 (d, J=8.8 Hz, 1H), 7.67～7.65 (m, 1H), 4.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.8, 159.7, 154.3, 135.6, 131.1, 128.3, 123.4, 121.1, 54.0.

Methyl 6-bromobenzo[d]thiazole-2-carboxylate (**6c**):[8] Purification by flash chromatography (petroleum ether/EtOAc, V∶V=15∶1) gave a white solid (242.1 mg, 89%). m.p. 78.5～80.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12 (d, J=2.0 Hz, 1H), 8.09 (d, J=8.8 Hz, 1H), 7.69～7.67 (m, 1H), 4.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.9, 158.6, 152.1, 138.4, 131.1, 126.7, 124.8, 122.0, 53.9.

Methyl 5-chlorobenzo[d]thiazole-2-carboxylate (**6d**):[8] Purification by flash chromatography (petroleum ether/EtOAc, V∶V=15∶1) gave a white solid (207.0 mg, 91%). m.p. 94.0～95.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (d, J=2.0 Hz, 1H), 7.90～7.87 (m, 1H), 7.53～7.50 (m, 1H), 4.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.8, 159.9, 154.0, 135.1, 133.5, 128.5, 125.2, 123.0, 53.9.

Methyl benzo[d]oxazole-2-carboxylate (**6e**):[8] Purification by flash chromatography (petroleum ether/ EtOAc, V∶V=15∶1) gave a white solid (162.8 mg, 92%). m.p. 82.0～83.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, J=8.0 Hz, 1H), 7.68 (d, J=8.4 Hz, 1H), 7.54 (t, J=7.8 Hz, 1H), 7.47 (t, J=7.8 Hz, 1H), 4.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.1, 152.7, 151.0, 140.6, 128.4, 126.0, 122.3, 111.9, 53.9.

Methyl 5-methoxybenzo[d]oxazole-2-carboxylate (**6f**). Purification by flash chromatography (petroleum ether/ EtOAc, V∶V=15∶1) gave a white solid (188.4 mg, 91%). m.p. 102.8～103.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, J=9.2 Hz, 1H), 7.28 (d, J=2.4 Hz, 1H), 7.15～7.12 (m, 1H), 4.08 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.4, 157.0, 153.2, 145.8, 141.5, 118.3, 112.2, 103.6, 56.1, 53.7; HRMS (ESI) calcd $C_{10}H_{10}NO_4$ $[M+H]^+$ 208.0610, found 208.0614.

Methyl 5-methylbenzo[d]oxazole-2-carboxylate (**6g**):[8] Purification by flash chromatography (petroleum ether/ EtOAc, V∶V=15∶1) gave a white solid (166.2 mg, 87%). m.p. 110.8～112.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, J=8.4 Hz, 1H), 7.38 (s, 1H), 7.22 (d, J=8.8 Hz, 1H), 4.02 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.1, 152.2, 151.4, 139.4, 138.5, 127.6, 121.6, 111.7, 53.8, 22.2.

Methyl 5-chlorobenzo[d]oxazole-2-carboxylate (**6h**):[8] Purification by flash chromatography (petroleum ether/ EtOAc, V∶V=15∶1) gave a white solid (188.3 mg, 89%). m.p. 87.4～88.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, J=6.0 Hz, 1H), 7.61 (d, J=8.8 Hz, 1H), 7.52～7.49 (m, 1H), 4.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.7, 153.7, 149.5, 141.6, 131.7, 129.0, 122.0, 112.8, 54.0.

Methyl 6-methylbenzo[d]oxazole-2-carboxylate (**6i**):[8]

Purification by flash chromatography (petroleum ether/EtOAc, V∶V=15∶1) gave a white solid (171.9 mg, 90%). m.p. 89.5～91.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (d, J=8.4 Hz, 1H), 7.45 (s, 1H), 7.29～7.26 (m, 1H), 4.08 (s, 3H), 2.53 (s, 3H); ^{13}C{^{1}H} (100 MHz, $CDCl_3$) δ: 157.2, 152.2, 151.4, 139.4, 138.5, 127.6, 121.6, 111.8, 53.7, 22.2.

Methyl 6-phenylbenzo[*d*]oxazole-2-carboxylate (**6j**): Purification by flash chromatography (petroleum ether/EtOAc, V∶V=15∶1) gave a white solid (253.3 mg, 93%). m.p. 90.5～91.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (d, J=2.0 Hz, 1H), 7.77～7.70 (m, 2H), 7.62～7.60 (m, 2H), 7.48 (t, J=7.2 Hz, 2H), 7.40 (t, J=7.2 Hz, 1H), 4.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.0, 153.2, 150.5, 141.3, 140.4, 140.1, 129.1, 128.2, 127.9, 127.7, 120.5, 111.9, 53.9; HRMS (ESI) calcd for $C_{15}H_{12}NO_3$ [M+H]$^+$ 254.0817, found 254.0814.

Methyl 5-bromobenzo[*d*]oxazole-2-carboxylate (**6k**):[8] (petroleum ether/EtOAc, V∶V=15∶1) gave a white solid (233.0 mg, 91%). m.p. 98.0～99.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J=1.6 Hz, 1H), 7.64～7.62 (m, 1H), 7.55～7.53 (m, 1H), 4.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.6, 153.5, 149.9, 142.0, 131.6, 125.1, 118.9, 113.2, 54.0.

Methyl 6-bromobenzo[*d*]oxazole-2-carboxylate (**6l**):[8] Purification by flash chromatography (petroleum ether/EtOAc, V∶V=15∶1) gave a white solid (225.3 mg, 88%). m.p. 101.5～130.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, J=1.6 Hz, 1H), 7.77～7.74 (m, 1H), 7.61～7.58 (m, 1H), 4.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.7, 153.0, 151.4, 139.7, 129.8, 123.3, 121.9, 115.4, 54.0.

Supporting Information ^{1}H NMR and ^{13}C NMR spectra of all desired products. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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