Check for updates

View Article Online
View Journal

NJC

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: B. Yu, P. Yang, X. Gao, Z. Yang, Y. Zhao, H. Zhang and Z. Liu, *New J. Chem.*, 2017, DOI: 10.1039/C7NJ01779K.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the author guidelines.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the ethical guidelines, outlined in our author and reviewer resource centre, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/njc

View Article Online
DOI: 10.1039/C7NJ01779K

Journal Name

ARTICLE

CsF-Promoted Carboxylation of Aryl(Hetaryl) Terminal Alkynes with Atmospheric CO_2 at Room Temperature†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

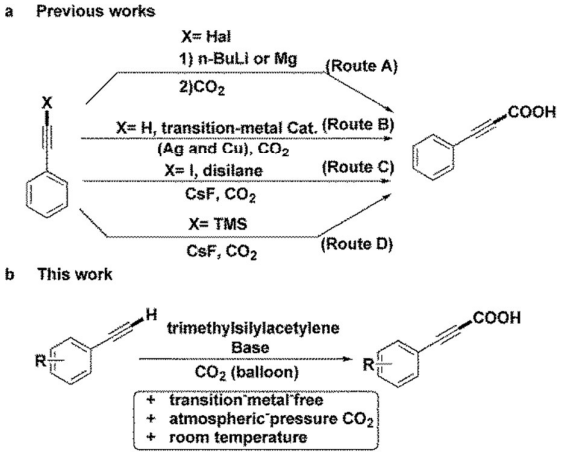
B. Yu,[a] P. Yang,[a,b] X. Gao,[a,b] Z. Z. Yang,[a] Y. F. Zhao,[a] H. Y. Zhang[a] and Z. M. Liu*[, a,b]

A CsF-promoted carboxylation of aryl(hetaryl) terminal alkynes with atmospheric CO_2 in the presence of trimethylsilylacetylene has been developed to give functionalized propiolic acids products at room temperature. A wide range of propiolic acids bearing functional groups was successfully obtained in good to excellent yields. Mechanistic studies demonstrate that in the carboxylation process alkynylsilane intermediate was first in situ generated, which was then trapped by CO_2, giving rise to the corresponding functionalized propiolic acids after acidification. The advantages of this approach include avoiding use of transition-metal catalysts, wide substrate scope together with excellent functional group tolerance, ambient condition and a facile work-up procedure.

Introduction

Recently, utilization of CO_2 as a starting material in organic synthesis has attracted much attention and emerged as a flourishing research area in terms of sustainable chemistry, since CO_2 is an abundant, inexpensive, nontoxic and renewable C1 source.[1-4] So far, CO_2 can be converted into many energy-related products and commodity chemicals, such as urea,[5] formamidine derivatives,[6] formic acids,[7] methanol,[8] benzimidazoles,[9] aromatic aldehydes[10] and so on. In particular, carboxylation of terminal alkynes with CO_2 is a promising and atom-economic way to the synthesis of alkynyl carboxylic acids. However, as a result of the thermodynamical stability of CO_2, high energy substrates, specific catalysts and harsh conditions are generally required for CO_2 transformation, thus its conversion under ambient conditions, especially at room temperature and atmospheric pressure is still challenging.

Aryl(hetaryl) propiolic acids and their derivatives are an important kind of organic intermediates with versatile applications in organic synthesis.[11-17] The synthesis of such functionalized propiolic acids in an environmentally benign way has become considerable relevance. At present, the most common approach to construction of alkynyl C-C bond involves the interception of aromatic lithium or magnesium reagents with CO_2 (Scheme 1, a, Route A).[18] However, the high nucleophilicity of lithium and magnesium acetylides limits functional groups compatibility of this route and requires prefunctionalization of alkynes. Thus far, the transition-metal-based catalysts have been demonstrated to catalyze the intermolecular C-H carboxylation of terminal alkynes with CO_2 (Scheme 1, a, route B).[19-26] Although these carboxylation methods are prominent examples in this field, they rely on catalysts derived from rare and expensive precious metals, which can be a significant limitation, particularly for large-scale syntheses. Transition-metal-free cross-coupling reaction has offered an attractive surrogate to metal-catalyzed processes to C-C bond formation due to their low cost, environmentally benign nature.[27-33] Sato and coworkers reported a very mild carboxylation of alkyl iodides with CO_2 using a strained four-



Scheme 1. Routes to the synthesis of propiolic acids. a, Reported routes. Route A, classical synthesis of aryl propiolic acids by reaction of organometallic species with CO_2. The organometallic species are typically prepared by deprotonation of terminal alkynes or by lithium halogen exchange of alkynyl halides. X'= Cl or Br; Hal, halogen. Route B, transition-metal-catalyzed carboxylation of terminal alkynes with CO_2. Route C, a strained disilane-propoted carboxylation of alkynyl halides with CO_2 under transition-metal-free conditions. Route D, carboxylation of alkynylsilanes with CO_2 mediated by CsF in DMSO. b, Route developed in this work: CsF-promoted carboxylation of aryl terminal alkynes with atmospheric CO_2/trimethylsilylacetylene at room temperature.

[a] Beijing National Laboratory for Molecular Sciences, Key Laboratory of Colloid, Interface and Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190;
[b] University of Chinese Academy of Sciences, Beijing 100049, China.

† Electronic Supplementary Information (ESI) available: ^{1}H and ^{13}C NMR spectrum， See DOI: 10.1039/x0xx00000x

Published on 18 July 2017. Downloaded by State University of New York at Binghamton on 29/07/2017 15:08:10.

New Journal of Chemistry Accepted Manuscript

Please do not adjust margins

View Article Online
DOI: 10.1039/C7NJ01779K

Published on 18 July 2017. Downloaded by State University of New York at Binghamton on 29/07/2017 15:08:10.

membered ring disline and CsF under transition-metal-free conditions (Scheme 1, route C).[34] More recently, Kondo reported the direct incorporation of CO_2 into alkynylsilanes mediated by CsF, affording propiolic acids under ambient conditions (Scheme 1, route D).[35] However, alkynylsilanes are usually synthesized via Pd/Cu catalyzed alkynylation of aryl triflates or halides with alkynes. Though such progress has been made, expensive and high-energy substrates or metal catalysts were used, and only limited propiolic acids were produced. Therefore, general and transition-metal-free protocols to produce aryl(hetaryl) propiolic acids are highly desirable.

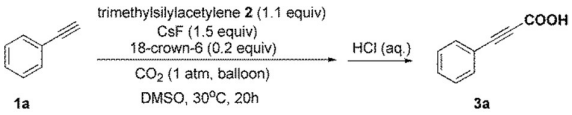
As part of our continuing studies on the transformation of CO_2 into useful chemicals, combined with our interest in the development of new methods for C-C bond formation using CO_2 as a C1 source,[36] herein we present a transition-metal-free strategy for carboxylation of aryl(hetaryl) terminal alkynes with CO_2 under ambient conditions. In this protocol trimethylsilylacetylene as a readily available and cheap silane coupling agent, combined with CsF, was used to promote the carboxylation (Scheme 1, b). This approach had a wide substrate scope, and various aryl(hetaryl) propiolic acids including benzene-1,4-di-propiolic and benzene-1,3,5-tri-propiolic acids could be obtained in good to excellent yields. Moreover, this protocol could be extended to gram scale production of phenylpropiolic acid. In addition, the postreatments on the carboxylated compounds with MeI and amines could afford the corresponding phenylpropiolic methyl esters and phenylpropiolic amides.

Results and discussion

Exploration of optimal conditions

At the outset of this investigation, the reaction conditions were explored using phenylalkyne (**1a)** as a model substrate, and the optimal conditions were obtained (for 1 mmol **1a** conversion, 1.1 equiv. of trimethylsilylacetylene, 1.5 equiv. of CsF, 0.2 equiv. of 18-crown-6, DMSO, 1 atm of CO_2, 30°C, 20h). The coupling reaction of **1a** and CO_2 afforded **3a** in an isolated yield of 92% at 100% conversion of **1a** under the optimized conditions (Table 1, entry 1). In the absence of either of CsF or trimethylsilylacetylene, no reaction took place (Entries 2, 3), indicating that both the base and trimethylsilylacetylene were indispensable. The absence of 18-crown-6 resulted in the reduction in the **3a** yield to 47% (Entry 4). As known, 18-crown-6 can coordinate with potassium cation, thus it may enhance the nucleophilicity of fluoride anion and the solubility of the catalyst. For comparison, other bases instead of CsF were tested. It was indicated that NEt_3 was ineffective for the reaction (Entry 5), while KF, K_2CO_3 and sodium tertbutoxide (NaO^tBu) gave rise to the desired product in declined yields (Entries 6-8). Excitingly, potassium tertbutoxides (KO^tBu) was very effective for this reaction, affording **3a** in a yield of 93% (Entry 9), comparable to CsF. Notably, it was found that KO^tBu could give rise to **3a** in a yield of 92% even in the absence of trimethylsilylacetylene. In the next set of experiments, other solvents including DMF, acetonitrile, 1,4-dioxane, THF, and

Table 1. CsF-promoted carboxylation of phenylacetylene with carbon dioxide[a]



Entry	catalyst system: change from ''standard'' conditions	Yield(%)[b]
1	none	92
2	no CsF	0
3	no Trimethylsilylacetylene	0
4	no 18-crown-6	47
5	NEt_3 instead of CsF	0
6	K_2CO_3 instead of CsF	43
7	KF instead of CsF	85
8	NaO^tBu instead of CsF	86
9	KO^tBu instead of CsF	93
10	CH_3CN instead of DMSO	65
11	THF instead of DMSO	42
12	1,4-dioxane instead of DMSO	40
13	Toluene instead of DMSO	23
14	DMF instead of DMSO	84

[a]Reaction conditions: phenylacetylene (**1a**, 1 mmol), trimethylsilylacetylene (**2**, 1.1mmol), CsF (1.5 equiv), 18-crown-6 (0.2 equiv), in DMSO (3 ml), at 30°C for 20h. [b]isolated yield.

toluene were examined in place of DMSO. It was found that the absence of the dipolar aprotic solvents led to the decrease in the yields of **3a** under otherwise identical conditions (Table 1, entries 10-13). In sharp contrast to this result, the dipolar aprotic solvent, e.g, DMF, improved the **3a** yield drastically to 84% (Table 1, entry 14).

Scope of the substrates

To demonstrate the general applicability of this protocol, the carboxylation of various terminal alkynes with CO_2 was preformed under the optimized reaction conditions. As shown in Table 2, the products were basically isolated as carboxylic acids. Interestingly, electron-rich, -neutral, and –deficient as well as heteroaromatic substrates were all carboxylated, producing corresponding carboxylic acids in good to excellent yields after acidification (Table 2, **3a-3v**). Notably, the isomers with the substituent at different positions (ortho-, meta-, and para positions) in the aryl ring showed similar activity (Table 2, **3d-3f, 3h-3j**), suggesting the substitution in the aryl ring had little impact on the activation of alkyne C-H bond. Remarkably, the reaction of heteroaromatic alkynes (i.e. 2-ethynylthiophen and 3-ethynylthiophen) with CO_2 also proceeded well, affording the corresponding products in high yields (Table 2, **3q** and **3r**). However, 2-ethynylpyridine and 3-ehtynylpyridine did not give the desired products under standard conditions, possibly because the newly formed propiolic acids were not stable. Instead, methyl ester products could be produced via treating the reaction solutions with MeI (Supporting Information, Scheme S1).

Applications of the protocol

New Journal of Chemistry Accepted Manuscript

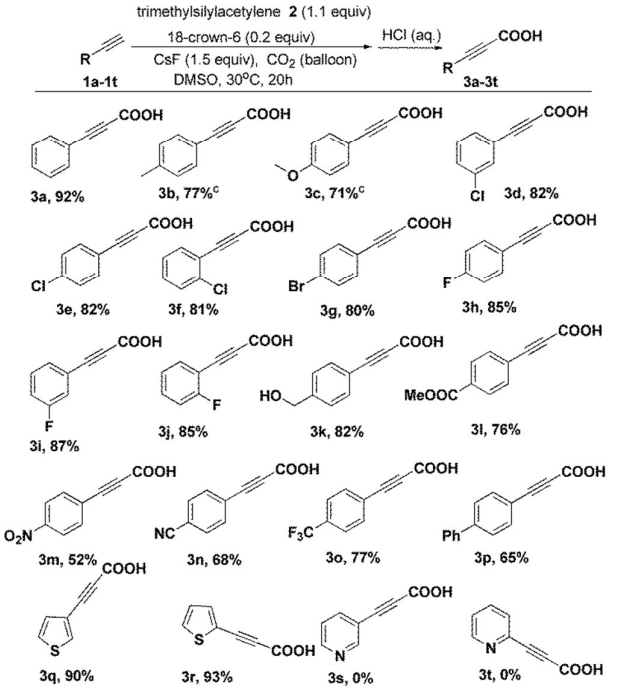
This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

View Article Online
DOI: 10.1039/C7NJ01779K

Published on 18 July 2017. Downloaded by State University of New York at Binghamton on 29/07/2017 15:08:10.

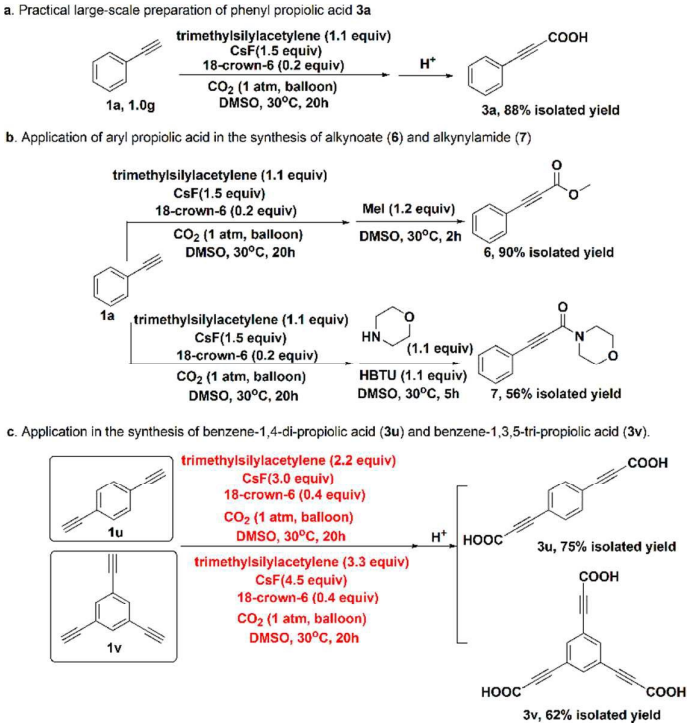
Table 2. CsF-promoted coupling of various terminal alkynes with carbon dioxide in DMSO[a,b]



[a]Reaction conditions: terminal alkynes (1a, 1 mmol), trimethylsilylacetylene (2, 1.1mmol), CsF (1.5 equiv), 18-crown-6 (0.2 equiv), in DMSO (3 ml), at 30°C for 20h. [b]isolated yield. [c]Reaction time: 24h.

The above protocol is practical and scalable since a satisfactory product yield (88%) was obtained when the carboxylation of phenylacetylene **1a** with CO_2 was performed on a 1.0 g scale (Scheme 2, a). Since propiolic acids are known to be capable of undergoing versatile transformations[37-43], the carboxylated products from the reactions of alkyneswith CO_2 could also readily transform into other kinds of value-added chemicals, as illustrated in Scheme 2. For example, methyl ether product was obtained in an isolated yield of 90% via treating the carboxylated compound with methyl iodide (Scheme 2, b). Alkynylamides is a kind of valuable intermediates with multiple usages.[44-46] The carboxylated compounds from phenylacetylenes with CO_2 could be further converted into alkynylamides via their reactions with amines. For instance, the treatment of phenylacetylene, CO_2 with morpholine in one-pot reaction under mild conditions afforded alkynylamide in 56% isolated yield, demonstrating the compatibility of our method with amine molecules of potential pharmaceutical importance.

Aromatic polycarboxylic acids, especially those with unsaturated bonds (i.e., -C=C- and -C≡C-), are promising feedstocks for the synthesis of advanced materials such as metal organic frameworks and functional polymers. However, their synthesis is challenging. Excitingly, the protocol presented in this work was successfully applied in the synthesis of benzene-1,4-di-propiolic and benzene-1,3,5-tri-propiolic acids that are useful building blocks of functional materials, and good product yields were obtained (Scheme 2, c).



Scheme 2. Applications of the trimethylsilylacetylene/CsF-promoted carboxylation of terminal alkynes.

Control experiments

To understand the nature of this trimethylsilylacetylene-involved carboxylation process and to gain insight into the possible reaction pathway, several control experiments were carried out as illustrated in Scheme 3. First, the reaction was conducted with isotopically labled $^{13}CO_2$ as the carboxylative reagent (Scheme 3, (a)). ^{13}C labled phenylpropiolic acid was obtained in a yield of 90% confirmed by ^{13}C NMR (Figure 1), suggesting that CO_2 involved the formation of the carboxylated product. Considering that without trimethylsilylacetylene the reaction did not occur (Table 1, entry 3; Scheme 3, (b)), the stoichiometric reaction of phenylacetylene and trimethylsilylacetylene was performed in the presence of N_2 replacing CO_2, and 1-phenyl-2-trimethylsilyacetylene intermediate was only obtained in an isolated yield of 95% (Scheme 3, (c)). With this intermediate as a starting material, bubbling CO_2 into the reaction solution under the optimized conditions resulted in the production of **3a** in an isolated yield of 94% (Scheme 3, (d)). These results suggest that 1-phenyl-2-trimethylsilyacetylene intermediate was in situ generated under the experimental conditions, which could further nucleophilically attack CO_2, providing **3a** after acidification.

Base on the above and previous studies[47-48], a possible reaction pathway was proposed as illustrated in Scheme 4. This carboxylation may in principle proceed in two steps. Firstly, the fluoride anion reacts with trimethylsilylacetylene to afford the hypervalent silicon intermediate **I**, thus reacting

New Journal of Chemistry Accepted Manuscript

Please do not adjust margins

View Article Online
DOI: 10.1039/C7NJ01779K

Published on 18 July 2017. Downloaded by State University of New York at Binghamton on 29/07/2017 15:08:10.

with phenylalkyne to form the crucial intermediates 1-phenyl-2-trimethylsilyacetylene **4a.** Subsequently, a fluoride anion attacks silicon atom of **4a** to afford carbanion of phenylalkyne, which in situ attacks to CO_2, affording the cesium carboxylate **5a**. After acidification of **5a**, phenyl propiolic acid **3a** is finally obtained.

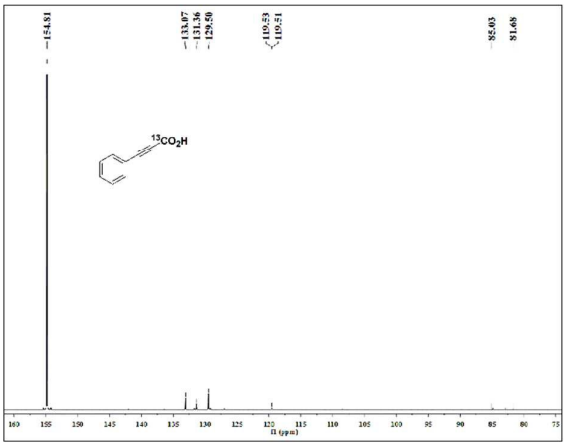
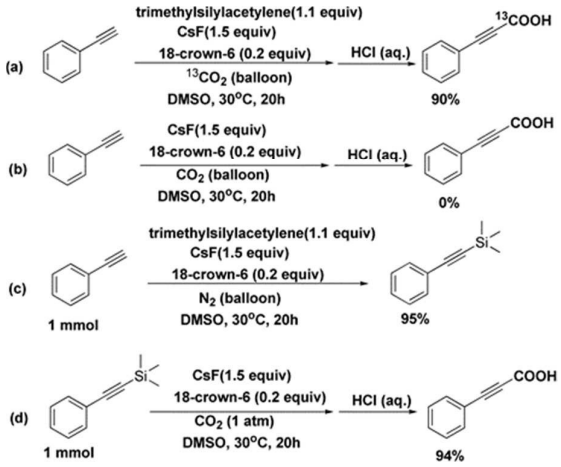


Figure 1. ^{13}C NMR spectrum of the carboxylated product from phenylacetylene with $^{13}CO_2$

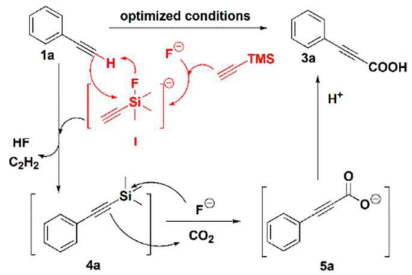


Sheme 3. Control experiments for mechanistic studies.

Experimental

General information

Alkynes, trimethylsilylacetylene and other chemicals were purchased from J&K or Innochem. Carbon dioxide (99.999%), ^{13}C-labled carbon dioxide (purity>99.9%, ^{13}C 99%, ^{18}O<1%), terminal alkynes, and other reagents were used without further purification. All reactions were monitored by thin-layer chromatography (TLC) using UV light as cisualizing agent. Column chromatography was performed with 230-300 mesh silica gel. ^1H and ^{13}C NMR spectra were recorded on a Bruker AvanceII 400M type (^1H NMR, 400 MHz; ^{13}C NMR, 101 MHz) spectrometer. Their peak frequencies were referenced versus an internal standard (TMS) shifts at 0 ppm for ^1H NMR and against the solvent ($CDCl_3$, 77.0 ppm) for ^{13}C NMR, respectively.



Scheme 4. Proposed reaction pathway for carboxylation of terminal alkynes.

Multiplicity abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*, Hz).

General procedure for carboxylation of terminal alkynes

The reaction was performed in a 10 mL Schlenk tube with a magnetic stirring bar. Typically, terminal alkyne (1.0 mmol), trimethylsilylacetylene (1.1 mmol), CsF (1.5 mmol) and 18-crown-6 (0.2 mmol) were added into dry DMSO (2 ml) loaded in the reactor. After purged with CO_2 for 3 times, the reactor was connected to a CO_2 ballon and moved to a water bath of 30°C. After being stirred for 20h, the reaction mixture was diluted with water (30 mL), and was extracted with CH_2Cl_2 (3 × 10 mL). The aqueous phase was acidified with HCl aqueous solution (6 M) and then extracted with diethyl ether (5 × 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the pure propiolic acid (for example, compound **3a**: 92%). The obtained product was weighed by a mass balacne, and identified by NMR analysis. For example, 3-phenylpropiolic acid (**3a**), white solid, 133.3 mg, isolated yield of 92%. ^1H NMR (400 MHz, DMSO) δ 7.68 – 7.62 (m, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 154.81, 133.07, 131.36, 129.50, 119.53, 119.51, 85.03, 81.68.

Experiment of isotopically labled $^{13}CO_2$

The carboxylation of phenylalkyne with $^{13}CO_2$ was performed under the standard conditions, and the procedure was similar to the general one. The desired product was obtained in an isolated yield of 90%. The product was then analyzed by ^{13}C NMR spectroscopy as shown in Figure 1.

Synthesis of 4a

Phenylacetylene (1.0 mmol) was added to a DMSO solution of trimethylsilylacetylene (1.1 mmol), CsF (1.5 mmol) and 18-crown-6 (0.2 mmol) in a 10 mL Schlenk tube with a magnetic stirring bar. The Schlenk tube was purged with N_2 for 3 times, and connected to a N_2 ballon, which was then moved to a water bath of 30°C. After being stirred for 20h, the reaction mixture was diluted with water (30 mL), and was extracted

New Journal of Chemistry Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

View Article Online
DOI: 10.1039/C7NJ01779K

Published on 18 July 2017. Downloaded by State University of New York at Binghamton on 29/07/2017 15:08:10.

with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude mixture. The residue was purified by silica gel flash column chromatography (petroleum ether) to give the desired product as a yellow liquid in 95% yield. The as-obtained product was identified by NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 6.5, 3.2 Hz, 2H), 7.33 (dd, *J* = 5.1, 1.8 Hz, 3H), 0.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.96, 128.46, 128.19, 123.22, 105.21, 94.05, 0.00.

Synthesis of 3a in gram scale

Phenylacetylene (10.0 mmol) was added to a DMSO solution of trimethylsilylacetylene (11 mmol), CsF (15 mmol) and 18-crown-6 (2 mmol) in a 100 mL Schlenk tube with a magnetic stirring bar. The reactor was purged with CO_2 for 3 times, and connected to a CO_2 ballon, which was then moved to a water bath of 30°C. After being stirred for 20h, the reaction mixture was diluted with water (200 mL), and was extracted with CH_2Cl_2 (3 × 50 mL). The aqueous phase was acidified with aqueous HCl solution (6 M) and then extracted with diethyl ether (5 × 50 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the pure **3a** in an isolated yield of 88%.

Synthesis of 6

Phenylacetylene (1.0 mmol) was added to a DMSO solution of trimethylsilylacetylene (1.1 mmol), CsF (1.5 mmol) and 18-crown-6 (0.2 mmol) in a 10 mL Schlenk tube with a magnetic stirring bar. The Schlenk tube was purged with CO_2 for 3 times, and connected to a CO_2 ballon, which was then moved to a water bath of 30°C. After being stirred for 20h, the solution of MeI (1.2 mmol MeI in 2 ml anhydrous DMSO) was added via a syringe. After 2h, the reaction mixture was diluted with water (30 mL), and was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude mixture. Subsequently, the mixture was purified by silica gel flash column chromatography (petroleum ether/EtOAc 10:1) to give the pure **6** as light yellow liquid in 90% yield.[49] The as-obtained product was identified by NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.37 – 7.32 (m, 1H), 7.24 (t, *J* = 7.4 Hz, 2H), 3.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.26, 132.83, 130.60, 128.52, 119.45, 86.27, 80.32, 52.57.

Synthesis of 7

Phenylacetylene (1.0 mmol) was added to a DMSO solution of trimethylsilylacetylene (1.1 mmol), CsF (1.5 mmol) and 18-crown-6 (0.2 mmol) in a 10 mL Schlenk tube with a magnetic stirring bar. The Schlenk tube was purged with CO_2 for 3 times, and connected to a CO_2 ballon, which was then moved to a water bath of 30°C. After being stirred for 15 h, the solution of morpholine (1.1 mmol morpholine and 1.2 mmol HBTU (O-(1H-benzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluoro-phosphate) in 3ml anhydrous DMF) was added via syringe. After 5h, the reaction mixture was diluted with water (30 mL), and was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude mixture, which was purified by silica gel flash column chromatography (petroleum ether/EtOAc 5:1), giving pure **7** as light yellow powder in 56% yield.[50] The resultant product was identified by NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.35 (ddd, *J* = 16.0, 11.7, 4.5 Hz, 3H), 3.83 – 3.79 (m, 2H), 3.75 – 3.70 (m, 2H), 3.67 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.22, 132.35, 130.16, 128.52, 120.25, 91.23, 80.74, 47.32, 41.99.

Synthesis of 3u and 3v

1,4-Diethynylbenzene or 1,3,5-triethynylbenzene (1.0 mmol) was added to a DMSO solution of trimethylsilylacetylene (1.1 equiv.), CsF (1.5 equiv.) and 18-crown-6 (0.2 equiv.) in a 10 mL Schlenk tube with a magnetic stirring bar. The Schlenk tube was purged with CO_2 for 3 times, and connected to a CO_2 ballon, which was then moved to a water bath of 30°C. After being stirred for 20h, the reaction mixture was diluted with water (30 mL), and was extracted with CH_2Cl_2 (3 × 20 mL). The aqueous phase was acidified with aqueous HCl solution (6 M) and then extracted with diethyl ether (5 × 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum, giving pure products in 75% (**3u**) and 62% (**3v**) isolated yield, respectively.[49] 3, 3'-(1,4-Phenylene)dipropiolic acid **(3u),** 160.5 mg, pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.44, 133.41, 121.62, 84.29, 83.51. 3, 3',3''-(1,3,5-Phenylene)tripropiolic acid **(3v),** 174.8 mg, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.26, 137.97, 121.54, 83.63, 81.65.

Conclusions

In conclusion, we have developed a new approach for carboxylation of terminal alkynes with CO_2 under ambient conditions, affording the corresponding aromatic propiolic acids in good to excellent yields. A broad range of substrates were proved to be well tolerable. This transition-metal-free protocol provides an alternative convenient and simple strategy for efficient access to construct C-C bond using CO_2 as a C1 source. Further application of this carboxylation methodology in the synthesis of diverse alkynylamides is currently under investigation.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21503239, 21533011, 21402208, 21403252).

References

New Journal of Chemistry Accepted Manuscript

Please do not adjust margins

View Article Online
DOI: 10.1039/C7NJ01779K

Published on 18 July 2017. Downloaded by State University of New York at Binghamton on 29/07/2017 15:08:10.

1 M. Cokoja, C. Bruchmeier, B. Rieger, W. A. Herrmann, F. E. Kuhn, *Angew. Chem. Int. Ed.* 2011, **50**, 8510-8537;
2 S. Wesselbaum, T. vom Stein, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed.* 2012, **51**, 7499-7502;
3 C. D. Gomes, O. Jacquet, C. Villiers, P. Thuery, M. Ephritikhine, T. Cantat. *Angew. Chem. Int. Ed.* 2012, **51**, 187-190;
4 A.; Tlili, X. Frogneux, E. Blondiaux, T. Cantat. *Angew. Chem. Int. Ed.* 2014, **53**, 2543-2545
5 F. Shi, Y. Q. Deng, T. L. SiMa, J. J. Peng, Y. L. Gu, B. T. Qiao, *Angew. Chem. Int. Ed.* 2003, **42**, 3257-3260
6 O. Jacquet, C. D. Gomes, M. Ephritikhine, T. Cantat, *Chem CatChem.* 2013, **5**, 117-120
7 Z. F. Zhang, S. Q. Hu, J. L. Song, W. J. Li, G. Y. Yang, B. X. Han, *ChemSusChem.* 2009, **2**, 234-238
8 C. A. Huff, M. S. Sanford, *J. Am. Chem. Soc.* 2011, **133**, 18122-18125
9 B. Yu, H. Y. Zhang, Y. F. Zhao, S. Chen, Z. M. Liu, *Green. Chem.* 2013, **15**, 95-99
10 B. Yu, Y. F. Zhao, H. Y. Zhang, J. L. Xu, L. D. Hao, X. Gao, Z. M. Liu, *Chem. Commun.* 2014, **50**, 2330-2333;
11 G. C. E. Raja, F. M. Irudayanathan, H. S. Kim, J. Kim, S. Lee, *J. Org. Chem.* 2016, **81**, 5244-5249;
12 L. Z. Zhang, Z. J. Hang, Z. Q. Liu, *Angew. Chem. Int. Ed.* 2015, **55**, 236-239.
13 L. Ackermann, *Angew. Chem. Int. Ed.* 2011, **50**, 3842-3844; .
14 H. Mizuno, J. Takay, N. Iwasawa, *J. Am. Chem. Soc.* 2011, **133**, 1251-1253;
15 D. M. Dalton, T. Rovis, *Nat. Chem.* 2010, **2**, 710-711;
16 T. Mita, K. Michigami, Y. Sato, *Org. Lett.* 2012, **14**, 3462-3465;
17 B. Yu, J. N. Xie, C. L. Zhong, W. Li, L. N. He, *ACS Catal.,* 2015, **5**, 3940-3944.
18 A. Polyzos, M. O'Brien, T. P. Petersen, I. R. Baxendale, S. V. Ley, *Angew. Chem. Int. Ed.* 2011, **50**, 1190-1193;
19 L. J. GooBen, N. Rodriguez, F. Manjolinho, P. P. Lange, *Adv. Synth. Catal,* 2010, **352**, 2913-2917;
20 X. Zhang, W. W. Zhang, X. Ren, L. L. Zhang, X. B. Lu, *Org. Lett.*, 2011, **13**, 2402-2405;
21 W. Z. Zhang, W. J. Li, X. Zhang, H. Zhou, X. B. Lu, *Org. Lett.*, 2010, **12**, 4748-4751;
22 D. Y. Yu, Y. G. Zhang, *Proc. Natl. Acad. Sci. U.S.A.*, 2010, **107**, 20184-20189;
23 S. H. Kim, K. H. Kim, S. H. Hong, *Angew. Chem. In. Ed.* 2014, **53**, 771-774;
24 X. H. Liu, J. G. Ma, Z. Y. Niu, G. M. Yang, P. Cheng, *Angew. Chem. Int. Ed.* 2015, **54**, 1002-1005;
25 Y. Fukue, S. Oi, Y. Inoue, *J. Chem. Soc., Chem. Commun.*, 1994, 2091-2091;
26 F. Manjolinho, M. Arndt, K. GooBen, L. J. GooBen, *ACS Catal.*, 2012, **2**, 2014-2021
27 S. E. Denmark, G. L. Beutner, *Angew. Chem., Int. Ed*., 2008, **47**, 1560-1638;
28 D. Y. Yu, Y. G. Zhang, *Green Chem.*, 2011, **13**, 1275-1279;
29 E. Nakamura, I. Kuwajima, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 498-499;
30 S. Matsukawa, I. Sekine, *Synth. Commun.*, 2009, **39**, 1718-1721;
31 K. Wadhwa, V. R. Chintareddy, J. G. Verkade, *J. Org. Chem.*, 2009, **74**, 6681-6690;
32 R. B. Lettan II, K. A. Scheidt, *Org. Lett.,* 2005, **7**, 3227-3230;
33 V. R. Chintareddy, K. Wadhwa, J. G. Verkade, *J. Org. Chem.*, 2011, **76**, 4482-4488.
34 T. Mita, K, Suga, K. Sato, Y. Sato, *Org. Lett*. 2015, **17**, 5276-5279
35 M. Y. Kobayashi, K. Inamoto, Y. Tanaka, Y. Kondo, *Org. Biomol. Chem.*, 2013, **11**, 3773-3775
36 B. Yu, Z. Z. Yang, Y. F. Zhao, L. D. Hao, H. Y. Zhang, X. Gao, B. X. Han, Z. M. Liu, *Chem. Eur. J.* 2016, **22**, 1097-1102.
37 S. Cai, J. Zeng, Y. Bai, X. W. Liu, *J. Org. Chem.*, 2012, **77**, 801-807;
38 A. C. Mantovani, T. A. C. Goulart, D. F. Back, G. Zeni, *Chem. Eur. J.,* 2014, **20**, 12663-12668;
39 H.; Zhu, J. Stochigt, Y. Yu, H. Zou, *Org. Lett.,* 2011, **13**, 2792-2794;
40 D. R. Stuart, P. Alsabeh, M. Kuhn, K. Fagnou, *J. Am. Chem. Soc*., 2010, **132**, 18326-18339;
41 A. Saito, A. Taniguchi, Y. Kambara, Y. Hanzawa, *Org. Lett*., 2013, **15**, 2672-2675;
42 D. Gao, T. G. Back, *Chem. Eur. J.,* 2012, **18**, 14828-14840;
43 C. Li, Y. Zhang, P. Li, L. Wang, *J. Org. Chem.*, 2011, **76**, 4692-4696.
44 I. M. McDonald, R. A. Mate, F. C. Zusi, H. Huang, J. E. Macor, *Bioorg. Med. Chem. Lett.* 2013, **23**, 1684-1688;
45 C. Eibl, L. Munoz, I. Tomassoli, C. Stokes, R. L. Papke, D. Gundisch, *Bioorg. Med. Chem.* 2013, **21**, 7309-7329;
46 J. Hwang, J. Choi, K. Park, W. Kim, K. H. Song, S. Lee, *Eur. J. Org. Chem*., 2015, **2015**， 2235-2243;
47 X. F. Liu, R. Ma, C. Qiao, H. Cao, L. N. He, *Chem. Eur. J.*, 2016, **22**, 16489-16493;
48 M. Fujita, T. Hiyama, *J. Am. Chem. Soc.*, 1984, **106**, 4629-4630;
49 B. Yu, J. N. Xie, C. L. Zhong, W. Li, L. N. He, *ACS Catal.,* 2015, **5**, 3940-3944;
50 J. D. Goodreid, P. A. Duspara, C. Bosch, R. A. Batey, *J. Org. Chem.*, 2014, **79**, 943-954.

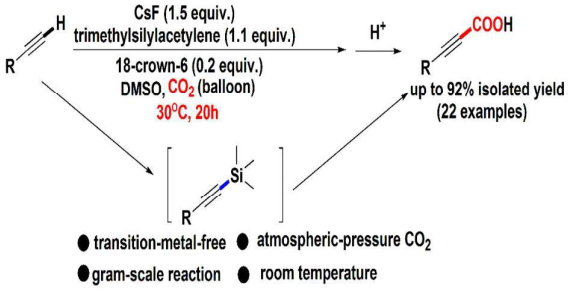
New Journal of Chemistry Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

View Article Online
DOI: 10.1039/C7NJ01779K

Published on 18 July 2017. Downloaded by State University of New York at Binghamton on 29/07/2017 15:08:10.



A CsF-promoted carboxylation of aryl(hetaryl) terminal alkynes with atmospheric CO_2 in the presence of trimethylsilylacetylene at room temperature was developed.

New Journal of Chemistry Accepted Manuscript