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**To be cited as:** *Helv. Chim. Acta* 10.1002/hlca.201900258

**Link to VoR:** <http://dx.doi.org/10.1002/hlca.201900258>

# Anhydrous conditions enable the catalyst-free carboxylation of aromatic alkynes with CO<sub>2</sub> under mild conditions.

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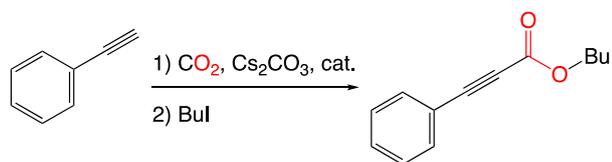
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**Abstract:** The direct carboxylation of aromatic alkynes with CO<sub>2</sub>, a cheap and widely available C<sub>1</sub> source, is the most attractive method for the synthesis of carboxylic acids. Here we show that direct carboxylation of terminal alkynes can be simply performed in near-quantitative yield in 4 hours with anhydrous Cs<sub>2</sub>CO<sub>3</sub> under mild conditions without need of a metal catalyst

**Keywords:** alkynes • carbon dioxide fixation • propiolic acids • C-H activation • cesium carbonate

## Introduction

The utilization of CO<sub>2</sub> as a C<sub>1</sub> source is attractive due to its low toxicity, low price and growing abundance in the atmosphere.<sup>[1],[2],[3],[4]</sup> Recent years have seen the emergence of many reactions building complexity with CO<sub>2</sub>,<sup>[5],[6]</sup> examples include the synthesis of cyclic carbonates<sup>[7],[8],[9]</sup> methylated amines<sup>[10]</sup>, formylated amines<sup>[11]</sup>, propiolic carboxylic acids,<sup>[12],[13],[14]</sup> esters<sup>[15],[16],[17]</sup> as well as numerous heterocycles.<sup>[18]</sup> Due to the high thermodynamic stability of CO<sub>2</sub>, it is generally considered that robust catalytic tools are required for its efficient transformations. Of the reactions mentioned above, the carboxylation of alkynes is interesting due to the importance of propiolic acid derivatives in medicinal chemistry.<sup>[15]</sup> Many studies have been carried out to optimize the conditions for the carboxylation of terminal alkynes using a broad range of homogeneous and heterogeneous catalysts based on transition or rare earth metals. (Scheme 1).<sup>[15],[19],[20],[21]</sup> In all the reported metal catalysed reactions, a base is also required to promote deprotonation of the alkyne, and the utilization of Cs<sub>2</sub>CO<sub>3</sub> in DMF or DMSO appears to be a privileged system. Base promoted direct carboxylation of terminal alkynes by Cs<sub>2</sub>CO<sub>3</sub> was reported to occur in the absence of catalyst only when using significantly higher temperatures and CO<sub>2</sub> pressure (120 ° C and 2.5 bar of CO<sub>2</sub>) compared to the metal-catalysed reaction.<sup>[22]</sup> Here, we show that under rigorous anhydrous conditions dry Cs<sub>2</sub>CO<sub>3</sub> allows for the convenient base-promoted, catalyst-free carboxylation of aromatic alkynes under mild conditions and in excellent yields.



**Scheme 1** Carboxylation of phenylacetylene using Cs<sub>2</sub>CO<sub>3</sub> as the base and CO<sub>2</sub> as the carboxylation reagent.

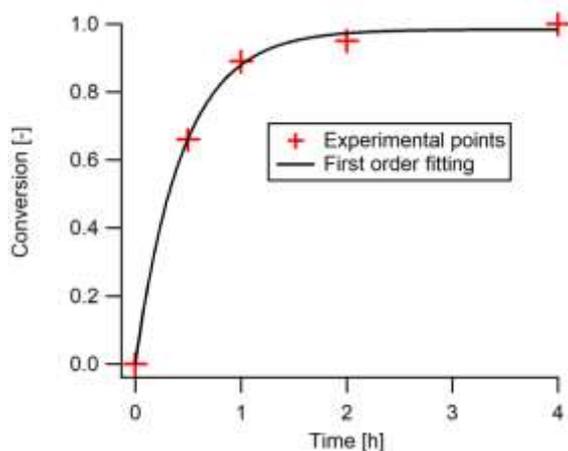
## Results and Discussion

Phenylacetylene was taken a model substrate and since the reaction is reversible, even under mild conditions, the product is converted in situ into the corresponding ester by reaction with 1-iodobutane (Table 1).<sup>[15],[23]</sup> Initially, the reaction was conducted in DMSO at 40 °C for 24 h under 1 atm. CO<sub>2</sub> in presence of two equivalents of Cs<sub>2</sub>CO<sub>3</sub>. A non-negligible yield of 33% was obtained (Table 1, entry 1) in line with previous results showing that the reaction proceeds to some extent under very mild conditions even in the absence of a catalyst.<sup>[24]</sup> We found that, on increasing the temperature to 60 °C and then to 80 °C the yields increases up to 99 % with an isolated yield of 91% (Table 1, entries 2, 3, Figure S1). The increase in yield with temperature is attributed to the increased solubility of the base in DMSO with temperature, and to faster deprotonation kinetics.<sup>[25]</sup> To demonstrate the ability of the base to deprotonate (at least partially) the acidic C-H bond, the reaction between phenylacetylene and Cs<sub>2</sub>CO<sub>3</sub> was monitored by <sup>1</sup>H NMR spectroscopy (Figure S2), at room temperature. The signal assigned to the aliphatic proton disappeared after 1 h at 80 °C, confirming deprotonation of the alkyne. In presence of water (1 :2 with respect to Cs<sub>2</sub>CO<sub>3</sub>) only partial deprotonation is observed (Figure S3). Indirectly, these results suggest that the rate determining step of the C-H carboxylation reaction is the deprotonation of the alkyne. The reaction of the deprotonated alkyne with <sup>13</sup>C CO<sub>2</sub> resulted in the instantaneous formation of the 3-phenylpropionate salt, detected by <sup>13</sup>C NMR spectroscopy (appearance of a signal at 155.8 ppm assigned to the carboxylic group, Figure S5).

The reaction does not proceed when it is conducted in DMF or THF (Table 1 entries 4 and 5), where Cs<sub>2</sub>CO<sub>3</sub> is markedly less soluble, indicating that the solubility of Cs<sub>2</sub>CO<sub>3</sub> is important for good activity, presumably due to the deprotonation rate that is accelerated when the base is soluble.<sup>[26],[27]</sup> Low yields are also obtained with sub-stoichiometric amounts of anhydrous Cs<sub>2</sub>CO<sub>3</sub> (Table 1, entry 6).

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Remarkably, at 80 °C the time required for a near-quantitative conversion of the substrate is much shorter compared to those previously reported in literature (14-24 h), even if catalysts are used and/or harsher conditions are applied.<sup>[28],[26],[27],[22]</sup> Notably, high yields are only reached after 12 h when the AgPF<sub>6</sub> catalyst was used in DMF with stoichiometric amounts of Cs<sub>2</sub>CO<sub>3</sub> and 2 atm. CO<sub>2</sub>.<sup>[20]</sup> The time-dependent yields measured at 80 °C show that the reaction is essentially first order with respect to the substrate with an estimated kinetic constant of 2 h<sup>-1</sup>, and reaches the maximum yield after approximately 3 h (Figure 2, Table 1, entries 7-9). To ensure that the carboxylic group is derived from CO<sub>2</sub> and not Cs<sub>2</sub>CO<sub>3</sub>, an experiment was conducted in absence of CO<sub>2</sub> and no reaction was observed (Table 1, entry 10).



**Figure 2.** Time-dependent yields for the catalyst-free carboxylation of phenylacetylene. Reaction condition: PhCCH (28 mg, 0.28 mmol), Cs<sub>2</sub>CO<sub>3</sub> (183 mg, 0.56 mmol, 2 eq.), CO<sub>2</sub> (1 atm.), DMSO (1 mL), 80 °C.

**Table 1.** Optimization of reaction conditions. Reaction conditions: phenylacetylene (0.28 mmol), CO<sub>2</sub> (1 atm), Cs<sub>2</sub>CO<sub>3</sub> (183 mg, 0.56 mmol, 2 eq.), DMSO (1 mL). Product trapped with butyl iodide (1.1 eq.). [a] Yields determined by GC using n-decane as internal standard. [b] Isolated product. [c] 0.2 eq. of Cs<sub>2</sub>CO<sub>3</sub>. [d] Without CO<sub>2</sub>.

Entry	Solvent	T [°C]	Time [h]	Yield [%] <sup>[a]</sup>
1	DMSO	40	24	33
2	DMSO	60	4	30
3	DMSO	80	4	> 99, 91 <sup>[b]</sup>
4	DMF	80	4	4
5	THF	80	4	< 1
6 <sup>[c]</sup>	DMSO	80	4	6
7	DMSO	80	2	95
8	DMSO	80	1	83
9	DMSO	80	0.5	66
10 <sup>[d]</sup>	DMSO	40	24	< 1

<sup>[a]</sup>Yields determined by GC using n-decane as internal standard. <sup>[b]</sup>Isolated product. <sup>[c]</sup>0.2 eq. of Cs<sub>2</sub>CO<sub>3</sub>. <sup>[d]</sup>Without CO<sub>2</sub>.

Our results under catalyst-free conditions, show that the low to modest yields reported for the catalyst-free reaction in DMSO can be easily optimized by increasing the temperature to 80 °C to afford the product in near-quantitative yield. Since the reproducibility of carboxylation reaction promoted by weak bases as Cs<sub>2</sub>CO<sub>3</sub> is likely to be affected by the presence of water, even under forcing conditions (high temperature, overpressure),<sup>[29]</sup> we investigated the effect of stoichiometric amounts of water in the used mild conditions.

Addition of carefully controlled amounts of water (0.1, 0.2 and 1 eq. with respect to Cs<sub>2</sub>CO<sub>3</sub>) to the system leads to a significant reduction in yield (Table 2, entries 1-3, 80, 43 and <1 %, respectively). Hence, to ensure reproducible high yields under catalyst-free conditions, water must be excluded from the reaction mixture, and anhydrous solvents and reagents must be used. The detrimental effect of water is not unique to metal free carboxylation reactions. Notably, to emphasize the general detrimental effect of water on Cs<sub>2</sub>CO<sub>3</sub> promoted reactions we performed the metal catalysed reaction, using the performant AgPF<sub>6</sub> under the reported conditions,<sup>[20]</sup> but in the presence of H<sub>2</sub>O (1 eq.). Under these conditions, 4 % product was obtained (Table 2, entry 4).

These results indicate that rigorously anhydrous conditions (thoroughly dried solvents, anhydrous Cs<sub>2</sub>CO<sub>3</sub> and reagents, rigorous Schlenk techniques) should be used in base promoted carboxylation reactions.

**Table 2.** Effect of water on the catalysed and catalyst-free reaction. Reaction conditions: phenylacetylene (0.28 mmol), CO<sub>2</sub> (1 atm), DMSO (1 mL). Product trapped with butyl iodide (1.1 eq.). Yields determined by GC using n-decane as internal standard.

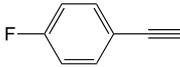
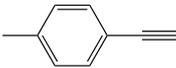
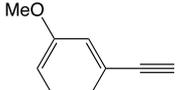
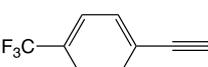
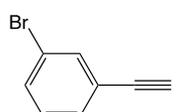
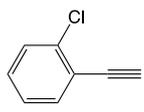
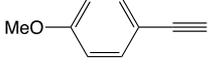
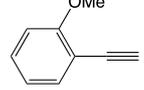
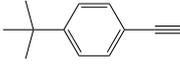
Entry	Notes	T [°C]	Time [h]	Yield [%]
1	0.1 eq H <sub>2</sub> O	80	4	80
2	0.2 eq H <sub>2</sub> O	80	4	43
3	1 eq H <sub>2</sub> O	80	4	< 1
4	AgPF <sub>6</sub> (4 %), 1 eq H <sub>2</sub> O	80	4	< 1

The catalytic activity of transition metal ions based on copper or silver in DMF (where Cs<sub>2</sub>CO<sub>3</sub> is not able to deprotonate terminal alkynes) reported by other authors can be rationalized by the ability of those metals to coordinate the substrate, weakening the C-H bond, and accelerating the deprotonation of the alkyne, as proposed in computational studies.<sup>[30],[31]</sup> However, our results strongly suggest that the carboxylation of aromatic terminal alkynes in DMSO essentially proceeds via an uncatalysed acid-base reaction and the addition of catalyst is not crucial.

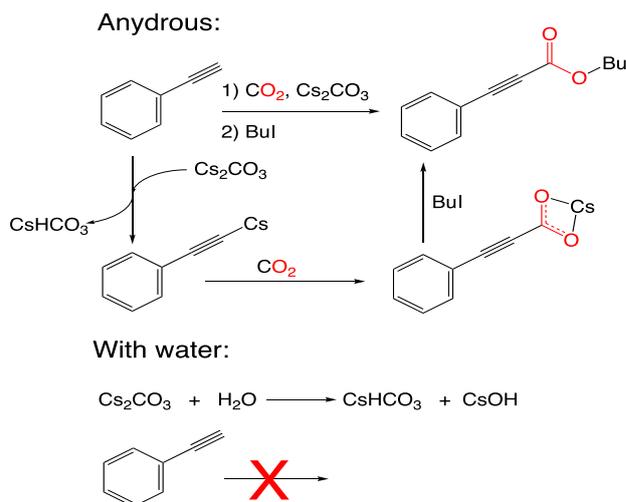
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The catalyst-free carboxylation was explored for various phenyl acetylene derivatives under the reaction conditions optimized for phenyl acetylene. Quantitative yields were obtained in four hours for aromatic alkynes with electron withdrawing groups in the aromatic ring and for both *p*-methyl phenyl acetylene and *m*-methoxy phenyl acetylene. (Table 3, Entry 1- 7), while good yields were instead achieved for less acid alkynes (Table 3, Entry 7 - 10).

**Table 3.** Carboxylation of phenyl acetylene derivatives. Reaction conditions: alkyne (0.28 mmol), CO<sub>2</sub> (1 atm), DMSO (1 mL). Product trapped with butyl iodide (1.1 eq.). Yields determined by GC using *n*-decane as internal standard. <sup>[a]</sup>Isolated yield.

Entry	Alkyne	Time [h]	Yield [%]
1		4	> 99, 92 <sup>[a]</sup>
2		4	> 99
3		4	> 99
4		4	> 99, 95 <sup>[a]</sup>
5		4	> 99
6		4	> 99
7		4	> 99
8		4	88
9		4	75
10		4	60

The mechanism of the base-promoted transformation is therefore postulated to require the following steps: deprotonation of the alkyne by the carbonate base, insertion of CO<sub>2</sub>, nucleophilic attack of the carboxylate anion onto the alkyl halide in the final step. Figure 3 summarizes the key mechanistic steps and postulates the main deactivation pathway due to water, i.e. acidification of the reaction mixture inhibiting the deprotonation of the alkyne.



**Scheme 2** Proposed steps for the uncatalysed carboxylation of PhCCH using CO<sub>2</sub> as in the absence (top) and presence (bottom) of water.

## Conclusions

In conclusion, we demonstrated that carboxylation of phenylacetylene can be promoted in quantitative yield under anhydrous conditions using Cs<sub>2</sub>CO<sub>3</sub> as the base in DMSO under mild conditions and in short reaction times (80 °C, 1 atm. CO<sub>2</sub>, 4 h). When moisture is present in the reaction mixture, even reported catalysts such as AgPF<sub>6</sub> are unable to catalyse the reaction. Hence, the C-H carboxylation of alkynes proceeds mainly *via* an acid-base mechanism. We believe that these results can be generalized to many base-promoted CO<sub>2</sub> reactions.

## Experimental Section

### General methods.

Loading of reagents for carboxylation was carried out under an inert argon atmosphere using an MBraun glovebox equipped with a purifier unit or using standard Schlenk-type techniques. Glassware was dried overnight at 150 °C prior to use. Unless otherwise noted, reagents were acquired from commercial sources and used without further purification. The solvents and the reagents were purchased from Sigma Aldrich or Eurisotop (deuterated solvents) in their anhydrous form, conditioned under argon and dried with molecular sieves (4 Å) for two weeks. Water content in DMSO was tested using quantitative <sup>1</sup>H NMR spectroscopy (see supporting information). Cs<sub>2</sub>CO<sub>3</sub> was purchased from Sigma Aldrich and dried under vacuum (10<sup>-3</sup> bar) for 5 days at 60 °C prior to use. Shorter drying times result in the deleterious presence of water and reduced catalytic performance (Table S1, see supporting information). <sup>1</sup>H and <sup>13</sup>C NMR experiments were carried out using NMR tubes adapted with J. Young valves. The NMR spectra were recorded on Bruker 400 or 800 MHz. <sup>1</sup>H chemical shifts are reported in ppm and were measured relative to residual solvent peaks, which were assigned relative to an external TMS standard set at 0.00 ppm. Gas chromatography-mass spectrometry (GC-MS) of liquid samples was performed on an Agilent 7890B Gas Chromatograph together with Agilent 7000C MS triple quad

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detector using He as the carrier gas. The yields were determined by the internal standard method using n-decane as the internal standard.

*Typical procedure for the base-promoted carboxylation reaction.*

To ensure reproducibility with respect to temperature and time, four reactions were conducted simultaneously.<sup>[32]</sup> Four 25 mL round bottom flasks were each charged with 183 mg (0.56 mmol, 2 eq) of anhydrous Cs<sub>2</sub>CO<sub>3</sub>, 30 μL of phenyl acetylene (0.28 mmol, 1 eq), and 1 mL of DMSO. The individual reaction mixtures were stirred to afford pale yellow suspensions. The mixtures were frozen and then 1 atm CO<sub>2</sub> was introduced to each flask after removing the argon atmosphere under mild vacuum. Subsequently, the mixtures were quickly warmed to 80 °C in a pre-heated oil bath under continuous stirring at 400 rpm for 4 hours. Then each mixture was cooled to 40 °C and 35 μL of 1-iodobutane (0.3 mmol, 1.1 eq) were added under air. After 1 h, 53 μL of n-decane (0.28 mmol, 1 eq) were added as internal standard together with 4 ml of AcOEt. The suspension was filtered to remove the cesium carbonate and hydrogen carbonate formed during the reaction and the filtrate was analyzed by GC-MS/FID.

For the reaction conducted with other substrates the same procedure described above was used, except that an equimolar amount of other acetylene derivatives was employed.

For the reactions conducted with different solvents, temperature, amount of base or time, the same procedure described above was used, except for that other solvents, other temperature, other amount of base or other times were employed.

For the reaction conducted in presence of AgPF<sub>6</sub> the same procedure described above was used, except that AgPF<sub>6</sub> was added to the reaction flask under argon atmosphere before the addition of CO<sub>2</sub>.

For the reaction conducted without CO<sub>2</sub> the same procedure described above was used, except that CO<sub>2</sub> was not added to the flasks.

For the reactions conducted in presence of water the same procedure described above was used, except that H<sub>2</sub>O was added to the flasks through a septum outside of the glovebox.

*Synthesis of the phenylpropionic esters by direct carboxylation.*

A 25 mL round bottom flask was charged with 549 mg (1.68 mmol, 2 eq) of anhydrous Cs<sub>2</sub>CO<sub>3</sub>, 90 μL of phenyl acetylene (0.84 mmol, 1 eq), and 3 mL of DMSO. The mixture was frozen and then 1 atm CO<sub>2</sub> was introduced in the flask after removing the argon atmosphere under mild vacuum. Subsequently, the mixture was quickly warmed to 80 °C in a pre-heated oil bath and maintained at to 80 °C under continuous stirring at 400 rpm for 4 hours. The mixture was then cooled to 40 °C and 105 μL of 1-iodobutane (0.9 mmol, 1.1 eq) were added under air. After 1 h, water (5 mL) was added to the system and the mixture was extracted three times with Et<sub>2</sub>O (4 mL each). The combination of the organic phases was dried under vacuum affording the butyl 3-phenylpropionate as viscous oil (152 mg, 91% yield).

<sup>1</sup>H NMR spectrum of butyl 3-phenylpropionate (THF-d<sub>8</sub>, 400 MHz, 298 K): δ = 7.58-7.60 (d, 2H, J = 8 Hz), 7.38-7.48 (m, 2 H), 7.30-7.31 (d, 1H, J = 4 Hz),

4.17-4.20 (t, 2H), 1.62-1.69 (m, 2H), 1.37-1.47 (m, 2H), 0.93-0.97 (t, 3H) (Figure S1). HRMS (APPI/LTQ-Orbitrap) m/z calc. for C<sub>13</sub>H<sub>15</sub>O<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup>: 203.1067; Found 203.1064.

The synthesis of butyl 3-(4-fluorophenyl)propionate and 3-(4-methoxyphenyl)propionate was performed using the same conditions except for the final extraction of the ester from water which was performed using CH<sub>2</sub>Cl<sub>2</sub> instead of ether (three times with 4 mL).

<sup>1</sup>H NMR spectrum of butyl 3-(4-fluorophenyl)propionate (CD<sub>3</sub>CN, 400 MHz, 298 K): δ = 7.64-7.68 (m, 2H), 7.17-7.22 (m, 2H), 4.20-4.23 (t, 2H), 1.63-1.70 (m, 2H), 1.36-1.45 (m, 2H), 0.93-0.96 (m, 3H). HRMS (ESI/QTOF) m/z calc. for C<sub>13</sub>H<sub>14</sub>FO<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup>: 221.0978; Found 221.0977

<sup>1</sup>H NMR spectrum of butyl 3-(4-methoxyphenyl)propionate (CD<sub>3</sub>CN, 400 MHz, 298 K): δ = 7.33-7.37 (t, 1H), 7.18-7.20 (d, 1H, J = 8 Hz), 7.15 (s, 1H), 7.08-7.10 (m, 1H), 4.20-4.23 (t, 2H), 3.80 (s, 3H) 1.63-1.70 (m, 2H), 1.36-1.46 (m, 2H), 0.93-0.97 (t, 3H). HRMS (ESI/QTOF) m/z calc. for C<sub>14</sub>H<sub>16</sub>O<sub>3</sub>Ag<sup>+</sup> [M + Ag]<sup>+</sup>: 339.0150; Found 339.0163 (addition of Ag<sup>+</sup> is required to observe the peak).

## Supplementary Material

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/MS-number>.

## Acknowledgements

This work was supported by Ecole Polytechnique Fédéral de Lausanne (EPFL), from the Swiss National Science Foundation grant number 200021\_178793 and by Swiss Competence Center for Heat and Electricity Storage (PJD).

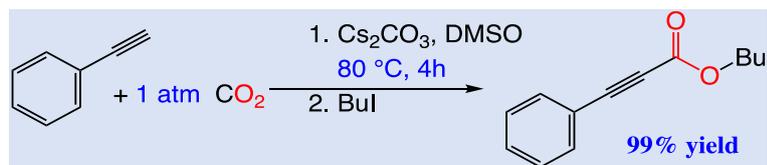
**Author Contribution Statement.** DT, FDB, PD, and MM planned the research and wrote the manuscript. MM supervised the research in all aspects. DT performed and analyzed all the experiments, F.D.B carried out and analyzed the GC-MS experiments;

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