Recently, this protocol was expanded to less reactive organometallic reagents where catalytic insertion CO_2 into less polarized metal-carbon bonds (C-Sn, C-Zn, C-B) with high chemoselectivity and under mild reaction conditions was achieved. Generally, such reactions take place under mild reaction conditions. However widespread use of these methods is limited by the synthesis of related organometallic reagents as precursors and the restricted substrate scope. In the past decades, several interesting systems have been reported for metal mediated reductive carboxylation of alkenes and alkynenes with CO_2 to form carboxylic acids or esters. However, most of those systems need either stoichiometric amount of transition metals as reactants or excess amount of organometallic reagents for transmetallation processes. The development of catalytic systems for synthesis of carboxylic acid product by direct CO_2 carboxylation without using stoichiometric organometallic reagents is highly desired, especially for commercial applications. An alternative possibility to achieve the catalytic synthesis carboxylic acid from CO_2 is by direct C-H bond activation and carboxylation, but unfortunately, this is still an undeveloped field.

Previously known methods for the preparation of alkynyl carboxylic acids include CO_2 insertion into metal-carbon bond of organometallic reagents, hydrolysis of bromide and related derivatives and the oxidation of preoxidized substrates, such as alcohols or aldehydes. Despite the efficiency of these conventional procedures, they are restricted by the severe reaction conditions and the organometallic reagent that dramatically limited the synthesis and application of a wide scope of functionalized propiolic acids.

Object of the Invention

It is the object of the present invention to substantially overcome or at least ameliorate one or more of the above disadvantages.

Summary ~~of the Invention~~

In a first aspect of the ~~invention~~disclosure there is provided a process for converting a terminal alkyne into an alkynoic acid comprising exposing the alkyne to carbon dioxide in the presence of a copper(I) species, a base and a complexing agent capable of complexing copper(I).

The following options may be used in conjunction with the first aspect, either individually or in any suitable combination.

The copper(I) species may be a copper(I) halide, e.g. copper (I) chloride. It may be present in catalytic amount relative to the terminal alkyne. It may be present at less than about 10mol% relative to the terminal alkyne, or less than about 5 or 2mol%, or at about 1

more than one of any one or more of these. It may comprise a mixture of two or more alkynes, whereby the process produces a mixture of alkynoic acids. In the event that the alkyne contains more than one (e.g. 2 or 3) terminal alkyne groups, the process may produce predominantly or exclusively a monocarboxylic acid. By adjusting conditions, in some cases, a dicarboxylic acid may be formed from an alkyne having two terminal alkyne groups. The alkyne may have a carbon atom other than the terminal alkyne carbon atom bonded to the non-terminal alkyne carbon atom. The alkyne may have structure X-C≡C-H, where X is bonded to the C≡C group by a C-C bond.

In an embodiment there is provided a process for converting a terminal alkyne into an alkynoic acid comprising exposing the alkyne in a dipolar aprotic solvent such as DMF to carbon dioxide at about 1 atmosphere pressure and about ambient temperature in the presence of a carbonate salt such as caesium carbonate, a catalytic amout of a copper(I) halide and a catalytic amount of a diaminoalkane.

In another embodiment there is provided a process for converting a terminal alkyne into an alkynoic acid comprising exposing the alkyne in a dipolar aprotic solvent such as DMF to carbon dioxide at about 1 atmosphere pressure and about ambient temperature in the presence of a carbonate salt such as caesium carbonate, a catalytic amout of a copper(I) halide and a catalytic amount of a poly-N-heterocyclic carbene.

In another embodiment there is provided a process for converting converting a terminal alkyne into an alkynoic acid comprising exposing the alkyne to a poly-N-heterocyclic carbene reagent in which about 50% of carbene sites are complexed with copper(I) and about 50% of carbene sites are complexed with carbon dioxide, said process being conducted at about ambient temperature in a dipolar aprotic solvent such as DMF.

In a second aspect of the ~~invention~~disclosure there is provided a process for converting a terminal alkyne into an alkynoic acid comprising exposing the alkyne to carbon dioxide in the presence of a carbonate salt at a temperature of at least about 60°C and a partial pressure of carbon dioxide of at least about 1 atmosphere.

The following options may be used in conjunction with the second aspect, either individually or in any suitable combination.

The carbonate salt may be, or may comprise, an alkaline metal carbonate. It may be, or may comprise, caesium carbonate. It may be present in equimolar or greater amount relative to the terminal alkyne. It may be present in a molar excess of about 0, 5, 10, 15, 20, 24, 30, 35, 40, 45 or 50%, optionally more than 50%, over the terminal alkyne.