

Editor choice paper

# Indirect palladium catalysed methoxycarbonylation of trichloroethylene

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## Abstract

The palladium catalysed alkoxy carbonylation of trichloroethylene has been studied. Under standard conditions (with classical phosphine as ligand of Pd) no reaction takes place. On the other hand, we have shown that a simple procedure allows to convert trichloroethylene into its monoiodo analogue. The methoxycarbonylation of this last compound to give methyl dichloroacrylate is easily achieved using a simple catalyst precursor such as  $\text{PdCl}_2(\text{PPh}_3)_2$ .

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## 1. Introduction

Carbonylation reactions of aryl, benzyl, allyl or vinyl halides (or pseudo halides) catalysed mainly by palladium represent an efficient tool to synthesize carboxylic acid derivatives and this methodology has been widely applied in organic synthesis. However in this context, catalytic carbonylation reaction of trichloroethylene (TCE) has never been reported to the best of our knowledge. In the same way, no *gem*- nor *vic*-dichlorovinyl substrate have been described to undergo this reaction and only few chlorovinyl compounds furnish aminocarbonylation or hydroxycarbonylation products [1–3].

Moreover a survey of the literature showed that trichloroethylene has seldom been used in homogeneous catalytic reactions with transition metal complexes. The only published report deal with catalytic cross-coupling reactions with Grignard reagents to achieve carbon–carbon bond formation. Thus, the reactions of TCE with organomagnesium compounds in the presence of phosphinepalladium or phosphinenickel catalyst lead to products where the 1 or 2 position are substituted [4,5].

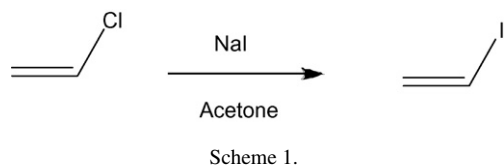
Amatore et al. [6] have demonstrated in contradiction with a precedent study [7] that after work-up, two major complexes are present in solution when  $\text{Pd}(\text{PPh}_3)_4$  was allowed to react with TCE: *trans*- $[\text{Cl}_2\text{C}=\text{CHPdII}(\text{PPh}_3)_2\text{Cl}]$  (80%) **1** and

*(Z)*-*trans*- $[\text{ClCH}=\text{CCIPdII}(\text{PPh}_3)_2\text{Cl}]$  (20%) **2**. However they pointed out that in nucleophilic substitution or cross-coupling reactions involving such carbon–halogen vinylic bonds, the final distribution of products depends not only on the overall oxidative addition process but on the nucleophile strength as well.

In fact, the first steps of the mechanism described for 1,2-dichloroethylene are totally reversible and proceeds through the formation of a  $\eta^2$ -dichloroalkenepalladium(0) before the real step of oxidative addition leading to a *cis*- $\sigma$ -chlorovinylpalladium intermediate. The slow rearrangement of the *cis*- $\sigma$ -chlorovinylpalladium complex to the more stable *trans*-isomer is probably never involved in catalytic reactions.

In the context of our ongoing efforts to develop carbonylation reactions, we focused our interest on chlorovinyl compounds. Some of our preliminary works on the subject have shown that TCE, 1,2 and 1,1-dichloroethylene are totally reluctant to the alkoxy carbonylation reaction catalysed by triphenylphosphinepalladium complexes although the crucial step of oxidative addition is possible when carbon monoxide is absent (*vide supra*). Previous works concerning various substrates have pointed out that carbon monoxide is able to slow down or inhibit oxidative addition process [8,9]. In the case of methoxycarbonylation of benzyl chloride at low carbon monoxide pressure and temperature [10], we have shown it competes with this substrate to react with the palladium(0) centre and to give rise to the formation of inert palladium carbonyl compounds.

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None of the experimental conditions tested successfully in the former study (especially the low pressures) allowed here the reaction to proceed.

Then, it appeared that if the same kind of competition between CO and TCE was implied, a possible route to perform alkoxy-carbonylation of TCE might be to increase the rate of the overall oxidative addition.

The carbon–iodine bond is known to undergo a much more rapid oxidative addition than the carbon–chlorine one [11] and the substitution of one of the chlorine atom on the TCE would furnish an isomer of dichloroiodoethene which would have to be more reactive toward the palladium(0) species.

However, the synthesis of such molecules has not been described. Thus we first undertook a study in order to synthesize these compounds. In particular we have focused our attention on (Z)-1,2-dichloro-1-iodoethene since this product should react with the catalytic species to give iodo analogues of complex 2. Thus oxidative addition of this compound on the Pd atom is expected to be easy even under CO.

## 2. Results and discussion

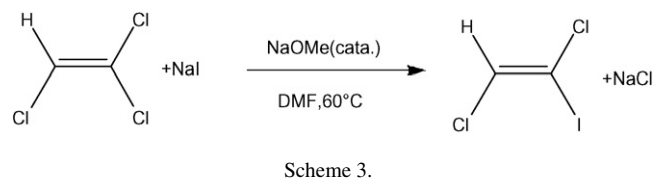
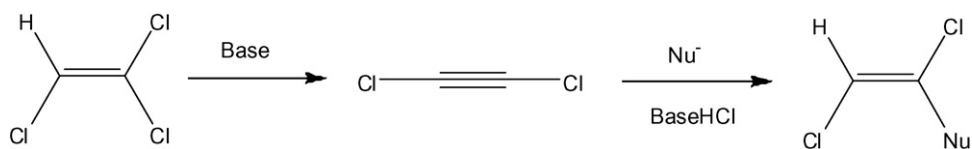
### 2.1. Synthesis of (Z)-1,2-dichloro-1-iodoethene

The most direct and attractive way that can be envisioned to synthesize dichloroiodoethenes is a direct chloride atom substitution on TCE which could be carried out by action of NaI on TCE in acetone (Scheme 1). However various attempts have only led to very low amounts of the expected product (GC yields  $\leq 1\%$ ). This finding is not surprising since it is known that Finkelstein reaction at vinylic centre needs harsh conditions and has only been described for few substrates [12–14].

In the same way, it is known that Copper(I)iodide assisted halogen exchange fails to transform chloroalkenes to iodo-analogous [15].

However, substitution reactions on TCE are possible via an elimination–addition mechanism [16]. Actually, in the presence of bases, dichloroethyne is formed in a first step before a stereoselective nucleophilic addition leading in most cases to final products with *trans*-Cl,Cl configuration (Scheme 2).

Thus, reaction of TCE with sodium iodide as nucleophile species in the presence of various bases was studied in order to obtain (Z)-1,2-dichloro-1-iodoethene (DCIE).



Our first attempts performed with couples solvent/base: acetone/triethylamine, and methanol/NaOMe did not furnish the target product. On the other hand, the couples DMF/NaOMe, DMF/(NaH–MeOH) (it should be noted that the combination KH–MeOH has been used in the synthesis of dichloroethyne [17]) and DMF/NaH allowed to synthesize the product approximately in the same way (Scheme 3) although the last couple suffer from lack of reproducibility. The results are shown in Table 1.

However, it is noteworthy that dichloroethyne intermediate is a toxic compound with low boiling point (29 °C under 743 mmHg), that ignites spontaneously and may even explodes on contact with air [18]. The concentration of this compound in the medium depends on the amount of base added at the beginning of the reaction and its maximum is reached within a few minutes as monitored by GC analysis. It is so important to pointed out that the reaction is catalytic in base and avoids to accumulate a lot of dichloroethyne in solution on a short period of time. For instance, when experiments were conducted at temperatures over 75 °C even under nitrogen atmosphere, the substance decomposed, producing black carbon and flames in the reflux condenser. Thus safe conditions of DCIE production adopted afterwards were: temperature of 60 °C and relatively small amounts of base.

Under these conditions, with a twofold excess of TCE with respect of NaI, fairly good yields have been obtained, but the reactions did not go to completion in 8 h. GC analyses showed the formation of only one isomer of DCIE with only small amounts of two by-products (<8–10%). The structure of the later have been attributed on the basis of mass spectrometry: 1,1,2-trichloro-2-iodoethene and 1,2-dichloro-1,2-diiodoethene. As it is known that trichlorovinyl anions can react with CCl<sub>4</sub> under PTC conditions to lead to tetrachloroethylene [19], it might be so possible that both trichlorovinyl and iododichlorovinyl anions could attack an iodine atom of DCIE to furnish these compounds and dichloroethyne (Scheme 4).

The reaction proceeded more rapidly when the amount of TCE was increased (Table 2) and the reaction became nearly quantitative (in I<sup>−</sup>) within eight hours for a ratio TCE/NaI of about 16 (entry 4). A further increase of TCE amount slowed down the reaction, probably owing to a diminution of sodium iodide solubility in the medium (entry 5).

The stereochemistry of DCIE isomer obtained is not easy to confirm. In the literature, the configuration of related ethylenic

Table 1  
DCIE synthesis with different bases

Entry	DMF (mL)	Base	(mmol)	Reaction time (h)	Yield <sup>a</sup> DCIE (%)
1	12	MeOH/NaH	1.25/1	6	65
				8	68
2	18	MeOH/NaH	1.25/1	6	73
				8	77
3	18	MeOH/NaH	1.87/1.5	6	77
				8	80
4	18	MeOH/NaH	0.47/1.5	6	72
				8	75
5	18	NaOMe	1.5	6	76
				8	77
6	18	NaH	1.5	6	82
				8	82

Reaction conditions: TCE (89 mmol), NaI (21.3 mmol), 60 °C.

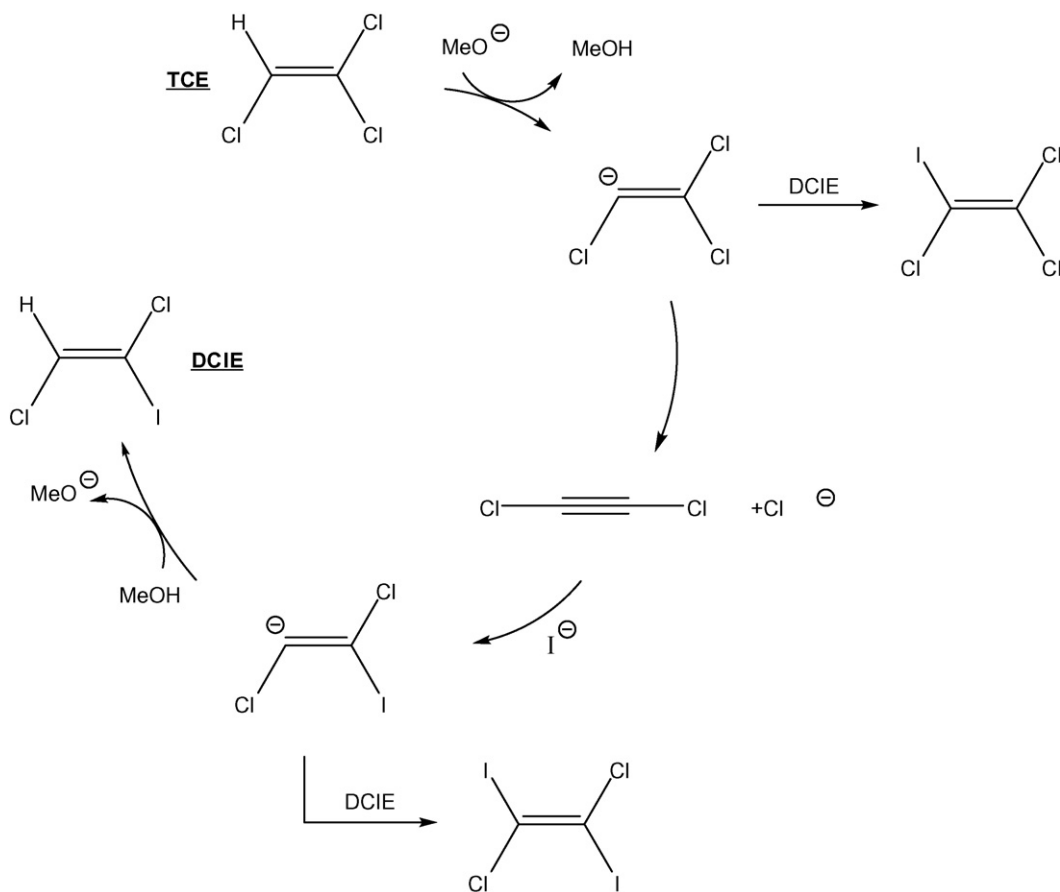
<sup>a</sup> GC yield based on sodium iodide.

compounds have been determined from X-ray structures of solid product [20], but generally configurations were assumed to be *trans*-Cl,Cl [20,21] or were based on comparison of experimental vs calculated chemical shifts of vinylic protons when *Z* and *E* isomers could be prepared [22].

For our part, we carried out a reduction of DCIE on magnesium in methanol at ambient temperature. The reaction of

magnesium with methanol to form magnesium methanolate allowed to get an highly active surface of metal which reduced easily and quantitatively DCIE to *E*-1,2-dichloroethylene (Scheme 5).

The fact that we only got the less stable isomer of 1,2-dichloroethylene [23] led us to conclude to the *Z*-form configuration of our product.



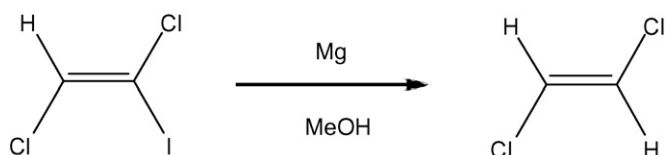
Scheme 4.

Table 2  
Effect of TCE amount

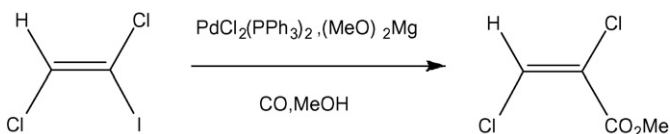
Entry	TCE (mmol)	DMF (mL)	Reaction time (h)	Yield <sup>a</sup> of DCIE (%)
1	44.5	18	6	63
			8	65
2	89	18	6	77
			8	80
3	178	18	6	86
			8	89
4	356	18	6	90.5
			8	99
5	534	18	6	71.5
			8	75

Reaction conditions: NaI (21.3 mmol), MeOH/NaH (1.87/1.5 mmol), 60 °C.

<sup>a</sup> GC yield based on sodium iodide.



Scheme 5.



Scheme 6.

## 2.2. Alkoxy carbonylation of (Z)-1,2-dichloro-1-iodoethene

The methoxycarbonylation of DCIE was first carried out in methanol under CO pressure (60 bar) with 5 mol% of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> as catalyst, in the presence of Mg(OMe)<sub>2</sub> (Scheme 6). This compound was chosen as base in order to minimize Michael addition onto the desired dichloroacrylate

[24]. This base is indeed much less nucleophile than sodium methanolate as we have already described it [25]. The more significant results are presented in Table 3.

With a stoichiometric amount of methoxide anions, methyl (*E*)-1,2-dichloroacrylate [26,27] was effectively produced with retention of configuration concomitantly with several other unknown heavier products. The reaction did not go to completion within 21 h (entry 1). The total conversion of DCIE, in the same time, was reached by doubling the amount of base but the yield of product was reduced and passed through a maximum (56% after 5 h) before decreasing (45% after 21 h) (entry 2). The same result was obtained but the reaction time was shortened (the yields reached its maximum after 1 h—entry 3) when the reaction medium was heated before introducing carbon monoxide (it must be pointed out that the substrate was not consumed during the period of heating). This protocol was adopted in our following study to avoid deactivation of a part of catalyst by forming palladium carbonyl complexes as mentioned above. Diminution of pressure by a factor of ten slowed down the reaction but did not improve the yield (entry 4).

Surprisingly, when the reaction was led in a schlenk tube under atmospheric pressure of carbon monoxide, one of the by-products **3** became the predominant product (entry 5). It was so easy to isolate and characterize it as 2-chloro-3,3-dimethoxypropanoate.

A plausible reaction sequence of formation of **3**, in which the last step has been described with sodium methanolate as base [28] is depicted in Scheme 7.

It seems then that subsequent addition of methoxide ions onto the carbonylated product would be facilitated at low concentration of carbon monoxide due to very low pressure and also to the fact that transfer of CO from gas phase into solution is obviously less efficient in schlenk tube with a magnetic stirrer than in autoclave with a mechanical agitation system. This result suggests that under higher CO pressure some of other by-products arise from further carbonylation reactions as confirmed by GC-MS analyses.

Best yields of methyl dichloroacrylate were achieved by using triethylamine as base (entries 6 and 7) showing so that fur-

Table 3  
Methoxycarbonylation of DCIE

Entry	Base	PCO (bar)	Temperature (°C)	Conversion/yield <sup>a</sup> (%) reaction time			
				0.5 h	3 h	5 h	21 h
1	Mg(OMe) <sub>2</sub>	60	60	34/25	54/43	65/46	75/51
2	Mg(OMe) <sub>2</sub>	60	60	35/30	54/46	75/56	100/45
3 <sup>b</sup>	Mg(OMe) <sub>2</sub>	60	60	67/52	78/56 <sup>d</sup>	100/47	
4 <sup>b</sup>	Mg(OMe) <sub>2</sub>	6	60	30/17	48/31	63/41	86/45
5 <sup>b,c</sup>	Mg(OMe) <sub>2</sub>	1.1	50	17/3	65/12	86/6	
6 <sup>b</sup>	NEt <sub>3</sub>	60	60	34/24	66/44 <sup>d</sup>	100/61	
7 <sup>b</sup>	NEt <sub>3</sub>	60	40	15/10	28/24	40/32	90/67
8 <sup>b</sup>	Pyridine	60	60			0/0	

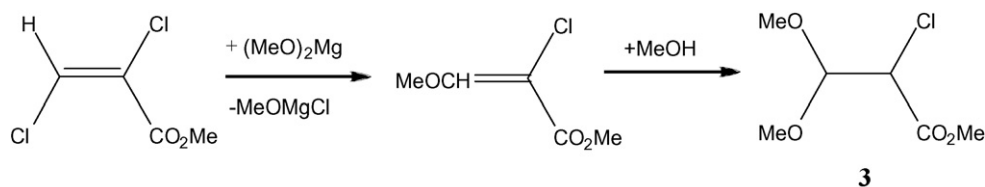
Reaction conditions: DCIE (5.15 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.28 mmol), MeOH (50 mL), base (5.2 mmol except entry 1 2.6 mmol).

<sup>a</sup> GC yield.

<sup>b</sup> Solution was heated at the temperature of the experiment for 0.5 h before introducing carbon monoxide.

<sup>c</sup> Reaction carried out in a schlenk tube in 25 mL of methanol under constant pressure.

<sup>d</sup> 1 h.



Scheme 7.

ther transformations of the product are limited with decreasing the base strength. Therefore, given the good performance of this amine, we tried to perform the reaction with weaker bases such as pyridine. However in this case the reaction was ineffective (entry 8).

### 3. Conclusion

The oxidative addition of vinyl chlorides to Pd(0)–phosphine complexes easily occurs in the absence of CO, for instance, as the first step of cross-coupling reaction of trichloroethylene with Grignard reagents. In contrast, under CO this catalytic step is much more difficult and alkoxy-carbonylation of trichloroethylene does not take place when Pd is liganded to usual phosphine. However, we have shown that indirect methoxycarbonylation of TCE can be easily achieved with moderate to good yields and selectivities by converting the substrate to its mono-iodo analogue. This finding indicates that the presence of carbon monoxide is clearly responsible of the lack of reactivity of TCE towards palladium catalyst. Actually under CO pressure, CO competes with the phosphine as ligand of palladium and owing its  $\pi$ -acceptor character its coordination reduces the electronic density on the metal centre and therefore the activity of Pd complexes towards oxidative insertion into the C–Cl bond decreases.

## 4. Experimental

### 4.1. General procedure

All experiments were carried out with reagents purchased from Aldrich or Acros and used as received. DMF was dried over calcium hydride and methanol was distilled over magnesium.

GC analyses were performed on a Chrompack CP 9001 apparatus equipped with a flame ionisation detector and a CPSil 5CB (25 m  $\times$  0.32 mm  $\times$  5  $\mu$ m, Chrompack) capillary column.  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectra were recorded on a AC-300 Bruker spectrometer at 23  $^\circ\text{C}$ ; chemical shifts are reported in parts per million downfield from TMS. GC/MS: electron impact (EI) technique was used to analyse the crude of reaction. Gas chromatography was performed on a Trace GC (Thermoelectron, San Jose, USA). RTx-5MS (Restek, Evry, France) column 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m. MS analysis were performed on a Polaris Q from Thermoelectron (San Jose, USA).

Catalytic reactions of methoxycarbonylation were carried out in a stainless steel 160 mL autoclave (Parr) equipped with a mechanical stirrer. The batch reactor was enclosed in an electric furnace whose temperature was monitored and controlled by a thermocouple and a PID temperature controller.

### 4.2. Typical procedure for DCIE synthesis

A mixture of TCE (32 mL, 356 mmol), methanol (0.06 g, 1.87 mmol), NaI (3.2 g, 21.3 mmol), ethylbenzene (0.1 g, 0.94 mmol) as GC internal standard and DMF (18 ml) was degazed in a round bottom flask equipped with a reflux condenser. NaH 60% in mineral oil (0.06 g, 1.5 mmol) was added and the reaction mixture was stirred under nitrogen at 60  $^\circ\text{C}$  for 8 h. Aliquots of solution were sampled for GC analysis.

### 4.3. Reduction of DCIE

DCIE (0.3 g, 1.35 mmol) and ethylbenzene (0.1 g, 0.94 mmol) as GC internal standard were dissolved in methanol (13 mL), and magnesium powder (0.1 g, 4.1 mmol) was added. The solution was purged with  $\text{N}_2$  and allowed to stir at room temperature for 1 h.

### 4.4. Typical procedure for the methoxycarbonylation of DCIE

Magnesium powder (0.126 g, 5.2 mmol) was added to 25 mL of methanol in a Schlenk tube. After reaction, DCIE (1.15 g, 5.15 mmol), ethylbenzene (0.5 g, 4.7 mmol) and  $\text{PdCl}_2(\text{PPh}_3)_2$  (0.2 g, 0.28 mmol) in 25 mL of methanol were introduced under  $\text{N}_2$ . The mixture was charged into the reactor under  $\text{N}_2$  and heated at 60  $^\circ\text{C}$  for 0.5 h. Then, it was pressurized with 60 bar of carbon monoxide. Aliquots of solution were sampled for GC analysis.

### 4.5. Isolation and characterization of products

#### 4.5.1. DCIE

After reaction without ethylbenzene, about 80% of TCE was removed by rotary evaporation, water (60 mL) added and the mixture was extracted with pentane (120 mL). Pentane was washed twice by water (2 mL  $\times$  60 mL) and after separation dried over  $\text{MgSO}_4$ . Solvents were removed in vacuo and the resulting oil was distilled to yield 2.8 g (60%) of DCIE (bp 70  $^\circ\text{C}$  at 67 mmHg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.73(s, 1H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  78.85, 127.17. GC-MS(EI 70 eV)  $m/z$  (%): 226(11, M+4), 224(65, M+2), 222(100, M), 187(4), 152(6), 127(23, I), 99(10), 97(64), 95(100).

#### 4.5.2. By-products of DCIE synthesis

1,1,2-Trichloro-2-iodoethene. GC-MS(EI 70 eV)  $m/z$  (%): 262(4, M+6), 260(30, M+4), 258(97, M+2), 256(100, M), 221(4), 186(8), 151(3), 133(15), 131(46), 129(4), 98(3), 96(14), 94(23).

1,2-Dichloro-1,2-diiodoethene. GC-MS(EI 70 eV) *m/z* (%): 352(10, M + 4), 350(61, M + 2), 348(100, M), 254(71, I<sub>2</sub>), 225(8), 223(49), 221(75), 188(7), 186(20), 151(6), 127(18, I), 98(5), 96(31), 94(43).

#### 4.5.3. Methyl (E)-1,2-dichloroacrylate

After reaction without ethylbenzene, methanol was removed by rotary evaporation, the mixture was taken up in ether (40 mL) and washed with water (2 mL × 20 mL) and dried over MgSO<sub>4</sub>. The brown oil was distilled under reduced pressure and the first fraction furnished 0.22 g of the compound with a purity of 90%. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.84 (s, 3H), 6.84 (s, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 53.09, 123.19, 124.22, 161.05. GC-MS(EI 70 eV) *m/z* (%): 158(2, M + 4), 156(12, M + 2), 154(21, M), 127(7), 125(47), 123(74), 119(100), 99(5), 97(33), 95(48).

Authentic samples were prepared by reaction of methyl propynoate with cupric chloride [26].

#### 4.5.4. Methyl 2-chloro-3,3-dimethoxypropanoate 3

After reaction without ethylbenzene, methanol was removed by rotary evaporation, the mixture was taken up in ether (40 mL) and washed with water (2 mL × 20 mL) and dried over MgSO<sub>4</sub>. The brown oil was purified by column chromatography on silica gel (petroleum ether/methanol, 97: 3) to give 0.15 g of the compounds. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.39(s, 3H), 3.41(s, 3H), 3.76(s, 3H), 4.23 (d, *J* = 7.5 Hz, 1H), 4.64 (d, *J* = 7.5 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 52.99, 54.16, 55.42, 55.72, 103.66, 167.80. GC-MS(EI 70 eV) *m/z* (%): 182(0.3, M), 153(2.9), 151(10), 75(100).

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