

## Review Article

Hydroxymethylation of unsaturated hydrocarbons with CO<sub>2</sub>: An overview

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## ABSTRACT

The objective of this review is to summarize recent progress and advances in the synthesis of hydroxymethyl-alcohols through the direct hydroxymethylation of unsaturated hydrocarbons using CO<sub>2</sub> as the carbonyl source with insightful mechanistic discussions. Depending on the unsaturated substrates employed the paper is divided into three sections. The first section focuses exclusively on hydroxymethylation of alkenes. The second covers hydroxymethylation of allenes. The third section gives a brief overview of the hydroxymethylation of alkynes.

## 1. Introduction

In the current industrialized age, fossil fuel combustion is the single largest source of air pollution due to the agglomeration of carbon dioxide (CO<sub>2</sub>) in the atmosphere, which is responsible for both global warming and ocean acidification [1]. On the other hand, CO<sub>2</sub> can be regarded as a plentiful, inexpensive, nontoxic, and renewable one-carbon (C1) feedstock in the synthetic organic chemists' toolbox. As a consequence, a number of innovative research activities on the conversion of CO<sub>2</sub> to value-added chemicals have been undertaken in recent years [2–14]. Hydroformylation of unsaturated hydrocarbons with CO<sub>2</sub> is one of the well-established CO<sub>2</sub> conversion reactions, which leads to the production of aldehydes [15]. Noteworthy, hydroformylation is the first step in the construction of diverse organic compounds (e.g., carboxylic acids, nitriles, amines, alcohols) from the aldehyde intermediates [16]. Among these products, primary alcohols are widely utilized as industrial solvents and precursors of plasticizers and detergents [17]. In reality, current industrial manufacturing of this special class of alcohols mostly utilizes a two-step process involving hydroformylation of unsaturated hydrocarbons to aldehydes, and subsequent hydrogenation to alcohols [18]. During the past years, significant efforts have been dedicated to the development of strategies to shorten this sequence, preferably by designing one-pot sequential

hydroformylation/hydrogenation protocols, in which the desired alcohol would be directly collected from the reaction mixture [19]. In this context, recently, hydroxymethylation of unsaturated hydrocarbons using CO<sub>2</sub> as the carbonyl source has emerged as one of the most powerful strategies for the direct synthesis of alcohols. To the best of our awareness, a comprehensive review on this extremely interesting research arena has not been published yet. In continuation of our preceding reviews [20,21], herein, we will cover proof-of-concept investigations of how CO<sub>2</sub> can be used in organic chemistry in alkene and alkyne hydroxymethylation (Fig. 1). While industrial processes like hydroformylation can be conducted on large scales, the corresponding hydroxymethylation of unsaturated hydrocarbons using CO<sub>2</sub> would require scale-up and engineering advances to reach similar scales, at which point the volumes of CO<sub>2</sub> use may become substantial and impact greenhouse effects.

## 2. Hydroxymethylation of alkenes

In the present section, we will describe the existing literature on the synthesis of primary alcohols through the direct hydroxymethylation of respective alkenes with CO<sub>2</sub> in the presence of a reducing agent. Needless to say that using hydrogen as a reducing agent is the most promising and environmentally friendly pathway for this transformations.

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However, alternative to hydrogen, hydrosilanes have been also in the forefront due to their ready accessibility, air-stable, safe and nontoxic nature and easy handling procedure. The section is divided into two major sub-sections. The first covers hydroxymethylations using molecular hydrogen as the reducing agent, while the second focuses exclusively on hydroxymethylation reaction using of hydrosilanes as the reducing agents.

### 2.1. Molecular hydrogen as reducing agent

One of the earliest reports of the synthesis of alcohols through the direct hydroxymethylation of alkenes with CO<sub>2</sub> was disclosed by Tominaga and Sasaki in 2000 [22], who showed that the combination of 2.0 mol% H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub> and 8 mol% LiCl, along with the utilization of molecular hydrogen (40 atm) as a reductant, enabled the hydroxymethylation of a small series of alkenes **1** with CO<sub>2</sub> (40 atm) effectively to give primary alcohols **2** in modestly to high yields (Scheme 1). Ru<sub>3</sub>(CO)<sub>12</sub> was also found to be effective catalyst for this conversion; however, RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> proved to be quite inert. Notably, LiCl plays an essential role in the process. In the absence of an additive salt, only the hydrogenation of C—C double bond proceeded. Apparently, this transformation proceeds through the formation of carbon monoxide (CO) via the water-gas shift (WGS) equilibrium (CO<sub>2</sub> + H<sub>2</sub> ⇌ CO + H<sub>2</sub>O), following the hydroformylation of alkene through the addition of CO and H<sub>2</sub> to the C—C double bond to form aldehyde intermediate, which could be further reduced by H<sub>2</sub> to yield alcohols. Three years later, Haukka and co-workers reported that [Ru(CO)<sub>3</sub>Cl<sub>2</sub>]<sub>2</sub>/Li<sub>2</sub>CO<sub>3</sub> combination could act as efficient catalytic system for hydroxymethylation of 1-hexene under the condition of a CO<sub>2</sub>/H<sub>2</sub> (1:1) atmosphere in *N*-methyl-2-pyrrolidone (NMP) [23]. Although the desired cyclohexylmethanol **2a** was obtained in 85 % yield within 17 h, the requirement for a high total pressure (60 atm) and a high reaction temperature (150 °C), may limit the range of applications this protocol. Moreover, due to high boiling point of NMP, solvent separation process is difficult. Soon after, Sasaki's research group revealed an alternative catalytic system which could effectively catalyze this CO<sub>2</sub> conversion reaction in toluene [24]. This include: Ru<sub>3</sub>(CO)<sub>12</sub> as the catalyst and [BMI]Cl (BMI = 1-*n*-butyl-3-methylimidazolium) as the additive. However, drastic conditions were still required.

In 2004, Tominaga and Sasaki provided a further example of primary alcohols **4** synthesis directly from the corresponding alkenes **3** employing their original procedure (Table 1) [25]. Although various terminal and internal alkenes were compatible substrates under the reaction conditions, the regioselectivity was poor and in most cases a mixture of both linear and branched alcohols were obtained. It is noteworthy that compared to the reactions using CO under the same conditions, most of the reactions using CO<sub>2</sub> gave the desired alcohols almost comparable to much higher yields. However, this method did not work well for 1,1-disubstituted and terminal aromatic alkenes. Electrospray ionization-mass spectrometry (ESI-MS) analysis of the reaction solution in the hydroxymethylation of cyclohexene revealed formation of four kinds of ruthenium anionic complexes including a tetranuclear complex ([H<sub>3</sub>Ru<sub>4</sub>(CO)<sub>12</sub>]<sup>-</sup>) (I); a trinuclear complex ([HRu<sub>3</sub>(CO)<sub>10</sub>]<sup>-</sup>) which may derived from ([HRu<sub>3</sub>(CO)<sub>11</sub>]<sup>-</sup>) (II); a mononuclear complex ([RuCl<sub>3</sub>(CO)<sub>3</sub>]<sup>-</sup>) (III); and its cyclohexene complex

([RuCl<sub>2</sub>(CO)<sub>3</sub>(C<sub>6</sub>H<sub>10</sub>)]<sup>-</sup>) (IV). In order to compare the catalytic performance, the authors prepared the complexes I, II and III, then applied them as catalysts for hydroxymethylation of cyclohexene with carbon monoxide. The results indicated that complexes I and II were faintly active for this reaction, but mononuclear complex III was completely inactive. Surprisingly, when the merge of complexes I and II with complex III was used, the catalytic activity was significantly enhanced and that the former combination was more active than the latter; its catalytic activity was increased approximately 40 times as fast as that of the tetranuclear complex I alone. Based on these observations, the authors speculated that complex III may provide a coordination site for substrates while complex I induce hydrogen donation. The authors depicted a plausible mechanism as shown in Scheme 2. Shortly afterwards, Arai and colleagues investigated the impact of CO<sub>2</sub> and H<sub>2</sub> pressures on the total conversion and the product distribution of the above-mentioned reaction [26]. It was shown that increasing total pressure of CO<sub>2</sub> and H<sub>2</sub> enhanced the yield of aldehyde and its hydrogenation to primary alcohol was assisted with increasing H<sub>2</sub> pressure but suppressed with increasing CO<sub>2</sub> pressure. In a related study, Tominaga disclosed that only 0.5 mol% of Ru<sub>3</sub>(CO)<sub>12</sub> could effectively catalyze hydroxymethylation of 1-hexene with CO<sub>2</sub> and H<sub>2</sub> employing mixed ionic liquid [BMI][Cl + NTF<sub>2</sub>] as the reaction medium [27]. However, in this seminal work, only one example was provided, without any substrate scope exploration.

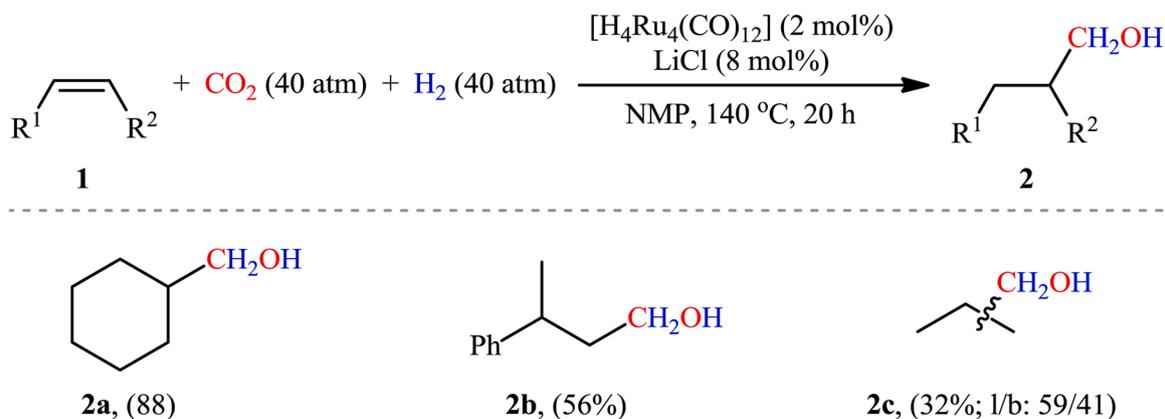
In 2014, Dupont's research team developed a novel Ru-based catalytic system in which the ionic liquids [BMI•Cl] or [BMMI•Cl] (BMMI = 3-butyl-1,2-dimethylimidazolium) reacted in the presence of H<sub>3</sub>PO<sub>4</sub> with Ru<sub>3</sub>(CO)<sub>12</sub> to produce Ru-hydride-carbonyl-carbene species *in situ* that are efficient catalysts for hydroxymethylation of alkenes with CO<sub>2</sub> and H<sub>2</sub> [28]. Thus, under the optimal reaction conditions [120 °C and 60 atm CO<sub>2</sub>/H<sub>2</sub> (1:1) for 17 h], various terminal, internal, as well as 1, 1-disubstituted alkenes **5** were functionalized to the corresponding alcohols **6** in satisfactory yields (Scheme 3). However, like previous works styrene did not respond to the reaction and unsymmetrical alkenes such as indene gave mixtures of possible regioisomers.

In the same year, the combination of Ru<sub>3</sub>(CO)<sub>12</sub> and bulky phosphite ligand (L5) was found by Beller and co-workers as efficient and selective catalyst for hydroxymethylation of alkenes with CO<sub>2</sub>/H<sub>2</sub> [29]. In this reaction, various internal and terminal alkenes **7** proceeded well to afford the desired alcohols **8** with moderate to excellent yields, even ethylene (H<sub>2</sub>C = CH<sub>2</sub>) also converted into propanol in a 51 % yield (Scheme 4). Notably, the unwanted hydrogenation of alkenes was prevented to a certain extent.

Concurrently, the group of Kondratenko developed a library of nanosized gold catalysts supported on potassium doped titanium oxide with various potassium weight concentrations [1K-Au/TiO<sub>2</sub> (1.0 wt% K), 2K-Au/TiO<sub>2</sub> (2.1 wt% K), 3K-Au/TiO<sub>2</sub> (2.9 wt% K)] and applied for converting CO<sub>2</sub> with ethylene and H<sub>2</sub> into propanol in a continuous-flow single-channel reactor with a feed ratio of unity for CO<sub>2</sub>, H<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub> [30]. The results demonstrated that the activity and selectivity significantly depend on gold nanoparticles size, which can be tuned by deposition method applied to the formation of silver nanoparticles (Au NPs) and by promoting with K. The best *oxo*-selectivity (propanol plus propanal) was observed with 2K-Au/TiO<sub>2</sub>. In accordance with experimental findings, the authors suggested that CO<sub>2</sub> adsorption takes place



Fig. 1. Direct hydroxymethylation of unsaturated hydrocarbons with CO<sub>2</sub>.



**Scheme 1.** Ru-catalyzed hydroxymethylation of alkenes **1** with CO<sub>2</sub> and H<sub>2</sub> developed by Tominaga and Sasaki.

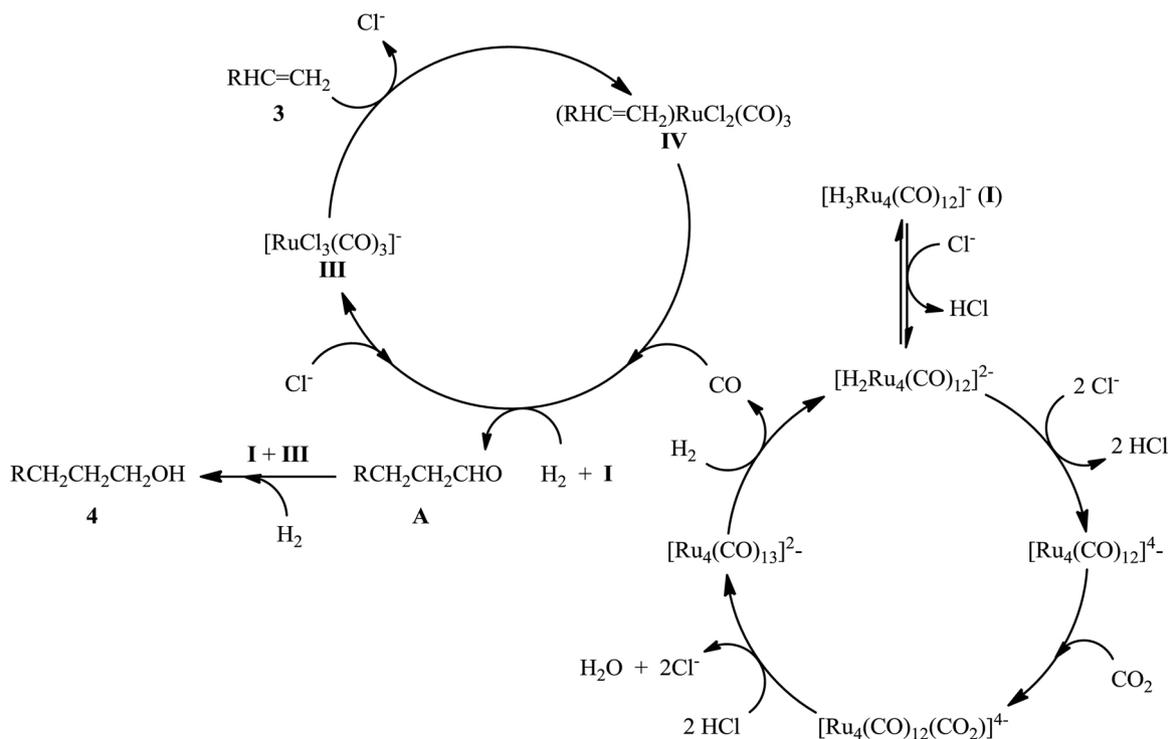
**Table 1**

Synthesis of primary alcohols **4** through the direct hydroxymethylation of alkenes **3** with CO<sub>2</sub> using of H<sub>2</sub> as a reducing agent.

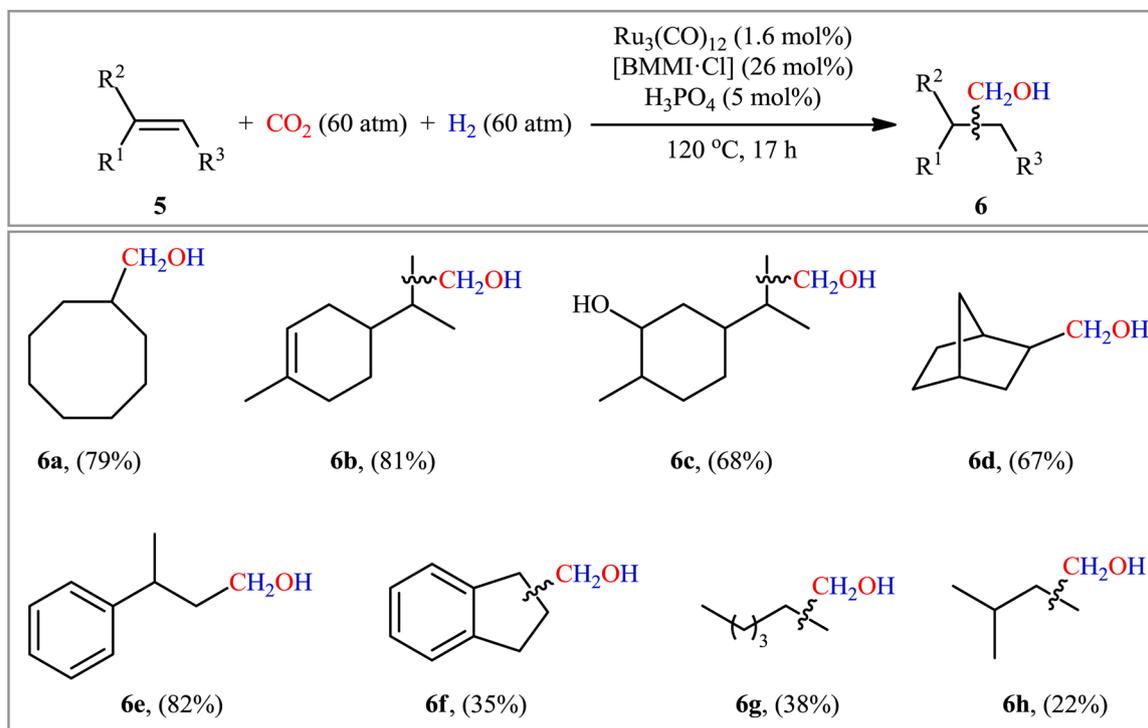
Entry	Substrate	Yield (%)	l/b ratio
1	Cyclooctene	81	–
2	3-Hexene	74	57/43
3	2-Hexene	73	60/40
4	1-Hexene	70	59/41
5	α-Methylstyrene	48	100/0
6	1,1-Diphenylethylene	9	100/0
7	Styrene	4	60/40
8	<i>Trans</i> -stilbene	58	–
9	<i>Cis</i> -stilben	26	–

on bare and K-modified TiO<sub>2</sub>, while H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> are activated on Au NP. It should be mentioned that upon increasing in K loading, the NP become larger and their distribution broader. Later, the same research team reported that Cs-Au/TiO<sub>2</sub>, K-Au/SiO<sub>2</sub>, and K-Au/SiO<sub>2</sub> catalysts were also efficient for the titled reaction [31–34].

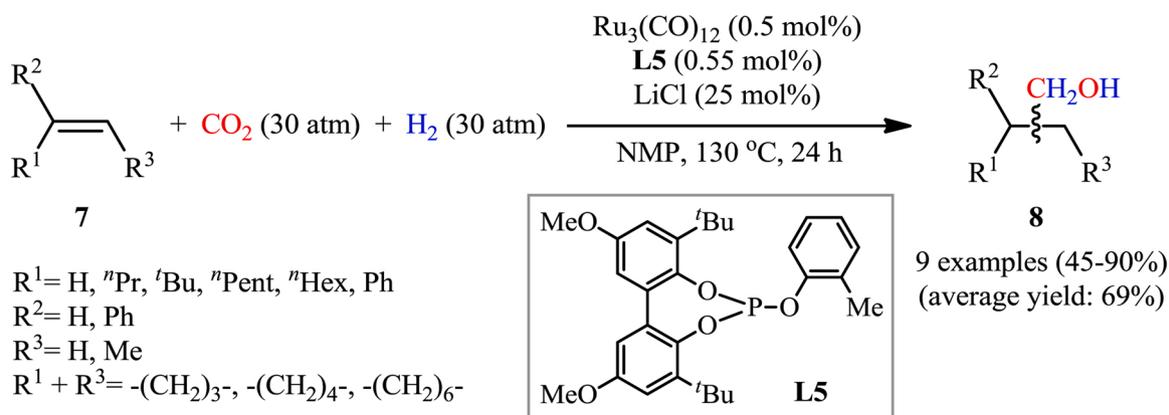
Along this line, recently, the L. He group further described the Ru-catalyzed hydroxymethylation of alkenes **9** with CO<sub>2</sub>/H<sub>2</sub> to afford primary alcohols **10** (Scheme 5) [35]. In this case, [Ru(CO)<sub>3</sub>Cl<sub>2</sub>]<sub>2</sub> combined with Co<sub>2</sub>(CO)<sub>8</sub> was used as the catalyst under 30 atm of CO<sub>2</sub>/H<sub>2</sub> at 140 °C. Small amounts of [BMI]Cl and AcOH were used as the additives. The cyclic alkenes were highly active and 1,1-alkyl-aryl substituted alkenes were also successfully converted to the corresponding alcohols in modest yields and excellent regioselectivities. Terminal and 1,1-dialkyl substituted alkenes could proceed yet with good yields, but poor regioselectivities. In cases of dienes (e.g., 1,5-cyclooctene, 1,7-octadiene), products with one double bond being reduced were formed. The reaction is noteworthy in that it could be conducted successfully on a gram scale as exemplified by fabrication of 3,5,5-trimethylhexan-1-ol on a 30 mmol scale (61 %).



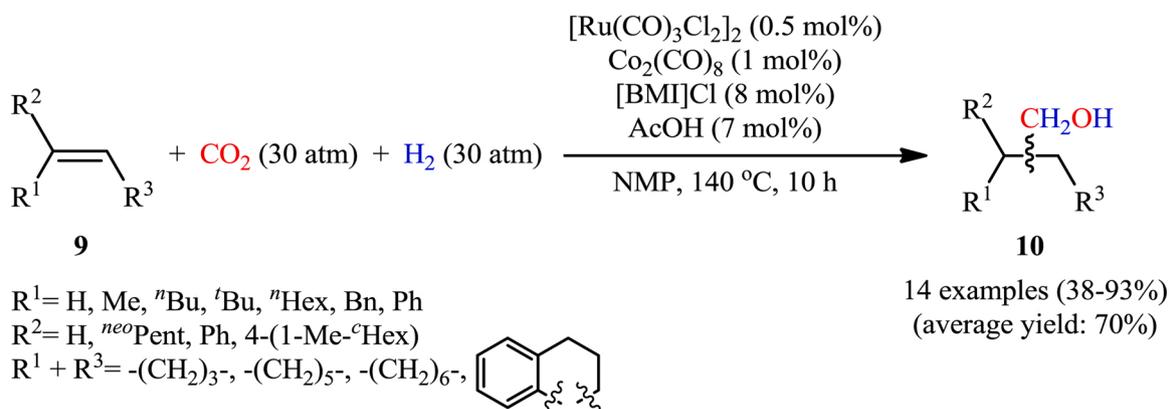
**Scheme 2.** Plausible mechanism for Ru-catalyzed hydroxymethylation of alkenes **3** with CO<sub>2</sub> and H<sub>2</sub>.



**Scheme 3.** Synthesis of alcohols **6** through the treatment of alkenes **5** with CO<sub>2</sub>/H<sub>2</sub> in the presence of a metal/ionic liquid binary catalytic system.



**Scheme 4.** Beller's synthesis of primary alcohols **8**.



**Scheme 5.** Reductive hydroxymethylation of alkenes **9** with CO<sub>2</sub>/H<sub>2</sub> catalyzed by heterobimetallic ruthenium-cobalt system.

## 2.2. Hydrosilane as reducing agents

In 2017, the group of Yu realized an elegant enantioselective copper-catalyzed reductive hydroxymethylation of alkenes with atmospheric CO<sub>2</sub> using hydrosilane as reducing agents [36]. They carefully studied the reaction variables (e.g., ligand, reductant, and solvent) for the Cu(OAc)<sub>2</sub>-catalyzed hydroxymethylation of 4-phenylstyrene (the model substrate) and found that implementation of the reaction in the presence of 6 mol% of (*R*)-DTBM-SEGPHOS as a chiral ligand and 8 equiv. of (EtO)<sub>3</sub>SiH as the reducing agent in cyclohexane at 60 °C was the optimum reaction condition. Various electron-rich and electron-deficient styrene derivatives **11** were well tolerated by this reaction under the standard conditions and gave the desired chiral homobenzylic alcohols **12** in good to almost quantitative yields with remarkable levels of enantioselectivity (Scheme 6a). A relatively wide panel of common functional groups such as halide, amine, ether, and ester functionalities at different positions of phenyl rings of styrenes were well compatible by this transformation, thus indicating its broad applicability. Of note, the authors further extended the substrate scope of their synthetic strategy to the more challenging 1,3-dienes. It was shown that under the identical conditions, a library of (*E*)-1-phenyl-1,3-butadienes **13** underwent hydroxymethylation to afford the target 1,4-addition products **14** in high yields and excellent regio-, enantio-, and (*Z*)-selectivities (Scheme 6b). Intriguingly, the synthetic applicability of this transformation was exemplified by high yielding preparation of a natural product (*R*)-(-)-curcumene and commercial drug (*S*)-(+)-ibuprofen. A catalytic cycle was proposed for this CO<sub>2</sub> reduction protocol (Scheme 7). Firstly, L<sup>\*</sup>CuH **A** is formed in the presence of silane. Then, insertion of alkene **11** into the CuH— bond with high regioselectivity and enantioselectivity generates the species **B** followed by its reaction with CO<sub>2</sub> to form copper carboxylate **C**. Subsequently, reduction of **C** by hydrosilane provides copper alkoxide intermediate **D**. Lastly, σ-bond metathesis of **D** with hydrosilane regenerates species **A** and affords silyl ether **E**, which is converted to alcohol **12** after desilylation.

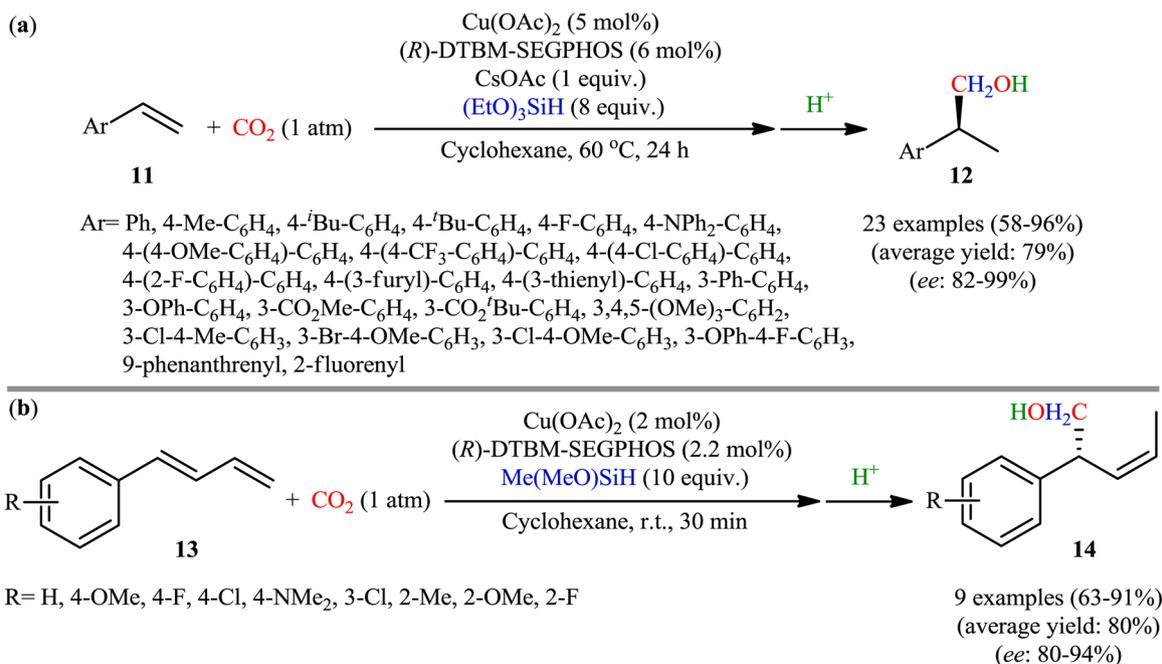
Quite recently, a detailed density functional theory (DFT) study suggested that the dimeric copper(I) species **V**, generated in the mixture of Cu(OAc)<sub>2</sub>, bidentate triaryl phosphine 2,2'-bis(diphenylphosphino)-1,1'-biphenyl (dppb), and (MeO)<sub>3</sub>SiH might be the catalytically active

species in the above-mentioned transformation (Scheme 8) [37].

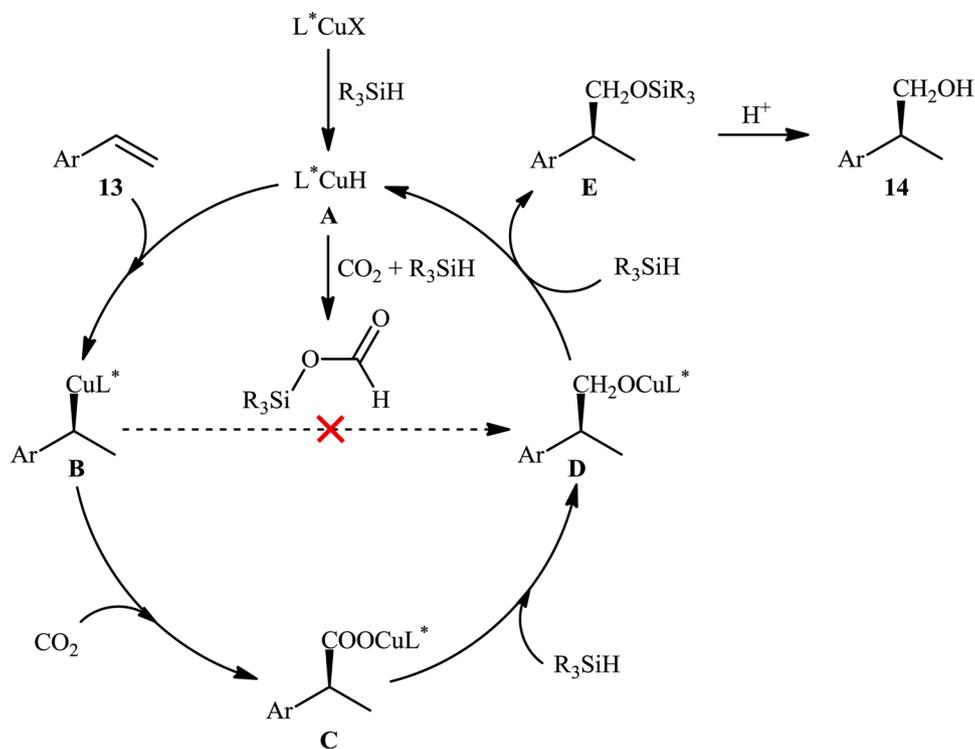
Recently, the same group further reported the highly selective construction of homoallylic alcohols with all-carbon quaternary centers via Cu-catalyzed asymmetric functionalization of 1,3-dienes with CO<sub>2</sub> using Me(MeO)<sub>2</sub>SiH as reducing agent [38]. A variety of functionalized 1,3-dienes including 1,1-aryl-alkyl and 1,1-dialkyl-substituted, as well as 1,1,4-trisubstituted 1,3-dienes **15** were directly converted to chiral 1,4-addition products **16** with high chemo-, regio-, *E/Z*-, and enantioselectivities (Scheme 9). The authors utilized DFT calculations to gain a theoretical explanation for the observed regio-, and stereo-selectivity. The computations indicated that 1,2-hydrocupration of 1,3-diene to form chiral secondary-allylcopper intermediate **INT-1** was enantio-determining step, which further induced the chirality of the quaternary carbon center via the Zimmerman-Traxler-type transition state (Fig. 2).

## 3. Hydroxymethylation of allenes

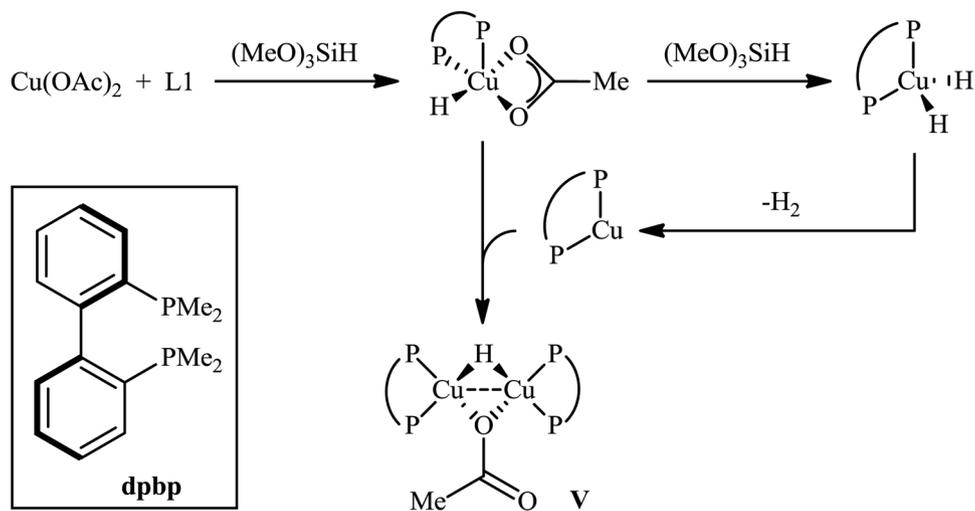
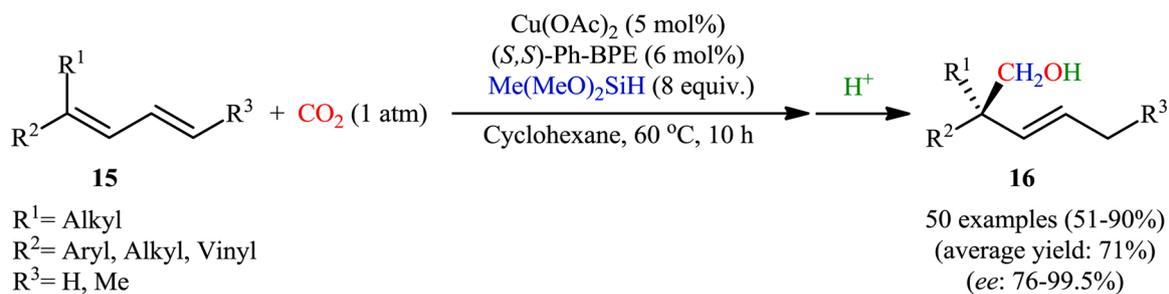
In 2015, Fujihara and Tsuji along with their co-workers described a beautiful regioselective copper-catalyzed hydroxymethylation of allenes **17** by employing CO<sub>2</sub> as C1 source and hydrosilane as reductant, providing an efficient approach for the synthesis of homoallylic alcohols **18** (Scheme 10) [39]. The reaction was successfully applied to mono-substituted, 1,1-disubstituted, and tri-substituted allenes with a variety of functional groups. Interestingly, in all cases, CO<sub>2</sub> was exclusively added at the more hindered carbon in the C=C double bond, giving rise to branched allylic alcohols. It is worthwhile to note that by increasing the amount of the base from 5 mol % to 100 mol% and replacing of the Xy-Xantphos ligand with <sup>o</sup>IPr, the product could be completely switched from homoallylic alcohols to β,γ-unsaturated carboxylic acids. The mechanism proposed by the authors for the formation of homoallylic alcohols **18** was depicted in Scheme 11, which was started with the addition of copper hydride **A** (generated *in situ* by the reaction of CuCl with a base and a hydrosilane) to allene **17** at the less hindered site to form allylcopper intermediate **B**, followed by regioselective reaction with CO<sub>2</sub> at the γ-position via six-membered transition state to produce copper carboxylate **C**. Later, further reduction of this intermediate by the hydrosilane generated a copper alkoxide **E** via the silyl copper ketal derivative **D**. Subsequently, σ-bond metathesis with the hydrosilane



**Scheme 6.** (a) Cu-catalyzed region- and enantio-selective hydroxymethylation of styrene derivatives **11** with CO<sub>2</sub> using (EtO)<sub>3</sub>SiH as reducing agent; (b) Yu's hydroxymethylation of 1-phenyl-1,3-butadienes **13**.



Scheme 7. Proposed catalytic cycle for the reaction in Scheme 6a.

Scheme 8. Formation of the dimeric copper(I) species V via the reaction of Cu(OAc)<sub>2</sub>, dpbp, and (MeO)<sub>3</sub>SiH.Scheme 9. Cu-catalyzed asymmetric hydroxymethylation of 1,3-dienes **15** with CO<sub>2</sub> developed by Yu.

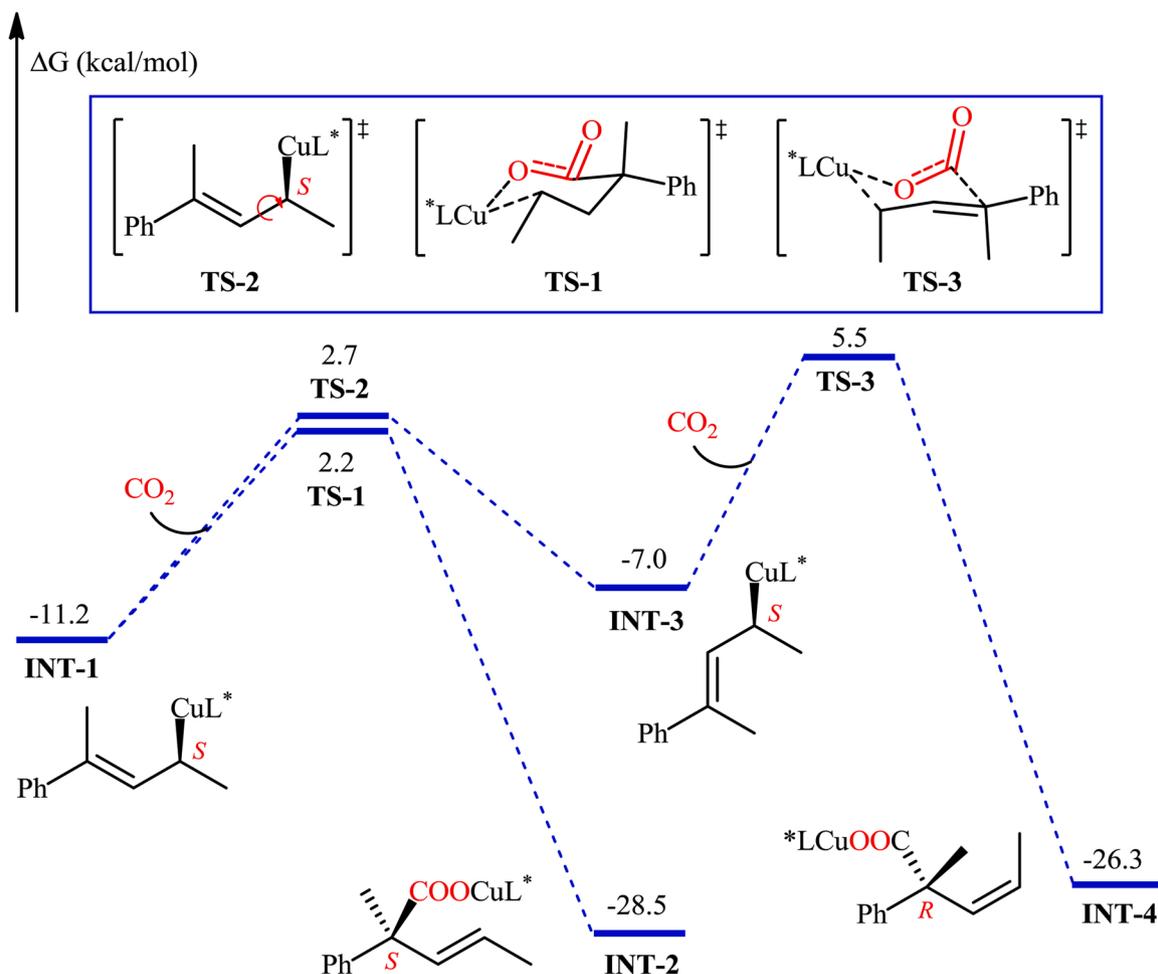
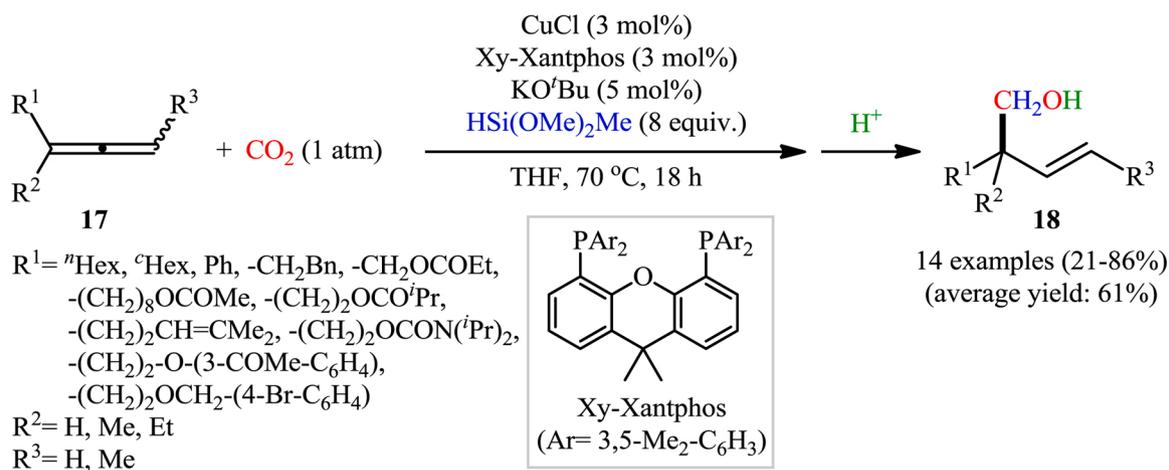


Fig. 2. Free energy profiles for the formation of chiral copper carboxylate species.

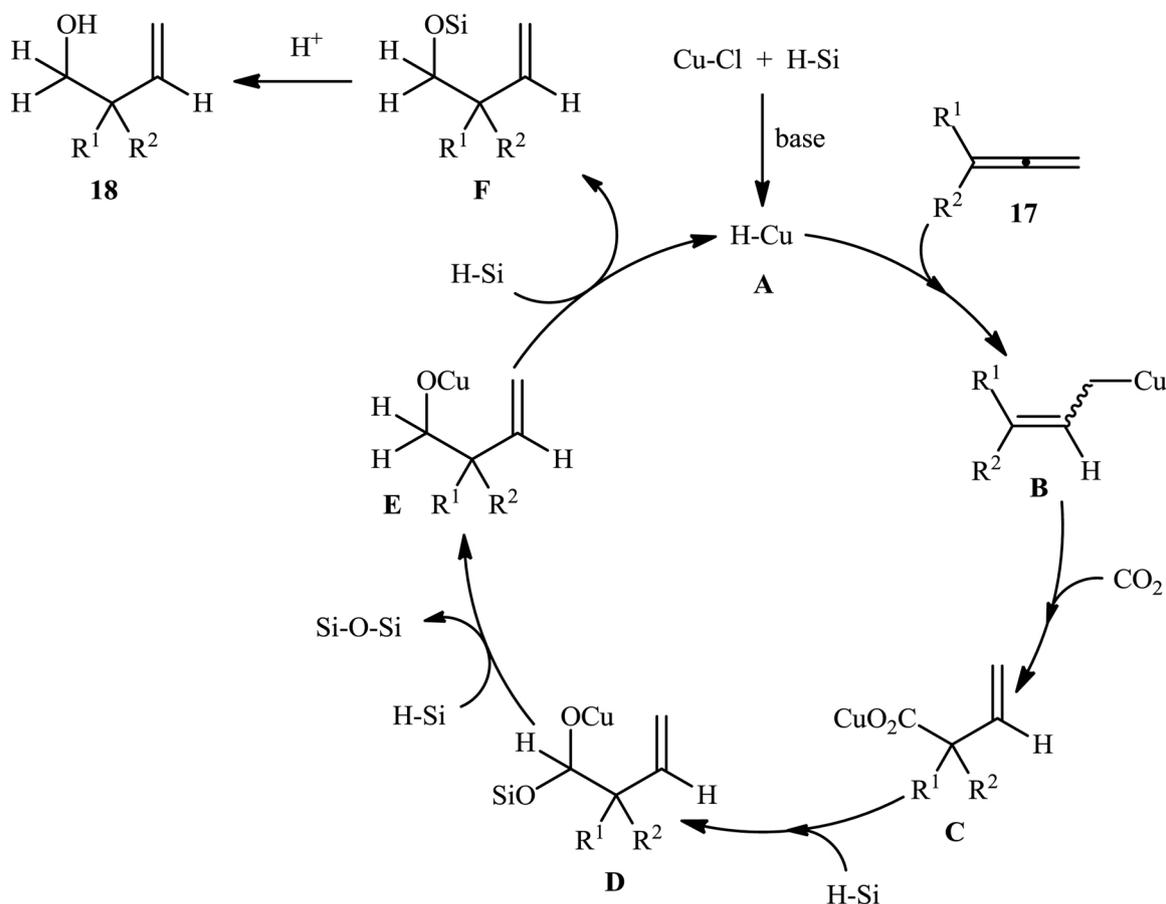


Scheme 10. Tsuji's synthesis of homoallylic alcohols **18**.

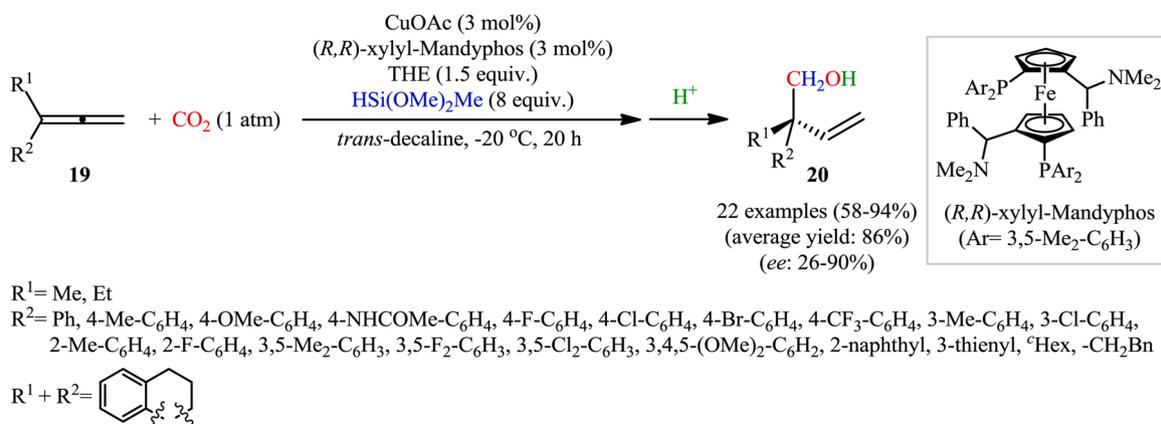
occurred to yield silyl ether **F** and regenerate **A** as the active catalyst species. Finally, protonation (workup) of **F** afforded the desired product **18**.

Recently, the enantioselective version of this transformation was disclosed by Ding et al. [40], who realized that the treatment of 1, 1-disubstituted allenes **19** with CO<sub>2</sub> and hydrosilane (Me(OMe)<sub>2</sub>SiH) in the presence of CuOAc as a catalyst, (*R,R*)-xylyl-Mandyphos as a chiral ligand, and 2,2,2-trifluoroethanol (TFE) as an additive afforded

the chiral homoallylic alcohols **20** bearing all-carbon quaternary centers in good to near quantitative yields and fair to excellent enantioselectivities (Scheme 12). Notably, this CO<sub>2</sub>-fixation reaction can be easily scaled up to produce multigram quantities of chiral homoallylic alcohols without sacrificing the yield or outcome of the protocol. The authors nicely showed the synthetic utility of the prepared chiral homoallylic alcohols in the preparation of various useful chiral chemicals (e.g., quaternary aldehydes,  $\delta$ -lactones, dihydrofurans). Moreover, they



Scheme 11. Proposed mechanism for the formation of homoallylic alcohols **18**.



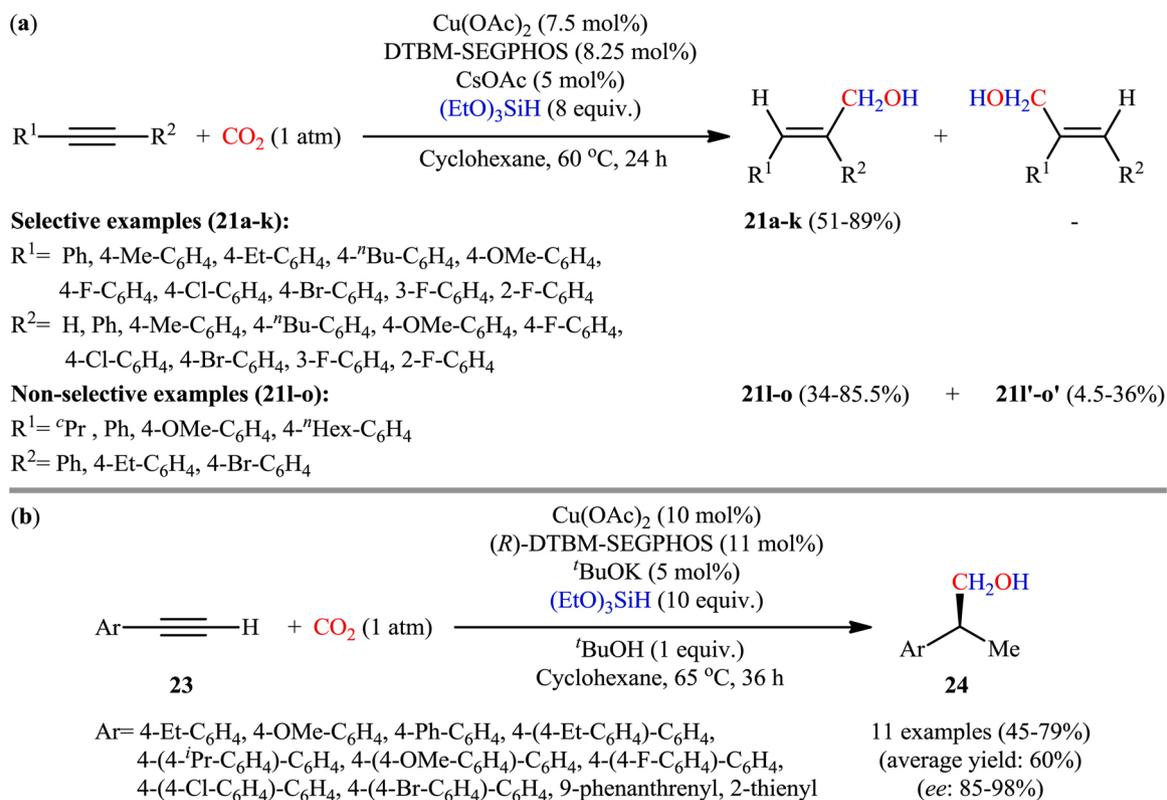
Scheme 12. Cu-catalyzed enantioselective hydroxymethylation of 1,1-disubstituted allenes **19** with atmospheric CO<sub>2</sub>.

successfully applied their protocol in the high yielding preparation of chiral drug (S)-atromepine.

#### 4. Hydroxymethylation of alkynes

After pioneering work by Gooßen's research group on the synthesis of *n*-alcohols through the sequential carboxylation and hydrogenation of terminal alkynes with CO<sub>2</sub> and molecular hydrogen [41], the first and only example of the direct hydroxymethylation of alkynes with CO<sub>2</sub> was very recently published by He, Ma, and co-workers [42]. In this study, fifteen allylic alcohols **22** were selectively synthesized through the treatment of various functionalized alkynes **21** with atmospheric CO<sub>2</sub> and HSi(OEt)<sub>3</sub> as the carbonyl and hydride sources, respectively, in the

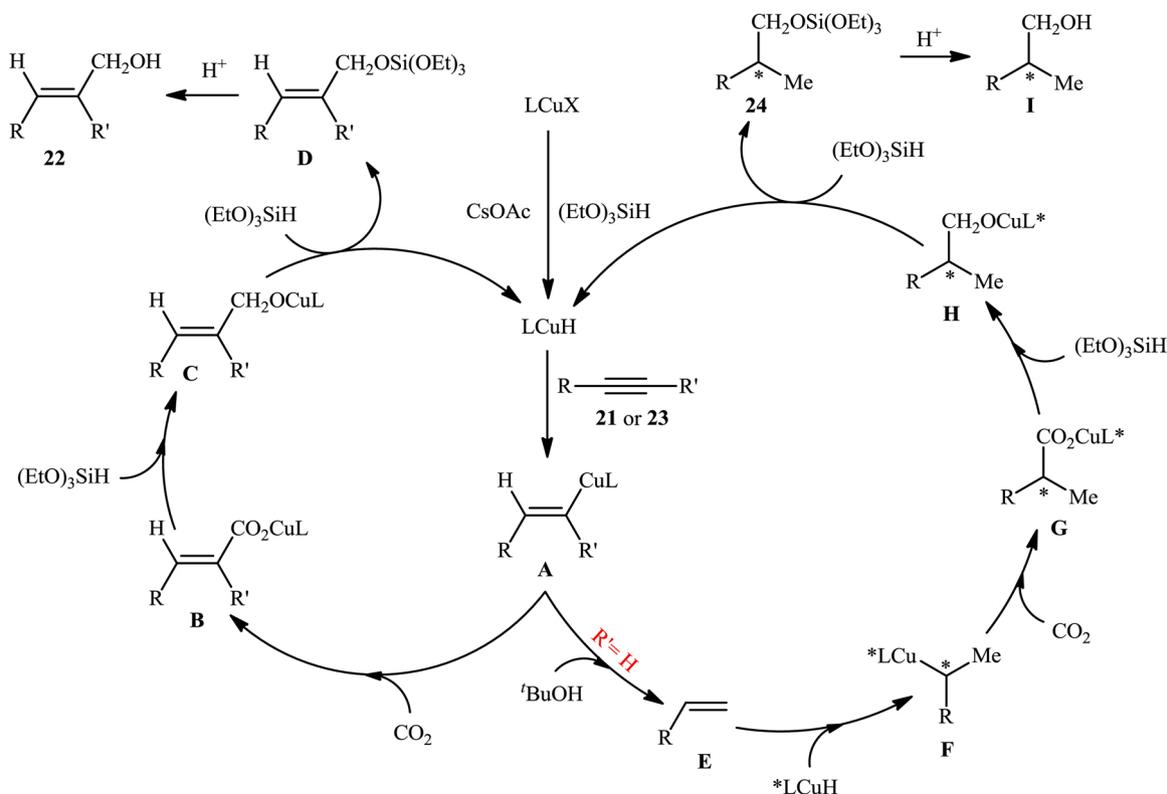
presence of Cu(OAc)<sub>2</sub>/CsOAc/DTBM-SEGPHOS (5,5'-Bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole, [(4,4'-bi-1,3-benzodioxole)-5,5'-diyl]bis[bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphine]) combination as the catalytic system in cyclohexane at 60 °C (Scheme 13a). The optimized protocol tolerated both terminal and internal alkynes and afforded the desired allylic alcohols in modest to excellent yields and outstanding (*Z*)-selectivities. Listed below are some important information of the reactions: (i) the relative reaction rates of various alkynes followed the order: alkyl-aryl internal alkynes > aryl-aryl internal alkynes > terminal alkynes; (ii) the addition of CO<sub>2</sub> to terminal alkynes predominantly occurred at the terminal carbon; and (iii) unsymmetrical internal alkynes output a mixture of regioisomers. Interestingly, the addition of a proton source triggered the reductive



**Scheme 13.** (a) Hydroxymethylation of alkynes **21** with CO<sub>2</sub>; (b) Reductive hydroxymethylation of terminal alkynes **23**.

hydroxymethylation *via* a cascade sequence. Thus, by addition of <sup>t</sup>BuOH to the reaction mixture and switching of DTBM-SEGPHOS to (*R*)-DTBM-SEGPHOS, a variety of (hetero)aromatic terminal alkynes **23** reacted with CO<sub>2</sub> and HSi(OEt)<sub>3</sub> to give the corresponding enantiopure

homobenzylic alcohols **24** in moderate to good yields with high levels of enantioselectivity (Scheme 13b). Based on a series of control experiments and reported studies, the author suggested a plausible catalytic cycle for the formation of allylic and homobenzylic alcohols, which is



**Scheme 14.** Mechanistic possibilities for the fabrication of allylic alcohols **22** and homobenzylic alcohols **24**.

displayed in Scheme 14. In both cases, the reaction starts with the generation of vinylcopper intermediate A through the hydrocupration of *in situ* generated LCuH to the alkyne. In the absence of a proton source, intermediate A reacts with CO<sub>2</sub> to give the copper carboxylate B, which after reduction with HSi(OEt)<sub>3</sub> converts to intermediate C. Next, transmetalation of this intermediate with hydrosilane affords silyl ether D and regenerates the LCuH species. Finally, protonation of intermediate D provides the observed homoallylic alcohol 22 (Scheme 14, cycle A). While in the presence of a proton source (tBuOH), prior protonation of vinylcopper A forms the alkene E, that after hydrocupration gives benzylic copper species F. Subsequently, carboxylation of intermediates F leads to carboxylcopper species G. Later, reduction of G with hydrosilane yields silyl ether intermediate H. Finally, protonation of intermediate H affords the desired homobenzylic alcohol 24 (Scheme 14, cycle B). Finally, it should be noted that transition metal complexes play important role in hydroxymethylation of unsaturated hydrocarbons with CO<sub>2</sub> and synthesis of organic compounds [43–61].

## 5. Conclusion

Primary alcohols are not only recognized as powerful and valuable building blocks for organic synthesis but also extensively used in industry as solvents as well as plasticizers and detergents raw materials. Today in industry, this class of alcohols are mainly produced through a multiple-step process consisting of hydroformylation of alkenes, purification of the generated aldehydes, and then hydrogenation of aldehydes to alcohols using molecular hydrogen. Therefore, it is highly desired to develop a one-pot tandem hydroformylation/hydrogenation process in which the alcohol would be directly collected from the reaction mixture. As showed in this review, recently direct reductive hydroxymethylation of unsaturated hydrocarbons with CO<sub>2</sub> has emerged as an efficient new method for the construction of primary alcohols which beside the simplification and shortening of the synthetic schemes merits from inexpensive and easily available starting materials. As illustrated, various unsaturated hydrocarbons including alkenes, allenes, and alkynes were applicable to this page of alcohol synthesis. Importantly, several chiral catalytic systems were also developed which allow the preparation of optically active products with high degree of enantioselectivities. Moreover, most of the reactions summarized in this Mini-Review can be scaled up to the gram quantities without difficulty. Nevertheless, there are still many challenges that have yet to be resolved. For example: (a) most of the reactions outlined in this review required harsh conditions (high temperature and/or high CO<sub>2</sub> pressure). Thus, there is a need for further studies exploring the novel catalytic systems, which can allow these transformations under milder and more practical conditions; (b) the asymmetric synthesis of alcohols using CO<sub>2</sub> as the hydroxymethyl source is a great challenge and of course further research should be focused on development of efficient methodologies for the asymmetric synthesis of alcohols using this chemistry; and (c) due to infancy of this chemistry, the substrate scope is still narrow and generality of this synthetic procedure should be more examined.

## Declaration of Competing Interest

The authors report no declarations of Interest.

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