Cobalt- and rhodium-catalyzed carboxylation using carbon dioxide as the C1 source

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Abstract

Carbon dioxide (CO_2) is one of the most important materials as renewable chemical feedstock. In this review, the Co- and Rh-catalyzed transformation of CO_2 via carbon–carbon bond-forming reactions is summarized. Combinations of metals (cobalt or rhodium), substrates, and reducing agents realize efficient carboxylation reactions using CO_2. The carboxylation of propargyl acetates and alkenyl triflates using cobalt complexes as well as the cobalt-catalyzed reductive carboxylation of α,β-unsaturated nitriles and carboxyamides in the presence of Et_2Zn proceed. A Co complex has been demonstrated to act as an efficient catalyst in the carboxylation of allylic $C(sp^3)$–H bonds. Employing zinc as the reductant, carboxyzincation and the four-component coupling reaction between alkyne, acrylates, CO_2, and zinc occur efficiently. Rh complexes also catalyze the carboxylation of arylboronic esters, $C(sp^2)$–H carboxylation of aromatic compounds, and hydrocarboxylation of styrene derivatives. The Rh-catalyzed [2 + 2 + 2] cycloaddition of diynes and CO_2 proceeds to afford pyrones.

Introduction

Carbon dioxide (CO_2) is one of the most important materials as renewable feedstock [1-4]. However, the thermodynamic and kinetic stability of CO_2 sometimes limits its utility. Classically, harsh reaction conditions such as high temperature and high pressure of CO_2 were required. To overcome these problems, the use of transition-metal catalysts has been considered as a fundamental and reliable method. In the last decade, considerable attention has been focused on the development of the catalytic fixation of CO_2 via carbon–carbon (C–C) bond formation

using a variety of organic compounds as starting materials [5-20]. A key factor for the successful catalytic fixation of CO_2 is the carbon–metal bond formation when transition metals are used as the catalyst. In addition, the choice of suitable reducing agents is also crucial for realizing effective carboxylation reactions.

In this review, the Co- and Rh-catalyzed transformations of CO_2 via C–C bond-forming reactions are summarized. First, we

describe Co-catalyzed carboxylation reactions, including the carboxylation of propargyl acetates and alkenyl triflates. Then, the Co-catalyzed reductive carboxylation of α,β-unsaturated nitriles and carboxyamides is addressed. In addition, a Co catalyst can catalyze the allylic C(sp^3)–H carboxylation of allylarenes when a suitable ligand is used. In the presence of zinc powder, the Co-catalyzed carboxyzincation of alkynes and the four-component coupling reaction between alkyne, acrylates, CO$_2$, and zinc proceed in an efficient manner. Visible-light-driven hydrocarboxylation reactions are shown. We also summarize carboxylation reactions catalyzed by rhodium that is a homologous element of cobalt. Carboxylations of arylboronic esters are described. Rh complexes are also effective catalysts in C(sp^2)–H carboxylation reactions. Employing Et$_2$Zn or visible light, the Rh-catalyzed hydrocarboxylation of styrene derivatives has been achieved. Furthermore, the formation of pyrones from diynes and CO$_2$ can be effectively catalyzed by Rh complexes.

## Review
Cobalt catalysts
Carboxylation of propargyl acetates

Allyl and propargyl electrophiles, such as halides and esters, are well known as efficient reagents in transition-metal-catalyzed C–C bond-forming reactions [21-23]. In particular, the carboxylation of allyl esters with CO$_2$ has been catalyzed by Pd or Ni under electrochemical reaction conditions [24,25]. For catalytic reactions using reducing agents, Martin reported Ni-catalyzed regiodivergent carboxylation of allyl acetates in the presence of Mn as the reductant [26]. Mita and Sato found that Pd-catalyzed carboxylation of allylic alcohols proceeded using Et$_2$Zn as the reducing agent [27]. The carboxylation of propargyl chlo-

ride was reported as one of the examples concerning the Ni-catalyzed carboxylation of benzyl chlorides [28].

We have found that Co complexes can catalyze the carboxylation of propargyl acetates with CO$_2$ using Mn powder as the reducing agent [29]. Thus, the carboxylation of a propargyl acetate **1a** was performed in the presence of CoI$_2$(phen) (phen = 1,10-phenanthroline) and Mn powder (3.0 equiv) in *N,N*-dimethylacetamide (DMA) under an atmospheric pressure of CO$_2$ at room temperature (Scheme 1). Under optimized reaction conditions, the carboxylated product **2a-Me** was obtained in 83% yield after derivatization to the corresponding methyl ester. In the absence of the Co catalyst, **2a-Me** was not obtained. Moreover, Mn powder proved to be essential for the carboxylation to proceed. Using CoI$_2$(bpy) (bpy = 2,2′-bipyridine) as the catalyst afforded **2a-Me** in 76% yield, whereas CoI$_2$(PPh$_3$)$_2$ and CoI$_2$(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane) suppressed the carboxylation.

The carboxylation of various propargyl acetates containing the trimethylsilyl (TMS) group as the R^1 group proceeded under the optimal reaction conditions, affording the corresponding carboxylic acids **2b–e** in good-to-high yields (Scheme 2). Notably, the ester and chloro functionalities in **2b** and **2c**, respectively, were compatible with the reaction conditions. For the carboxylation of tertiary-alcohol-derived acetates to the corresponding carboxylic acids **2d,e**, CoI$_2$(bpy) was found to be an effective catalyst. The yields of product **2** decreased when less bulky substituents (R^1) were used. Thus, **1f** (R^1 = *tert*-butyldimethylsilyl) afforded the corresponding product **2f** in 88% yield, whereas **1g** (R^1 = *t*-Bu) and **1h** (R^1 = Cy) afforded **2g** and **2h** in 57% and 26% yields, respectively.
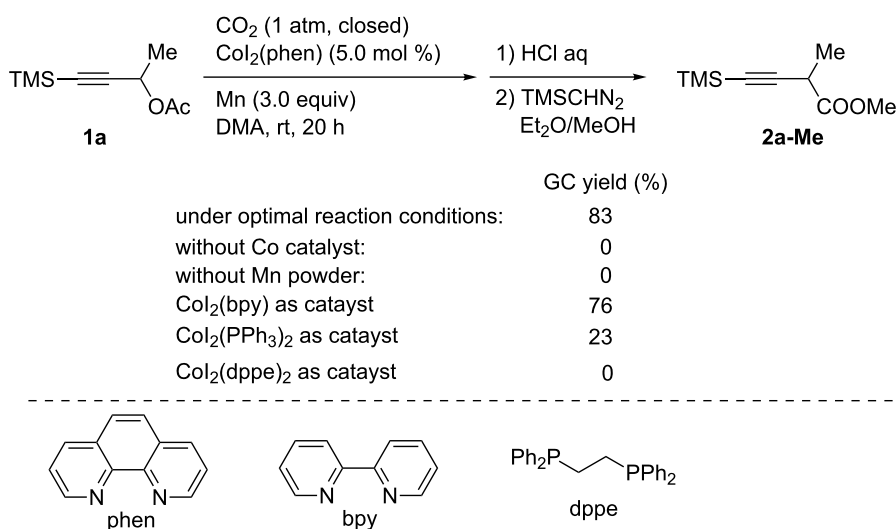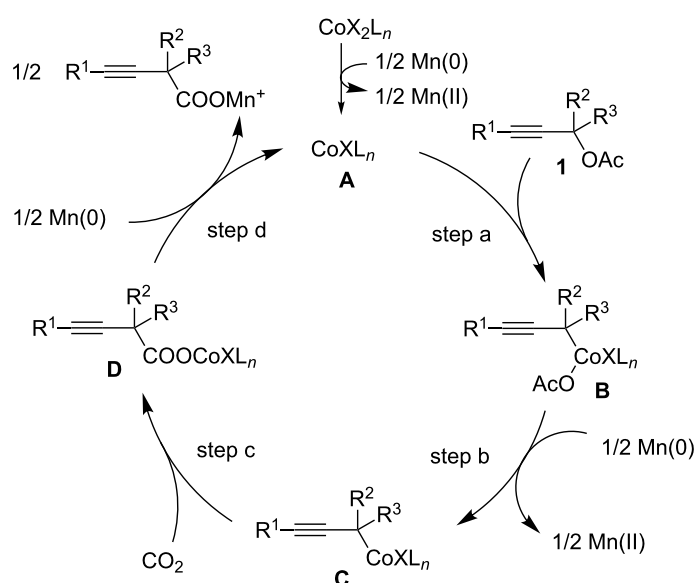

Scheme 1: Optimization of the Co-catalyzed carboxylation of **1a**.
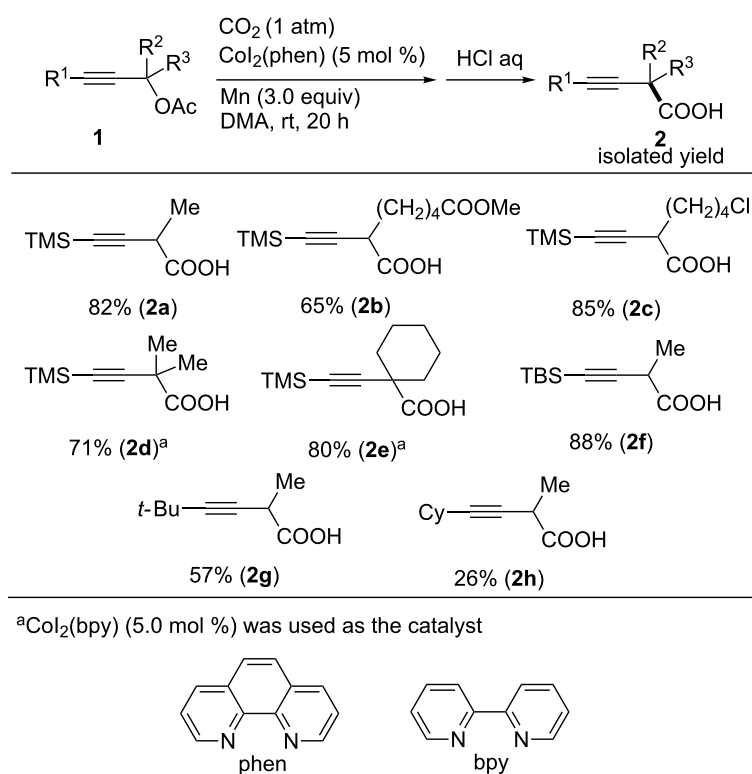
Scheme 2: Co-catalyzed carboxylation of propargyl acetates **1**.

Scheme 3 presents a plausible reaction mechanism for this transformation. Accordingly, a Co(I) catalytic species **A** is first generated by the reduction of Co(II) with Mn. Secondly, the oxidative addition of the C–O bond in **1** occurs, affording Co(III)

intermediate **B** (step a) [30]. Next, the propargyl Co(III) species **B** is reduced by Mn, producing the corresponding propargyl Co(II) intermediate **C** (step b). Subsequently, the nucleophilic Co species **C** reacts with CO_2, which provides carboxylate

Scheme 3: Plausible reaction mechanism for the Co-catalyzed carboxylation of propargyl acetates **1**.

Co(II) intermediate **D** (step c). Finally, the reduction of **D** with Mn affords the corresponding carboxylate, regenerating the Co(I) catalytic species **A** (step d).

Carboxylation of alkenyl and aryl triflates

The catalytic carboxylation of aryl halides and pseudohalides using CO_2 is an important reaction to yield benzoic acid derivatives. In 2009, Martin reported the Pd-catalyzed carboxylation of aryl bromides using $ZnEt_2$ as the reductant [31]. In 2012, we first reported the Ni-catalyzed carboxylation of aryl chlorides and vinyl chlorides using Mn powder as the suitable reductant [32]. These reactions can be performed under mild conditions, i.e., an atmospheric pressure of CO_2 at room temperature.

We also reported the Co-catalyzed carboxylation of alkenyl and aryl trifluoromethanesulfonates (triflates) as substrates [33]. As a model reaction (Scheme 4), alkenyl triflate **3a** was selected as the substrate, and the carboxylation of **3a** was performed using Mn powder (1.5 equiv) as the reductant in DMA as the solvent under an atmospheric pressure of CO_2 at room temperature. Employing $CoI_2(Me_2phen)$ (Me_2phen = 2,9-dimethyl-1,10-phenanthroline) as the catalyst, **4a-Me** was obtained in 86% yield after esterification. Other bidentate ligands such as bpy, phen, and dppe were not suitable for this reaction. Control experiments revealed that both the Co catalyst and the Mn reductant were indispensable to the reaction.

The carboxylation of diverse alkenyl triflates was also examined. As a result, the desired carboxylic acids **4a–k** were ob-
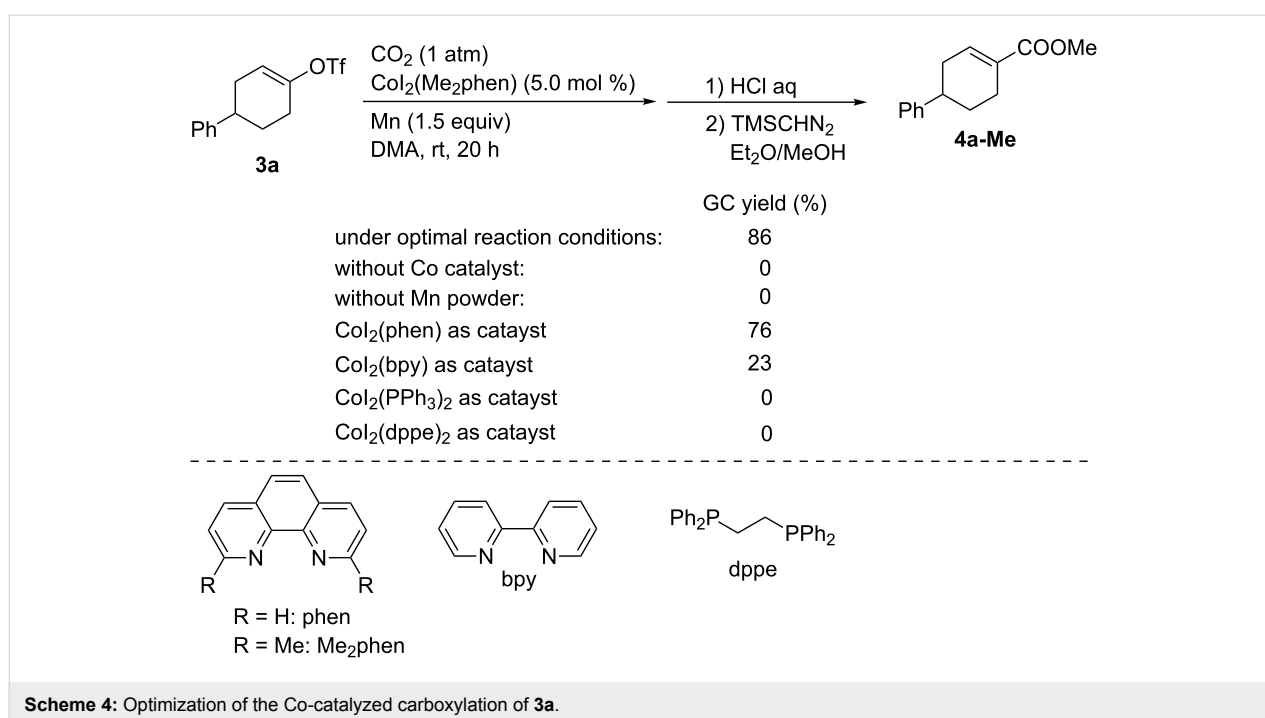
tained in good-to-high yields, as shown in Scheme 5. Notably, the ester and *p*-toluenesulfonate functionalities in **4c** and **4d**, respectively, were tolerated. An indole-functionalized substrate **3f** was converted into its corresponding carboxylic acid **4f**. Conjugated alkenyl triflates **3g–i** were also subjected to the reaction, and the desired carboxylic acids **4g–i** were obtained in moderate-to-high yields. Furthermore, the seven-membered cyclic substrate **3j** that was derived from cycloheptanone afforded its corresponding conjugated carboxylic acid **4j** in 75% yield. The alkenyl triflate **3k** prepared from the corresponding aldehyde was also carboxylated, and its corresponding product **4k** was obtained in moderate yield.

The catalyst $CoI_2(Me_2phen)$ was also effective with sterically hindered aryl triflates: the carboxylation of mesityl triflate (**5**) at 40 °C proceeded successfully, affording **6** in 77% yield (Scheme 6)
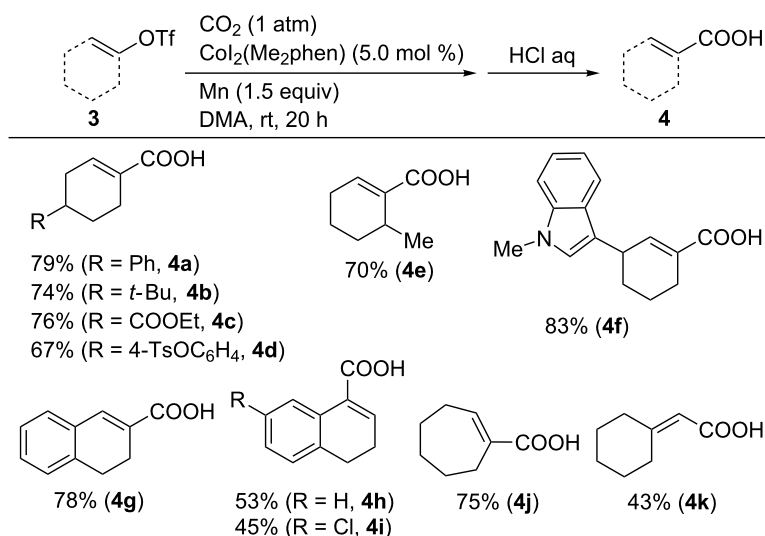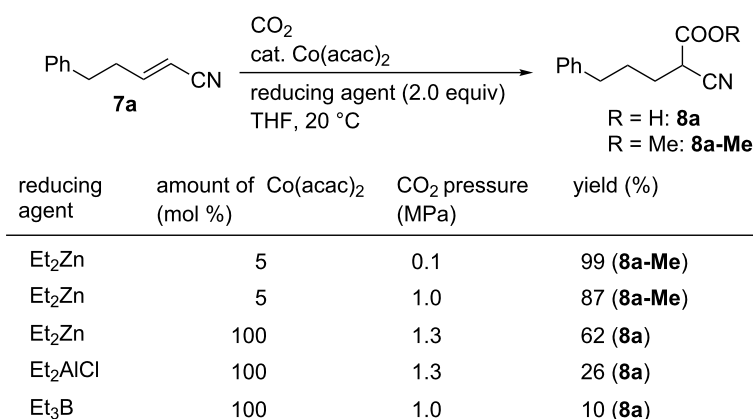
Carboxylation of α,β-unsaturated nitriles and esters

α,β-Unsaturated carbonyl compounds are good substrates for conjugate additions that use a catalytic amount of a metal complex and a stoichiometric amount of reductant, as exemplified by the reductive aldol reaction of α,β-unsaturated nitriles catalyzed by cobalt using phenylsilane as the reductant [34].

Yamada found that the reductive carboxylation of α,β-unsaturated compounds with CO_2 proceeded in the presence of Co catalysts and reductants (Scheme 7) [35,36]. When the reaction of 5-phenylpent-2-enenitrile (**7a**) was performed in the pres-


	GC yield (%)
under optimal reaction conditions:	86
without Co catalyst:	0
without Mn powder:	0
$CoI_2(phen)$ as catayst	76
$CoI_2(bpy)$ as catayst	23
$CoI_2(PPh_3)_2$ as catayst	0
$CoI_2(dppe)_2$ as catayst	0

Scheme 4: Optimization of the Co-catalyzed carboxylation of **3a**.

Scheme 5: Co-catalyzed carboxylation of vinyl triflates **3**.
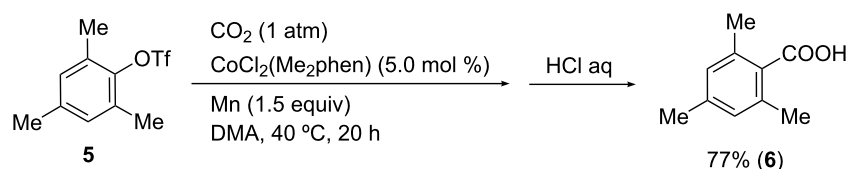
Scheme 6: Co-catalyzed carboxylation of a sterically hindered aryl triflate **5**.

reducing agent	amount of Co(acac)$_2$ (mol %)	CO$_2$ pressure (MPa)	yield (%)
Et$_2$Zn	5	0.1	99 (**8a-Me**)
Et$_2$Zn	5	1.0	87 (**8a-Me**)
Et$_2$Zn	100	1.3	62 (**8a**)
Et$_2$AlCl	100	1.3	26 (**8a**)
Et$_3$B	100	1.0	10 (**8a**)

Scheme 7: Optimization of the Co-catalyzed carboxylation of **7a**.

ence of catalytic Co(acac)$_2$ and with Et$_2$Zn as the reductant, the carboxylation proceeded to yield **8a-Me** after its derivatization to the corresponding methyl ester. In these reactions, the selection of the reductant is crucial: other reductants such as Et$_2$AlCl and Et$_3$B yielded the corresponding product in low yields even after using a stoichiometric amount of Co(acac)$_2$ at high pressure.

Under the optimal reaction conditions with the Co(acac)$_2$/Et$_2$Zn system, various α,β-unsaturated nitriles were carboxylated to the corresponding products, which were isolated as methyl esters (Scheme 8). Thus, compound **7** bearing alkyl, ether, ester, and halide substituents exhibited good reactivity. Cinnamonitrile afforded **8f-Me** in 81% yield using 10 mol % of catalyst. α-Phenyl-substituted α,β-unsaturated nitrile also reacted with
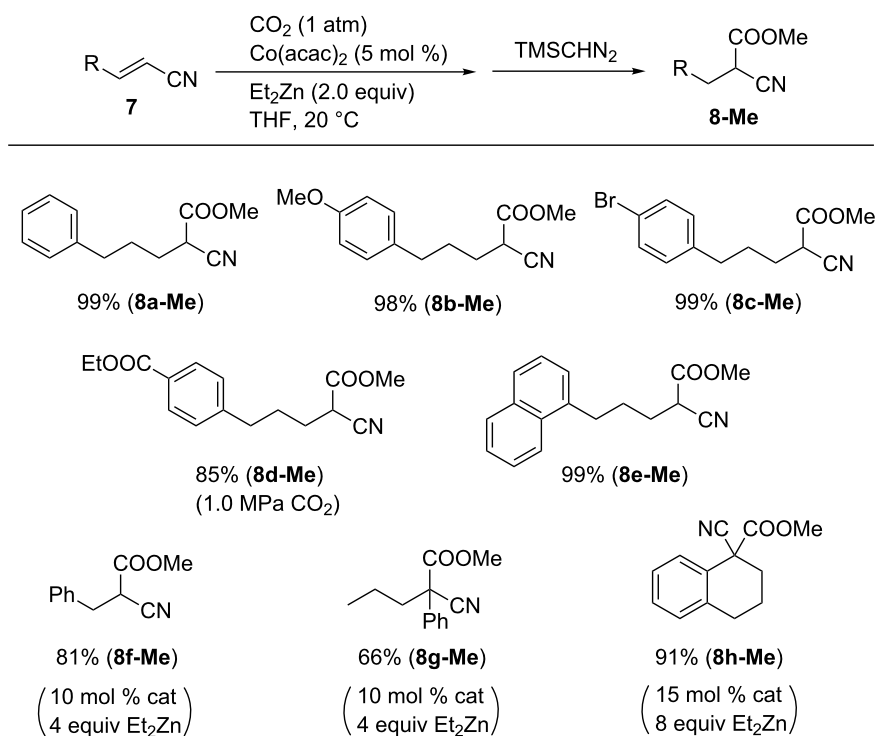
Scheme 8: Scope of the reductive carboxylation of α,β-unsaturated nitriles **7**.

CO_2, affording the carboxylated product **8g-Me** in good yield. In addition, compound **8h-Me** was obtained from the reaction of α-cyano-substituted dihydronaphthalene **7h** with CO_2 in the presence of 15 mol % of catalyst and 8 equiv of Et_2Zn.

The $Co(acac)_2/Et_2Zn$ system can also be applied to carboxylate α,β-unsaturated carboxamides **9** (Scheme 9). By using 10 mol % of $Co(acac)_2$ and 4 equiv of Et_2Zn, *N*-methylanilide derivatives **9a–f** were smoothly converted into the corresponding products **10a–f** in high yields. Trifluoromethyl and chloro substituents were tolerated in these reactions, judging by the formation of products **10c-Me** and **10d-Me**. With regard to other amide groups, morpholides **9g–i** could be used and benzylmethylamide- and diethylamide-bearing substrates, which afforded the corresponding products **10j-Me** and **10k-Me**, albeit with moderate yields.

## Allylic C(sp³)–H bond carboxylation

The development of methods for the catalytic carboxylation of less reactive C–H bonds with CO_2 is crucial regarding both C–H activation and CO_2 fixation processes. Mita and Sato reported a cobalt-catalyzed allylic C–H carboxylation of allyl-arenes (Scheme 10), in which 1-allyl-4-phenylbenzene (**11a**) was reacted with CO_2 (1 atm) in the presence of $AlMe_3$ (3 equiv) using catalytic amounts of a Co precursor and ligands

[37]. The catalytic system comprising $Co(acac)_2$ and Xantphos (4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) afforded the corresponding carboxylated product **12a-Me** in an NMR yield of 71% after CH_2N_2 treatment. In the reaction mixture, olefin isomers were also generated in 20% yield. The ligands were found to have a strong influence in yields and selectivity. Thus, the use of DPEphos (2,2′-bis(diphenylphosphino)di-phenyl ether), dppf (1,1′-bis(diphenylphosphino)ferrocene), dppp (1,3-bis(diphenylphosphino)propane), and bpy as ligands afforded the olefin isomerization product as the major product. Further screening of the reaction conditions revealed that the amount of $AlMe_3$ was critical: the product yield increased with decreasing $AlMe_3$ to 1.5 equiv. The concentration of **11a** also affected the efficiency of the reaction, and the isomerization of olefins could be suppressed at lower concentrations of **11a**, affording the desired **12a-Me** in 58% yield. With the addition of 1 equiv of CsF, the carboxylation was further accelerated to give **12a-Me** in 71% yield.

Using optimized reaction conditions, the substrate scope was examined (Scheme 11). Allylbenzene was converted into its corresponding carboxylated product **12a** in an isolated 68% yield, and various functionalized allylarenes bearing trifluoromethyl (**11b**) and alkoxy (**11c,d**) substituents were tolerated. The selectivity of the reaction was demonstrated with
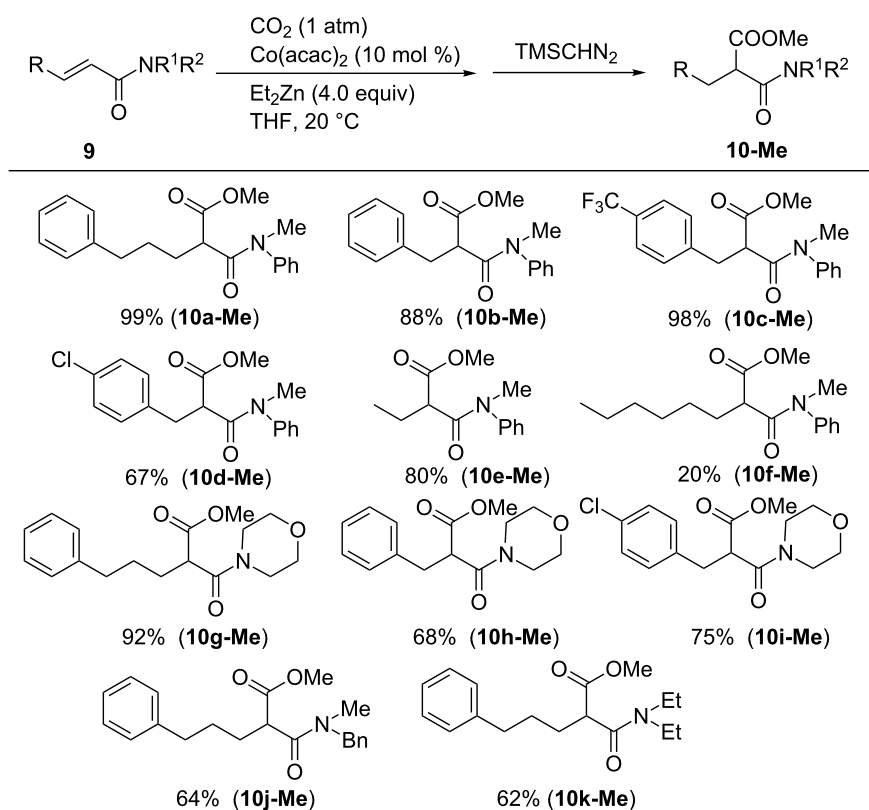
Scheme 9: Scope of the carboxylation of α,β-unsaturated carboxamides **9**.
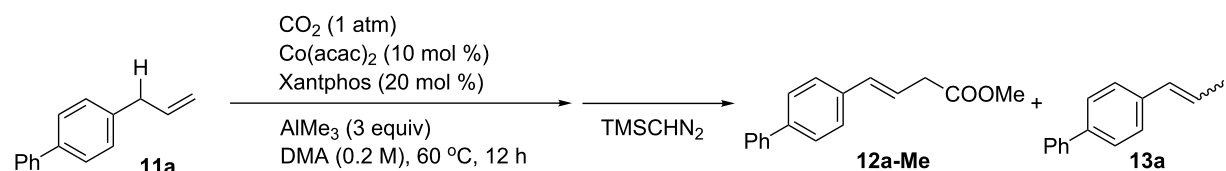
|	NMR yield (%)	
	12a-Me	**13a**
under the reaction conditions:	32	41
DPEphos as ligand	0	77
dppf as ligand	0	91
dppp as catayst	0	86
bpy as catayst	0	90
AlMe₃ (1.5 equiv)	45	31
AlMe₃ (1.5 equiv), 0.05 M in DMA	58	14
AlMe₃ (1.5 equiv), 0.05 M in DMA CsF (1 equiv)	71	20
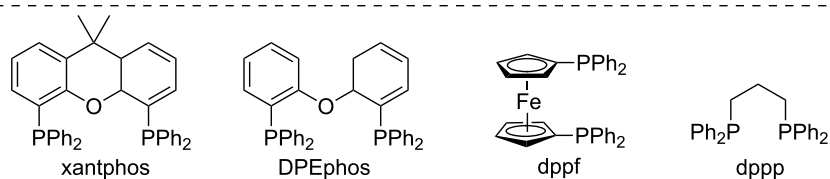
Scheme 10: Optimization of the Co-catalyzed carboxylation of **11a**.
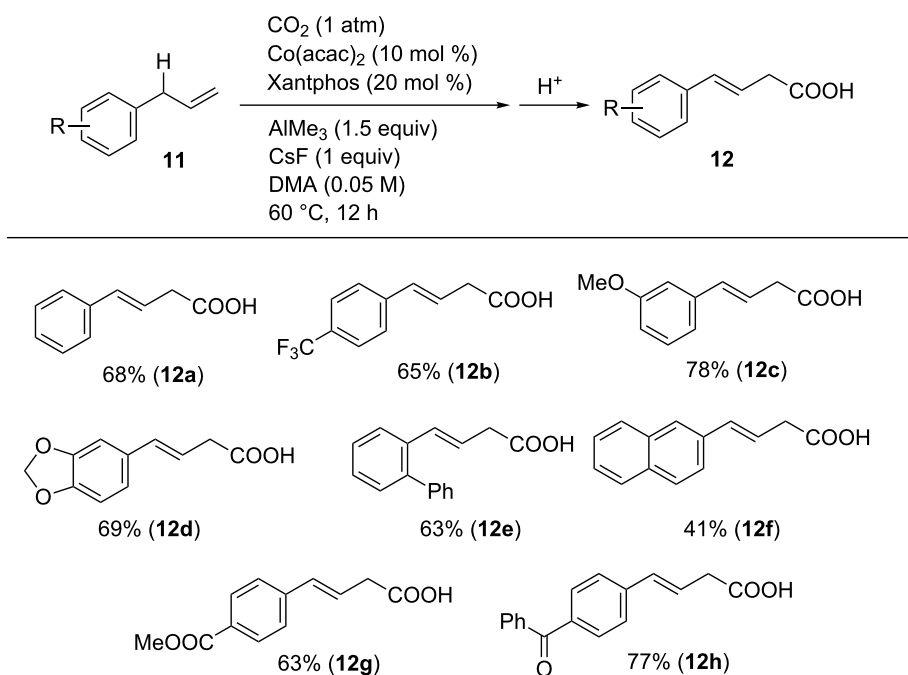
Scheme 11: Scope of the carboxylation of allylarenes **11**.

substrates **11g** and **11h** containing ester and ketone moieties, respectively, which are generally more reactive toward nucleophiles than CO_2.
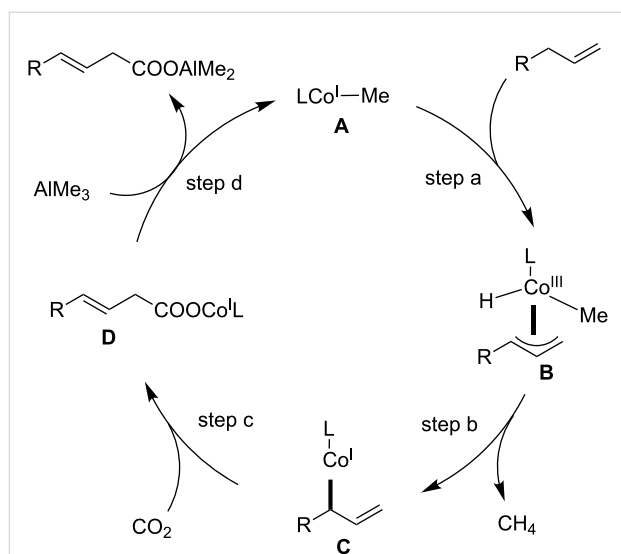
Notably, the Co-catalyst system was found to be applicable for the carboxylation of 1,3-diene derivatives **14** with CO_2

(Scheme 12), which afforded various hexa-3,5-dienoic acid derivatives. Diene **14a** was converted into the corresponding carboxylic acid **15a** in good yield. In addition, 1,4-dienes having cyclohexenyl and geminal diphenyl substituents (**14b** and **14c**) produced their corresponding linear carboxylic acids **15b** and **15c** in 78% and 57% yields, respectively. Substrate **14e**
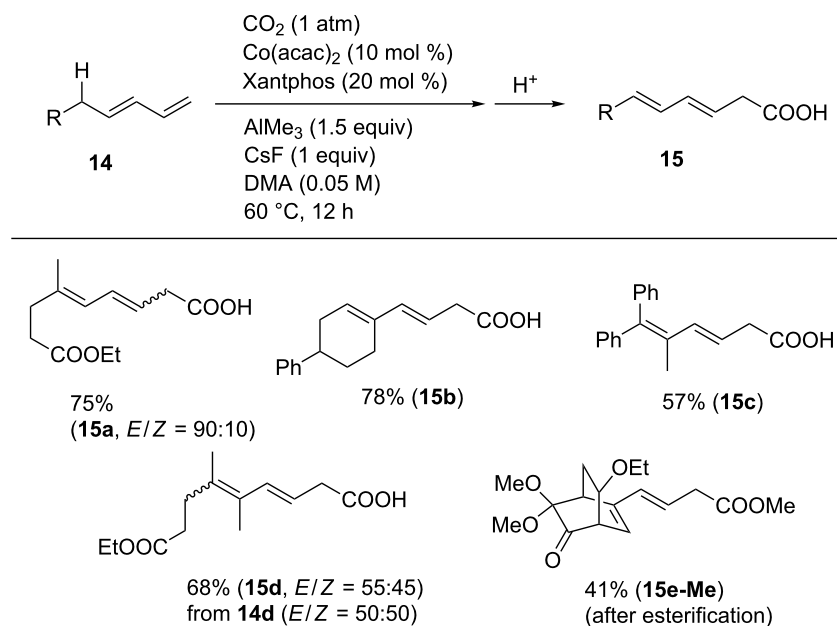
Scheme 12: Scope of the carboxylation of 1,4-diene derivatives **14**.

containing a bicyclo[2.2.2]octane framework with ketone and dimethyl ketal moieties was also converted and the corresponding product was isolated as the methyl ester **15e-Me** after esterification.

For the Co-catalyzed C(sp^3)–H carboxylation of allylarenes, a mechanism shown in Scheme 13 can be envisaged. The process starts with the generation of a low-valent methyl-Co(I) species **A** by the reaction of the Co(II) complex with AlMe$_3$. The C–C double bond of the substrate then coordinates to the metal, and
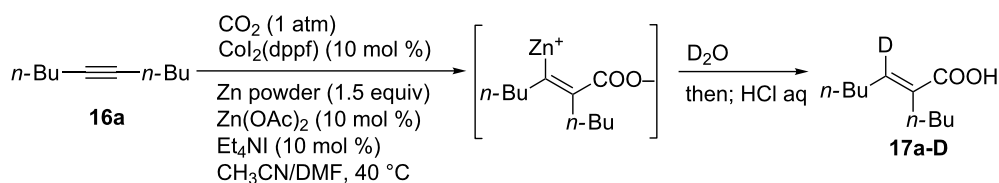
the subsequent cleavage of the adjacent allylic C–H bond affords η^3-allyl-Co(III) species **B** (step a). Subsequently, the reductive elimination of methane from **B** yields the low-valent allyl-Co(I) species **C** (step b). Then, C–C bond formation at the γ-position occurs via a reaction with CO$_2$, affording the carboxylate Co species **D** (step c). Finally, a linear carboxylated product is obtained by the transmetalation between **D** and AlMe$_3$, with the concomitant regeneration of methyl-Co(I) **A** (step d).
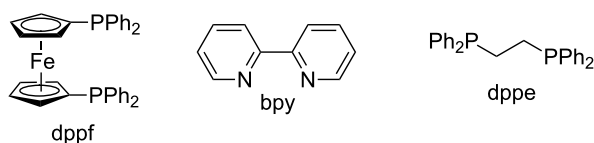
Carboxyzincation of alkynes

The good reactivity and high functional-group compatibility of organozinc compounds render them as important reagents in organic synthesis [38,39]. For their preparation, direct and useful methods such as the transition-metal-catalyzed carbozincation of alkynes that affords stereodefined alkenylzinc compounds have been developed. To date, a variety of organozinc reagents (RZnX and R$_2$Zn: R = aryl, alkyl, alkenyl, alkynyl, allyl, and benzyl groups) have been used in these reactions, and the corresponding alkenylzinc compounds can be prepared.

In this context, we reported the first carboxyzincation of alkynes using CO$_2$ and Zn metal powder in the presence of a cobalt complex as the catalyst (Scheme 14) [40]. 5-Decyne (**16a**) was treated with Zn powder (1.5 equiv) in the presence of CoI$_2$(dppf) (10 mol %), Zn(OAc)$_2$ (10 mol %), and Et$_4$NI (10 mol %) in a mixture of CH$_3$CN and DMF (v/v = 10:1) under an atmospheric pressure of CO$_2$ at 40 °C. When the reaction mixture was quenched with D$_2$O (>99% D), deuterated **17a-D** was obtained in a ^{1}H NMR yield of 80% with excellent deuterium incorporation ratio (94%) at the β-position. Al-

Scheme 13: Plausible reaction mechanism for the Co-catalyzed C(sp^3)–H carboxylation of allylarenes.

	NMR yield (%)
under optimal reaction conditions:	86
without Co catalyst:	0
without Zn(OAc)$_2$:	53
without Et$_4$NI	43
CoI$_2$(dppe) as catalyst	<5
CoI$_2$(bpy) as catalyst	0

Scheme 14: Optimization of the Co-catalyzed carboxyzincation of **16a**.

though Zn(OAc)$_2$ and Et$_4$NI were not indispensable for the reaction to proceed, these two additives caused an increased product yield. In contrast, the reaction did not occur in the absence of the catalyst. The use of the dppf ligand also proved to be essential, because other ligands such as dppe and bpy were not effective in the reaction.

After the reaction with 4-octyne (**17b**) under the aforementioned conditions, the reactions with I$_2$ and (PhSe)$_2$ produced **17b-I** and **17b-Se** in good yields (Scheme 15). Notably, **16b** was successfully subjected to the Pd-catalyzed Negishi coupling with aryl bromide, affording the corresponding sterically congested alkene **17b-Ar** in 56% yield after two steps. The Negishi coupling with benzyl chloride and the Cu-catalyzed allylation of allyl bromide also afforded the corresponding products **17b-Bn** and **17b-Allyl**, respectively, in good yields.

The reaction successfully proceeded even with unsymmetrical internal alkynes. For instance, 1-(1-naphthyl)-1-hexyne (**16c**) afforded **17c-D** in 82% yield with excellent regioselectivity (Scheme 16). Thienyl-substituted alkynes such as **16d** and **16e** selectively furnished **17d-D**, **17d-Allyl**, and **17e-D**. Unsymmetrical internal alkynes bearing 4-Me$_2$NC$_6$H$_4$ and 4-MeOC$_6$H$_4$ moieties (**16f** and **16g**) afforded **17f-D**, **17g-D**, and **17g-Ar** regioselectively after treatment with D$_2$O or aryl iodide/Pd catalyst.

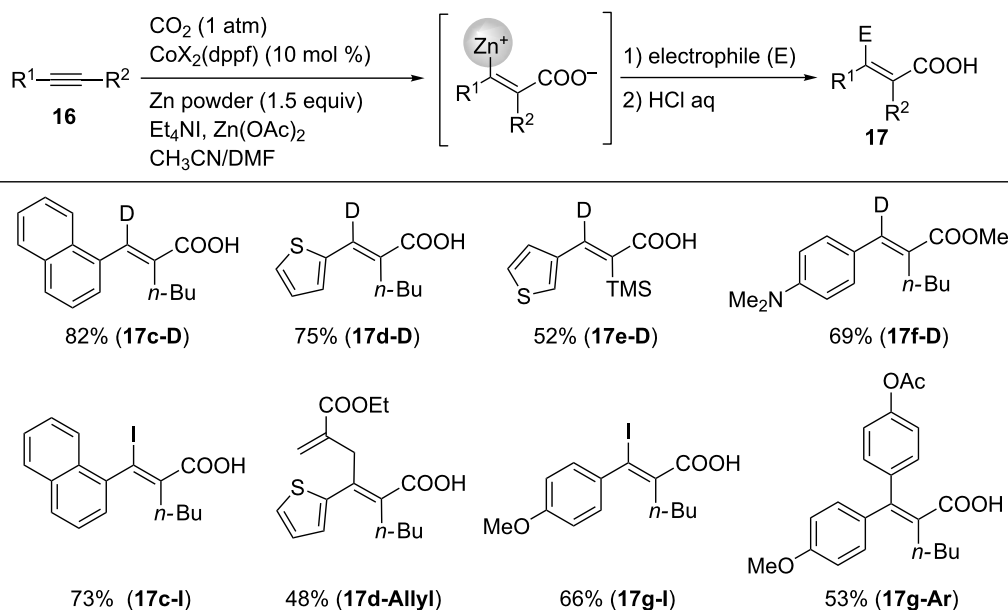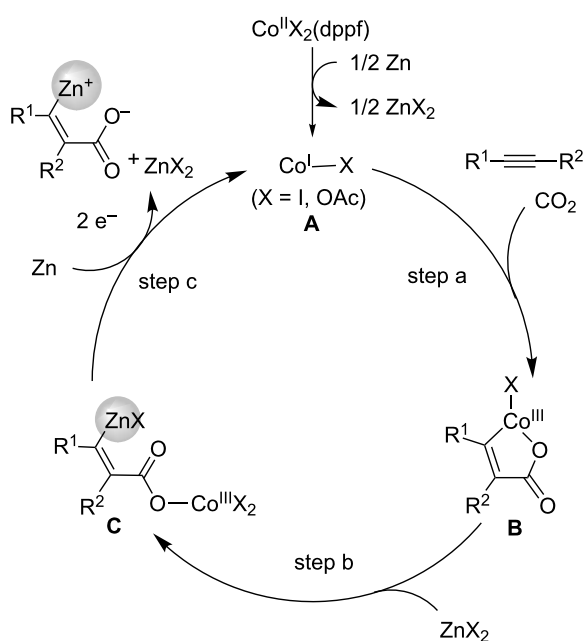A possible reaction mechanism for the carboxyzincation reaction is displayed in Scheme 17. First, the Co(II) precursor is reduced to Co(I) (**A**) in the presence of metallic Zn. The oxidative cyclization of **A** with alkyne **16** and CO$_2$ affords cobaltacycle **B** (step a). Next, the transmetalation between **B** and the Zn(II) species occurs, which affords the alkenylzinc intermediate **C** (step b) [41], which is then reduced with Zn powder, thereby giving the carboxyzincated product and regenerating Co(I) species **A** (step c).

We also achieved the four-component coupling of alkynes **16**, acrylates **18**, CO$_2$, and Zn metal, as depicted in Scheme 18 [40]. As a model reaction, the reaction using diphenylacetylene (**16h**), butyl acrylate (**18a**), CO$_2$, and Zn was performed. After treatment with H$_2$O and allyl bromide, the corresponding products **19a-H** and **19a-Allyl** were obtained in high yields. Chloro and trifluoromethyl functionalities were well tolerated under the reaction conditions, and **19b-Me** and **19c-Me** were obtained in 55% and 57% yields, respectively. The reaction of unsymmetrical 1-phenyl-1-hexyne with **18a** afforded **19d-H** and **19d-Et** regioselectively. In addition, an alkyne with a thiophene ring regioselectively produced the desired product **19e-Me** after methylation with MeI. It is noteworthy that an alkynoate was also converted into the corresponding product **19f-Me** in good yield. Methyl, ethyl, and *tert*-butyl acrylates **18b**, **18c**, and **18d**, respectively, also afforded the corresponding products. The product of the reaction with acrylamide **18e** was also obtained.

Scheme 19 shows a plausible reaction mechanism for this four-component coupling reaction. In a similar manner to that described for the carboxyzincation, the reduction of the Co(II)
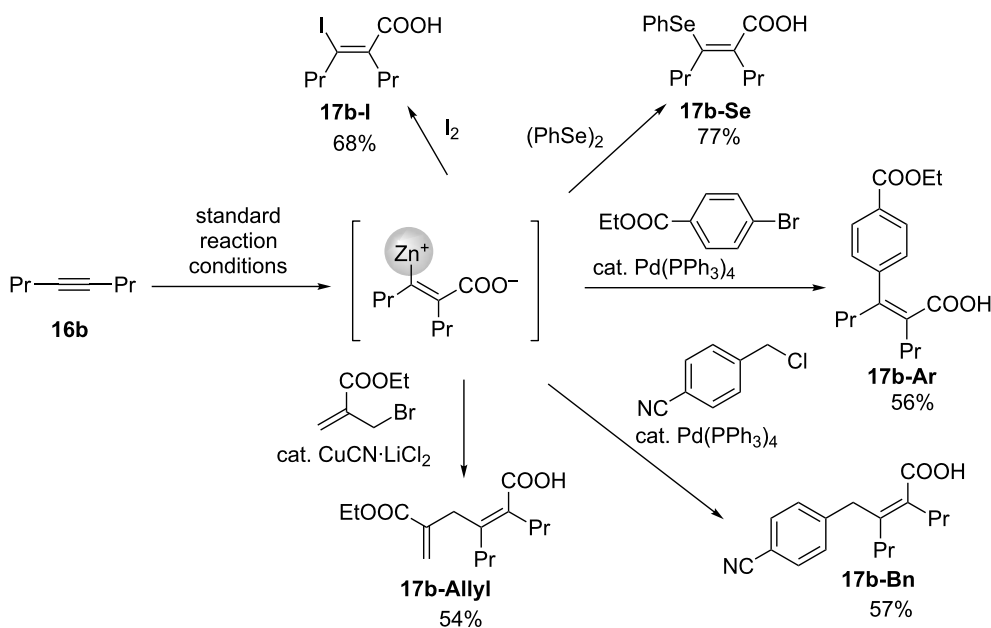
Scheme 15: Derivatization of the carboxyzincated product.

Scheme 16: Co-catalyzed carboxyzincation of alkynes **16**.

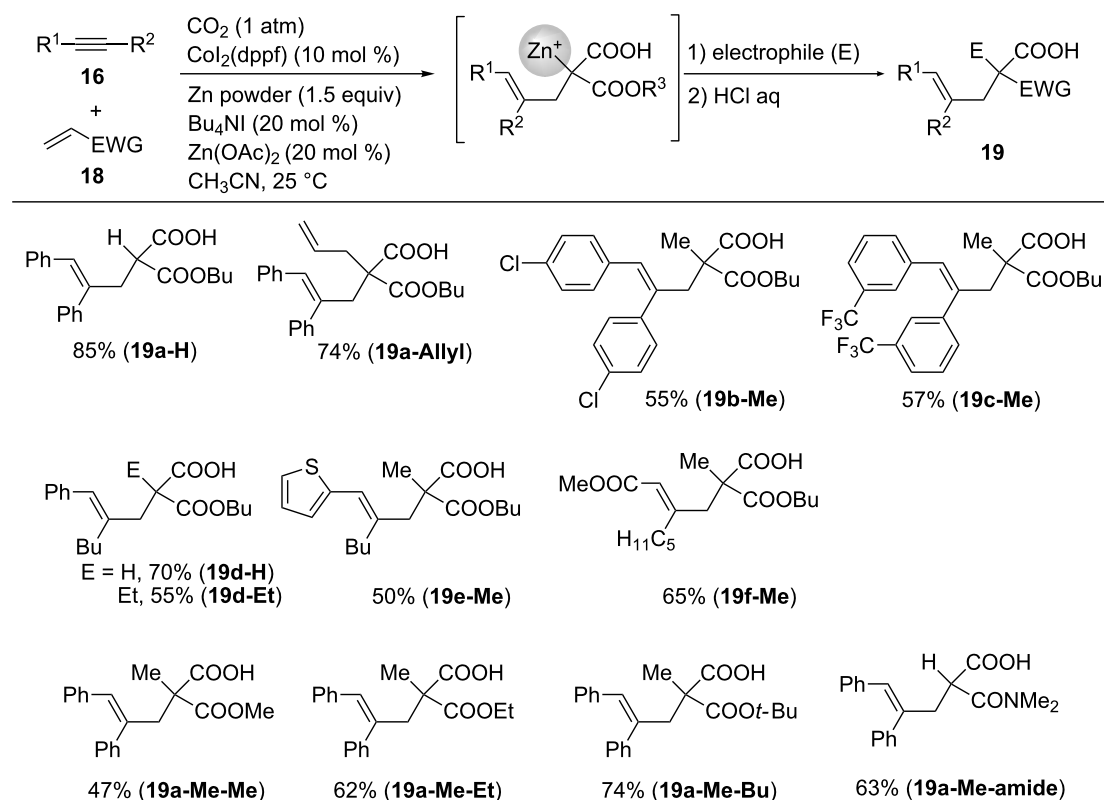**Scheme 17:** Plausible reaction mechanism for the Co-catalyzed carboxyzincation of alkynes **16**.

precursor to Co(I) species **A** in the presence of Zn metal activates the catalytic cycle. Next, the oxidative cyclization of **A**, alkyne **16**, and acrylate **18** proceeds regioselectively, and cobaltacycle **B** is formed (step a) [42]. Then, the insertion of CO_2 into the Co–C(sp^3) bond occurs, and the seven-membered Co intermediate **C** is obtained (step b). The transmetalation of **C**

with the Zn(II) species proceeds then to afford the alkenylzinc species **D** (step c). The subsequent two-electron reduction of **D** with Zn metal occurs, and the alkenylzinc intermediate **E** is subsequently obtained, along with the regeneration of Co(I) species **A** (step d). After 1,4-migration of zinc in **E**, product **19** is obtained (step e).
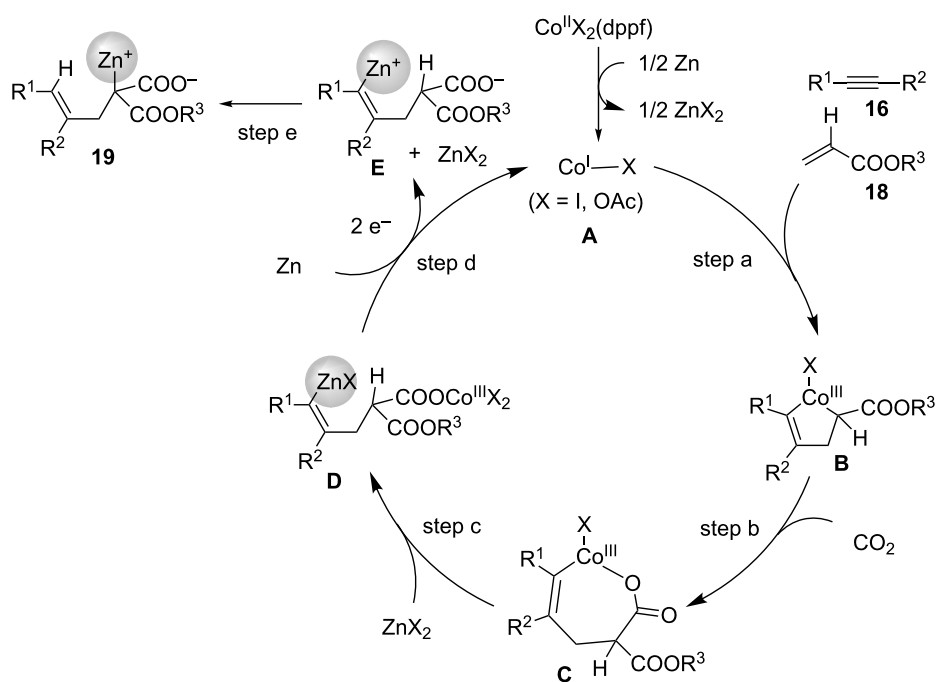
Visible-light-driven hydrocarboxylation of alkynes

The Use of photoenergy to organic synthesis is of importance, since the highly reactive intermediate can be generated by photochemical reaction such as electron transfer and energy transfer [43-45]. Among them, light-energy-driven CO_2 fixation reactions via C–C bond formation are promising in terms of mimicking photosynthesis. In 2015, Murakami et al. found the direct carboxylation reaction with CO_2 under photo-irradiation reaction conditions [46]. Jamison et al. also reported the synthesis of α-amino acid derivatives using amine and CO_2 [47]. Iwasawa disclosed the Pd-catalyzed carboxylation of aryl halides using CO_2 in the presence of an Ir photo-redox catalyst under visible-light irradiation conditions [48].

Zhao and Wu reported the visible-light-driven hydrocarboxylation of alkynes in the presence of a Co catalyst [49]. The reaction of alkynes was carried out using CoBr$_2$/dcype (dcype = bis(dicyclohexylphosphino)ethane) as catalysts in the presence of [Ir(ppy)(dtbpy)](PF$_6$) and iPr$_2$NEt as photoredox catalyst and a sacrificial reagent, respectively, in acetonitrile under an atmospheric pressure of CO_2 (Scheme 20). 1-Phenyl-1-propyne (**16n**) afforded hydrocarboxylated products as a mixture of

Scheme 18: Co-catalyzed four-component coupling of alkynes **16**, acrylates **18**, CO_2, and zinc.


Scheme 19: Proposed reaction mechanism for the Co-catalyzed four-component coupling.
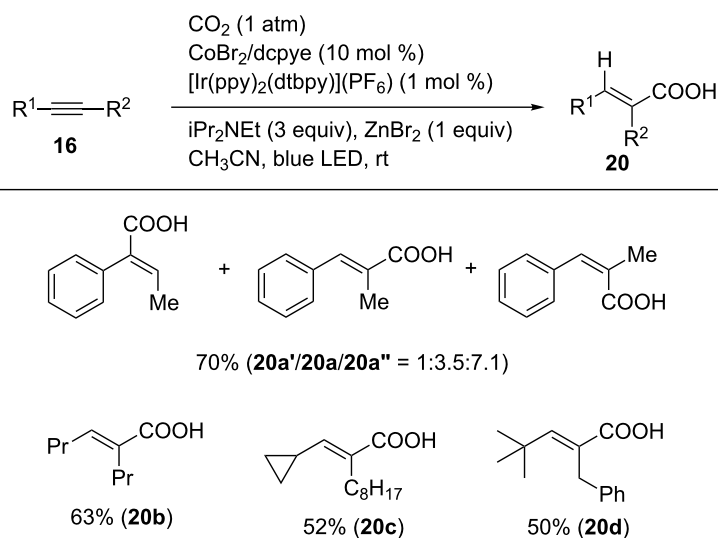
Scheme 20: Visible-light-driven hydrocarboxylation of alkynes.

regio- and stereoisomers. 4-Octyne (**16b**) afforded the product **20b** in good yield. Other unsymmetrical internal alkynes were converted to the corresponding products regioselectively.

The same protocol could be expanded to the synthesis of γ-hydroxybutenolides by using arylalkynes bearing *ortho*-esters of the aromatic ring (Scheme 21) [49]. Various alkynes **21** were
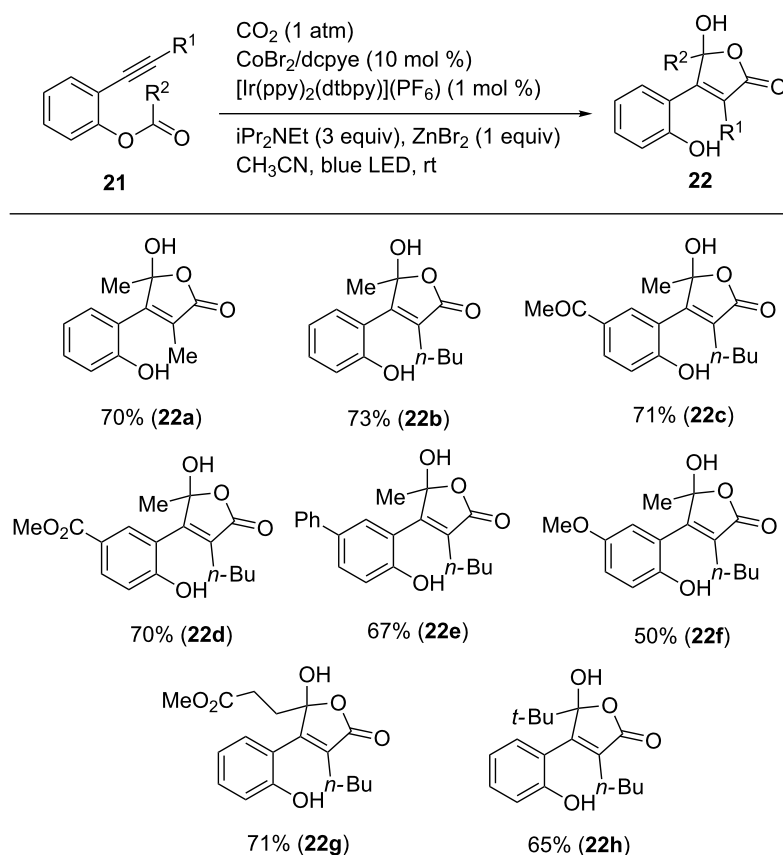
Scheme 21: Visible-light-driven synthesis of γ-hydroxybutenolides from *ortho*-ester-substituted aryl alkynes.

converted to the corresponding products in moderate-to-good yields. Notably, ketone (**22c**) and ester (**22d,g**) functionalities were tolerated in the reaction. A bulky ester moiety took part in the reaction and the corresponding product **22h** was obtained in good yield.

Furthermore, the same group discovered the one-pot synthesis of coumarin derivatives via hydrocarboxylation/alkene isomerization/cyclization reactions (Scheme 22) [49]. A key of the sequential reactions is a use of aromatic alkynes bearing a momo-protected hydroxy group at the *ortho* position on the aromatic ring (**23**). The corresponding coumarin derivatives were obtained in moderate-to-good yields. Notably, ketone (**24e**), ester (**24d**) moieties were tolerated in the reaction. In addition, 2-quinolones (**24f** and **24g**) were obtained using alkynes bearing a Boc protected carbamate in place of the MOM protected ether.

Scheme 23 shows a plausible reaction mechanism for these reactions. First, the Co(II) precursor is reduced to Co(I) **A** by the aid of an Ir photoredox catalyst and an amine under irradiation. The oxidative cyclization of **A** with **23** and CO_2 affords cobaltacycle **B** (step a). Next, the protonation of **B** affords an intermediate **C** (step b). Finally, two-electron reduction of Co(III) in **C** occurs and Co(I) species **A** regenerates (step c). $ZnBr_2$ may facilitate the step. Under the irradiation conditions, an *E*-isomer with aryl moiety can undergo a reversible isomerization to form the corresponding *Z*-isomer. Acid-mediated cyclization affords a coumarin derivative.

Rhodium catalysts
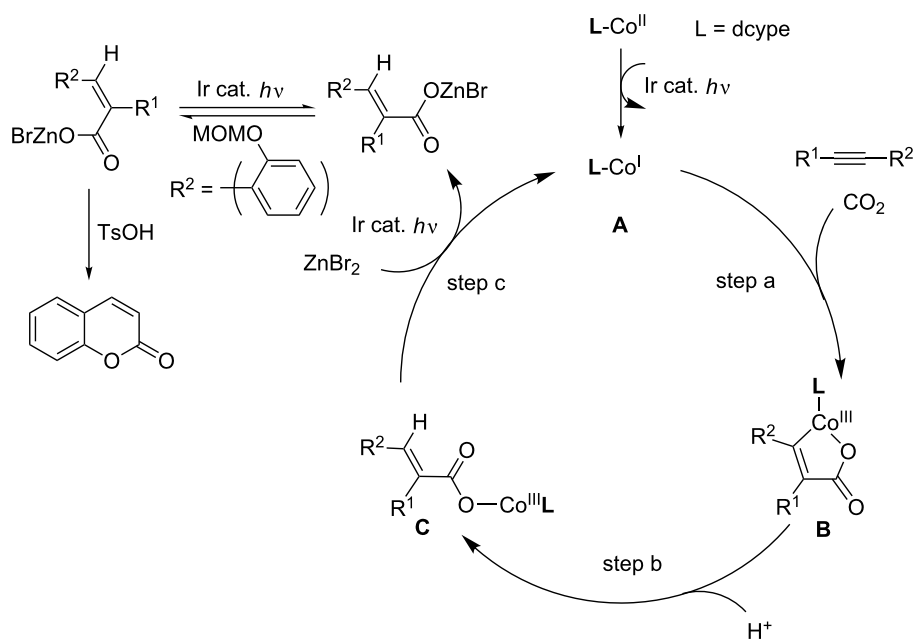## Carboxylation of aryl and alkenylboronic esters

Aryl and alkenylboronic acids or their esters are of interest in organic synthesis because they are commonly used for C–C bond-forming reactions such as Pd-catalyzed Suzuki–Miyaura coupling reactions [50-53].

Iwasawa et al. reported the Rh-catalyzed carboxylation of arylboronic esters using CO_2 (Scheme 24) [54]. The reaction of **25a** was performed using a catalytic amount of $[Rh(OH)(cod)]_2$ and 1,3-bis(diphenylphosphino)propane (dppp) in the presence of CsF as a base in 1,4-dioxane at 60 °C. Under these reaction conditions, the desired carboxylated product **26a** was obtained in 75% yield. A variety of arylboronic esters (**25b–i**) were converted into the corresponding carboxylic acids **26b–i** in good-to-high yields. It is noteworthy that ketone, ester, and nitrile functionalities in **26d**, **26e**, and **26f**, respectively, were tolerated in the reaction. Sterically hindered substrates could be subjected to the reaction, and **26g** was obtained from **25g**. Moreover, a substrate having a heteroaromatic ring (**25i**) was converted into its corresponding carboxylic acid **26i**.

Alkenylboronic esters **27** were also converted into the corresponding α,β-unsaturated carboxylic acids **28** using $[RhCl(nbd)]_2$ (nbd = norbornadiene) as a catalytic precursor (Scheme 25) [54]. When an alkyl-substituted substrate was examined, the *p*-methoxy-substituted dppp derivative was found to be the suitable ligand.
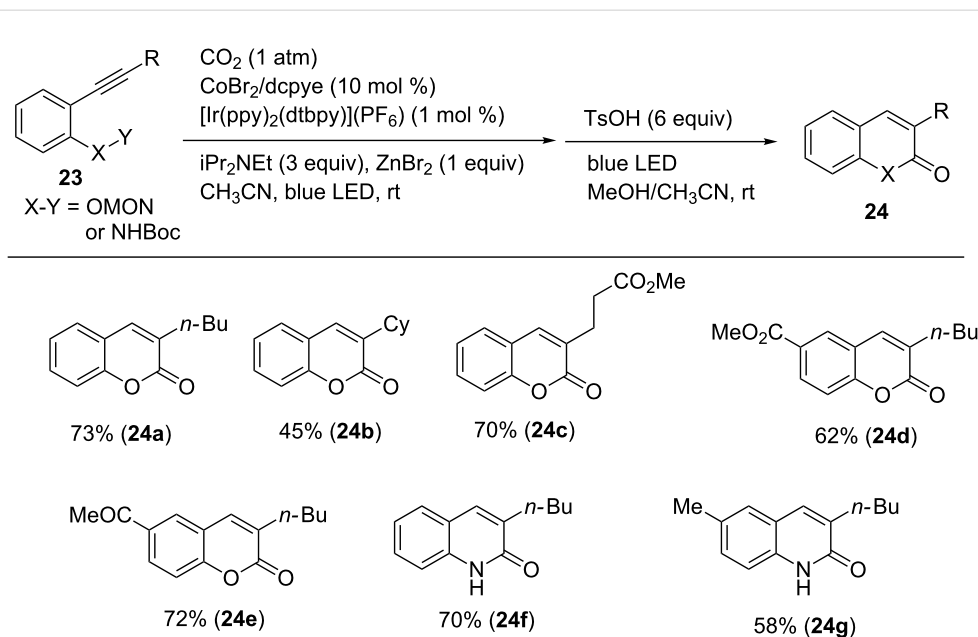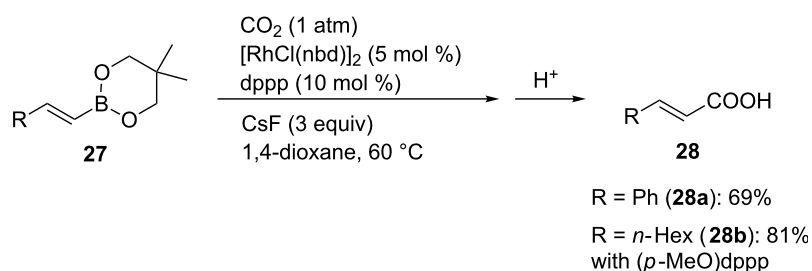

Scheme 22: One-pot synthesis of coumarines and 2-quinolones via hydrocarboxylation/alkyne isomerization/cyclization.

Scheme 23: Proposed reaction mechanism for the Co-catalyzed carboxylative cyclization of *ortho*-substituted aromatic alkynes.
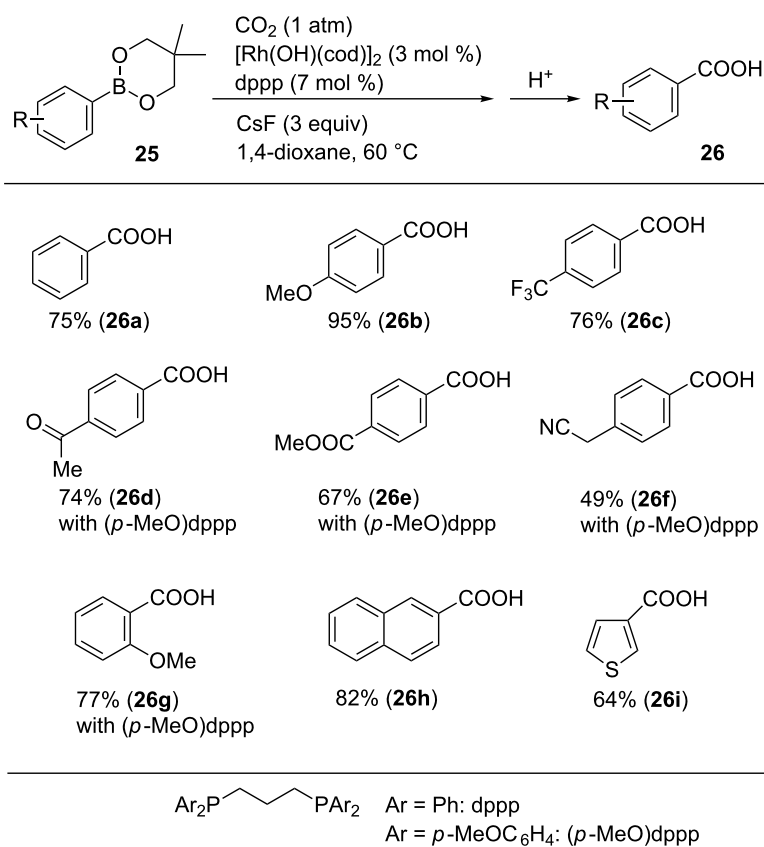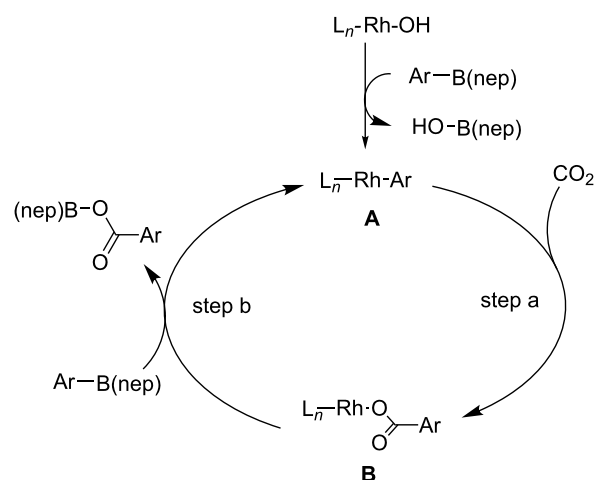

Scheme 24: Rh-catalyzed carboxylation of arylboronic esters **25**.

Scheme 25: Rh-catalyzed carboxylation of alkenylboronic esters **27**.

For this transformation, the reaction mechanism depicted in Scheme 26 was proposed. The catalytic cycle is activated by the generation of aryl-Rh intermediate **A** from the reaction of the Rh(I) species with the corresponding arylboronic ester. Next, the reaction of **A** with CO_2 proceeds with the concomitant generation of the corresponding carboxylate Rh species **B** (step a). Finally, transmetalation between **B** and the arylboronic ester affords the product, along with the aryl-Rh intermediate **A** (step b)

Scheme 26: Plausible reaction mechanism for the Rh-catalyzed carboxylation of arylboronic esters **25**.

After this contribution, the Cu-catalyzed carboxylation of aryl and alkenylboronic esters was independently reported by the groups of Iwasawa and How [55,56].
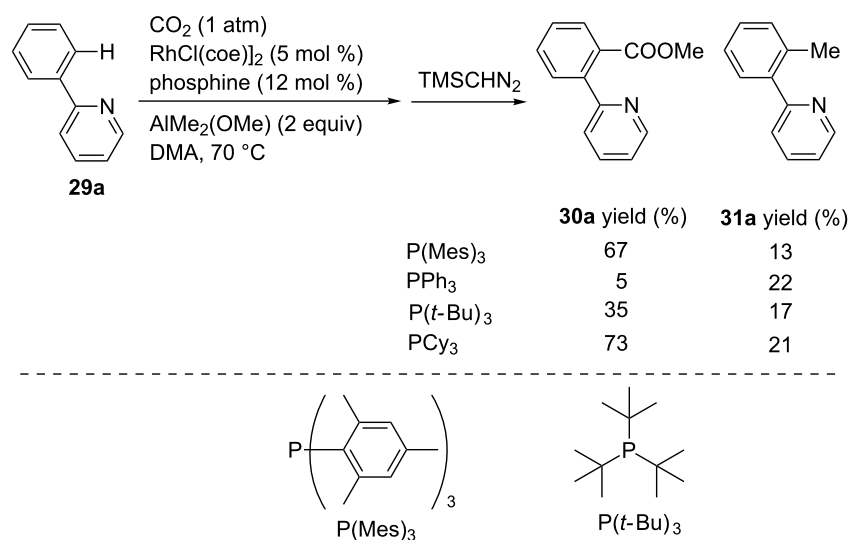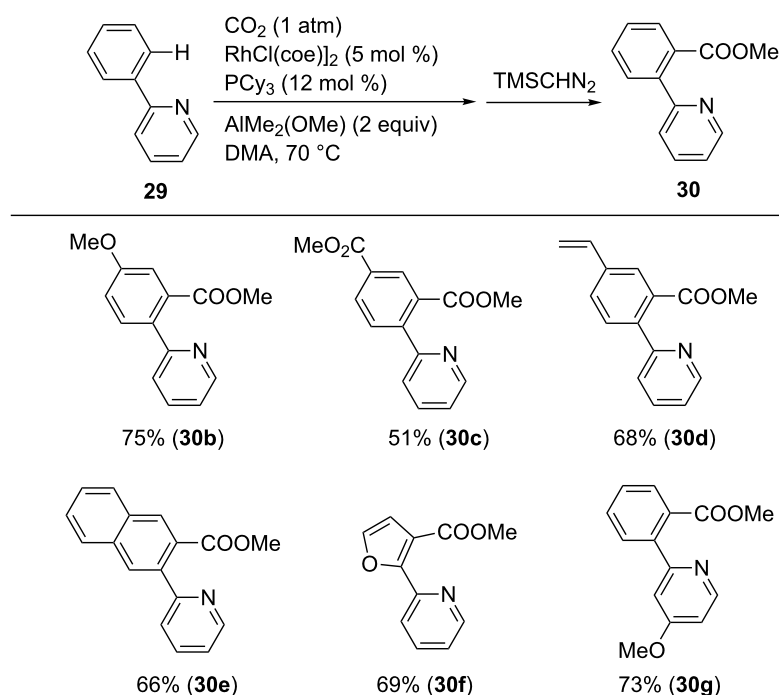
Direct C(sp^2)–H bond carboxylation

As described above, C–H carboxylations with CO_2, particularly C(sp^2)–H carboxylation reactions, have attracted much research interest. As a consequence, Nolan [57] and Hou [58] independently reported Cu-catalyzed carboxylations using heteroarenes as substrates, which occur at the relatively acidic C–H bond.

Regarding Rh as the catalyst, Iwasawa et al. first reported a rhodium-catalyzed chelation-assisted C(sp^2)–H carboxylation using methylaluminum as a reducing reagent (Scheme 27) [59]. Subsequently, the reaction of 2-phenylpyridine (**29a**) was performed using AlMe$_2$(OMe) in DMA at 70 °C. Employing [RhCl(coe)]$_2$ (coe = cyclooctene) and P(Mes)$_3$ ((P(Mes)$_3$ = tris(2,4,6-trimethylphenyl)phosphine) as the catalyst, the carboxylated product **30a** was obtained in 67% yield, along with the formation of a methylated byproduct **31a**. Other phosphine ligands such as PPh$_3$, P(*t*-Bu)$_3$, and PCy$_3$ afforded the product in low-to-good yields.

Under the optimal reaction conditions using PCy$_3$ as the ligand, various 2-pyridylarenes **29** were converted into the corresponding products **30** (Scheme 28). Substrates bearing either electron-donating or electron-withdrawing substituents at the aryl ring afforded the corresponding products. Interestingly, a terminal alkenyl group remained intact after the reaction (**30d**). Furthermore, substrates bearing naphthyl or furyl rings were carboxylated, and the corresponding products, **30e** and **30f**, respectively, were obtained in good yields.

A plausible reaction mechanism for this Rh-catalyzed chelation-assisted C(sp^2)–H bond carboxylation is shown in Scheme 29. First, a low-valent methyl–Rh(I) species **A** is generated by transmetalation. Secondly, a pyridine ring in the substrate coordinates to the Rh center, which prompts the cleavage of the adjacent C–H bond, affording Rh(III) species **B** (step a). Subsequently, the reductive elimination of methane from **B** affords the low-valent Rh(I) species **C**. Then, C–C bond formation with CO_2 proceeds, and Rh carboxylate **D** is formed. Finally, the carboxylated product is obtained by the transmetalation between **D** and AlMe$_2$(OMe), and methyl–Rh(I) **A** is regenerated.

Later, Iwasawa et al. achieved the Rh-catalyzed direct carboxylation of arenes without any directing group (Scheme 30) [60,61]. The reactions proceeded using a catalytic amount of Rh complex bearing dcype (dcype = 1,2-bis(dicyclohexylphosphino)ethane) as the ligand and AlMe$_2$(OEt) as a reducing agent

Scheme 27: Ligand effect on the Rh-catalyzed carboxylation of 2-phenylpyridine **29a**.

	30a yield (%)	**31a** yield (%)
P(Mes)$_3$	67	13
PPh$_3$	5	22
P(t-Bu)$_3$	35	17
PCy$_3$	73	21

**Scheme 28:** Rh-catalyzed chelation-assisted C(sp^2)–H bond carboxylation with CO_2.

in a mixture of DMA and 1,1,3,3-tetramethylurea (TMU) as a solvent. Under the reaction conditions, benzene (**32a**) was converted into benzoic acid (**33a**, TON: 37) at 85 °C. The monosubstituted arenes such as toluene (**32b**), fluorobenzene (**32c**), and trifluoromethylbenzene (**32d**) afforded the corresponding carboxylic acids **33b**, **33c**, and **33d** in good TON. *o*-Xylene yielded its corresponding mixture of carboxylic acids **33e**. When 1,3-bis(trifluoromethyl)benzene (**32f**) was used as the substrate at 145 °C, the corresponding carboxylic acid **33f** was site-selectively obtained in good TON. Benzofuran (**32h**) and indole (**32i**) also gave the carboxylic acids, which were isolated as their methyl esters.
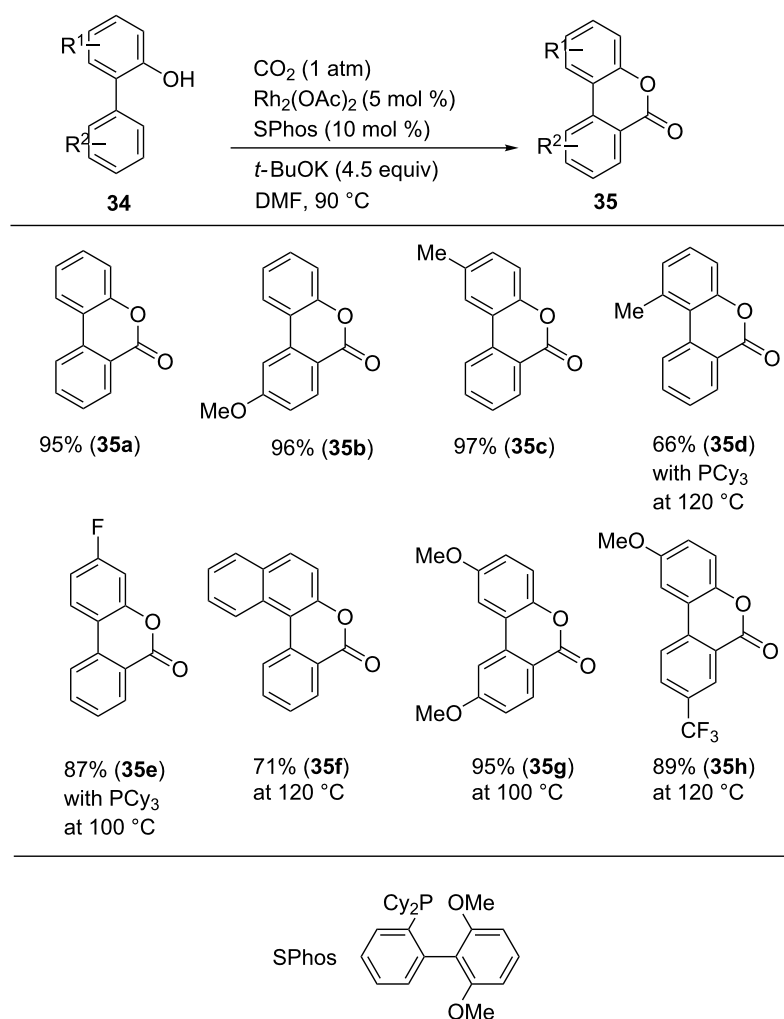
Li and co-workers reported the Rh-catalyzed site-selective C(sp^2)–H carboxylation reaction using 2-arylphenols as the substrates (Scheme 31) [62]. The desired reactions proceeded using
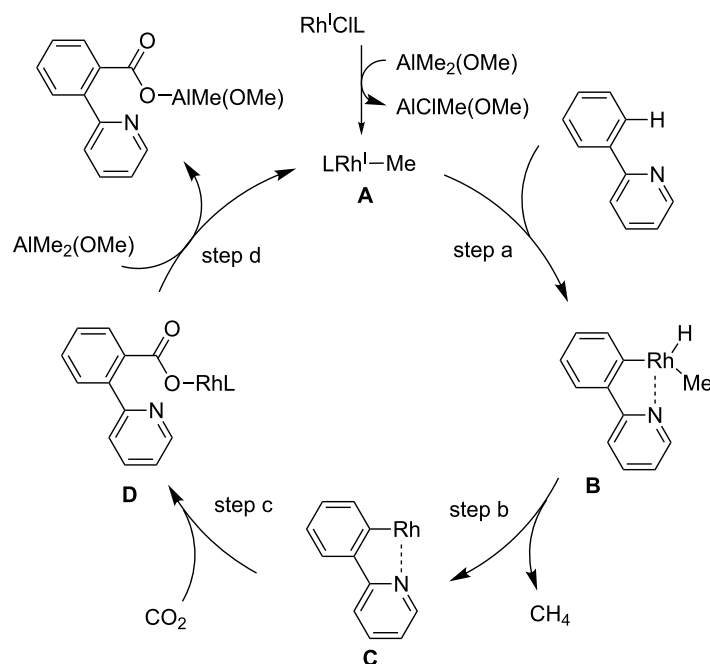
Scheme 29: Reaction mechanism for the Rh-catalyzed $C(sp^2)$–H carboxylation of 2-pyridylarenes **29**.
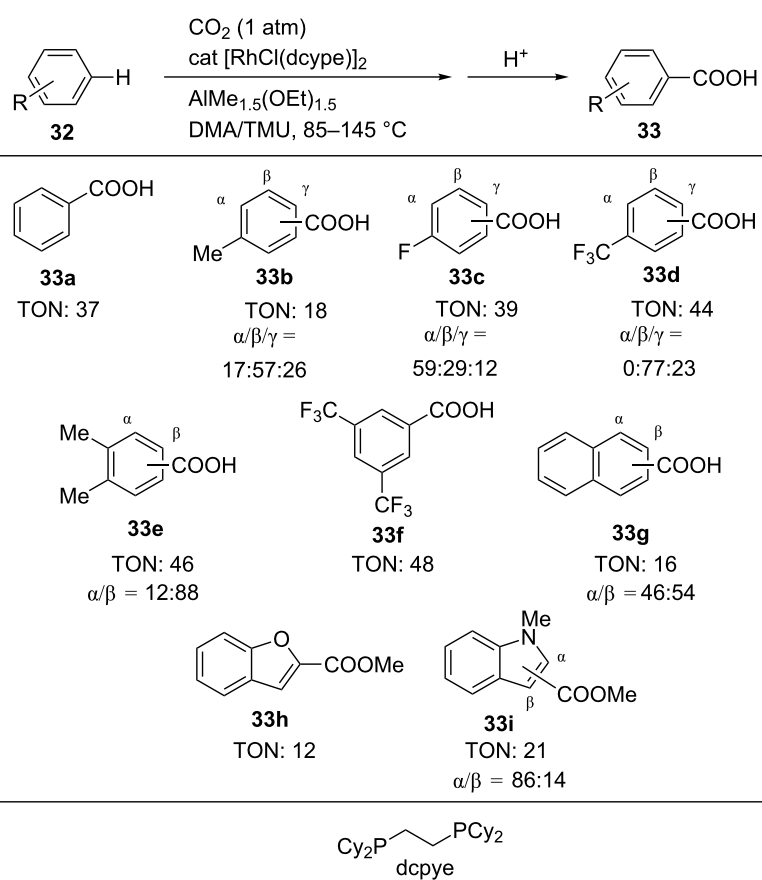
Scheme 30: Carboxylation of $C(sp^2)$–H bond with CO_2.

Scheme 31: Carboxylation of C(sp²)–H bond with CO_2.

a $Rh_2(OAc)_4$/SPhos catalyst system and *t*-BuOK as a base in DMF. Under the optimal reaction conditions, the reaction with 2-phenylphenol (**34a**) afforded dibenzopyranone (**35a**) in 95% yield. Other substituted 2-arylphenol derivatives (**34b–h**) were converted to the corresponding dibenzopyranones (**35b–h**) in good-to-high yields. Notably, sterically hindered substrates (**34d** and **34f**) were allowed by elevating the reaction temperature.

A plausible reaction mechanism is shown in Scheme 32. First, a phenoxide **34'** generated by the reaction of 2-arylphenol with *t*-BuOK reacts with a Rh complex **A** to generate a Rh complex **B** (step a). Then, chelation-assisted C–H bond activation proceeds to generate a rhodacycle **C** (step b). The reaction of **C** with CO_2 affords an eight-membered rhodacycle intermediate **D** (step c). Next, **D** is converted to the corresponding rhodium complex **E** by ligand exchange with KOAc (step d). Possibly

another ligand exchange between **E** and KOAc regenerates the Rh complex **A** (step e). The desired product (**35**) is obtained after lactonization.

Hydrocarboxylation of arylalkenes

Hydrocarboxylation is an essential carboxylation reaction. To date, transition-metal-catalyzed hydrocarboxylation reactions using alkynes [63-66], alkenes [67,68], allenes [69-71] and 1,3-dienes [72,73] have been reported. In this regard, Mikami et al. reported the Rh-catalyzed hydrocarboxylation of styrene derivatives depicted in Scheme 33 [74]. The desired reaction proceeded using $[RhCl(cod)]_2$ as a catalyst and Et_2Zn as a reducing agent in DMF at 0 °C. As a result, diverse styrene derivatives **36a–f** bearing an electron-withdrawing group were converted into their corresponding carboxylic acids **37a–f** in moderate-to-high yields. Notably, the ester, ketone, and amide functionalities of **37a**, **37c**, and **37d**, respectively, were toler-
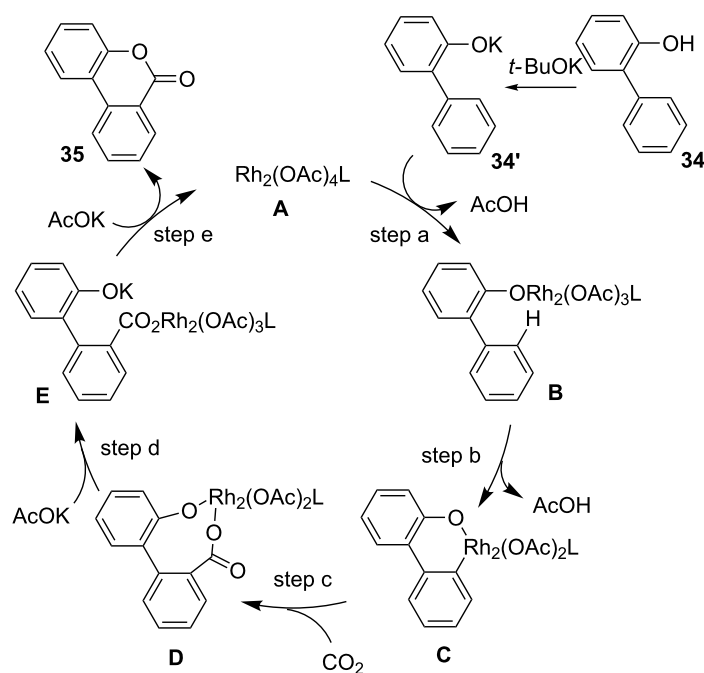
Scheme 32: Reaction mechanism for the Rh-catalyzed C(sp^2)–H carboxylation of 2-arylphenols **34**.
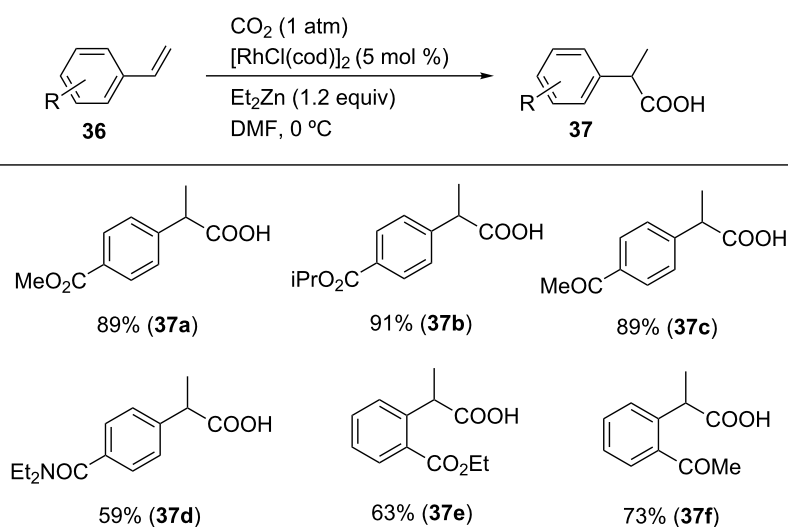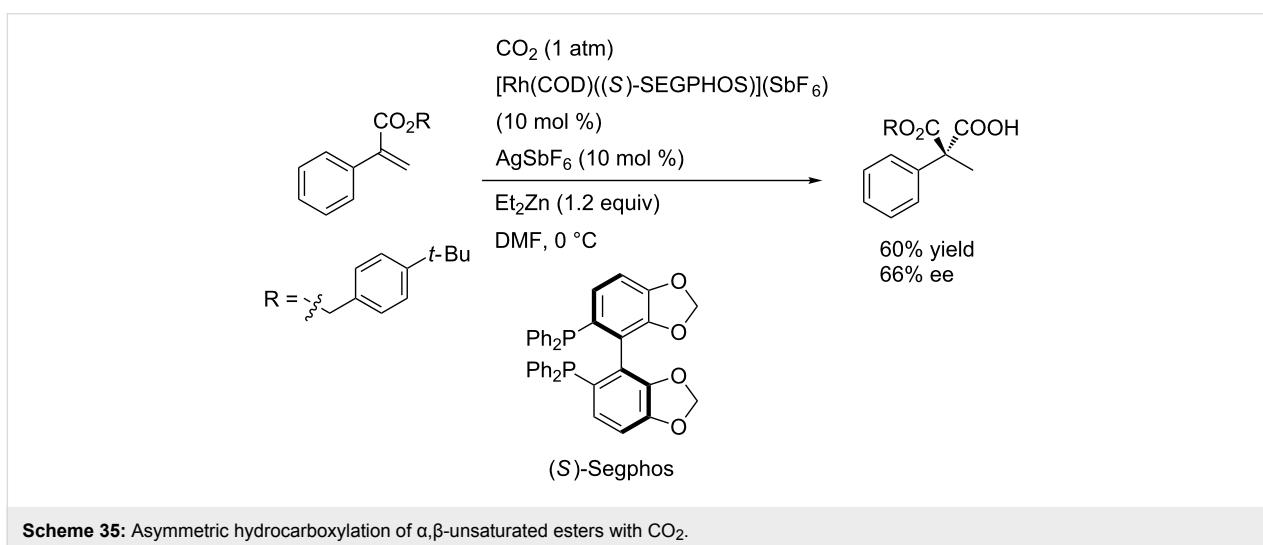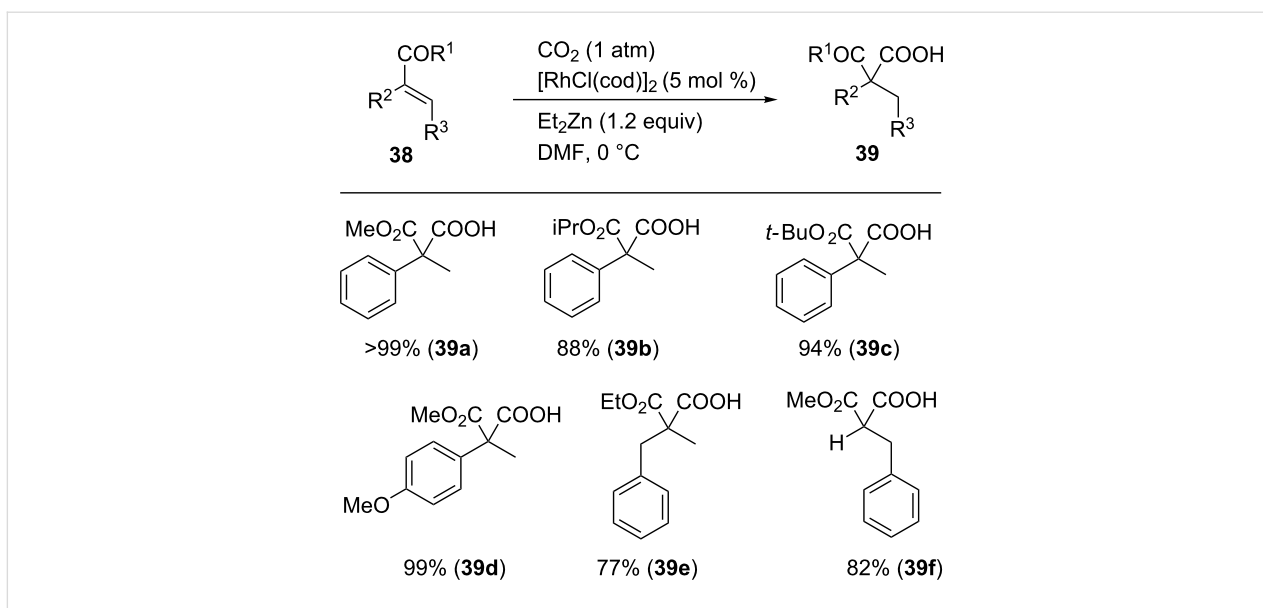

Scheme 33: Hydrocarboxylation of styrene derivatives with CO_2.

ated in the reaction. However, substrates such as 4-methoxy-styrene or styrene did not yield the desired products.

The same Rh-catalytic system proved to be applicable to the carboxylation of α,β-unsaturated esters **38** (Scheme 34). A variety of substrates **38a–f**, including those containing an electron-donating substituent or benzyl-substituted esters, were converted into their corresponding products **39a–f** in good-to-high yields.

Notably, the asymmetric hydrocarboxylation was archived by using a chiral bisphosphine as a ligand (Scheme 35).

Scheme 36 illustrates a plausible reaction mechanism for this transformation. First, transmetalation between the Rh(I) and Zn reagents generates ethyl–Rh(I) species **A**, from which β-hydrogen elimination occurs to yield the hydride-Rh intermediate **B** (step a). Subsequently, the hydrorhodation of the C–C double bond occurs, affording an

Scheme 34: Hydrocarboxylation of α,β-unsaturated esters with CO_2.

Scheme 35: Asymmetric hydrocarboxylation of α,β-unsaturated esters with CO_2.

alkyl-Rh(I) species **C** (step b). Then, C–C bond formation with CO_2 proceeds to give Rh carboxylate **D** (step c) Finally, the carboxylated product is obtained by the transmetalation between **D** and Et_2Zn, with the concomitant regeneration of ethyl–Rh(I) **A** (step d).
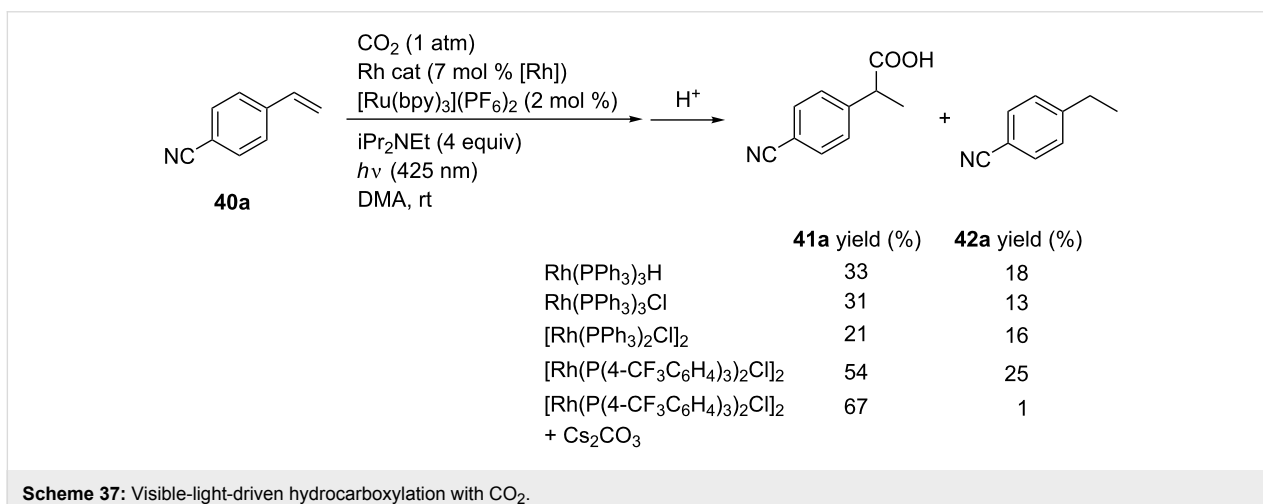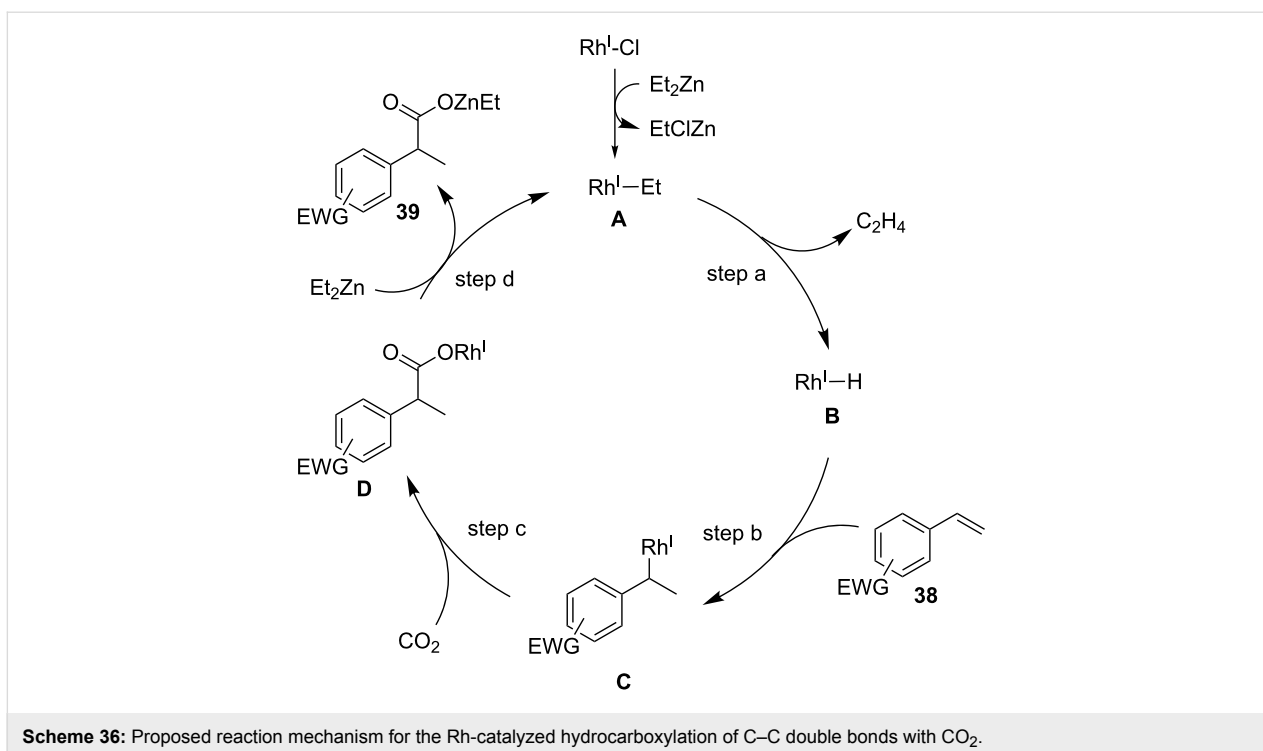
Visible light-driven hydrocarboxylation of alkenes

Iwasawa et al. reported the Rh-catalyzed hydrocarboxylation of alkenes driven by visible-light irradiation conditions in the presence of a photoredox catalyst (Scheme 37) [75]. A model reaction using 4-cyanostyrene (**40a**) was carried out using $iPrNEt_2$ as a sacrificial electron donor in the presence of $[Ru(bpy)_3](PF_6)_2$ as a photoredox catalyst under visible-light irradiation (425 nm). Employing $Rh(PPh_3)_3H$ as a catalyst, the

desired hydrocarboxylated product **41a** was obtained in 33% yield along with the formation of reduced product **42a**. $Rh(PPh_3)_3Cl$ and $[Rh(PPh_3)_2Cl]_2$ were not efficient while a use of $[Rh(P(4-CF_3C_6H_4)_3)_2Cl]_2$ afforded **41a** in 54% yield. Finally, an addition of Cs_2CO_3 dramatically reduced the byproduct and **41a** was obtained in 67% yield.

Under the optimal reaction conditions, several substrates were examined and the corresponding hydrocarboxylated products were obtained in moderate yields (Scheme 38).

[2 + 2 + 2] Cycloaddition of diynes with CO_2

The [2 + 2 + 2] cycloaddition of diynes with CO_2 is an important reaction in the field of CO_2 fixation. In these reactions,

Scheme 36: Proposed reaction mechanism for the Rh-catalyzed hydrocarboxylation of C–C double bonds with CO_2.

**Scheme 37:** Visible-light-driven hydrocarboxylation with CO_2.

cyclic esters such as pyrones can be obtained, which are classically catalyzed by Ni complexes [76-78]. Tanaka et al. reported that a Rh complex with a suitable bidentate ligand was an efficient catalyst for the [2 + 2 + 2] cycloaddition reaction (Scheme 39) [79]. The reaction of **43a** was performed using 20 mol % [Rh(cod)$_2$]BF$_4$ and a bidentate phosphine in 1,2-dichloroethane at room temperature. Prior to the addition of **43a**, the mixture of [Rh(cod)$_2$]BF$_4$ and phosphine was stirred for 30 min. Then, **43a** was added dropwise to the mixture over 10 min, and the resulting reaction mixture was further stirred for 16 h. As ligands, SEGPHOS, BIPHEP, and DPPF were ineffective, but BINAP and H$_8$-BINAP afforded the product **44a** in

moderate yields. Notably, the addition of **43a** over 120 min improved the yield even at low catalyst loadings (5 mol %). A high (94%) yield was eventually obtained by reducing the prestirring time to 5 min.

A variety of diynes having different tether units (**43a–g**) were converted into the corresponding pyrones **44a–g** in good-to-high yields within 1 h (Scheme 40). Ester, ketone, and hydroxy groups were tolerated in the reaction. In the case of an unsymmetrical diyne bearing methyl and isopropyl groups (**43g**), a mixture of regioisomers **44g** + **44g′** was obtained in high yield with high regioselectivity.
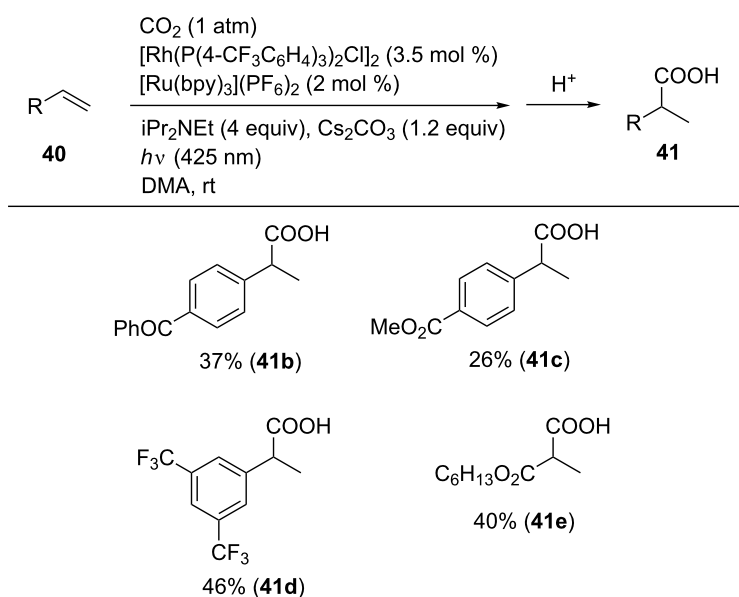
Scheme 38: Visible-light-driven Rh-catalyzed hydrocarboxylation of C–C double bonds with CO_2.
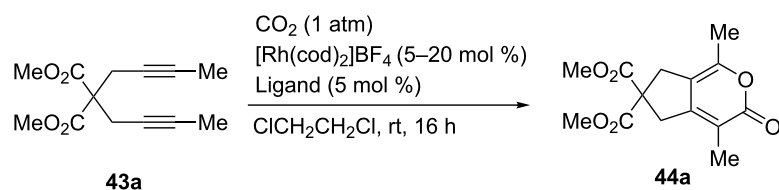

ligand	loading (mol %)	prestirring time (min)	addition time (min)	yield (%)
SEGPHOS	20	30	10	19
BIPHEP	20	30	10	9
DPPF	20	30	10	25
BINAP	20	30	10	41
H_8-BINAP	20	30	10	48
H_8-BINAP	5	30	10	18
H_8-BINAP	5	30	120	78
H_8-BINAP	5	5	120	94
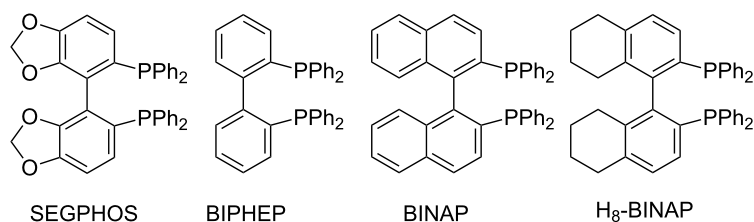
Scheme 39: Optimization of reaction conditions on the Rh-catalyzed [2 + 2 + 2] cycloaddition of diyne **42a** and CO_2.

For this transformation, the reaction pathways depicted in Scheme 41 can be envisaged. The Rh(I) species **A** reacts with a diyne to afford rhodacycle **B** (step a). Then, the reaction of **B** with CO_2 produces the seven-membered rhodium intermediate C (step b), from which reductive elimination occurs to yield its corresponding pyrone and the Rh(I) species **A** (step c). Alternatively, the oxidative cyclization of **A** proceeds as one of the C–C triple bonds of the diyne and CO_2 react regioselectively,
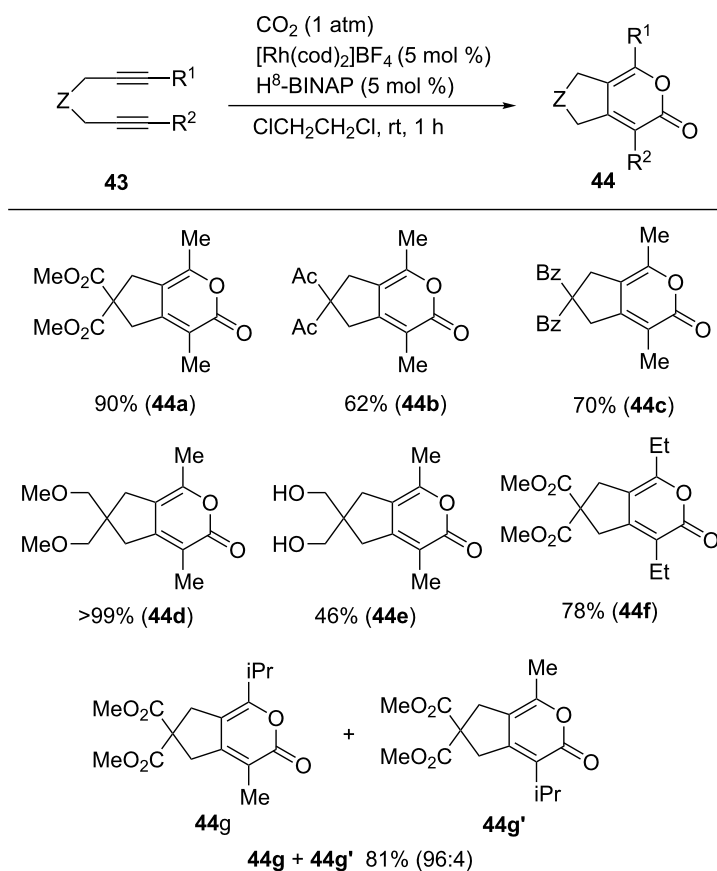
Scheme 40: [2 + 2 + 2] Cycloaddition of diyne and CO_2.
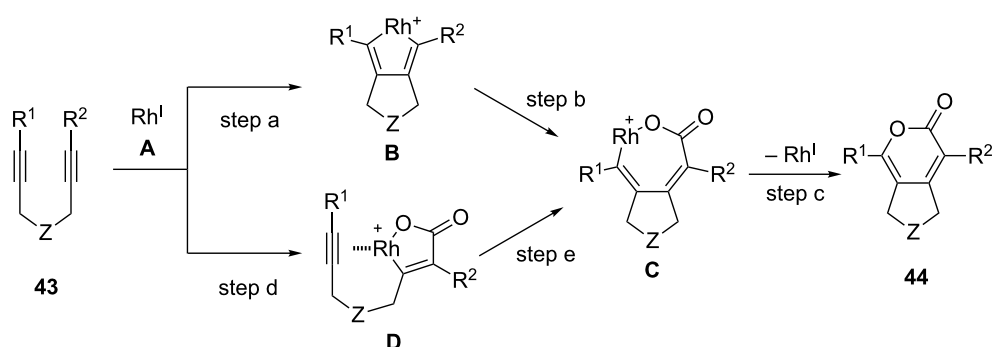
Scheme 41: Proposed reaction pathways for the Rh-catalyzed [2 + 2 + 2] cycloaddition of diyne and CO_2.

and rhodacycle **D** is subsequently formed (step d). Then, the insertion of the alkyne into the Rh–C bond occurs to give rhodacycle **C** (step e).

Conclusion

In this review, the Co- and Rh-catalyzed transformation of CO_2 via carbon–carbon bond-forming reactions is summarized. Co complexes can catalyze the carboxylation of propargyl acetates

and alkenyl triflates. The cobalt-catalyzed reductive carboxylation of α,β-unsaturated nitriles and carboxyamides proceeds using Et_2Zn. In addition, a cobalt complex proved to be an efficient catalyst in the allylic $C(sp^3)$–H carboxylation. In the presence of zinc as the reagent, carboxyzincation and the four-component coupling reaction between alkyne, acrylates, CO_2, and zinc occur efficiently. Rh complexes also catalyze the carboxylation of aryl and vinylboronic esters, the $C(sp^2)$–H carboxyla-

tion of aromatic compounds, and the hydrocarboxylation of styrene derivatives. The Rh-catalyzed [2 + 2 + 2] cycloaddition of diynes and CO_2 proceeds to afford pyrenes. Combinations of metals (cobalt or rhodium), substrates, and reducing agents can realize efficient carboxylation reactions using CO_2 under mild reaction conditions. Furthermore, the development of novel carboxylation reactions using clean reducing agents such as non-metallic organic reductants such as amine, water, or hydrogen gas can be envisaged in the near future.

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