

Highly Regio- and Stereoselective Three-Component Nickel-Catalyzed *syn*-Hydrocarboxylation of Alkynes with Diethyl Zinc and Carbon Dioxide**

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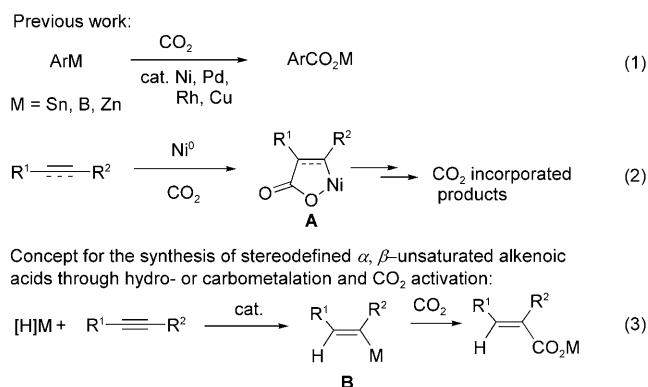
In memory of Xinwei Ma

Activation of carbon dioxide and converting it into useful chemical feedstock have attracted much attention owing to the fact that CO₂ is abundant, inexpensive, nontoxic, and environmentally benign.^[1] However, the challenges still to be overcome are its lack of thermodynamic and kinetic stability. For the reaction of allylic tin species,^[2] aryl boronates, and limited examples of 1-alkenyl boronates,^[3] aryl or alkyl zinc substrates^[4,5] can react with carbon dioxide, usually under palladium, nickel, copper, or rhodium catalysis [Scheme 1, Eq. (1)]. In addition, a stoichiometric amount of Ni or Ti reagents have been used to mediate the reaction of CO₂ with

alkene,^[6] diene,^[7] alkyne,^[8] or allene^[9] substrates to form five-membered metallaoxacyclic intermediates **A**, which may undergo further reactions to afford carboxylation products [Scheme 1, Eq. (2)]. There are very limited reports on the catalytic reactions of alkyne^[10] or allene^[11] substrates involving **A**-type intermediate using 20 mol % of [Ni(cod)₂] and 10 equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene.

Furthermore, there are a few reports on substituted alkynes that can undergo a stereoselective titanium- or rhodium-catalyzed *syn*-hydrozincation^[12,13] or rhodium- or nickel-catalyzed carbocation^[13,14] reaction [Scheme 1, Eq. (3)]. With this notion in mind, we envisioned that organozinc reagents generated in situ from hydro- or carbocation of unsaturated hydrocarbon species may react with CO₂ to afford the corresponding carboxylic acids in a convenient manner [Scheme 1, Eq. (3)]. Rovis and co-workers reported the hydrozincation/carboxylation of styrenes with [Ni(acac)₂] (10 mol %; acac = acetylacetonate) and Cs₂CO₃ (20 mol %).^[15] Takaya and Iwasawa reported such a hydrocarboxylation of allene with 1–2.5 mol % of a silyl pincer-type palladium complex.^[16] However, it should be noted that both reports involve the reaction of very reactive allylic or benzylic metallic species with CO₂. So far, there are no such reports on alkyne substrates; the challenge here would be the lower reactivity of the 1-alkenyl zinc generated in situ towards CO₂^[17] and the regioselectivity of the alkynes. Herein, we report the concise highly regio- and stereoselective three-component nickel-catalyzed (1–3 mol %) *syn*-hydrocarboxylation of alkynes^[11,12] with diethyl zinc and the subsequent efficient reaction with carbon dioxide mediated by CsF to afford stereodefined and synthetically useful 2-alkenoic acids. This reaction has been applied to the highly regio- and stereoselective synthesis of 3-alkylideneoxindole^[18] and α -alkylidene- γ -butyrolactam.^[19]

Initially, diphenylacetylene (**1a**) was treated with CO₂ in the presence of 10 mol % of [Ni(cod)₂], 20 mol % of PCy₃, and 3 equivalents of ZnEt₂. Pleasingly, 10 % of the expected *syn*-hydrocarboxylation product, that is, (*E*)-2,3-diphenylacrylic acid **2a**, was formed together with 25 % of the hydrolysis product **4a** (Table 1, entry 1). Various bases were then screened with no obvious improvement (Table 1, entries 2–4). Then we tested the effect of inorganic salts such as ZnBr₂, LiCl, KF, and CsF as the ligand^[3a,b,20] (Table 1, entries 5–8). We observed that when 3 equivalents of CsF were used, the hydrocarboxylation product **2a** was formed in 59 % yield together with 11 % of the ethylcarboxylation product, that is,



Scheme 1. Previous work and our concept for CO₂ activation.

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entry 2 of Table 2, entry 4 of Table 3, and Equation 1 in Scheme 3.

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Table 1: Optimization of reaction conditions.^[a]

Entry	[Ni(cod) ₂] [mol %]	Ligand/additive (equiv)	T [°C]	t [h]	Yield [%] ^[b]		
					2a	3a	4a
1	10	PCy ₃ (0.20)	RT	31	10	4	25
2	10	K ₃ PO ₄ (3)	RT	31	11	< 1.6	26
3	10	Cs ₂ CO ₃ (3)	RT	25	< 1	n.d.	13
4	10	K ₂ CO ₃ (3)	RT	29	6	< 1	46
5	10	ZnBr ₂ (3)	RT	31	3	3	27
6	10	LiCl (3)	RT	31	53	3	12
7	10	KF (3)	RT	31	35	1.4	16
8	10	CsF (3)	RT	22	59	11	4
9	1	CsF (3)	60	1.5	80	4	< 1
10 ^[c]	1	CsF (1)	60	1.5	84	3	2
11 ^[c]	1	CsF (0.5)	60	1.5	52	1	11

[a] Reaction conditions: The reaction was carried out with 0.5 mmol of **1a**, the indicated amount of [Ni(cod)₂], ligand or additive, 3 equiv of ZnEt₂ (1 M in hexane, 1.5 mL), and about 1 L of CO₂ (a balloon) in CH₃CN (3 mL) at the indicated temperature. [b] Yield based on ¹H NMR analysis. [c] 3 equiv of ZnEt₂ (1.5 M in toluene, 1.0 mL). cod = cycloocta-1,5-diene, Cy = cyclohexyl, n.d. = not determined.

(*E*)-2,3-diphenylpent-2-enoic acid (**3a**; Table 1, entry 8). Screening of the temperature and the catalyst loading led to the observation that when the reaction was conducted at 60 °C, the yield of **2a** was improved to 80 % while the amount of **3a** was lowered to 3 % with using just 1 mol % of [Ni(cod)₂] (Table 1, entry 9). Furthermore, when the solution of ZnEt₂ in toluene was used instead of that in hexane, the yield was further improved even with just 1 equivalent of CsF (Table 1, entry 10). Lowering the amount of CsF to 0.5 equivalents led to a much lower yield of **2a** (Table 1, entry 11).

With the optimized conditions in hand, we began to explore the scope of this reaction (Table 2). Symmetrical alkyne substrates were studied first (Table 2, entries 1–5). Electron-rich aryl alkynes gave higher yields (Table 2, entries 2–4 vs. entry 1). The reaction of dialkyl-substituted alkynes was less effective with a yield of 62 % for product **2e** (Table 2, entry 5). When R¹ is an aryl (Table 2, entries 6–10) or 2-thienyl group (Table 2, entry 11) and R² is the tertiary butyl group, the product is regioselective. The structure of **2h** was confirmed by its X-ray crystal structure analysis (Figure 1).^[21] The reaction was conducted on a 7.0 mmol scale to afford the product in a higher yield (Table 2, entry 6 vs. entry 7).

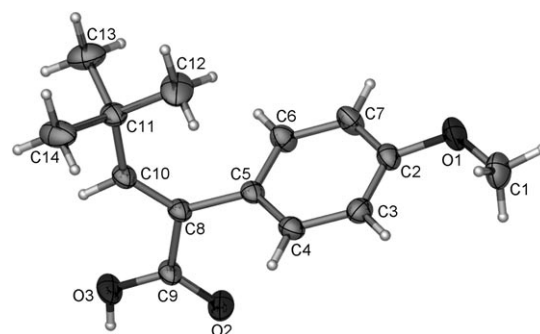
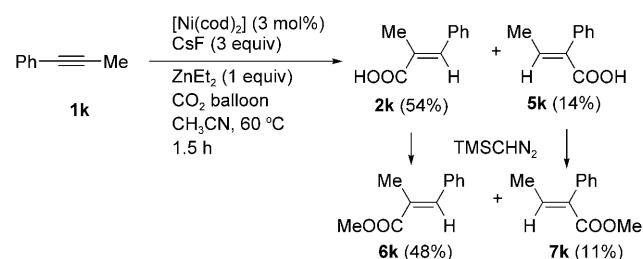
The reaction of 1-phenyl-1-propyne was also regioselective (≈4:1), and afforded the *syn*-products **5k** and **2k** with the CO₂H group connected to the sp² carbon atom bearing the methyl group; The product **2k** is the major product (Scheme 2).

To improve the regioselectivity, an amino group was introduced to the starting alkyne substrates. Pleasingly, (*E*)-amino acid **9a** was produced exclusively in an excellent yield and with high regio- and stereoselectivity when 1-phenyl-2-(*o*-(*N*-tosylphenyl)acetylene **8a** was used (Table 3, entry 1).

Table 2: Nickel-catalyzed hydrocarboxylation of alkynes.^[a]

Entry	R ¹	R ²	[Ni(cod) ₂] [mol %]	Yield of 2 [%] ^[b]
1	Ph	Ph	1	81 (2a)
2 ^[c]	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -MeOC ₆ H ₄	1	89 (2b)
3	<i>p</i> -MeC ₆ H ₄	<i>p</i> -MeC ₆ H ₄	1	89 (2c)
4	<i>m</i> -MeC ₆ H ₄	<i>m</i> -MeC ₆ H ₄	1	91 (2d)
5 ^[d]	<i>n</i> Pr	<i>n</i> Pr	3	62 (2e)
6	Ph	<i>t</i> Bu	3	79 (2f)
7 ^[e]	Ph	<i>t</i> Bu	3	91 (2f)
8	α -naphthyl	<i>t</i> Bu	3	88 (2g)
9	<i>p</i> -MeOC ₆ H ₄	<i>t</i> Bu	3	81 (2h)
10	<i>p</i> -FC ₆ H ₄	<i>t</i> Bu	3	77 (2i)
11	2-thienyl	<i>t</i> Bu	3	68 (2j)

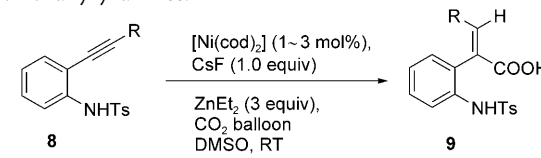
[a] Reaction conditions: The reaction was carried out with 0.5 mmol of alkyne, the indicated amount of [Ni(cod)₂], 0.5 mmol of CsF, 1.5 mmol of ZnEt₂ (1.5 M in toluene, 1.0 mL), and about 1 L of CO₂ (a balloon) in CH₃CN (3 mL) at 60 °C. [b] Yields of isolated products. [c] 1.5 equiv of CsF. [d] 3 equiv of CsF. [e] 7.0 mmol of the alkyne, 0.21 mmol of [Ni(cod)₂], 7.0 mmol of CsF, and 21 mmol of ZnEt₂ (1.5 M in toluene, 14.0 mL), and about 1.5 L of CO₂ (a balloon) in CH₃CN (42 mL).


Figure 1. ORTEP plot of **2h** shown with ellipsoids at the 30 % probability level.

Scheme 2. Nickel-catalyzed hydrocarboxylation of **1k**. Yields of **2k** and **5k** were determined by ¹H NMR analysis. TMS = trimethylsilyl.

Further study shows that exclusive regio- and stereoselectivity was also observed when R is *t*Bu, *n*Bu, cyclopropyl, or 2-thienyl (Table 3, entries 2–5).

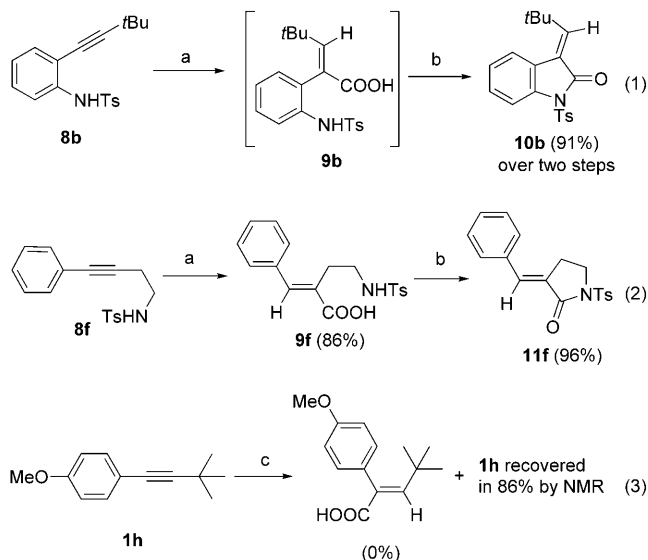
The amino acid **9b** could be easily transformed into 3-alkylideneoxindole **10b**^[18] with the aid of EDCI (Scheme 3, Eq. (1)). Notably, in this reaction the crude product **9b** was be

Table 3: Nickel-catalyzed highly regio- and stereoselective hydrocarboxylation of alkynyl amines.^[a]



Entry	R	[Ni(cod) ₂] [mol %]	t [h]	Yield of 9 [%] ^[b]
1	Ph (8a)	1	6	95 (9a)
2	<i>t</i> Bu (8b)	3	3	94 (9b)
3	<i>n</i> Bu (8c)	3	3	95 (9c)
4	cyclopropyl (8d)	3	3	91 (9d)
5	2-thienyl (8e)	1	6	96 (9e)

[a] Reaction conditions: The reaction was carried out with 0.5 mmol of alkyne, the indicated amount of [Ni(cod)₂], 0.5 mmol of CsF, and 1.5 mmol of ZnEt₂ (1.5 M in toluene, 1.0 mL), and about 1 L of CO₂ (a balloon) in DMSO (3 mL) at RT (25–30 °C). [b] Yield of isolated product. DMSO = dimethyl sulfoxide, Ts = 4-toluenesulfonyl.



Scheme 3. Synthesis of 3-alkylideneoxindole **10b** and α -alkylidene- γ -butyrolactam **11f**. a) [Ni(cod)₂] (3 mol %), CsF (1.0 equiv), ZnEt₂ (3 equiv), CO₂ (a balloon), DMSO, RT, 3 h; b) EDCI (1.2 equiv), CH₂Cl₂, –10 °C $\rightarrow$ RT; c) 1. [Ni(cod)₂] (1.0 equiv), CsF (1.0 equiv), CO₂ (a balloon), CH₃CN, 60 °C, 11 h; 2. HCl. Amount of **1h** recovered was determined by ¹H NMR analysis. EDCI = (1-ethyl-3-(3-dimethylamino-propyl) carbodiimide HCl.

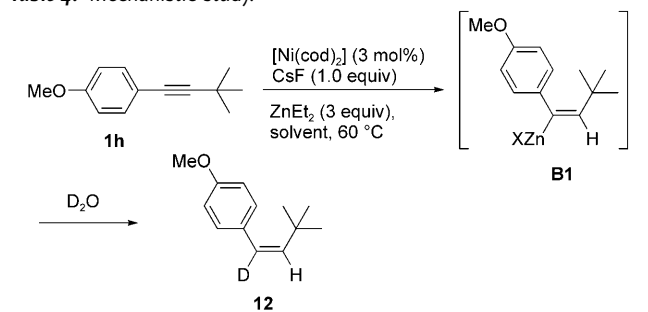
directly transformed into **10b** without purification. Such a strategy can also be applied to 4-phenylbut-3-ynyl *N*-tosylamide **8f** for the efficient and highly regio- and stereoselective synthesis of α -alkylidene- γ -butyrolactam **11f**^[19] (Scheme 3, Eq. (2)).

According to Yamamoto and co-workers^[8a] if the reaction proceeds via the cyclometalation mechanism (Scheme 1, Eq. (2)), the reaction of an alkyne, CO₂, and a stoichiometric amount of [Ni(cod)₂] would directly afford the hydrocarboxylation product upon protonolysis. However, the reaction of alkyne **1h** and CO₂ with 1 equivalent of [Ni(cod)₂] under the

standard reaction conditions failed to afford the expected hydrocarboxylation product, with **1h** being recovered in 86 % yield (based on ¹H NMR analysis) after 11 hours followed by quenched with HCl (Scheme 3, Eq. (3)). This result indicates that the reaction should proceed via a different mechanism.

To further probe the mechanism, a couple of control experiments of alkyne **1h** were conducted in the absence of CO₂. The reaction of **1h** with ZnEt₂ in the presence of 3 mol % of [Ni(cod)₂] and 1 equivalent of CsF for 5 minutes followed by quenching with D₂O provided *cis*-alkene **12** in 46 % yield (based on ¹H NMR analysis) with a D incorporation of 34 % (Table 4, entry 1). We reasoned that the low D

Table 4: Mechanistic study.

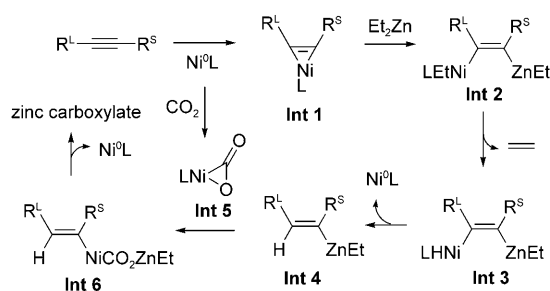


Entry	Solvent	t [min]	Yield of 12 [%] ^[b]	%D in 12	Yield of 1h [%] ^[b]
1	CH ₃ CN	5	46	34	48
2 ^[a]	CH ₃ CN	30	25	78	67
3	CD ₃ CN	30	43	92	49
4	CD ₃ CN	90	43	91	47
5 ^[c]	CH ₃ CN	5	78	32	11

[a] The reaction was carried out in the absence of CsF. [b] Yield determined by ¹H NMR analysis. [c] 7 mol % of [Ni(cod)₂].

incorporation was caused by the deprotonation of the hydrozincation intermediate **B1** with the solvent (MeCN) in the absence of CO₂, and this was confirmed by running the reaction in CD₃CN (Table 4, entry 3). In addition, it is interesting to observe that the reaction stopped at 53 % conversion even after 90 minutes (Table 4, entry 4). Finally it was observed that the reaction with 7 mol % of [Ni(cod)₂] afforded **12** in 78 % yield (based on ¹H NMR analysis) with 32 % of D incorporation, however, in the absence of CsF, the D incorporation in **12** increased to 78 % with a yield of 25 % (based on ¹H NMR analysis) for **12** (compare Table 4, entry 1 vs. entry 2). This outcome indicates that CsF is not only accelerating the hydrozincation reaction but also increasing the reactivity of the alkenyl zinc intermediate **B1**.^[17a,22] Here, it should be noted that the subsequent reaction of intermediate **B1** with CO₂ also increase the efficiency of the nickel catalyst (compare the results in Table 4 with that presented in Table 2, entry 9).

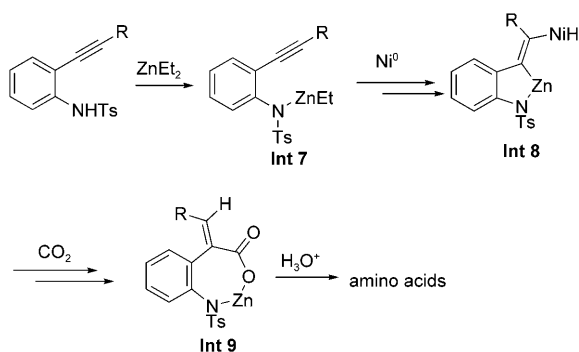
Based on these findings, a possible mechanism was proposed and is shown Scheme 4. The Ni⁰ species first reacts with the alkyne to form **Int 1**, which was followed by transmetalation with ZnEt₂ to form **Int 2**, and this explains the *syn* stereoselectivity. The beta hydride elimination and subsequent reductive elimination generates the **B1**-type



Scheme 4. A plausible mechanism. R^L = large group, R^S = small group.

intermediate of (*E*)-alkenyl zinc **Int 4** and regenerates Ni^0 . At the same time, Ni^0 reacts with CO_2 to produce Aresta's complex **Int 5**,^[23] which undergoes transmetalation with **Int 4** and subsequent reductive elimination to yield the zinc carboxylate and Ni^0 to complete the catalytic cycle.^[24] Arnold et al. have reported that F^- may react with CO_2 to form FCO_2^- , which increases the reactivity of the $C=O$ bond in CO_2 .^[25] This outcome explains the high catalytic activity of $[Ni(cod)_2]$.

The origin of exclusive regioselectivity of hydrocarboxylation of alkynyl amines comes from the directing ability of the amino group (Table 3, Scheme 3, and Scheme 5). Deprotonation with $ZnEt_2$ would readily form **Int 7**, followed by the nickel(0)-catalyzed intramolecular hydrozincation of alkynes and insertion of carbon dioxide to produce the amino acids.



Scheme 5. The origin of exclusive regioselectivity of hydrocarboxylation of alkynyl amines.

In conclusion, we have developed the first example of efficient nickel-catalyzed three-component highly regio- and stereoselective *syn*-hydrocarboxylation of alkynes using CO_2 mediated by CsF. This catalytic system is most efficient with just 1–3 mol % of $[Ni(cod)_2]$ needed for the smooth activation of CO_2 . It is also the first example of nickel-catalyzed^[12,13] hydrozincation of alkynes forming the stereodefined 1-alkenyl zinc species in situ. We have also provided the first reaction of 1-alkenyl zinc species with carbon dioxide. Hydrocarboxylation of alkynyl amines would give regio- and stereodefined amino acids, which could be easily transformed into 3-alkylideneoxindole or α -alkylidene- γ -butyrolactam derivatives. Owing to the high efficiency for CO_2

activation and the potential usefulness of the products, this reaction will be of much interest. Further studies in this area are being pursued in our laboratory.

Experimental Section

Procedure for the preparation of (*E*)-4,4-dimethyl-2-phenylpent-2-enoic acid (**2f**; Table 2, entry 7): To an oven dried 250 mL Schlenk flask were added $[Ni(cod)_2]$ (57.8 mg, 0.21 mmol), CsF (1.0638 g, 7.0 mmol), alkyne **1f** (1.1080 g, 7.0 mmol), and CH_3CN (42 mL) under argon. The mixture was then frozen in a liquid nitrogen bath with the argon being completely replaced by CO_2 (≈ 1.5 L, and the CO_2 gas was dried by passing it through two gas washing bottles with conc. H_2SO_4), and then the reaction flask was allowed to stand until the mixture thawed with the CO_2 balloon still attached. To the resulting suspension was added $ZnEt_2$ (1.5 M in toluene, 14.0 mL) via a syringe. After being stirred at 60°C for 1.5 h (until reaction was complete as evident by TLC), the resulting mixture was quenched with 3 M HCl (30 mL). The aqueous layer was extracted with EtOAc (20 mL $\times$ 5) and the organic layer was washed with brine, and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel (petroleum ether/acetone = 10/1 $\rightarrow$ 5/1) to afford **2f** (91%, 1.3071 g) as a white solid. M.p. = 132–133°C (petroleum ether/ethyl ether); 1H NMR (300 MHz, $CDCl_3$): δ = 11.96 (bs, 1 H, COOH), 7.38–7.26 (m, 3 H, ArH), 7.20–7.08 (m, 3 H, ArH and HC=C), 0.92 ppm (s, 9 H, *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.8, 155.8, 135.6, 130.7, 130.1, 127.6, 127.5, 34.4, 30.2 ppm; MS (m/z): 204 (M^+ , 76.2), 143 (100); IR (KBr): $\tilde{\nu}$ = 3400–2500 (br), 1675, 1631, 1598, 1496, 1421, 1366, 1269, 1208, 926, 785, 703 cm^{-1} ; Elemental analysis calcd for $C_{13}H_{16}O_2$: C 76.44, H 7.90; found: C 76.34, H 8.18.

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