CO_2 Activation

DOI: 10.1002/ange.201007128

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

*Suhua Li, Weiming Yuan, and Shengming Ma**

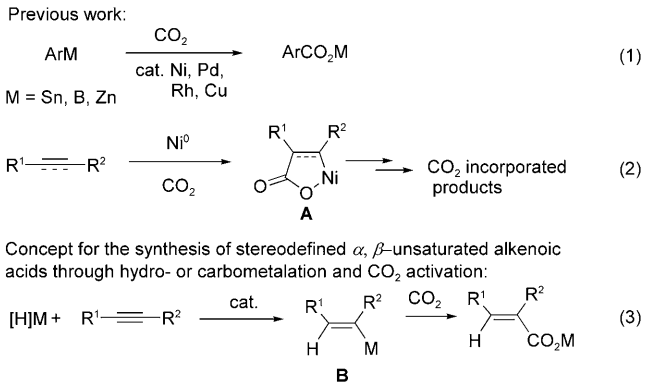
In memory of Xinwei Ma

Activation of carbon dioxide and converting it into useful chemical feedstock have attracted much attention owing to the fact that CO_2 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 CO_2 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 carbozincation[13,14] reaction [Scheme 1, Eq. (3)]. With this notion in mind, we envisioned that organozinc reagents generated in situ from hydro- or carbozincation of unsaturated hydrocarbon species may react with CO_2 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 Cs_2CO_3 (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 CO_2. So far, there are no such reports on alkyne substrates; the challenge here would be the lower reactivity of the 1-alkenylic zinc generated in situ towards CO_2[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 CO_2 in the presence of 10 mol% of $[Ni(cod)_2]$, 20 mol% of PCy_3, and 3 equivalents of $ZnEt_2$. 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 $ZnBr_2$, 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,

Previous work:



Concept for the synthesis of stereodefined α, β–unsaturated alkenoic acids through hydro- or carbometalation and CO_2 activation:

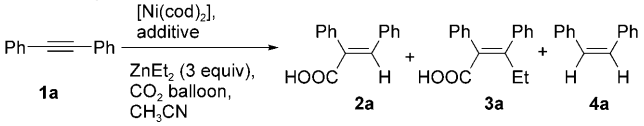
Scheme 1. Previous work and our concept for CO_2 activation.

[*] S. Li, Prof. Dr. S. Ma
State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences
354 Fenglin Lu, Shanghai 200032 (P.R. China)
Fax: (+86) 21-6260-9305
E-mail: masm@sioc.ac.cn
W. Yuan, Prof. Dr. S. Ma
Shanghai Key Laboratory of Green Chemistry and Chemical Process, Department of Chemistry, East China Normal University
3663 North Zhongshan Lu, Shanghai 200062 (P.R. China)

[**] Financial support from the Major State Basic Research and Development Program (2009CB825300), National Natural Science Foundation of China (20732005), and Project for Basic Research in Natural Science Issued by Shanghai Municipal Committee of Science (08dj1400100) is greatly appreciated. We thank Mr. Guobin Chai of our research group for reproducing the results presented in entry 2 of Table 2, entry 4 of Table 3, and Equation 1 in Scheme 3.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201007128.

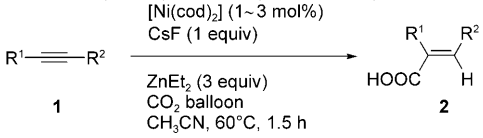
Table 1: Optimization of reaction conditions.[a]



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_3PO_4 (3)	RT	31	11	<1.6	26
3	10	Cs_2CO_3 (3)	RT	25	<1	n.d.	13
4	10	K_2CO_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 $ZnEt_2$ (1 M in hexane, 1.5 mL), and about 1 L of CO_2 (a balloon) in CH_3CN (3 mL) at the indicated temperature. [b] Yield based on ^1H NMR analysis. [c] 3 equiv of $ZnEt_2$ (1.5 M in toluene, 1.0 mL). cod = cycloocta-l,5-diene, Cy = cyclohexyl, n.d. = not determined.

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]	p-$MeOC_6H_4$	p-$MeOC_6H_4$	1	89 (**2b**)
3	p-MeC_6H_4	p-MeC_6H_4	1	89 (**2c**)
4	m-MeC_6H_4	m-MeC_6H_4	1	91 (**2d**)
5[d]	*n*Pr	*n*Pr	3	62 (**2e**)
6	Ph	*t*Bu	3	79 (**2f**)
7[e]	Ph	*t*Bu	3	91 (**2f**)
8	α-naphthyl	*t*Bu	3	88 (**2g**)
9	p-$MeOC_6H_4$	*t*Bu	3	81 (**2h**)
10	p-FC_6H_4	*t*Bu	3	77 (**2i**)
11	2-thienyl	*t*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 $ZnEt_2$ (1.5 M in toluene, 1.0 mL), and about 1 L of CO_2 (a balloon) in CH_3CN (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 $ZnEt_2$ (1.5 M in toluene, 14.0 mL), and about 1.5 L of CO_2 (a balloon) in CH_3CN (42 mL).

(*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 $ZnEt_2$ 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 R^1 is an aryl (Table 2, entries 6–10) or 2-thienyl group (Table 2, entry 11) and R^2 is the tertiary butyl group, the product is regiospecific. 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 CO_2H group connected to the sp^2 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).

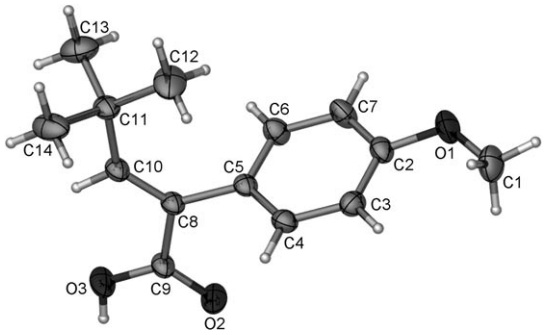
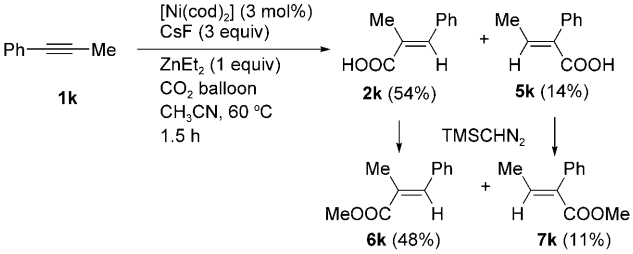


Figure 1. ORTEP plot of **2h** shown with ellipsoids at the 30% probability level.

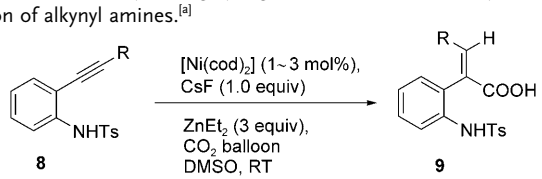


Scheme 2. Nickel-catalyzed hydrocarboxylation of **1k**. Yields of **2k** and **5k** were determined by ^1H NMR analysis. TMS = trimethylsilyl.

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).

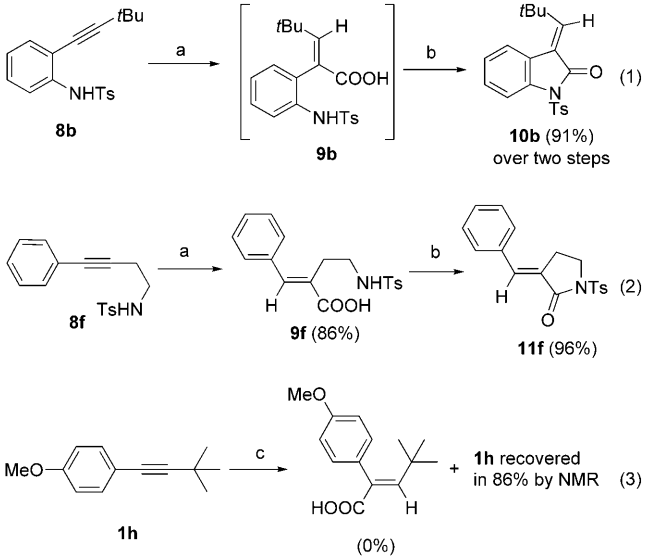
The amino acid **9b** could be easily transformed into 3-alkylideneoxindole **10b**[18] with the aid of EDCI (Scheme 3, Eq. (1)). Notably, in this reaction the crude product **9b** was be

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	*t*Bu (**8b**)	3	3	94 (**9b**)
3	*n*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 $ZnEt_2$ (1.5 M in toluene, 1.0 mL), and about 1 L of CO_2 (a balloon) in DMSO (3 mL) at RT (25–30 °C). [b] Yield of isolated product. DMSO = dimethyl sulfoxide, Ts = 4-toluenesulfonyl.



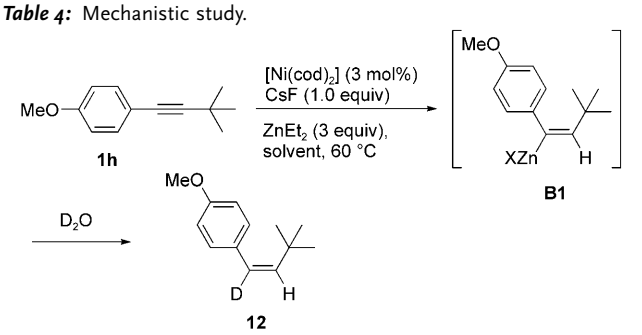
Scheme 3. Synthesis of 3-alkylideneoxindole **10b** and α-alkylidene-γ-butyrolactam **11f**. a) $[Ni(cod)_2]$ (3 mol%), CsF (1.0 equiv), $ZnEt_2$ (3 equiv), CO_2 (a balloon), DMSO, RT, 3 h; b) EDCI (1.2 equiv), CH_2Cl_2, −10 °C→RT; c) 1. $[Ni(cod)_2]$ (1.0 equiv), CsF (1.0 equiv), CO_2 (a balloon), CH_3CN, 60 °C, 11 h; 2. HCl. Amount of **1h** recovered was determined by ^{1}H NMR analysis. EDCI = (1-ethyl-3-(3-dimethylaminopropyl) 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, CO_2, and a stoichiometric amount of $[Ni(cod)_2]$ would directly afford the hydrocarboxylation product upon protonlysis. However, the reaction of alkyne **1h** and CO_2 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 ^{1}H 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 CO_2. The reaction of **1h** with $ZnEt_2$ in the presence of 3 mol% of $[Ni(cod)_2]$ and 1 equivalent of CsF for 5 minutes followed by quenching with D_2O provided *cis*-alkene **12** in 46% yield (based on ^{1}H NMR analysis) with a D incorporation of 34% (Table 4, entry 1). We reasoned that the low D

Table 4: Mechanistic study.

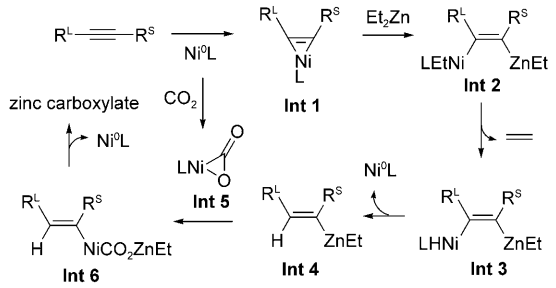


Entry	Solvent	*t* [min]	Yield of **12** [%][b]	%D in **12**	Yield of **1h** [%][b]
1	CH_3CN	5	46	34	48
2[a]	CH_3CN	30	25	78	67
3	CD_3CN	30	43	92	49
4	CD_3CN	90	43	91	47
5[c]	CH_3CN	5	78	32	11

[a] The reaction was carried out in the absence of CsF. [b] Yield determined by ^{1}H HMR 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 CO_2, and this was confirmed by running the reaction in CD_3CN (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 ^{1}H NMR analysis) with 32% of D incorportation, however, in the absence of CsF, the D incorportation in **12** increased to 78% with a yield of 25% (based on ^{1}H 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 CO_2 also increase the efficiency of the nickel catalyst (compare the results in Table 4 with that presented in Table 2, entry 9).

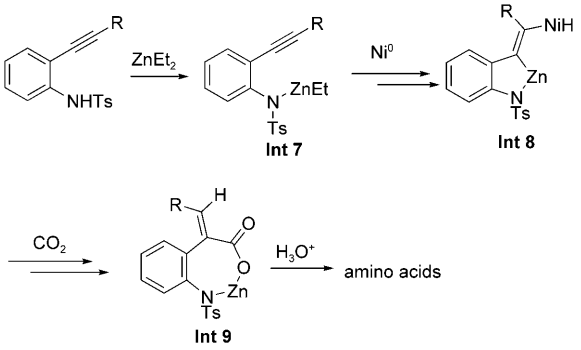
Based on these findings, a possible mechanism was proposed and is shown Scheme 4. The Ni^0 species first reacts with the alkyne to form **Int 1**, which was followed by transmetalation with $ZnEt_2$ to form **Int 2**, and this explains the *syn* stereoselectivity. The beta hydride elimination and subsequent 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 hydrocaroxylation 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 ($\approx$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 × 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→5/1) to afford **2f** (91%, 1.3071 g) as a white solid. M.p. = 132–133 °C (petroleum ether/ethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.96 (bs, 1H, COOH), 7.38–7.26 (m, 3H, ArH), 7.20–7.08 (m, 3H, ArH and HC=C), 0.92 ppm (s, 9H, *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.

Received: November 12, 2010
Revised: December 12, 2010
Published online: February 17, 2011

Keywords: alkynes · carbon dioxide · hydrocarboxylation · inorganic fluoride · nickel

[1] For recent reviews, see: a) J. Louie, *Curr. Org. Chem.* **2005**, *9*, 605; b) T. Sakakura, J.-C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365; c) M. Aresta, A. Dibenedotto, *Dalton Trans.* **2007**, 2975; d) G. A. Olah, A. Goeppert, G. K. S. Prakash, *J. Org. Chem.* **2009**, *74*, 487; e) M. Mori, *Eur. J. Org. Chem.* **2007**, 4981; f) A. Correa, R. Martin, *Angew. Chem.* **2009**, *121*, 6317; *Angew. Chem. Int. Ed.* **2009**, *48*, 6201.

[2] a) M. Shi, K. M. Nicholas, *J. Am. Chem. Soc.* **1997**, *119*, 5057; b) R. Johansson, O. F. Wendt, *Dalton Trans.* **2007**, 488.

[3] a) K. Ukai, M. Aoki, J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2006**, *128*, 8706; b) J. Takaya, S. Tadami, K. Ukai, N. Iwasawa, *Org. Lett.* **2008**, *10*, 2697; c) T. Ohishi, M. Nishiura, Z. Hou, *Angew. Chem.* **2008**, *120*, 5876; *Angew. Chem. Int. Ed.* **2008**, *47*, 5792.

[4] a) C. S. Yeung, V. M. Dong, *J. Am. Chem. Soc.* **2008**, *130*, 7826; b) H. Ochiai, M. Jang, K. Hirano, H. Yorimitsu, K. Oshima, *Org. Lett.* **2008**, *10*, 2681.

[5] For palladium-catalyzed direct carboxylation of aryl bromides in the presence of $ZnEt_2$ with CO_2, see: A. Correa, R. Martin, *J. Am. Chem. Soc.* **2009**, *131*, 15974.

[6] a) H. Hoberg, Y. Peres, A. Milchereit, *J. Organomet. Chem.* **1986**, *307*, C38; b) H. Hoberg, Y. Peres, C. Krüger, Y.-H. Tsay, *Angew. Chem.* **1987**, *99*, 799; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 771; c) H. Hoberg, A. Ballesteros, A. Sigan, C. Jegat, A. Milchereit, *Synthesis* **1991**, 395.

[7] a) M. Takimoto, M. Mori, *J. Am. Chem. Soc.* **2001**, *123*, 2895; for nickel-catalyzed carboxylative cyclization of bis-1,3-dienes, see:

b) M. Takimoto, M. Mori, *J. Am. Chem. Soc.* **2002**, *124*, 10008; c) M. Takimoto, Y. Nakamura, K. Kimura, M. Mori, *J. Am. Chem. Soc.* **2004**, *126*, 5956.

[8] a) S. Saito, S. Nakagawa, T. Koizumi, K. Hirayama, Y. Yamamoto, *J. Org. Chem.* **1999**, *64*, 3975; b) M. Takimoto, K. Shimizu, M. Mori, *Org. Lett.* **2001**, *3*, 3345; c) M. Aoki, M. Kaneko, S. Izumi, K. Ukai, N. Iwasawa, *Chem. Commun.* **2004**, 2568; d) Y. Six, *Eur. J. Org. Chem.* **2003**, 1157; e) Y. Six, *J. Chem. Soc. Perkin Trans. 1* **2002**, 1159.

[9] a) M. Takimoto, M. Kawamura, M. Mori, *Org. Lett.* **2003**, *5*, 2599; b) M. Aoki, S. Izumi, M. Kaneko, K. Ukai, J. Takaya, N. Iwasawa, *Org. Lett.* **2007**, *9*, 1251; c) M. Murakami, N. Ishida, T. Miura, *Chem. Lett.* **2007**, *36*, 476.

[10] a) K. Shimizu, M. Takimoto, Y. Sato, M. Mori, *Org. Lett.* **2005**, *7*, 195; b) K. Shimizu, M. Takimoto, Y. Sato, M. Mori, *Synlett* **2006**, 3182.

[11] M. Takimoto, M. Kawamura, M. Mori, Y. Sato, *Synlett* **2005**, 2019.

[12] For titanium-catalyzed hydrozincation of alkynes, see: Y. Gao, K. Harada, T. Hata, H. Urabe, F. Sato, *J. Org. Chem.* **1995**, *60*, 290.

[13] For rhodium-catalyzed hydro- and carbozincation of alkynamides, see: B. Gourdet, M. E. Rudkin, C. A. Watts, H. W. Lam, *J. Org. Chem.* **2009**, *74*, 7849.

[14] For nickel-catalyzed carbozincation of arylalkynes, see: a) T. Stüdemann, P. Knochel, *Angew. Chem.* **1997**, *109*, 132; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 93; b) T. Stüdemann, M. Ibrahim-Ouali, P. Knochel, *Tetrahedron* **1998**, *54*, 1299.

[15] C. M. Williams, J. B. Johnson, T. Rovis, *J. Am. Chem. Soc.* **2008**, *130*, 14936.

[16] J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2008**, *130*, 15254.

[17] For the rhodium or copper-catalyzed reaction of limited 1-alkenyl boronates with carbon dioxide, see Ref. [3]. There are reports on the reaction of aryl or alkyl zincs with carbon dioxide,[4] however, there is no reports on the reaction of 1-alkenyl zincs with carbon dioxide, except one example in: a) K. Kobayashi, Y. Kondo, *Org. Lett.* **2009**, *11*, 2035.

[18] This is a class of important compounds with a broad range of biological activities. For related references, see: a) L. Sun, N. Tran, F. Tang, H. App, P. Hirth, G. McMahon, C. Tang, *J. Med. Chem.* **1998**, *41*, 2588; b) M. Vieth, D. J. Cummins, *J. Med. Chem.* **2000**, *43*, 3020; c) C. L. Woodard, Z. Li, A. K. Kathcart, J. Terrell, L. Gerena, M. Lopez-Sanchez, D. E. Kyle, A. K. Bhattacharjee, D. A. Nichols, W. Ellis, S. T. Prigge, J. A. Geyer, N. C. Waters, *J. Med. Chem.* **2003**, *46*, 3877; d) B. J. Hare, W. P. Walters, P. R. Caron, G. W. Bemis, *J. Med. Chem.* **2004**, *47*, 4731; e) B. Pandit, Y. Sun, P. Chen, D. L. Sackett, Z. Hu, W. Rich, C. Li, A. Lewis, K. Schaefer, P.-K. Li, *Bioorg. Med. Chem.* **2006**, *14*, 6492; f) A. Andreani, S. Burnelli, M. Granaiola, A. Leoni, A. Locatelli, R. Morigi, M. Rambaldi, L. Varoli, M. W. Kunkel, *J. Med. Chem.* **2006**, *49*, 6922.

[19] For studies on the biological activities of α-alkylidene-γ-butyrolactams, see: a) C. Belaud, C. Roussakis, Y. Letourneux, N. ElAlami, J. Villieras, *Synth. Commun.* **1985**, *15*, 1233; b) T. Janecki, E. Błaszczyk, K. Studzian, A. Janecka, U. Krajewska, M. Różalski, *J. Med. Chem.* **2005**, *48*, 3516; c) H. Krawczyk, Ł. Albrecht, J. Wojciechowski, W. M. Wolf, U. Krajewska, M. Różalski, *Tetrahedron* **2008**, *64*, 6307; d) A. Albrecht, Ł. Albrecht, M. Różalski, U. Krajewska, A. Janecka, K. Studzianc, T. Janecki, *New J. Chem.* **2010**, *34*, 750.

[20] A. Togni, L. M. Venanzi, *Angew. Chem.* **1994**, *106*, 517; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 497.

[21] Crystal data for compound **2h**: $C_{14}H_{18}O_3$, MW = 234.28, monoclinic, space group $P21/c$, final R indices $[I > 2\sigma(I)]$, $R1 = 0.0451$, $wR2 = 0.1230$; R indices (all data), $R1 = 0.0518$, $wR2 = 0.1308$; $a = 5.9511(2)$ Å, $b = 8.4184(3)$ Å, $c = 26.7119(9)$ Å, $\alpha = 90°$, $\beta = 96.1180(10)°$, $\gamma = 90°$, $V = 1330.61(8)$ Å^3, $T = 296(2)$ K, $Z = 4$, reflections collected/unique 14842/2331 ($R_{int} = 0.0206$), number of observations $[> 2\sigma(I)]$ 2331, parameters: 154. CCDC 799934 (**2h**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[22] For additives that increase the activity of zincs, see: a) A. Metzger, M. A. Schade, P. Knochel, *Org. Lett.* **2008**, *10*, 1107; b) A. Metzger, S. Bernhardt, G. Manolikakes, P. Knochel, *Angew. Chem. Int. Ed.* **2010**, *122*, 4769; *Angew. Chem. Int. Ed.* **2010**, *49*, 4665.

[23] M. Aresta, C. F. Nobile, V. G. Albano, E. Forni, M. Manassero, *J. Chem. Soc. Chem. Commun.* **1975**, 636.

[24] When Ph_2Zn was treated with CO_2 mediated by 2.0 equivalents of CsF in CH_3CN under the catalysis of 1 mol% of $[Ni(cod)_2]$, 93% yield (based on ^{1}H NMR analysis) of PhCOOH was produced based on Ph_2Zn.

[25] D. W. Arnold, S. E. Bradforth, E. H. Kim, D. M. Neumark, *J. Chem. Phys.* **1995**, *102*, 3493.

