Communication

Cobalt-Catalyzed Allylic C(sp3)–H Carboxylation with CO2

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Cobalt-Catalyzed Allylic C(sp^3)–H Carboxylation with CO_2

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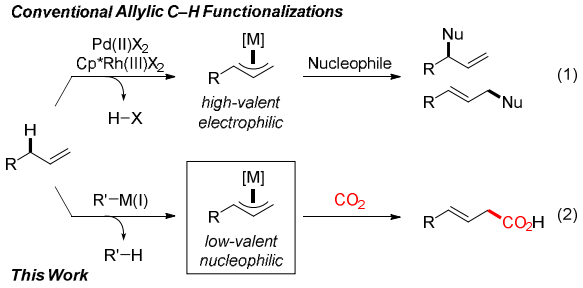
Supporting Information Placeholder

ABSTRACT: A catalytic carboxylation of the allylic C(sp^3)–H bond of terminal alkenes with CO_2 was developed with the aid of a cobalt/Xantphos complex. A wide range of allylarenes and 1,4-dienes were successfully transformed into the linear styrylacetic acid and hexa-3,5-dienoic acid derivatives in moderate to high yields, with excellent regioselectivity. The carboxylation showed remarkable functional group tolerability, so that selective addition to CO_2 occurred in the presence of other carbonyl groups such as amide, ester, and ketone. Since styrylacetic acid derivatives can be readily converted into optically active γ-butyrolactones through Sharpless asymmetric dihydroxylation, this allylic C(sp^3)–H carboxylation showcases a facile synthesis of γ-butyrolactones from simple allylarenes via short steps.

Transition metal-catalyzed direct functionalization of C–H bonds has been recognized as a potent and efficient platform for straightforward organic synthesis to not only construct carbon frameworks but also introduce various heteroatoms (B, N, O, Si, halogens, etc.) without the need for pre-functionalization of the poorly reactive C–H bonds.[1] However, catalytic functionalization of C(sp^3)–H bonds has seen much less development because of the inherent low reactivity and lability of the C(sp^3)–M (transition metal) complexes generated by C–H bond cleavage.[2] Besides, most of the reported methods for catalytic C–H addition to carbonyl electrophiles are restricted to highly reactive carbonyl compounds such as aldehydes, imines, α-ketocarbonyl compounds, and isocyanates.[3] Hence, the development of catalytic caboxylation of C(sp^3)–H bonds with the much less reactive carbon dioxide (CO_2) would be an innovative milestone in the fields of C–H activation and fixation chemistry of CO_2, an abundant, inexpensive, and nontoxic C1 feedstock.[4] Although catalytic carboxylation of acidic C–H bonds through deprotonation by basic metal complexes has been well studied,[5] there are only a few examples of C–H carboxylation apart from acid-base mechanism.[6] In addition, most of the past studies demonstrate the carboxylation of C(sp)–H and C(sp^2)–H bonds. Catalytic direct carboxylation of C(sp^3)–H bonds is still in its nascent stage, with only a few reported methods for methane carboxylation[7] and UV irradiation methods.[8,9] Hence, catalytic C(sp^3)–H carboxylation with CO_2 under mild conditions holds a formidable challenge that would open new horizons to the synthesis of aliphatic carboxylic acids.

To this end, we initially targeted terminal alkenes as substrates for C(sp^3)–H carboxylation. Allylic C(sp^3)–H functionalization using high-valent Pd(II) and Rh(III) catalysts has been widely studied, which allows direct substitution of the allylic C–H bond by a variety of nucleophiles through the generation of electrophilic η^3-allylmetal intermediates (Scheme 1, eq 1).[10] However, these methods do not meet the requirements of our planned carboxylation, since nucleophilic allylmetal species are necessary for the reaction with CO_2. We therefore envisaged the generation of a low-valent allylmetal species, some of which are generated through the cleavage of allylic C(sp^3)–H bonds by low-valent alkylmetal complexes (e.g., alkyl-Co(I) and Rh(I)) with the release of an alkane.[11,12] Although the reactivities of these allylmetal complexes have not been investigated, we hypothesized that a low-valent allylmetal complex shows high nucleophilicity toward CO_2 on the basis of the precedented transition metal-catalyzed carboxylation,[13] thus furnishing β,γ-unsaturated carboxylic acids (eq 2).

Scheme 1. Strategy for the Generation of a Nucleophilic Allylmetal Complex

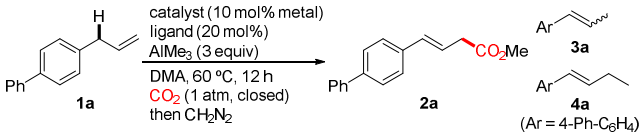


Based on the above hypothesis, we extensively investigated the reaction conditions for the carboxylation of allylarene **1a** under CO_2 atmosphere (1 atm, closed), using various metal salts, ligands, and alkylated reagents.[14] A combination of $Co(acac)_2$, Xantphos, and $AlMe_3$ provided the corresponding *trans*-styrylacetic acid methyl ester **2a** in 32% yield, together with olefin isomers in 41% yield after treatment with CH_2N_2 (Table 1, entry 1). Both Co(III) and Co(I) complexes were competent catalysts (entries 2 and 3) for this reaction; however, other transition metal salts such as Cr(II), Mn(I), Fe(III), Rh(I), Ir(I), Ni(II), and Cu(I) salts did not promote carboxylation but **1a** was recovered, and in some cases, olefin isomers were observed (entries 4-10).[15] Notably, the reaction offered extremely high linear/branch selectivity, so that only the linear carboxylated product **2a** was obtained. Encouraged by this result, we examined the effects of various ligands in the presence of $Co(acac)_2$. However, DPEphos, DPPF, DPPP, and 2,2'-bpy afforded the olefin isomerization product **3a** as the major product (entries 11-14). The reaction was strongly influenced even by subtle structural differences between Xantphos and DPEphos, implying that the oxygen atom in Xantphos might play a crucial role as a hemilabile ligand in this carboxylation (*vide infra*).

Next, the reaction conditions were further screened under the $Co(acac)_2$/Xantphos system. When the amount of $AlMe_3$ was reduced to 1.5 equiv, the yield of **2a** increased to 45% (entry 15).

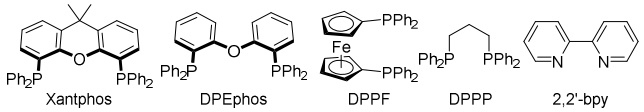
The concentration of **1a** also affected the efficiency, in which lower concentration suppressed olefin isomerization to afford the desired **2a** in 58% yield (entry 16). The addition of 1 equiv of CsF further accelerated the carboxylation to provide **2a** in 71% yield (entry 17).[16]

Table 1. Condition Screening



entry	metal salt	Ligand	yields (%)[a]			
			2a	**3a**[b]	**4a**	**1a**
1	$Co(acac)_2$	Xantphos	32	34/7	13	-
2	$Co(acac)_3$	Xantphos	21	58/9	-	-
3	$CoCl(PPh_3)_3$	Xantphos	22	54/12	5	4
4	$CrCl_2$	Xantphos	-	-/-	-	99
5	$MnBr(CO)_5$	Xantphos	-	-/-	-	98
6	$Fe(acac)_3$	Xantphos	-	9/2	-	86
7	$[Rh(cod)Cl]_2$	Xantphos	-	25/6	-	67
8	$[Ir(cod)Cl]_2$	Xantphos	-	5/-	-	93
9	$Ni(acac)_2$	Xantphos	-	27/3	-	69
10	CuI	Xantphos	-	6/2	-	89
11	$Co(acac)_2$	DPEphos	-	74/3	-	-
12	$Co(acac)_2$	DPPF	-	87/4	7	-
13	$Co(acac)_2$	DPPP	-	74/12	10	-
14	$Co(acac)_2$	2,2'-bpy	-	90/-	-	4
15[c]	$Co(acac)_2$	Xantphos	45	26/5	15	-
16[c,d]	$Co(acac)_2$	Xantphos	58	11/3	9	3
17[c,d,e]	**$Co(acac)_2$**	**Xantphos**	**71**	17/3	1	2

Reaction conditions: allylarene **1a** (0.2 mmol), catalyst (10 mol% of the metal), ligand (20 mol%), $AlMe_3$ (0.6 mmol), DMA (1.0 mL, 0.2 M), CO_2 (1 atm, closed), 12 h. [a]Yields were determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [b]Ratio of *E*/*Z* isomers. [c]1.5 equiv of $AlMe_3$ was used. [d]0.05 M in DMA (4.0 mL). [e]1 equiv of CsF (0.2 mmol) was added.



With the optimal conditions in hand, we next explored the substrate scope of the allylic C–H carboxylation of allylarenes under the $Co(acac)_2$/Xantphos/$AlMe_3$ system (Figure 1). Methyl esterification was unnecessary except in the case of **1o**, and a series of linear carboxylic acids were obtained with excellent regioselectivity. Additionally, a back extraction/crystallization sequence was effective for their purification process especially in case the product is a solid.[14] Electron-neutral allylarenes **1a-1d**, including the *ortho*-substituted **1c**, gave the corresponding linear carboxylic acids **5a-5d** in moderate to good yields. A variety of functionalized allylarenes bearing trifluoromethyl groups (**1e** and **1f**) and alkoxy groups (**1g-1i**) were tolerated under the present reaction conditions. Remarkably, pre-treatment of **1j** containing a phenolic hydroxy group with 0.5 equiv of $AlMe_3$ afforded an aluminum aryloxide, and subsequent carboxylation with 1.5 equiv of $AlMe_3$ furnished the corresponding carboxylic acid **5j** in 72% yield. The reaction proceeded selectively with CO_2 when using substrates containing amide (**1k**), ester (**1l**), and ketone (**1m**) carbonyls, which are generally reactive toward nucleophiles than is CO_2 and incompatible with the carboxylation using strongly nucleophilic organomagnesium and organolithium reagents. Furthermore, indole (**1n**) and quinoline (**1o**) derivatives were carboxylated to afford the products in 84% and 63% yields, respectively.

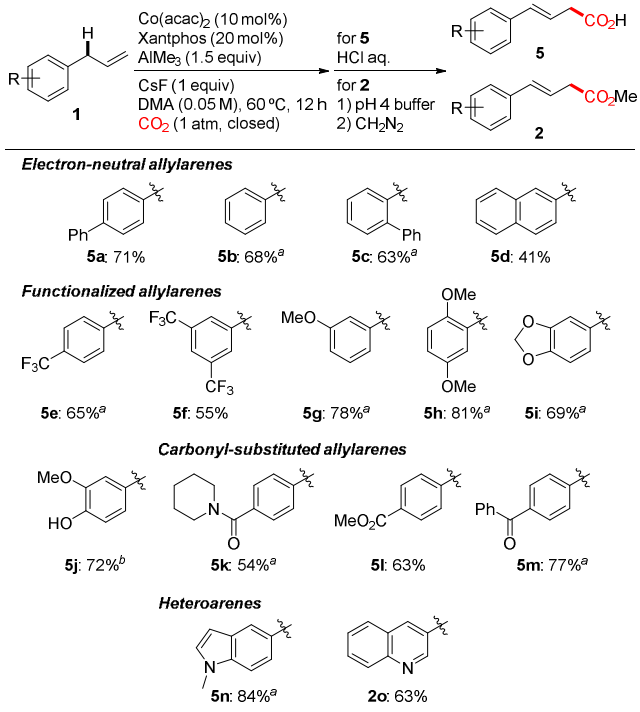


Figure 1. Substrate scope of allylarenes (0.4 mmol). Isolated yields are shown. [a]1-11% of olefin isomer (α,β-unsaturated carboxylic acid) was observed.[14] [b]2 equiv of $AlMe_3$ was used.

The efficient and highly regioselective carboxylation of allylarenes led us to examine the feasibility of using 1,4-dienes, which are assumed to show similar reactivity to allylarenes, as substrates. Indeed, a wide range of 1,4-diene derivatives were applicable to the cobalt-catalyzed carboxylation, and hexa-3,5-dienoic acid derivatives were obtained in good to high yields (Figure 2).

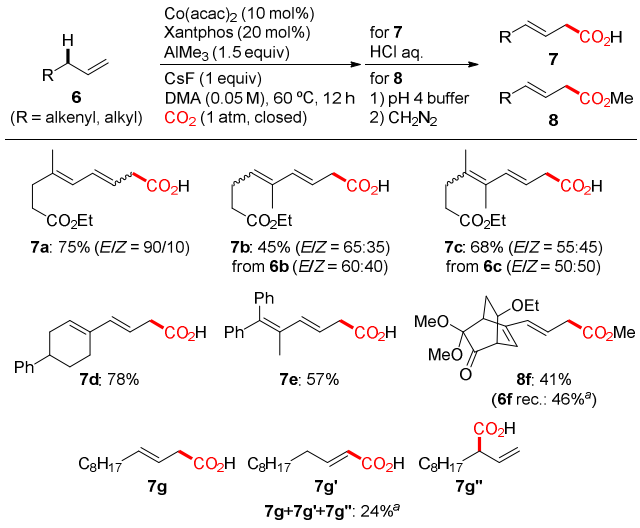


Figure 2. Substrate scope of 1,4-dienes and a simple alkene (0.4 mmol). Isolated yields are shown unless otherwise noted. [a]Yields were determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

Compounds **6a-6c** possessing different substitution patterns on the internal alkene moieties (**6b** and **6c** contain alkene regioisomers) exhibited different reactivities for the carboxylation of CO_2, but there was no significant change in the *E*/*Z* ratios of the inter-

nal alkenes.[14] 1,4-Dienes containing a cyclohexenyl moiety (**6d**) and *gem*-diphenyl moiety (**6e**) afforded the corresponding linear carboxylic acids **7d** and **7e** in 78% and 57% yields, respectively. The more structurally complicated bicyclo[2.2.2]octane-based 1,4-diene **6f** bearing ketone and dimethyl ketal moieties also underwent carboxylation; after careful work up using aq. citric acid/$NaCO_3$ buffer and methyl esterification, the corresponding ester **8f** was obtained in 41% yield, with 46% recovery of **6f**. This result indicated the dimethyl ketal moiety could be tolerated under the cobalt-catalyzed carboxylation conditions. Furthermore, carboxylation of a simple terminal alkene **6g** provided the carboxylic acids **7g**, **7g'**, and **7g"**. Even though the yield and regioselectivity of the reaction using **6g** were low, this result suggests the feasibility of extending the protocol to less reactive allylic C–H bonds.

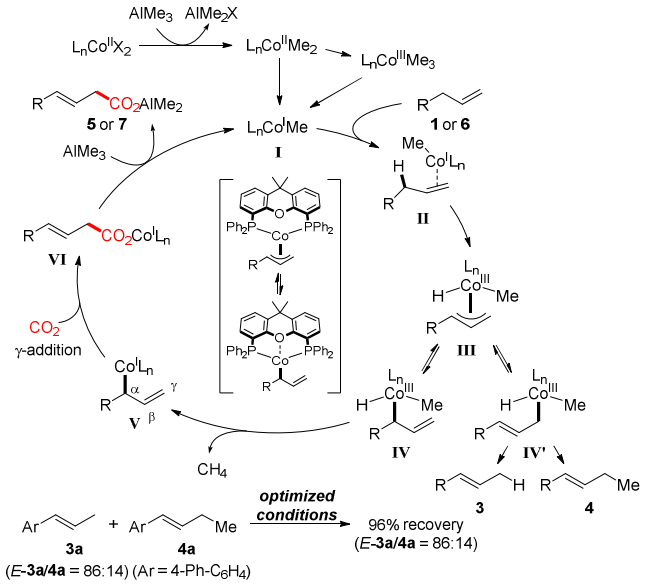


Figure 3. Proposed Catalytic Cycle.

Based on the obtained results, including significant ligand effects, we propose a plausible reaction pathway in Figure 3. Since cobalt catalysts with different valences (Co(I), Co(II), Co(III)) equally promoted the carboxylation, a low-valent methylcobalt(I) species **I** would first be generated from the cobalt salt, Xantphos, and $AlMe_3$.[17] Dialkylcobalt(II) is known to undergo disproportionation to form Co(I) and Co(III),[18] and the latter further produces Co(I) through reductive elimination. Next, the alkene in the substrate would coordinate to cobalt, thus facilitating the cleavage of the adjacent allylic C–H bond to produce η^3-allylcobalt species **III**. At this stage, the oxygen atom in the Xantphos ligand might coordinate to cobalt, which would assist the tautomerization of η^3-allylcobalt **III** to η^1-allylcobalt complexes **IV** and **IV'**.[19] The rigid backbone of Xantphos might work as a hemilabile ligand to promote the tautomerization; in contrast, in the case of DPEphos, which has a more flexible backbone, the oxygen atom is reluctant to coordinate to the cobalt center due to the free rotation of the Ar–O–Ar bond. Subsequently, two different ways are possible. Reductive elimination of methane from complex **IV** would lead to a low-valent allylcobalt species **V**,[11] which is stabilized by an aryl or alkenyl ligand.[20] Subsequently, C–C bond formation with CO_2 would proceed at the γ-position[21] to produce cobalt carboxylate **VI**. Transmetalation between **VI** and $AlMe_3$ would furnish the linear carboxylated product along with the regeneration of methylcobalt species **I**.

On the other hand, reductive elimination of complex **IV'** would generate the olefin isomerization product **3** and methylated product **4**. This reductive elimination step would be irreversible, since **3a** and **4a** were unreactive under the optimized carboxylation conditions. While further in-depth investigation is required to unveil the exact role of CsF in this carboxylation, its beneficial effect on the yield might be attributed to the interaction with CO_2, which allows for the dissolution of more CO_2 into the reaction system rather than the generation of the tetracoordinate fluoroaluminate complex.[16,22]

The cobalt-catalyzed allylic C–H carboxylation provides a new synthetic strategy for linear styrylacetic acid derivatives from allylarenes, which could not be achieved by simple deprotonation using a strong base (e.g., ^{n}BuLi), followed by the reaction with CO_2.[23] Since styrylacetic acid derivatives have non-conjugated alkene and carboxylic acid moieties, a variety of transformations can be expected. In particular, styrylacetic acid derivatives are key synthons of various functionalized γ-arylbutyrolactones, which are structural motifs found in many natural products (Figure 4).[24] Indeed, several transformations of styrylacetic acid derivative **5i** into γ-butyrolactones could be achieved (Scheme 2). Carboxylic acid **5i** derived from the commercially available safrole **1i** was readily converted into *anti*-β-iodo- and *anti*-β-hydroxy-γ-lactone **9i** and **10i** in good yields by treatment with Oxone®/KI[25] and dimethyldioxirane (DMDO),[26] respectively. Besides, Sharpless asymmetric dihydroxylation of the corresponding ester **2i** furnished the optically active *syn*-β-hydroxy-γ-butyrolactone **11i** in 80% yield with 99% ee.[27] These protocols provide a stereodivergent synthesis of γ-arylbutyrolactones from allylbenzene derivatives via short steps. Furthermore, **5h** was stereoselectively converted into a similar lactone **11h**, which is a key intermediate in the synthesis of tricyclic pharmacophores, through the oxa-Pictet-Spengler reaction and subsequent oxidation.[28]

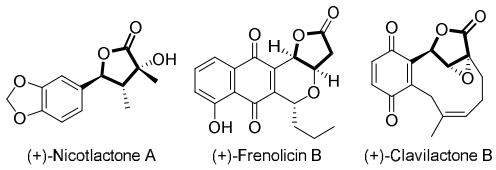
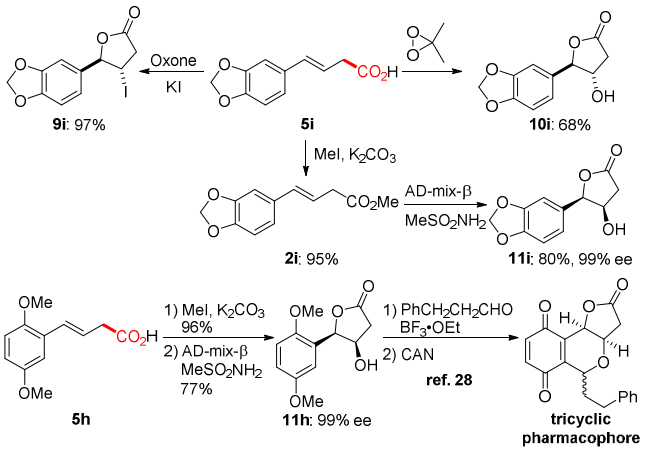


Figure 4. γ-Arylbutyrolactone-Based Bioactive Natural Products.

Scheme 2. Synthesis of γ-Arylbutyrolactones



In summary, we have developed a catalytic direct allylic C(sp^3)–H carboxylation by using the $Co(acac)_2$/Xantphos/$AlMe_3$ system, which enabled highly regioselective transformation of allyl groups into linear 3-butenoic acid motifs with good functional group tolerance. The carboxylated products, styrylacetic acids, could be readily converted into γ-arylbutyrolactones. Further research into the synthetic application of the protocol is ongoing, and the results will be reported in due course.

ASSOCIATED CONTENT

Supporting Information

Supporting Information Available. The information is available free of charge via the Internet at http://pubs.acs.org.

Supplemental data, experimental procedures, and characterizations.

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Notes

The authors declare no competing financial interests.

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(23) The treatment of **1a** with ^{n}BuLi in the presence of HMPA in 0 ºC in THF followed by introduction of gaseous CO_2 gave regioisomeric mixture of carboxylated products in 68% combined yield (linear/branch = 57:43, see the SI). Besides, no carboxylated product was observed from 1,4-diene **6d** by the same protocol, suggesting that $Co(acac)_2$/Xantphos/$AlMe_3$ catalytic system is advantageous in terms of both regioselectivitity as well as reactivity.

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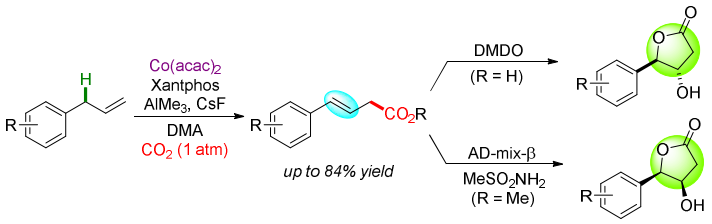

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