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Hydroesterification of Alkenes with Sodium Formate and Alcohols Promoted by Cooperative Catalysis of $Ru_3(CO)_{12}$ and 2-Pyridinemethanol

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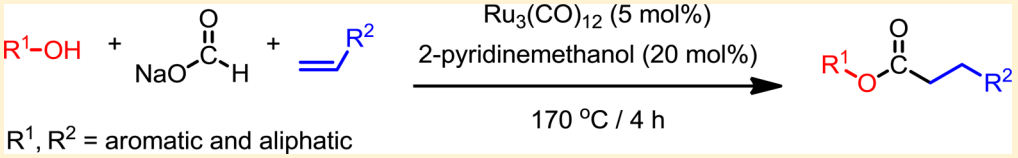
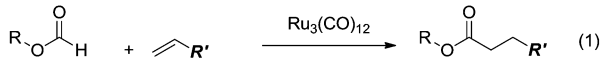
Supporting Information



ABSTRACT: A chelation-assisted hydroesterification reaction of alkenes with sodium formate and alcohols that involves cooperative catalysis by $Ru_3(CO)_{12}$ and 2-pyridinemethanol is described. In this three-component coupling reaction, sodium formate serves as the carbon monoxide source.

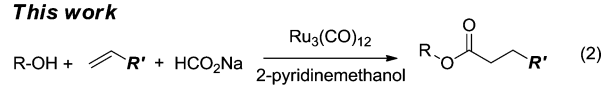
Transition-metal-catalyzed carbonylative esterification reactions are of current interest in organic synthesis because the resulting esters are important substances in the chemical, pharmaceutical, and perfume industries.[1] Among the various synthetic protocols to carry out these processes, chelation-assisted ruthenium-catalyzed hydroesterification reactions of alkenes with 2-pyridinemethyl formate is perhaps the best method (eq 1).[2] This reaction is facile because the 2-pyridyl

Previous report



(1)

This work



(2)

group acts as a chelating auxiliary for the cyclometalation step that generates CO and Ru(II) hydride, the latter of which is an important intermediate in the process. In addition, a rhodium-catalyzed hydroesterification reaction of alkenes with CO gas and stoichiometric amounts of 2-pyridinemethanol has also been devised.[3]

Studies carried out in recent years have shown that aryl or alkyl formates can be utilized in place of 2-pyridinemethyl formate for these processes.[4] All of these reactions utilize formate ester to generate the corresponding ester in which the 2-pyridinemethoxy or alkoxy group of the ester remains at its original position in the resulting ester. As a result, in order to utilize this procedure to prepare specific alkyl esters, a separate transesterification step with a desired alcohol is required. In a previous investigation, we developed a chelation-assisted hydroacylation reaction of alkenes with aldehydes that produces alkyl ketones and occurs under cooperative catalysis by a Rh(I)/2-aminopicoline system.[5] In this process, 2-amino-3-picoline serves as a chelation assistant that aids temporary installation of the metal onto the substrate during the C−H bond activation reaction and removal from the product after the reaction. We envisaged that 2-pyridinemethanol would also act as a chelation assistant in a new hydroesterification reaction depicted in eq 2. In studies probing this proposal, we also observed that sodium formate can be used as a carbonyl source. Herein we describe the results of an effort that has led to development of the new chelation-assisted strategy for the one-pot preparation of esters from alkenes, sodium formate, and alcohols promoted by the cooperative catalyst system comprising $Ru_3(CO)_{12}$ and 2-pyridinemethanol.

In studies aimed at determining the feasibility and optimal conditions for the new hydroesterification process, reactions of cyclohexene (**2a**) with 2-phenylethyl alcohol (**3a**) and sodium formate (**1**) were carried out at 170 °C for 4 h in the presence of $Ru_3(CO)_{12}$ (**4a**) (5 mol %) and 2-pyridinemethanol (**5a**) (20 mol %). This reaction produced 2-phenylethyl cyclohexanecarboxylate (**6a**) in 97% yield (Table 1, entry 1). We observed that the chelation auxiliary **5a** is indispensable for this process, as the reaction does not take place in its absence (entry 2). In addition, we found that the length of the linker between the 2-pyridyl and alcohol moieties in the cocatalyst is important, as 2-pyridone (**5b**) and 2-pyridineethanol (**5c**) are much less effective than **5a** in promoting the reaction (entries 3 and 4). The presence of pyridine-2,6-dimethanol (**5d**) and imidazolylmethanol **5e** (entries 5 and 6) as well as the addition of tetrabutylammonium iodide (TBAI) (entry 7)[2d] did not improve the efficiency of the reaction. Finally, a reaction carried

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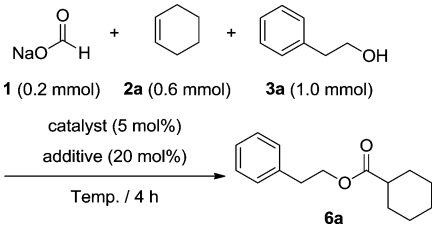
Table 1. Optimization of the Reaction Conditions

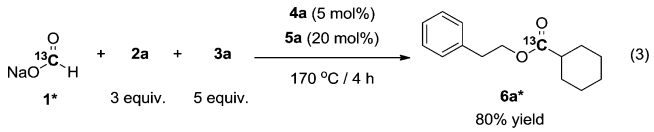


entry	Catalyst	additive	Temp. (°C)	yield(%)
1	$Ru_3(CO)_{12}$ (**4a**)	**5a**	170	97
2	**4a**	-	170	0
3	**4a**	**5b**	170	12
4	**4a**	**5c**	170	0
5	**4a**	**5d**	170	26
6	**4a**	**5e**	170	39
7[a]	**4a**	**5a**	170	32
8	**4a**	**5a**	150	50
9	$[Ru(p\text{-cymene})Cl_2]_2$ (**4b**)	**5a**	150	0
10	$[Ru(nbd)Cl_2]_2$ (**4c**)	**5a**	150	0
11	$Rh_4(CO)_{12}$ (**4d**)	**5a**	170	0

[a] 20 mol% of TBAI was added.

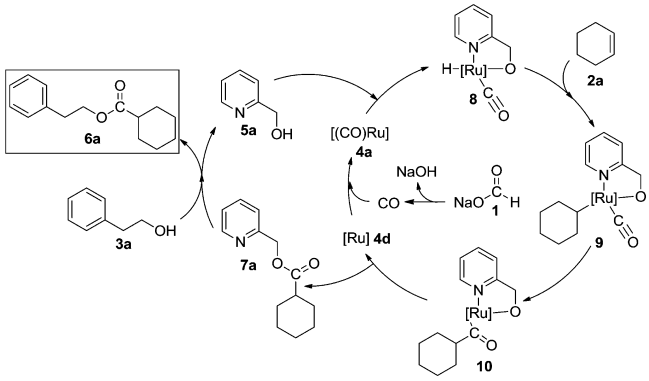
out at 150 °C took place much more slowly (entry 8). Other Ru(II) species including **4b**, **4c**, and $Rh_4(CO)_{12}$ (**4d**) did not show catalytic activity in this hydroesterification process (entries 9−11).

To determine the source of the carbonyl group in the ester product **6a**, ^{13}C-enriched sodium formate (**1***) was employed for the hydroesterification reaction (eq 3). The results of ^{13}C



NMR spectroscopic analysis showed that the carbonyl carbon in **6a*** is 26% enriched with ^{13}C, demonstrating that the carbonyl group of the ester product is derived from sodium formate (see the Supporting Information).[6] The findings suggest that the new hydroesterification reaction operates by the mechanistic pathway shown in Scheme 1. In this route, initial chelation-assisted O−H bond cleavage of 2-pyridinemethanol (**5a**) with $Ru_3(CO)_{12}$ (**4a**) generates the five-membered ruthenacyclic complex **8**.[7] Hydride insertion into cyclohexene (**2a**) then gives the cyclohexyl−Ru(II) intermediate **9**, which undergoes migratory insertion of the cyclohexyl group into coordinated CO in **9** to generate acyl−Ru(II) complex **10**. Reductive elimination in **10** produces ester **7a** along with Ru(0) intermediate **4d**, which regenerates catalyst **4a** by addition of CO formed by decomposition of sodium formate (**1**).

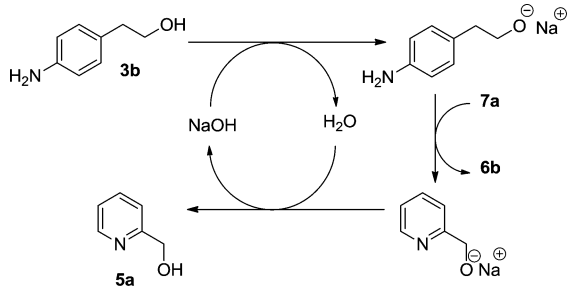
Scheme 1. Proposed Mechanism for the Hydroesterification Reaction of Alkenes with Sodium Formate and Alcohols under Cooperative Catalysis by Ru(0) and 2-Pyridinemethanol



Evidence exists for the proposal that CO and NaOH are formed from **1** at high temperatures (>150 °C). For example, the results of IR spectroscopic studies showed that **1** at high temperature generates CO gas, which is trapped by Rh(I) to form (CO)Rh(I) (IR peak at 2357 cm^{-1}).[8] Also, the generation of NaOH in this thermal process was confirmed by the observation of pH changes.[9]

In the mechanistic pathway, transesterification of the resulting 2-pyridylmethyl ester **7a** with 2-phenylethyl alcohol (**3a**) gives ester **6a** along with the starting material **5a**. Sodium formate-derived NaOH plays an important role in this transesterification process by serving as a base catalyst in the transesterification step.[10] This effect is seen in the hydroesterification reaction of 2-(4-aminophenyl)ethanol (**3b**), which possesses both an amino group and an alcohol group (Table 2, entry 2). Specifically, the reaction of **3b** with sodium formate and cyclohexene carried out under the standard conditions was observed to generate ester **6b** exclusively in 54% yield and none of the corresponding amide (Scheme 2). Thus, it appears that under the basic conditions, the alcohol moiety in **3b** is more nucleophilic than the aniline-type amine group.

Scheme 2. NaOH-Catalyzed Transesterification of 7a to 6b



The alcohol scope of the new catalytic hydroesterification reaction of cyclohexene was explored next. While benzyl alcohol (**3c**) is transformed into ester **6c** in 85% yield under the optimal conditions (Table 2, entry 3), phenol (**3d**) reacts to produce the corresponding ester **6d** in a much lower yield of 38% (entry 4). The source of this efficiency difference is likely to be the difference in the nucleophilicities of the alcohol and phenol. 2-Phenylethanols containing electron-donating and -withdrawing substituents at the *para* position on the aryl ring, such as methoxy (**3e**) and fluorine (**3f**), display similar

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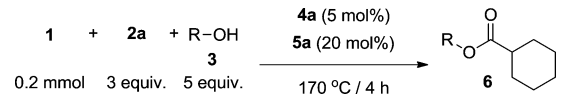
Table 2. Catalytic Hydroesterification Reactions of Various Alcohols with Sodium Formate



entry	alcohols	products	yield (%)
1	3a	6a	97
2	3b	6b	54
3	3c	6c	85
4	3d	6d	38
5	3e	6e	75
6	3f	6f	77
7	3g	6g	65
8	3h	6h	22
9	5a	7a	72
10	3i	6i	90
11	3j	6j	14
12	3k	6k	4
13	3l	6l	67
14	3m	6m	84

reactivities. The reaction of thiophenyl-substituted alcohol **3g** takes place in a moderate 65% yield to produce the corresponding ester **6g**, while the 4-pyridyl analogue **3h** reacts to form ester **6f** in only 22% yield. It is likely that the strongly coordinating pyridyl substituent in **3h** retards the complexation of Ru catalyst **4a** with **5a** that is required for chelation-assisted O–H bond cleavage. However, when **5a** is used as the starting alcohol, a 72% yield of the corresponding ester **7a** is generated.

Steric factors also influence the efficiency and regioselectivity (see below) of the transesterification reaction. This is exemplified by reactions with the 1° (**3i**), 2° (**3j**), and 3° (**3k**) alcohols, which form the corresponding esters in respective yields of 90%, 14%, and 4% (Table 2, entries 10–12).[11] Thus, it appears that steric hindrance effects the nucleophilicity of the alcohol in the anticipated manner. Finally, cycloalkylmethanols such as cyclohexylmethanol (**3l**) and cyclobutylmethanol (**3m**) also react efficiently under the optimal conditions (entries 13 and 14).

Reactions of various alkenes with 2-phenylethanol were examined (Table 3). Simple cycloalkenes **2a** and **2b** were observed to react to form the corresponding ester products **6a** and **6n** in yields of 97% and 64% (entries 1 and 2). Interestingly, norbornene (**2c**) reacts under the optimal conditions to form only the exo ester **6o** in 88% yield (entry 3).[12] Sterically hindered alkenes such as 3,3-dimethylbut-1-ene (**2d**) and α-methylstyrene (**2e**) serve as suitable substrates for the hydroesterification reaction. These alkenes regioselectively produce ester products **6p** and **6q** (94% and 87%, respectively; entries 4 and 5), wihich arise by addition to the terminal alkene carbons. These outcomes suggest that steric factors are important in forming the intermediate Ru complex **9** (Scheme 1). In this regard, it is interesting that the reaction of 1-hexene (**2f**) affords an 87% yield of a mixture of linear ester **6r** and branched ester **6s** in a 68/32 ratio (entry 6). Styrene (**2g**) also gives a product mixture of **6t** and **6u** in a 64/36 ratio in 66% yield (entry 7).

In the investigation described herein, we developed a new three-component hydroesterification reaction of alkenes with alcohols in the presence of sodium formate and the cooperative catalytic system comprising $Ru_3(CO)_{12}$ and 2-pyridinemethanol. The reaction follows a mechanistic route that consists of chelation-assisted hydroesterification and transesterification processes. In the reaction, sodium formate undergoes decomposition to form NaOH and carbon monoxide, the latter of which serves as the carbonyl source and the former promotes the transesterification step.

EXPERIMENTAL SECTION

General. Flash column chromatography was performed using 230–400 mesh silica gel, and column chromatography was monitored by analytical thin-layer chromatography (TLC) carried out on silica gel plates using UV light as a visualizing agent, *p*-anisaldehyde, ninhydrin, and $KMnO_4$ solution as staining solutions, and heat as a developing agent. pH values were recorded using a pH meter at room tempreature. Gas chromatographic analyses were performed on an Agilent 7890A instrument with an FID detector and an Agilent HP-5 capillary column. Mass chromatography analyses were performed using an HP-5MS column. IR spectra were recorded using an FT-IR spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with chemical shifts reported relative to residual deuterated solvent peaks. ^{1}H NMR spectra were referenced to $CDCl_3$ (δ 7.26 for ^{1}H) as an internal standard and are reported as follows: chemical shift (multiplicity, coupling constant, integration). Multiplicities are abbreviated as follows: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. ^{13}C NMR spectra were referenced to residual $CDCl_3$ (δ 77.26 for ^{13}C) as an internal standard. The analyzer type for high-resolution mass spectra was an ion-trap (orbitrap).

Materials. Commercially available reagent-grade chemicals and complexes **1**, **2a–g**, **3a–l**, **4a–b**, and **5a–d** were purchased and used as received, unless otherwise stated. Reagents **4c**[13] and **5e**[14] were prepared using literature procedures. ^{13}C-enriched sodium formate (**1***) was prepared by treatment of ^{13}C-enriched formic acid with NaOH in H_2O followed by removal of solvent. Cyclobutylmethanol (**3m**) was prepared by reduction of cyclobutanecarboxylic acid using $LiAlH_4$.

Typical Procedure: Preparation of 2-Phenylethyl Cyclohexanecarboxylate (6a) (Table 1). To a 1 mL pressure vial were added sodium formate (**1**) (16.8 mg, 0.2 mmol), cyclohexene (**2a**)

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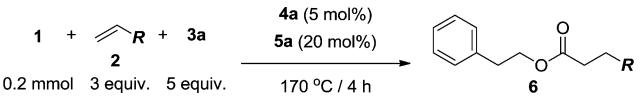
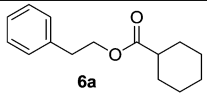
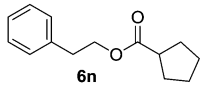
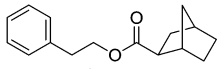
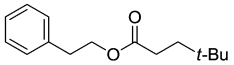
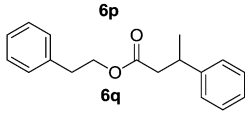
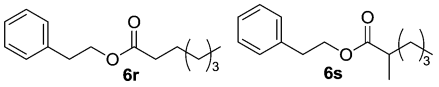
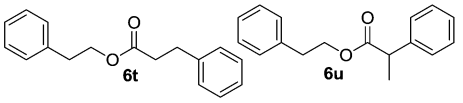
Table 3. Catalytic Hydroesterification of Various Alkenes with Sodium Formate



entry	olefins	products	yield (%)
1	 2a	 6a	97
2	 2b	 6n	64
3	 2c	 6o	88
4	 2d	 6p	94
5	 2e	 6q	87
6	 2f	 6r 6s	87 (68 / 32)[a]
7	 2g	 6t 6u	66 (64 / 36)[a]

(61.4 μL, 0.6 mmol), phenethyl alcohol (**3a**) (121 μL, 1.0 mmol), $Ru_3(CO)_{12}$ (**4a**) (6.4 mg, 0.01 mmol), and 2-pyridinemethanol (**5a**) (3.9 μL, 0.04 mmol). The mixture was stirred at 170 °C for 4 h. After cooling, the mixture was subjected to column chromatography (*n*-hexane/ethyl acetate = 10:1) on silica gel to give **6a** (45.0 mg, 97%) as a colorless oil.

*2-Phenylethyl Cyclohexanecarboxylate (**6a**).* [CAS no. 37139-88-1]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.29 (m, 2H), 7.24−7.21 (m, 3H), 4.28 (t, J = 7.0 Hz, 2H), 2.93 (t, J = 7.0 Hz, 2H), 2.27 (tt, J = 11.1, 3.5 Hz, 1H), 1.89−1.85 (m, 2H), 1.75−1.71 (m, 2H), 1.65−1.63 (m, 1H), 1.45−1.36 (m, 2H), 1.31−1.18 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.2, 138.1, 129.1, 128.6, 126.6, 64.7, 43.3, 35.3, 29.1, 25.9, 25.6.

*4-Aminophenethyl Cyclohexanecarboxylate (**6b**).* (26.7 mg, 54%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, J = 8.1 Hz, 2H), 6.64 (d, J = 8.1 Hz, 2H), 4.20 (t, J = 7.0 Hz, 2H), 3.56 (br s, 2H), 2.81 (t, J = 7.0 Hz, 2H), 2.26 (tt, J = 11.1, 3.4 Hz, 1H), 1.88−1.85 (m, 2H), 1.74−1.71 (m, 2H), 1.63−1.62 (m, 1H), 1.45−1.36 (m, 2H), 1.30−1.18 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.3, 144.7, 129.9, 128.1, 115.5, 65.2, 43.3, 34.4, 29.1, 25.9, 25.6; IR ($CDCl_3$) 3373, 2931, 2855, 1728, 1626, 1518, 1450, 1388, 1312, 1276, 1247, 1170, 1023, 823, 557, 513 cm^{-1}; HR-MS(ESI+) calcd for $C_{15}H_{21}NO_2Na^+$ $[M + Na]^+$ 270.1465, found 270.1455.

*Benzyl Cyclohexanecarboxylate (**6c**).* [CAS no. 22733-94-4] (37.1 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.31 (m, 5H), 5.11 (s, 2H), 2.36 (tt, J = 11.2, 3.6 Hz, 1H), 1.96−1.92 (m, 2H), 1.78−1.74 (m, 2H), 1.67−1.62 (m, 1H), 1.52−1.42 (m, 2H), 1.33−1.20 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.1, 136.5, 128.7, 128.2, 128.1, 66.0, 43.4, 29.2, 25.9, 25.6.

*Phenyl Cyclohexanecarboxylate (**6d**).* [CAS no. 3954-12-9] (15.5 mg, 38%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.35 (m, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.07−7.05 (m, 2H), 2.56 (tt, J = 11.2, 3.6 Hz, 1H), 2.09−2.05 (m, 2H), 1.85−1.80 (m, 2H), 1.71−1.66 (m, 1H), 1.64−1.54 (m, 2H), 1.41−1.26 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.8, 151.0, 129.5, 125.8, 121.7, 43.4, 29.1, 25.9, 25.5.

*4-Methoxyphenethyl Cyclohexanecarboxylate (**6e**).* (39.3 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 4.23 (t, J = 7.0 Hz, 2H), 3.78 (s, 3H), 2.86 (t, J = 7.0 Hz, 2H), 2.27 (tt, J = 11.1, 3.5 Hz, 1H), 1.88−1.85 (m, 2H), 1.74−1.72 (m, 2H), 1.64−1.62 (m, 1H), 1.44−1.36 (m, 2H), 1.31−1.21 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.2, 158.4, 130.1, 130.0, 114.0, 65.0, 55.4, 43.3, 34.4, 29.1, 25.9, 25.6; IR ($CDCl_3$) 2931, 2855, 727, 1612, 1512, 1450, 1300, 1244, 1165, 1131, 1033, 982, 822, 753, 562, 518 cm^{-1}; HR-MS(ESI+) calcd for $C_{16}H_{22}O_3Na^+$ $[M + Na]^+$ 285.1461, found 285.1456.

*4-Fluorophenethyl Cyclohexanecarboxylate (**6f**).* (38.5 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, J = 8.4, 5.4 Hz, 2H), 6.98 (t, J = 8.6 Hz, 2H), 4.24 (t, J = 6.8 Hz, 2H), 2.89 (t, J = 6.8 Hz, 2H), 2.26 (tt, J = 11.1, 3.5 Hz, 1H), 1.86−1.83 (m, 2H), 1.74−1.70 (m, 2H), 1.64−1.61 (m, 1H), 1.43−1.37 (m, 2H), 1.30−1.20 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.2, 161.8 (d, J = 242.8 Hz), 133.8 (d, J = 3.3 Hz), 130.5 (d, J = 7.8 Hz), 115.4 (d, J = 21.1 Hz), 64.7, 43.3, 34.5, 29.1, 25.9, 25.6; IR ($CDCl_3$) 2932, 2856, 1728, 1601, 1509, 1450, 1388, 1312, 1274, 1245, 1221, 1167, 1157, 1131, 1022, 824, 756, 555, 425 cm^{-1}; HR-MS(ESI+) calcd for $C_{15}H_{20}FO_2^+$ $[M + H]^+$ 251.1442, found 251.1425.

*2-(Thiophen-2-yl)ethyl Cyclohexanecarboxylate (**6g**).* (31.0 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, J = 5.1, 1.1 Hz, 1H), 6.94 (dd, J = 5.0, 3.4 Hz, 1H), 6.86−6.85 (m, 1H), 4.28 (t, J = 6.6 Hz, 2H), 3.14 (t, J = 6.6 Hz, 2H), 2.29 (tt, J = 11.2, 3.6 Hz, 1H), 1.91−1.87 (m, 2H), 1.76−1.72 (m, 2H), 1.65−1.58 (m, 1H), 1.47−1.38 (m, 2H), 1.32−1.19 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.2, 140.3, 127.0, 125.7, 124.2, 64.5, 43.3, 29.5, 29.1, 25.9, 25.6; IR ($CDCl_3$) 2930, 2854, 1728, 1450, 1311, 1245, 1165, 1038, 848, 691, 503 cm^{-1}; HR-MS(ESI+) calcd for $C_{13}H_{18}O_2SNa^+$ $[M + Na]^+$ 261.0920, found 261.0913.

*3-(Pyridin-4-yl)propyl Cyclohexanecarboxylate (**6h**).* (10.9 mg, 22%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 6.0 Hz, 2H), 7.09 (d, J = 5.9 Hz, 2H), 4.05 (t, J = 6.4 Hz, 2H), 2.66 (t, J = 7.5 Hz, 2H), 2.26 (tt, J = 11.2, 3.6 Hz, 1H), 1.97−1.90 (m, 2H), 1.89−1.85 (m, 2H), 1.75−1.71 (m, 2H), 1.63−1.60 (m, 1H), 1.45−1.36 (m, 2H),

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1.31−1.22 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.2, 150.3, 149.9, 124.0, 63.1, 43.3, 31.7, 29.3, 29.2, 25.9, 25.5; IR ($CDCl_3$) 2931, 2855, 1728, 1601, 1509, 1450, 1388, 1312, 1245, 1221, 1167, 1157, 1131, 1022, 895, 824, 756, 555, 504, 469 cm^{-1}; HR-MS(ESI+) calcd for $C_{15}H_{21}NO_2Na^+$ $[M + Na]^+$ 270.1465, found 270.1455.

*Heptyl Cyclohexanecarboxylate (**6i**).* [CAS no. 92319-47-6] (40.7 mg, 90%); ^1H NMR (400 MHz, $CDCl_3$) δ 4.04 (t, J = 6.7 Hz, 2H), 2.26 (tt, J = 11.2, 3.6 Hz, 1H), 1.90−1.87 (m, 2H), 1.76−1.72 (m, 2H), 1.64−1.57 (m, 3H), 1.47−1.38 (m, 2H), 1.32−1.25 (m, 11H), 0.89−0.86 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.5, 64.5, 43.5, 31.9, 29.2, 29.1, 28.9, 26.1, 26.0, 25.7, 22.8, 14.3.

*Isopropyl Cyclohexanecarboxylate (**6j**).* [CAS no. 6553-80-6] (4.8 mg, 14%); ^1H NMR (400 MHz, $CDCl_3$) δ 5.00−4.94 (m, 1H), 2.24−2.19 (m, 1H), 1.88−1.85 (m, 2H), 1.74−1.71 (m, 2H), 1.63−1.61 (m, 1H), 1.44−1.36 (m, 2H), 1.27−1.23 (m, 3H), 1.19 (d, J = 6.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.9, 67.2, 43.6, 29.2, 26.0, 25.6, 22.0.

*tert-Butyl Cyclohexanecarboxylate (**6k**).* [CAS no. 16537-05-6] (1.5 mg, 4%); ^1H NMR (400 MHz, $CDCl_3$) δ 2.16 (tt, J = 11.2, 3.6 Hz, 1H), 1.87−1.83 (m, 2H), 1.74−1.70 (m, 2H), 1.63−1.58 (m, 1H), 1.42 (s, 9H), 1.42−1.36 (m, 3H), 1.27−1.20 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.9, 79.8, 44.3, 29.3, 28.3, 26.0, 25.7.

*Cyclohexylmethyl Cyclohexanecarboxylate (**6l**).* [CAS no. 2611-02-1] (30.1 mg, 67%); ^1H NMR (400 MHz, $CDCl_3$) δ 3.85 (d, J = 6.5 Hz, 2H), 2.28 (tt, J = 11.2, 3.6 Hz, 1H), 1.91−1.87 (m, 2H), 1.72−1.60 (m, 9H), 1.47−1.38 (m, 2H), 1.31−1.16 (m, 6H), 0.99−0.90 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.4, 69.5, 43.5, 37.4, 29.9, 29.3, 26.6, 26.0, 25.9, 25.7.

*Cyclobutylmethyl Cyclohexanecarboxylate (**6m**).* (33.0 mg, 84%); ^1H NMR (400 MHz, $CDCl_3$) δ 4.00 (d, J = 6.6 Hz, 2H), 2.64−2.52 (m, 1H), 2.27 (tt, J = 11.2, 3.6 Hz, 1H), 2.06−1.98 (m, 2H), 1.92−1.78 (m, 4H), 1.76−1.70 (m, 4H), 1.62−1.59 (m, 1H), 1.47−1.37 (m, 2H), 1.31−1.17 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.5, 67.9, 43.4, 34.3, 29.2, 25.9, 25.6, 24.8, 18.6; IR ($CDCl_3$) 2931, 2856, 1730, 1450, 1246, 1132, 1035, 979, 913, 750 cm^{-1}; HR-MS(ESI+) calcd for $C_{12}H_{20}O_2Na^+$ $[M + Na]^+$ 219.1356, found 219.1346.

*Phenethyl Cyclopentanecarboxylate (**6n**).* [CAS no. 959061-87-1] (27.9 mg, 64%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.29 (m, 2H), 7.26−7.22 (m, 3H), 4.29 (t, J = 7.0 Hz, 2H), 2.94 (t, J = 7.0 Hz, 2H), 2.73−2.69 (m, 1H), 1.88−1.66 (m, 6H), 1.59−1.54 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.9, 138.1, 129.1, 128.6, 126.7, 64.9, 44.0, 35.3, 30.1, 25.9.

*exo-Phenethyl Bicyclo[2.2.1]heptane-2-carboxylate (**6o**).* (43.0 mg, 88%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.31 (m, 2H), 7.28−7.24 (m, 3H), 4.35−4.25 (m, 2H), 2.96 (t, J = 7.0 Hz, 2H), 2.47 (br s, 1H), 2.33−2.30 (m, 2H), 1.85−1.79 (m, 1H), 1.56−1.51 (m, 2H), 1.50−1.46 (m, 1H), 1.44−1.41 (m, 1H), 1.27−1.22 (m, 1H), 1.21−1.14 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.2, 138.1, 129.1, 128.6, 126.7, 64.9, 46.6, 41.0, 36.6, 36.1, 35.3, 34.2, 29.6, 28.8; IR ($CDCl_3$) 3028, 2953, 2871, 1727, 1604, 1497, 1454, 1386, 1349, 1311, 1269, 1215, 1169, 1064, 745, 697, 569, 494 cm^{-1}; HR-MS(ESI+) calcd for $C_{16}H_{20}O_2Na^+$ $[M + Na]^+$ 267.1351, found 267.1351.

*Phenethyl 4,4-Dimethylpentanoate (**6p**).* [CAS no. 213748-75-5] (44.1 mg, 94%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33−7.29 (m, 2H), 7.25−7.22 (m, 3H), 4.29 (t, J = 7.0 Hz, 2H), 2.95 (t, J = 7.0 Hz, 2H), 2.29−2.25 (m, 2H), 1.55−1.51 (m, 2H), 0.89 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.5, 138.0, 129.1, 128.6, 126.7, 65.0, 38.7, 35.3, 30.3, 30.2, 29.2.

*Phenethyl 3-Phenylbutanoate (**6q**).* (46.7 mg, 87%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33−7.29 (m, 4H), 7.27−7.19 (m, 6H), 4.26 (td, J = 7.1, 2.4 Hz, 2H), 3.27 (q, J = 7.5 Hz, 1H), 2.88 (t, J = 7.0 Hz, 2H), 2.66−2.53 (m, 2H), 1.29 (d, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.5, 145.8, 138.0, 129.0, 128.68, 128.67, 126.9, 126.7, 126.6, 64.9, 43.1, 36.6, 35.2, 22.0; IR ($CDCl_3$) 3063, 2934, 1731, 1603, 1495, 1455, 1161, 750, 697, 495 cm^{-1}; HR-MS(ESI+) calcd for $C_{18}H_{21}O_2^+$ $[M + H]^+$ 269.1536, found 269.1531.

*Phenethyl Heptanoate (**6r**).* [CAS no. 5454-11-5] (27.7 mg, 59%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.29 (m, 2H), 7.25−7.21 (m, 3H), 4.30 (t, J = 7.0 Hz, 2H), 2.94 (t, J = 7.0 Hz, 2H), 2.29 (t, J = 7.4 Hz, 2H), 1.66−1.56 (m, 2H), 1.31−1.28 (m, 6H), 0.91−0.87 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.9, 138.1, 129.1, 128.6, 126.7, 64.8, 35.3, 34.5, 31.6, 28.9, 25.1, 22.6, 14.2.

*Phenethyl 2-Methylhexanoate (**6s**).* (13 mg, 28%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.29 (m, 2H), 7.25−7.21 (m, 3H), 4.30 (td, J = 7.0, 1.3 Hz, 2H), 2.95 (t, J = 7.0 Hz, 2H), 2.45−2.37 (m, 1H), 1.67−1.58 (m, 1H), 1.43−1.34 (m, 1H), 1.31−1.19 (m, 4H), 1.12 (d, J = 6.9 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.0, 138.1, 129.1, 128.6, 126.6, 64.7, 39.7, 35.3, 33.6, 29.5, 22.7, 17.2, 14.1; IR ($CDCl_3$) 3030, 2860, 1729, 1455, 1381, 1170, 697, 571 cm^{-1}; HR-MS(ESI+) calcd for $C_{15}H_{22}O_2Na^+$ $[M + Na]^+$ 257.1512, found 257.1505.

*Phenethyl 3-Phenylpropanoate (**6t**).* [CAS no. 28049-10-7] (21.5 mg, 42%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.17 (m, 10H), 4.30 (t, J = 7.2 Hz, 2H), 2.95−2.90 (m, 4H), 2.63 (t, J = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.0, 140.7, 138.0, 129.1, 128.7, 128.5, 126.7, 126.4, 65.1, 36.1, 35.3, 31.1.

*Phenethyl 2-Phenylpropanoate (**6u**).* [CAS no. 66256-02-8] (12.1 mg, 24%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.19 (m, 8H), 7.11−7.09 (m, 2H), 4.34−4.23 (m, 2H), 7.40 (q, J = 7.2 Hz, 1H), 2.87 (td, J = 6.8, 1.6 Hz, 2H), 1.48 (d, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.6, 140.7, 138.0, 129.1, 128.8, 128.6, 127.7, 127.3, 126.6, 65.4, 45.7, 35.2, 18.6.

*Pyridin-2-ylmethyl Cyclohexanecarboxylate (**7a**).* [CAS no. 401516-10-7] (31.6 mg, 72%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 4.3 Hz, 1H), 7.67 (td, J = 7.7, 1.7 Hz, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.21−7.18 (m, 1H), 5.20 (s, 2H), 2.40 (tt, J = 11.3, 3.6 Hz, 1H), 1.97−1.93 (m, 2H), 1.77−1.73 (m, 2H), 1.64−1.61 (m, 1H), 1.51−1.42 (m, 2H), 1.32−1.21 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.8, 156.3, 149.5, 136.9, 122.9, 121.7, 66.6, 43.3, 29.2, 25.9, 25.6.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Determination of pH changes, FT-IR spectra, and ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(6) For comparison, when the reaction was carried out without sodium formate, a 15% yield of **6a** was obtained (based on presumed **1**). This result implies that a part of the carbonyl in **6a** comes from **4a**.

(7) The reaction of sodium formate (**1**) with 2-pyridinemethanol (**5a**) under $Ru_3(CO)_{12}$ catalyst did not take place at all. On the basis of this result, it can be concluded that the mechanism does not involve the formation of 2-pyridinylmethyl formate.

(8) (a) Liberation of CO from sodium formate (**1**) was identified by trapping with an Rh(I) complex. For example, a mixture of bis(cyclooctene)rhodium(I) chloride dimer and **1** was heated for 1 h at 170 °C to give a [(CO)Rh(I)] complex in which the IR peak of CO coordinated to Rh(I) appears at 2357 cm^{-1}. (b) For an example of a metal formate used as a carbonyl source, see: Pri-Bar, I.; Buchman, O. *J. Org. Chem.* **1988**, *53*, 624.

(9) (a) Sodium hydroxide generated from **1** was determined by measuring the pH of the aqueous solution before and after heating at 170 °C for 1 h; the initial pH of 6.9 increased to 9.1 after the reaction. (b) The pH of the reaction mixture was measured during the reaction; the pH of 6.52 at the initial stage gradually increased to 10.74 after 4 h.

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(12) The stereochemistry of ester **6o** was determined after conversion to the corresponding benzyl ester by comparison with known data in ref 4c.

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