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Cobalt- and Nickel-Catalyzed Carboxylation of Alkenyl and Sterically Hindered Aryl Triflates Utilizing CO_2

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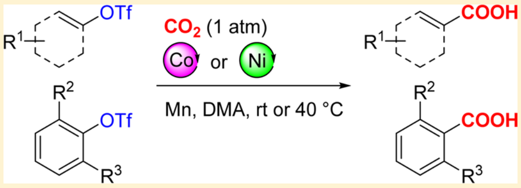
Ⓢ *Supporting Information*

ABSTRACT: A highly efficient cobalt-catalyzed reductive carboxylation reaction of alkenyl trifluoromethanesulfonates (triflates) has been developed. By employing Mn powder as a reducing reagent under 1 atm pressure of CO_2 at room temperature, diverse alkenyl triflates can be converted to the corresponding α,β-unsaturated carboxylic acids. Moreover, the carboxylation of sterically hindered aryl triflates proceeds smoothly in the presence of a nickel or cobalt catalyst.

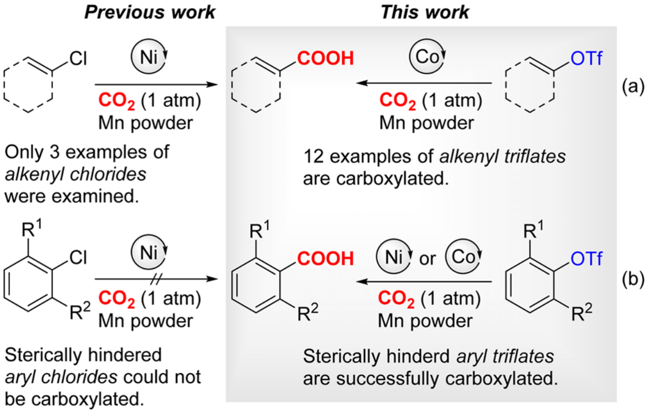


Carbon dioxide (CO_2) is considered an ideal C1-synthon for organic synthesis because of its nontoxicity, low cost, and availability as a renewable resource.[1] Therefore, the development of new catalytic methods enabling chemical fixation of CO_2 with concomitant C−C bond formation is considered an important current challenge.[2] In this regard, reductive catalytic carboxylation reactions of organic electrophiles with CO_2 have been studied intensively.[3−5] Catalytic carboxylation of aryl bromides with a palladium catalyst was reported by the Martin group in 2009 with an excess amount of pyrophoric Et_2Zn as a reducing reagent.[3b] In 2012, we reported the first catalytic carboxylation of less reactive aryl chlorides as well as alkenyl chlorides with a nickel catalyst.[4a] The reaction proceeded under 1 atm pressure of CO_2 at room temperature employing easy-to-handle Mn powder as a reducing reagent. Martin and co-workers have also developed nickel-catalyzed reductive carboxylation reactions of various organic halides and esters.[5]

Even the carboxylation reactions of aryl chlorides afford a wide variety of products with high functional group tolerance; the previous paper[4a] posed the following two significant problems: (1) only three simple alkenyl chlorides (without other functionalities) were employed as substrates, but reactivity of more easily accessible alkenyl triflates was not examined (Scheme 1a, left); (2) sterically hindered *ortho*-substituted aryl chlorides, even 2-chlorotoluene, did not afford carboxylated products with only low conversions of substrates (Scheme 1b, left).

In this paper, to compensate for the former results,[4a] we focus on the reactivity of alkenyl and aryl trifluoromethanesulfonates (triflates) as substrates. They are easily prepared from the corresponding ketones, aldehydes, or phenol derivatives and are often employed in synthetic organic chemistry as useful reagents.[6] Herein, we describe highly efficient reductive carboxylations of alkenyl triflates (Scheme 1a, right) and sterically hindered aryl triflates (Scheme 1b, right) employing Mn powder as a reducing reagent in the presence of a cobalt or nickel catalyst.[7,8]

Scheme 1. Reductive Carboxylation of Alkenyl and Sterically Hindered Aryl Electrophiles



The reaction of an alkenyl triflate **1a** was examined with Mn powder (1.5 equiv) as a reducing reagent under 1 atm pressure of CO_2 at room temperature (Table 1). The yield of α,β-unsaturated carboxylic acid (**2a**) was determined by gas chromatographic (GC) analysis after derivatization to the corresponding methyl ester (**2a-Me**). First, the carboxylation reaction of **1a** was carried out employing $NiBr_2$(**L1**) (5 mol %, **L1** = 2,2′-bipyridine) as a catalyst in the presence of additional **L1** (15 mol %) and tetraethylammonium iodide (Et_4NI, 10 mol %) in 1,3-dimethyl-2-imidazolidinone (DMI) solvent, i.e. under the optimal reaction conditions of the former carboxylation of alkenyl chlorides.[4a] In the reaction, **2a-Me** was obtained in 43% GC yield (entry 1), but ca. 30% of diene was afforded as the homocoupled product of **1a**. To improve the selectivity, we switched the catalyst to a cobalt complex that showed excellent catalytic activity for the carboxylation of propargyl acetates with CO_2.[4b] Use of CoI_2(**L1**) showed low catalytic activity in both

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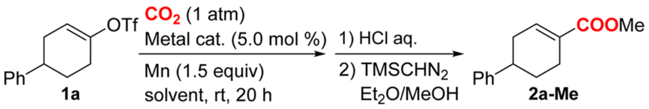
Table 1. Optimization of the Reaction Conditions with **1a**[a]



entry	metal catalyst	solvent	yield of **2a-Me** (%)[b]
1[c]	$NiBr_2(\mathbf{L1})$	DMI	43
2	$CoI_2(\mathbf{L1})$	DMI	10
3	$CoI_2(\mathbf{L1})$	DMA	23
4	$CoI_2(\mathbf{L2})$	DMA	76
5	$CoI_2(\mathbf{L3})$	DMA	86 (79)[d]
6	$CoI_2(PPh_3)_2$	DMA	0
7	CoI_2(dppe)	DMA	0
8[e]	$CoI_2(\mathbf{L3})$	DMA	32
9[f]	$CoI_2(\mathbf{L3})$	DMA	0
10	Without catalyst	DMA	0

[a] Reaction conditions: **1a** (0.25 mmol), metal catalyst (5.0 mol %), Mn powder (1.5 equiv) in solvent (0.50 mL), at room temperature for 20 h. [b] Determined by GC analysis using tridecane as an internal standard. [c] **L1** (15 mol %) and Et_4NI (10 mol %) were added. [d] Isolated yield of **2a** as the carboxylic acid. [e] Zn (1.5 equiv) was used in place of Mn. [f] Without Mn.

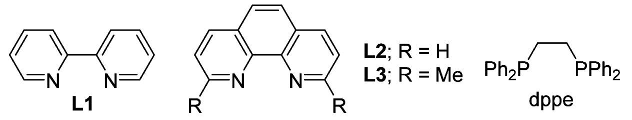
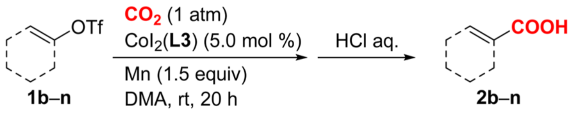
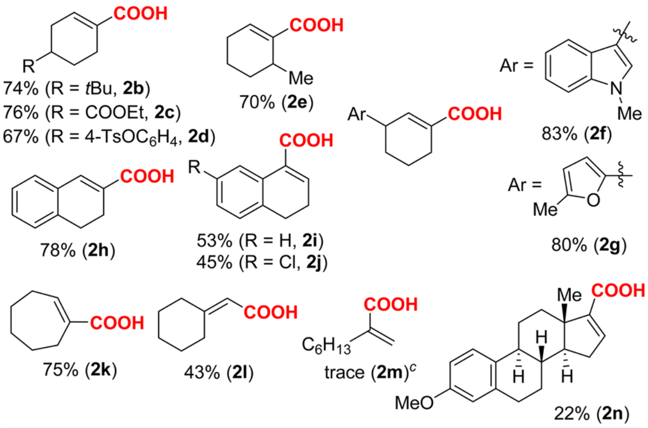


Table 2. Cobalt-Catalyzed Carboxylation of Alkenyl Triflates[a,b]





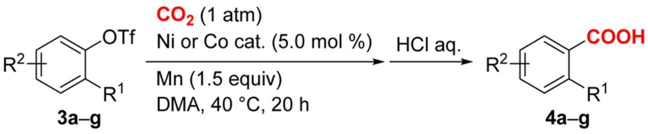
[a] Reaction conditions; **1** (0.25 mmol), $CoI_2(\mathbf{L3})$ (5.0 mol %), Mn powder (1.5 equiv) in DMA (0.50 mL) at room temperature for 20 h. [b] Isolated yield. [c] Determined by GC and GC-MS analysis after methylesterification.

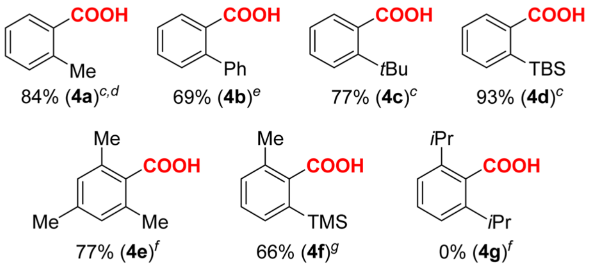
DMI and DMA solvents, but no homocoupling reaction of **1a** occurred (entries 2 and 3). The yield of **2a-Me** was increased substantially with 1,10-phenanthroline (**L2**) as the ligand (entry 4). Finally, $CoI_2(\mathbf{L3})$ (**L3** = 2,9-dimethyl-1,10-phenanthroline) as the catalyst afforded **2a-Me** in 86% yield and the corresponding carboxylic acid **2a** was isolated in 79% yield (entry 5).[9] The catalyst in situ prepared from CoI_2 and **L3** also worked well and afforded the product in 86% yield. Phosphine ligands were not effective at all (entries 6 and 7). In place of Mn, Zn powder afforded the product in low yield (entry 8). The cobalt catalyst and Mn powder were indispensable for this carboxylation reaction (entries 9 and 10).

Under the optimal reaction conditions (Table 1, entry 5), carboxylation of various alkenyl triflates was carried out (Table 2). Ester (**2c**), indole (**2f**), and furan (**2g**) moieties were well tolerated under the reaction conditions.[10] Importantly, the triflate moiety was selectively carboxylated even in the presence of *p*-toluenesulfonate (**2d**) and chloro (**2j**) functionalities which could be potentially reactive under the reductive carboxylation conditions. Conjugated alkenyl triflates (**1h**−**j**) were converted to the corresponding carboxylic acids (**2h**−**j**) in moderate to high yields. A seven-membered cyclic substrate (**1k**) also afforded the *α*,*β*-unsaturated carboxylic acid **2k** in 75% yield. An alkenyl triflate **1l** prepared from the corresponding aldehyde gave the product **2l** in moderate yield. Unfortunately, **1m** having an *exo*-methylene moiety gave a trace amount of product owing to extensive side reactions. An estrone-based alkenyl triflate (**1n**) furnished the product **2n** in 22% yield due to a preferential homocoupling reaction (41% yield) of **1n**.

As mentioned above, *ortho*-substituted aryl chlorides could not be carboxylated in our previous paper.[4a] Even 2-chlorotoluene did not give the desired carboxylation product. So, we changed the substrate from the aryl chloride to 2-methylphenyl triflate **3a**. To our delight, **3a** successfully furnished the carboxylated product **4a** in 84% isolated yield in the presence of $NiI_2(PPh_3)_2$ (5.0 mol %) and additional PPh_3 (10 mol %) at room temperature (Table 3). Other 2-substituted aryl triflates (**3b**−**d**) provided the corresponding benzoic acids (**4b**−**d**) in good to excellent yields. It is noteworthy that bulky substituents such as *tert*-butyl and TBS (*tert*-butyldimethylsilyl) moieties did not hamper the carboxylation reaction. As for more sterically hindered 2,6-disubstituted aryl triflates, 2,4,6-trimethylphenyl triflate **3e** only afforded the carboxylated product (**4e**) in 15% yield even at elevated temperature (60 °C) in the presence of the

Table 3. Cobalt- and Nickel-Catalyzed Carboxylation of Sterically Hindered Aryl Triflates[a,b]





[a] Reaction conditions: **3** (0.25 mmol), nickel or cobalt catalyst (5.0 mol %), Mn powder (1.5 equiv) in DMA (0.50 mL) at 40 °C for 20 h. [b] Isolated yield. [c] $NiI_2(PPh_3)_2$ (5.0 mol %) was used. [d] PPh_3 (10 mol %) was added, room temperature. [e] $NiI_2(\mathbf{L3})$ (5.0 mol %) was used, at room temperature. [f] $CoI_2(\mathbf{L3})$ (5.0 mol %) was used. [g] $CoI_2(\mathbf{L3})$ (10 mol %) was used.

nickel catalyst. In contrast, a cobalt catalyst CoI_2(**L3**) was found to be more active and successfully afforded **4e** in 77% yield at 40 °C. More sterically demanding 2-methyl-6-(trimethylsilyl)-phenyl triflate (**3f**) was also carboxylated to **4f** in 66% yield with a higher catalyst loading (10 mol %). However, 2,6-diisopropylphenyl triflate (**3g**) did not give the product (**4g**). Regarding less hindered substrates, phenyl triflate afforded benzoic acid in 54% yield utilizing $NiI_2(PPh_3)_2$ (5.0 mol %) and PPh_3 (10 mol %) as the catalyst.

In conclusion, we explored highly efficient reductive carboxylations of various alkenyl triflates employing a cobalt catalyst and Mn powder as a reducing reagent under 1 atm pressure of CO_2 at room temperature. Furthermore, the carboxylation of sterically hindered 2-substituted and 2,6-disubstituted aryl triflates proceeded smoothly with a nickel or cobalt catalyst.

EXPERIMENTAL SECTION

General Methods and Materials. DMA and DMI were distilled with CaH_2 and stored over activated MS-4A. Mn powder (≥99%) was purchased from Sigma-Aldrich and stored under a nitrogen atmosphere. Zn powder was activated by washing with HCl aq. and stored under a nitrogen atmosphere. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. IR spectra were obtained on an FT-IR spectrometer. ^1H and ^{13}C NMR spectra were measured with a spectrometer (500 or 400 MHz). The ^1H NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm), acetone-d_6 (2.05 ppm), or DMSO-d_6 (2.50 ppm). The ^{13}C NMR chemical shifts are reported relative to $CDCl_3$ (77.0 ppm), acetone-d_6 (29.0 ppm), or DMSO-d_6 (39.5 ppm). GC-MS data were recorded on a low-resolution EI-MS (quadrupole). High-resolution mass spectra were obtained with EI-HRMS (magnetic sector), ESI-HRMS (Orbitrap), APCI-HRMS (Orbitrap), and MALDI-HRMS (Orbitrap). GC analysis was carried out using a gas chromatographic analyzer equipped with a capillary column (0.25 mm i.d. × 30 m). UV/vis spectra were recorded with a spectrophotometer. Column chromatography was carried out on silica gel (spherical, neutral, 40−50 μm or 63-210 μm). TLC analyses were performed on commercial glass plates bearing a 0.25 mm layer of silica gel. Alkenyl triflates **1a**−**b**,[11] **1f**−**g**,[12] **1h**,[13] **1m**,[8c] and **1n**,[14] as well as aryl triflates **3a**,[15] **3b**,[16] **3c**,[15] **3d**,[17] **3e**,[18] and **3g**[18] were prepared according to the literature procedures. CoI_2(**L1**), CoI_2(**L2**), $CoI_2(PPh_3)_2$, CoI_2(dppe), $NiBr_2$(**L1**), and $NiI_2(PPh_3)_2$ were also prepared according to the literature procedures.[4b,19]

Preparation of CoI_2(L3) and NiI_2(L3). CoI_2(**L3**) was prepared according to a published method for $CoBr_2$(**L3**).[20] A 50 mL Schlenk flask was dried with a heating gun under vacuum. The flask was charged with CoI_2 (0.31 g, 1.0 mmol), 2,9-dimethyl-1,10-phenanthroline (**L3**, 0.23 g, 1.1 mmol), and ethanol (5 mL) under an Ar atmosphere. The resulting solution was stirred at 80 °C for 2 h. A light green solid was precipitated and isolated by filtration. The solid was filtered, washed with ethanol and hexane subsequently, and dried in vacuo. The desired complex was obtained in 83% yield (0.43 g, 0.83 mmol) and used without further purification. Stable under 250 °C; UV−vis (CH_3CN) λ_{max}, nm: 212, 272, 320, 390 (sh), 670 (br). Anal. Calcd for $C_{14}H_{12}CoI_2N_2\cdot 1/2CH_3CH_2OH$: C, 33.12; H, 2.78; N, 5.15. Found: C, 33.07; H, 2.53; N, 5.41. MALDI-HRMS (m/z): $[M-I]^+$ calcd for $C_{14}H_{12}CoIN_2$, 393.93717; found, 393.93678.

NiI_2(**L3**) was prepared by the same procedure (0.50 mmol scale, 0.23 g, 0.45 mmol, 89%). Light brown solid; mp 220−230 °C (dec); UV−vis (CH_3CN) λ_{max}, nm: 208, 248, 276, 360. Anal. Calcd for $C_{14}H_{12}NiI_2N_2\cdot 1/2CH_3CH_2OH$: C, 33.13; H, 2.78; N, 5.15. Found: C, 33.03; H, 2.56; N, 5.40. MALDI-HRMS (m/z): $[M-I]^+$ calcd for $C_{14}H_{12}IN_2Ni$, 392.93932; found, 392.93976.

General Procedure for Preparation of Alkenyl Triflates. To a mixture of ketone (10 mmol) and 2-chloropyridine (11 mmol) in CH_2Cl_2 (20 mL), the solution of Tf_2O (12 mmol) in CH_2Cl_2 (10 mL) was added dropwise at 0 °C and the mixture was stirred for 30 min at 0 °C. The resulting mixture was warmed to room temperature and stirred for 2 h. The reaction was quenched by adding H_2O (20 mL). The organic layer was washed with sat. $NaHCO_3$ aq. and brine and dried over $MgSO_4$. After filtration and removal of volatiles, the residue was purified with silica gel chromatography using hexane as an eluent.

*Ethyl 4-(Trifluoromethanesulfonyloxy)cyclohex-3-ene-1-carboxylate (**1c**).* Colorless oil (7.0 mmol scale, 1.0 g, 3.4 mmol, 49%); ^1H NMR (500 MHz, $CDCl_3$): δ 5.78−5.76 (m, 1H), 4.16 (q, J = 7.2 Hz, 2H), 2.62−2.57 (m, 1H), 2.48−2.40 (m, 4H), 2.17−2.11 (m, 1H), 1.97−1.89 (m, 1H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.9, 148.4, 118.5 (q, J_{C-F} = 320.1 Hz), 116.9, 60.8, 37.8, 26.6, 26.1, 25.0, 14.1. ESI-HRMS (m/z): [M + Na] calcd for $C_{10}H_{13}F_3O_5SNa$, 325.0328; found, 325.0322.

*4-[4-(Trifluoromethanesulfonyloxy)cyclohex-3-en-1-yl]phenyl 4-Methylbenzene-1-sulfonate (**1d**).* White solid (5.0 mmol scale, 1.6 g, 3.3 mmol, 66%); mp 93−95 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 6.95−6.92 (m, 2H), 5.84−5.82 (m, 1H), 2.86−2.81 (m, 1H), 2.56−2.24 (m, 7H), 2.06−2.01 (m, 1H), 1.94−1.86 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 148.8, 148.2, 145.3, 143.4, 132.5, 129.7, 128.5, 127.9, 122.5, 118.5 (q, J_{C-F} = 320.1 Hz), 117.8, 38.1, 31.4, 29.5, 27.6, 21.7. ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{20}H_{19}F_3O_6S_2Na$, 499.0467; found, 499.0456.

*3,4-Dihydronaphthalen-1-yl Trifluoromethanesulfonate (**1i**).*[8c] Colorless oil (7.0 mmol scale, 1.9 g, 6.7 mmol, 96%); ^1H NMR (500 MHz, $CDCl_3$): δ 7.36−7.33 (m, 1H), 7.28−7.24 (m, 2H), 7.18−7.16 (m, 1H), 6.01 (t, J = 4.7 Hz, 1H), 2.87 (t, J = 8.2 Hz, 2H), 2.51 (td, J = 8.2, 4.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 146.4, 136.2, 129.2, 128.7, 127.8, 126.9, 121.2, 118.6 (q, J_{C-F} = 320.4 Hz), 117.7, 26.9, 22.3.

*7-Chloro-3,4-dihydronaphthalen-1-yl Trifluoromethanesulfonate (**1j**).* Colorless oil (2.8 mmol scale, 0.55 g, 1.8 mmol, 63%); ^1H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, J = 1.8 Hz, 1H), 7.23 (dd, J = 8.1, 2.0 Hz, 1H), 7.11 (d, J = 7.9 Hz, 1H), 6.08 (t, J = 4.9 Hz, 1H), 2.83 (t, J = 8.1 Hz, 2H), 2.52 (td, J = 8.2, 4.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 145.2, 134.4, 132.9, 130.2, 129.0 (two peaks overlap absolutely, confirmed with the HMQC and HMBC spectra), 121.4, 119.2, 118.6 (q, J_{C-F} = 320.4 Hz), 26.2, 22.3. APCI-HRMS (m/z): $[M-H]^-$ calcd for $C_{11}H_7ClF_3O_3S$, 310.9762; found, 310.9760.

*1-Cyclohepten-1-yl Trifluoromethanesulfonate (**1k**).*[11] Pale brown oil (6.0 mmol scale, 0.52 g, 2.1 mmol, 35%); ^1H NMR (500 MHz, $CDCl_3$): δ 5.88 (t, J = 6.4 Hz, 1H), 2.53−2.51 (m, 2H), 2.17−2.14 (m, 2H), 1.74−1.61 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.1, 123.1, 118.6 (q, J_{C-F} = 320.1 Hz), 33.2, 29.9, 26.3, 24.8, 24.7.

*Cyclohexylidenemethyl Trifluoromethanesulfonate (**1l**).* Pale yellow oil (5.0 mmol scale, 0.40 g, 1.6 mmol, 33%); ^1H NMR (500 MHz, $CDCl_3$): δ 6.38 (s, 1H), 2.28−2.26 (br m, 2H), 2.07−2.05 (br m, 2H), 1.59−1.57 (br m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 133.8, 127.7, 118.7 (q, J_{C-F} = 321.1 Hz), 29.8, 27.5, 26.4, 26.04, 26.00. EI-HRMS (m/z): $[M]^+$ calcd for $C_8H_{11}F_3O_3S$, 244.0381; found, 244.0374.

Preparation of 6-Methylcyclohex-1-en-1-yl Trifluoromethanesulfonate (1e).[11] A mixture of potassium bis(trimethylsilyl)amide (KHMDS, 10 mL of 0.5 M toluene solution) and THF (25 mL) was cooled to −78 °C under an Ar atmosphere. To the solution was added dropwise the solution of 2-methylcyclohexanone (4.0 mmol) in THF (5.0 mL), and the resulting mixture was stirred at −78 °C for 1 h. Then, $PhNTf_2$ (5.0 mmol) was added in one portion, and the reaction mixture was allowed to warm to room temperature. After stirring for 6 h, H_2O (10 mL) was added, and the resulting mixture was extracted with Et_2O (2 × 20 mL). The combined organic layer was washed with brine and dried over $MgSO_4$. After filtration and removal of volatiles, purification of the residue by silica gel chromatography using hexane as an eluent gave **1e** (colorless oil, 0.53 g, 2.1 mmol, 53%). ^1H NMR (500 MHz, $CDCl_3$): δ 5.73 (td, J = 4.1, 1.2 Hz, 1H), 2.58−2.51 (m, 1H), 2.19−2.15 (m, 2H), 1.96−1.90 (m, 1H), 1.70−1.43 (m, 3H), 1.14 (d, J = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.4, 118.6 (q, J_{C-F} = 320.1 Hz), 118.2, 32.4, 31.5, 24.5, 19.2, 17.8.

Preparation of 2-Methyl-6-(trimethylsilyl)phenyl Trifluoromethanesulfonate (3f). A mixture of 2-bromo-6-methylphenol (10 mmol), TMSCl (10 mmol), and THF (20 mL) was cooled to 0 °C under an Ar atmosphere. To the solution was added dropwise triethylamine (10 mmol), and the resulting solution was allowed to warm to room temperature. After stirring for 2 h, white precipitate was filtered off and the filtrate was concentrated under vacuum to afford the crude mixture of (2-bromo-6-methylphenoxy)trimethylsilane. The crude mixture was placed in 100 mL round bottled flask and diluted with THF (20 mL) under Ar atmosphere. The mixture was cooled to −78 °C and *n*-BuLi in hexane (1.65 M, 9.1 mL, 15 mmol) was added slowly. The whole mixture was stirred for 1h at −78 °C. Then, Tf_2O (15 mmol) was added via syringe and the resulting solution was allowed to warm to room temperature. After stirring for 1 h, the reaction was quenched by adding H_2O and the mixture was extracted with Et_2O (2 × 20 mL). The combined organic layer was subsequently washed with $NaHCO_3$ aq. and brine, and dried over $MgSO_4$. After filtration and removal of all volatiles, purification of the residue by silica gel chromatography using hexane as an eluent gave **3f** (Colorless oil, 1.7 g, 5.3 mmol, 53%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, J = 6.7 Hz, 1H), 7.29−7.25 (m, 2H), 2.38 (s, 3H), 0.38 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.1, 134.8, 134.5, 133.7, 131.4, 127.9, 118.6 (q, J_{C-F} = 319.8 Hz), 17.3, 0.1. ESI-HRMS (m/z): $[M-H]^-$ calcd for $C_{11}H_{14}F_3O_3SSi$, 311.0390; found, 311.0392.

A Procedure for Carboxylation of 1a (Table 1, entry 5). A 20 mL Schlenk flask was charged with Mn powder (21 mg, 0.38 mmol) and dried with a heating-gun under vacuum. Then, the flask was charged with CoI_2(**L3**) (6.5 mg, 0.013 mmol). The flask was evacuated and refilled with CO_2. This sequence was repeated five times. Then, DMA (0.50 mL) and **1a** (59 μL, 0.25 mmol) were added via airtight syringes, and the resulting mixture was stirred at room temperature for 20 h. After the reaction, tridecane (50 μL, 0.21 mmol) as an internal standard, Et_2O (5 mL), and 1 M HCl aq. (3 mL) were added to the reaction mixture. After stirring for 10 min, the organic layer was separated, dried over $MgSO_4$, and filtrated. Then, methanol (1 mL) and $TMSCHN_2$ (2.0 M in Et_2O, 0.5 mL, 1.0 mmol) were added to the resulting solution, and it was stirred for 10 min. The yield of **2a-Me** was determined by GC analysis.

Representative Procedure for the Carboxylation of Alkenyl Triflates (1b−n) and Aryl Triflates (3a−g). A 20 mL Schlenk flask was charged with Mn powder (21 mg, 0.38 mmol) and dried with a heating gun under vacuum. Then, the flask was charged with CoI_2(**L3**) (6.5 mg, 0.013 mmol). The flask was evacuated and refilled with CO_2. This sequence was repeated five times. Then, DMA (0.50 mL) and **1** (0.25 mmol) were added via airtight syringes, and the resulting mixture was stirred at room temperature for 20 h. After the reaction, 1 M HCl aq. (3 mL) and Et_2O (5 mL) were added, and the whole solution was stirred at room temperature for 10 min. The mixture was extracted with Et_2O (5 mL × 5). The collected organic layer was combined and dried over anhydrous $MgSO_4$. After removal of volatiles, the residue was purified by silica gel chromatography using hexane/acetone (6/1, v/v) as an eluent.

*4-Phenylcyclohex-1-ene-1-carboxylic Acid (**2a**).*[4b] White solid (40 mg, 79%); ^1H NMR (500 MHz, $CDCl_3$): δ 7.33−7.30 (m, 2H), 7.23−7.21 (m, 4H), 2.83−2.77 (m, 1H), 2.58−2.51 (m, 2H), 2.38−2.31 (m, 2H), 2.07−2.03 (m, 1H), 1.80−1.72 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.9, 145.8, 141.8, 129.7, 128.5, 126.8, 126.3, 39.0, 33.9, 29.3, 24.4.

*4-tert-Butylcyclohex-1-ene-1-carboxylic Acid (**2b**).*[21] White solid (34 mg, 74%); ^1H NMR (500 MHz, $CDCl_3$): δ 7.14−7.12 (m, 1H), 2.52−2.48 (m, 1H), 2.31−2.25 (m, 1H), 2.16−2.08 (m, 1H), 2.00−1.90 (m, 2H), 1.31−1.25 (m, 1H), 1.18−1.10 (m, 1H), 0.89 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.0, 143.0, 129.6, 43.2, 32.1, 27.7, 27.1, 25.2, 23.5.

*4-(Ethoxycarbonyl)cyclohex-1-ene-1-carboxylic Acid (**2c**).* White solid (38 mg, 76%); mp 97−98 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.12−7.10 (br m, 1H), 4.18−4.14 (m, 2H), 2.59−2.45 (m, 4H), 2.29−2.22 (m, 1H), 2.13−2.08 (m, 1H), 1.76−1.68 (m, 1H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 175.0, 172.3, 140.2, 129.3, 60.6, 38.2, 28.0, 24.7, 23.1, 14.2. ESI-HRMS (m/z): $[M-H]^-$ calcd for $C_{10}H_{13}O_4$, 197.0819; found, 197.0815. IR (neat): 3100−2800 (br), 1720.5, 1683.9, 1645.3, 1379.1, 1249.9, 1174.7, 1141.9, 1089.8, 1033.9, 856.4, 763.8 cm^{-1}.

*4-{4-[(4-Methylbenzenesulfonyl)oxy]phenyl}cyclohex-1-ene-1-carboxylic Acid (**2d**).* White solid (62 mg, 67%); mp 238−240 °C; ^1H NMR (500 MHz, DMSO−D_6): δ 12.17 (br s, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 7.9 Hz, 2H), 7.27 (d, J = 8.9 Hz, 2H), 6.95−6.90 (m, 3H), 2.78−2.72 (m, 1H), 2.42−2.19 (m, 7H), 1.86−1.84 (m, 1H), 1.68−1.60 (m, 1H). ^{13}C NMR (126 MHz, DMSO−D_6): δ 167.9, 147.3, 145.7, 145.3, 138.1, 131.6, 130.2, 130.1, 128.3, 128.1, 121.8, 37.7, 32.8, 28.9, 24.4, 21.1. ESI-HRMS (m/z): $[M-H]^-$ calcd for $C_{20}H_{19}O_5S$, 371.0959; found, 371.0953. IR (neat): 3100−2800 (br), 1716.7, 1681.9, 1674.2, 1558.5, 1541.1, 1506.4, 1456.3, 1373.3, 1278.8, 1197.8, 1174.7, 1153.4, 1089.8, 864.1, 750.3, 723.3 cm^{-1}.

*6-Methylcyclohex-1-ene-1-carboxylic Acid (**2e**).*[8d] White solid (25 mg, 70%); ^1H NMR (500 MHz, $CDCl_3$): δ 7.10 (t, J = 4.0 Hz, 1H), 2.72−2.66 (m, 1H), 2.28−2.12 (m, 2H), 1.67−1.55 (m, 4H), 1.11 (d, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.1, 142.2, 134.7, 29.5, 27.5, 26.2, 20.2, 17.0.

*3-(1-Methyl-1H-indol-3-yl)cyclohex-1-ene-1-carboxylic Acid (**2f**).* White solid (53 mg, 83%); mp 166−168 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 10.89 (brs, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.29−7.28 (m, 2H), 7.24−7.21 (m, 1H), 7.11 (t, J = 7.3 Hz, 1H), 6.76 (s, 1H), 3.88 (brs, 1H), 3.71 (s, 3H), 2.38−2.35 (m, 2H), 2.06−2.01 (m, 1H), 1.83−1.75 (m, 2H), 1.71−1.66 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.3, 144.7, 137.2, 129.8, 126.7, 126.4, 121.7, 118.9, 118.9, 116.9, 109.3, 33.4, 32.6, 29.2, 23.9, 20.4. ESI-HRMS (m/z): $[M-H]^-$ calcd for $C_{16}H_{16}NO_2$, 254.1187; found, 254.1185. IR (neat): 3100−2800 (br), 1716.6, 1670.3, 1626.0, 1558.5, 1541.1, 1506.4, 1473.6, 1456.3, 1288.5, 1257.6, 808.2, 733.0 cm^{-1}.

*3-(5-Methylfuran-2-yl)cyclohex-1-ene-1-carboxylic Acid (**2g**).* Yellow solid (41 mg, 80%); mp 97−99 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.16−7.14 (m, 1H), 5.88 (d, J = 3.1 Hz, 1H), 5.86 (d, J = 3.1 Hz, 1H), 3.62−3.59 (m, 1H), 2.33−2.29 (m, 2H), 2.26 (s, 3H), 2.00−1.95 (m, 1H), 1.86−1.79 (m, 1H), 1.77−1.70 (m, 1H), 1.69−1.61 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.0, 154.4, 151.0, 141.3, 130.6, 105.9 (two peaks overlap absolutely, confirmed with the HMQC and HMBC spectra), 35.8, 27.1, 23.8, 20.2, 13.5. ESI-HRMS (m/z): $[M-H]^-$ calcd for $C_{12}H_{13}O_3$, 205.0870; found, 205.0867. IR (neat): 3100−2800 (br), 1683.9, 1635.6, 1558.5, 1508.3, 1417.7, 1288.5, 1020.3, 788.9 cm^{-1}.

*3,4-Dihydronaphthalene-2-carboxylic Acid (**2h**).*[22] Pale yellow solid (34 mg, 78%); ^1H NMR (500 MHz, DMSO-d_6): δ 12.45 (br s, 1H), 7.47 (s, 1H), 7.32 (d, J = 7.0 Hz, 1H), 7.28−7.21 (m, 3H), 2.81 (t, J = 8.4 Hz, 2H), 2.47 (t, J = 8.4 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 168.0, 136.5, 135.4, 132.3, 129.9, 129.3, 128.3, 127.5, 126.7, 26.9, 21.9.

*3,4-Dihydronaphthalene-1-carboxylic Acid (**2i**).*[23] Pale yellow solid (23 mg, 53%); ^1H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 4.7 Hz, 1H), 7.26−7.16 (m, 3H), 2.78 (t, J = 7.8 Hz, 2H), 2.47−2.43 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.9, 143.0, 136.2, 130.4, 129.9, 127.7, 127.5, 126.6, 126.2, 27.4, 23.7.

*7-Chloro-3,4-dihydronaphthalene-1-carboxylic Acid (**2j**).* White solid (24 mg, 45%); mp 189−191 °C; ^1H NMR (500 MHz, acetone-d_6): δ 8.03 (s, 1H), 7.38 (t, J = 4.9 Hz, 1H), 7.21 (app. d, J = 1.2 Hz, 2H), 2.76 (t, J = 7.9 Hz, 2H), 2.44 (td, J = 8.0, 5.0 Hz, 2H). ^{13}C NMR (126 MHz, acetone-d_6): δ 166.3, 142.4, 135.1, 132.9, 131.5, 128.98, 128.96, 127.1, 126.0, 26.4, 23.2. ESI-HRMS (m/z): $[M-H]^-$ calcd for $C_{11}H_8ClO_2$, 207.0218; found, 207.0215. IR (neat): 3100−2800 (br), 1716.7, 1683.9, 1558.5, 1541.1, 1506.4, 1489.1, 1473.6, 1456.3, 1174.7, 889.2, 835.2, 814.0, 715.6 cm^{-1}.

*Cyclohep-1-ene-1-carboxylic Acid (**2k**).*[21] Pale yellow solid (26 mg, 75%); ^1H NMR (500 MHz, $CDCl_3$): δ 7.35 (t, J = 6.7 Hz, 1H), 2.52 (dd, J = 5.5, 5.5 Hz, 2H), 2.32 (dd, J = 11.3, 6.4 Hz, 2H), 1.81−1.76 (m, 2H), 1.58−1.51 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.8, 147.3, 135.9, 32.0, 29.0, 36.9, 26.1, 25.6.

*2-Cyclohexylideneacetic Acid (**2l**).*[24] White solid (15 mg, 43%); ^1H NMR (500 MHz, $CDCl_3$): δ 5.63 (s, 1H), 2.83 (t, J = 5.8 Hz, 2H), 2.22 (t, J = 6.1 Hz, 2H), 1.68−1.59 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.2, 166.8, 112.5, 38.3, 30.1, 28.7, 27.9, 26.2.

*Product **2n**.* White solid (17 mg, 22%); mp 231−233 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.21 (d, J = 8.5 Hz, 1H), 6.97−6.96 (m, 1H), 6.72 (dd, J = 8.7, 2.6 Hz, 1H), 6.64 (d, J = 2.7 Hz, 1H), 3.78 (s, 3H), 2.96−2.85 (m, 2H), 2.42−2.27 (m, 4H), 2.17−2.11 (m, 1H), 1.94−1.90 (m, 1H), 1.75−1.60 (m, 4H), 1.51−1.42 (m, 1H), 0.97 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 169.8, 157.5, 146.4 (two peaks overlap absolutely, confirmed with the HMQC and HMBC spectra), 137.8, 132.7, 126.1, 113.9, 111.5, 55.8, 55.2, 46.0, 44.2, 37.1, 34.7, 31.9, 29.6, 27.7, 26.4, 16.0. ESI-HRMS (m/z): [M−H]$^-$ calcd for $C_{20}H_{23}O_3$, 311.1653; found, 311.1656. IR (neat): 3100−2800 (br), 2358.9, 1674.2, 1600.9, 1498.7, 1427.3, 1282.7, 1053.1, 964.4, 902.7, 808.2, 781.2, 731.0 cm^{-1}.

*2-Methylbenzoic Acid (**4a**).*[25] White solid (29 mg, 84%); ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.08 (d, J = 7.9 Hz, 1H), 7.46−7.43 (m, 1H), 7.30−7.27 (m, 2H), 2.67 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 173.6, 141.4, 133.0, 132.0, 131.6, 128.4, 125.9, 22.2.

*2-Phenylbenzoic Acid (**4b**).*[26] White solid (34 mg, 69%); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.94 (d, J = 7.9 Hz, 1H), 7.55 (td, J = 7.6, 1.2 Hz, 1H), 7.43−7.32 (m, 7H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 173.3, 143.4, 141.0, 132.1, 131.2, 130.7, 129.3, 128.4, 128.1, 127.3, 127.2.

*2-tert-Butylbenzoic Acid (**4c**).*[27] Pale yellow solid (34 mg, 77%); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.53−7.48 (m, 2H), 7.40 (td, J = 7.8, 1.4 Hz, 1H), 7.25 (td, J = 7.5, 1.1 Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 178.2, 148.2, 131.7, 130.5, 129.0, 127.1, 125.5, 36.0, 31.4.

*2-(tert-Butyldimethylsilyl)benzoic Acid (**4d**).* Carboxylation of **3d** was carried out on 0.50 mmol scale. White solid (0.11 g, 93%); mp 106−108 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.03 (d, J = 7.2 Hz, 1H), 7.71 (d, J = 7.2 Hz, 1H), 7.52 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.2 Hz, 1H), 0.95 (s, 9H), 0.34 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 174.6, 140.3, 137.1, 135.9, 131.3, 130.3, 128.6, 27.8, 18.3, −2.4. ESI-HRMS (m/z): [M−H]$^-$ calcd for $C_{13}H_{19}O_2Si$, 235.1160; found, 235.1157. IR (neat): 3200−2800 (br), 1683.9, 1562.3, 1417.7, 1275.0, 1259.5, 1149.6, 1114.91, 921.9, 839.0, 823.6, 808.2, 771.5, 736.8, 707.9 cm^{-1}.

*2,4,6-Trimethylbenzoic Acid (**4e**).*[28] White solid (32 mg, 77%); ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.88 (s, 2H), 2.42 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 175.9, 140.1, 136.2, 129.3, 128.8, 21.1, 20.3.

*2-Methyl-6-(trimethylsilyl)benzoic Acid (**4f**).* White solid (35 mg, 66%); mp 96−98 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.47 (d, J = 7.3 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.25 (d, J = 8.2 Hz, 1H), 2.50 (s, 3H), 0.34 (s, 9H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 177.2, 139.4, 136.9, 135.9, 132.3, 131.5, 129.8, 20.6, 0.1. ESI-HRMS (m/z): [M−H]$^-$ calcd for $C_{11}H_{15}O_2Si$, 207.0847; found, 207.0842. IR (neat): 3100−2800 (br), 1689.6, 1296.2, 1250.0, 1126.4, 879.5, 835.2, 792.7, 752.2 cm^{-1}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02307.

^{1}H NMR and ^{13}C NMR spectra for obtained compounds (PDF)

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Notes

The authors declare no competing financial interest.

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