Zinc-Mediated Allylation of Carbon Dioxide—The LiOAc Effect

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Brief discussion on the role of LiOAc

The role of LiOAc turned out to be intriguing. In the first place, traditionally, lithium salts help forming a RZnX•LiX' complex in zinc-mediated reactions, thus, increase the solubility of the metallic species.\(^1\) In the second place, the interaction between CO\(_2\) and acetate anion was earlier explored by computational studies by Steckel et al.\(^2\) It was also recently observed that that carbon dioxide could be captured by small size anions such as F\(^-\),\(^3\) CN\(^-\),\(^3\) to form a \(\sigma\)-bond anion-formate structure, thus, breaking the cumulative C=O bond in the inert CO\(_2\). Such anion-formate structure was proven by single-crystal X-ray diffraction study and photoelectronic spectra. Based on these previous findings, we proposed a rationale to illustrate the role of lithium acetate in this study (Scheme 1): on one hand it may improve the solubility of organometallic reagent in the reaction mixture; on the other hand it may lower the barrier of the nucleophilic attack by forming an acetoxyformate 4.

![Scheme 1](image)

Scheme 1. A rationale for the role of LiOAc.

Unfortunately, attempts in separating or identifying such intermediate(s) failed although some strong signals were indeed observed in the area from 1700 cm\(^{-1}\) to 1300 cm\(^{-1}\) when mixing CO\(_2\) with LiOAc in a solution of THF as monitored by in-situ IR measurement, which indicated the formation of some new carboxylate group(s) [Figures 1 (a)]. In comparison, mixing CO\(_2\) with LiCl in a solution of THF didn’t give any such new signal [Figures 1 (b)].
(a) In-situ IR study on LiOAc in THF under CO$_2$ atmosphere.

(b) In-situ IR study on LiCl in THF under CO$_2$ atmosphere.

**Figure 1.** In-situ IR studies on possible intermediate
General Information.

All reactions were carried out in a 25 mL Schlenk tube. Allylic bromides 1a-1p were prepared from the corresponding alcohols according to the literature reports. Allylic bromide 1q was purchased from Acros; 1r from TCI; 1s from Alfa-Aesar. Zinc powder was purchased from Sinopharm Chemical Reagent Co., Ltd (600 Mesh). All the metal powder was washed sequentially with 3 M aq HCl, acetone and diethyl ether (3 times for each) and dried under vacuum for 3 h before use. LiOAc was purchased from Energy Chemical. THF was distilled over sodium wire right before use. DCM and DMF were dried over CaH2 before distillation. The purity of CO2 is over 99.995% and used without further treatment. All the temperatures are referred to the bath temperature. NMR spectra were taken using TMS (1H, δ = 0), CDCl3 (13C CPD, δ = 77.0) and CFCl3 (19F CPD, δ = 0) as the internal standards.

Synthesis of β,γ-Unsaturated Carboxylic Acids by Carboxylation of Allyl Bromides with CO2 (Table 4 and Table 5).

1. Synthesis of 3-Phenyl-3-butenoic Acid (2a, mbky-10-067):

Typical procedure I: To an oven-dried 25 mL Schlenk tube equipped with a magnetic stirring bar were added zinc powder (68.5 mg, 1.05 mmol), LiOAc (66.2 mg, 1.00 mmol), 1a (197.6 mg, 1.00 mmol), and 5 mL of THF under an argon atmosphere. The mixture was then frozen with a liquid nitrogen bath and the argon inside was completely replaced by a balloon with CO2. The Schlenk tube was then allowed to stand until the mixture thawed with the CO2 balloon and was stirred at 20 °C for 24 h. The mixture was quenched with 10 mL of 3 M aq HCl and the aqueous layer was extracted with ethyl acetate (10 mL × 5). The combined organic layer was washed with 30 mL of brine, dried over anhydrous Na2SO4, filtrated and concentrated. The crude product was purified by column chromatography on silica gel to afford 133.6 mg of 2a (82%), eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 20/1 as a yellow solid: m.p. 47-48 °C (petroleum ether/ethyl acetate) (Lit. m.p.: 48-49 °C, petroleum ether/ethyl acetate; Lit. m.p.: 45-46 °C, petroleum ether): 1H NMR (300 MHz, CDCl3) δ 11.22 (bs, 1 H, COOH), 7.48-7.38 (m, 2 H,
ArH), 7.38-7.21 (m, 5 H, ArH), 5.58 (s, 1 H, one proton of CH2=), 5.25 (s, 1 H, one proton of CH2=), 3.54 (s, 2 H, CH2); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 178.0, 140.1, 139.3, 128.5, 127.9, 125.7, 116.8, 40.8; MS (m/z) 162 (M+, 91.78), 115 (100); IR (neat, cm$^{-1}$) 3500-2200(board), 1691, 1631, 1496, 1411, 1284, 1222, 1187, 1073, 1028. 2-Phenylpropene was formed in 3% yield as a main by-product as judged by $^1$H NMR.

The following compounds were prepared according to this Typical Procedure I.

2. Synthesis of 3-(1-Naphthyl)-3-butenoic Acid (2b, mbky-10-193):

$$\text{Br} \quad \text{Zn powder (1.05 equiv.)} \quad \text{LiOAc (1.0 equiv.)} \quad \text{CO}_2(\text{balloon}) \quad \text{THF, 20}^\circ\text{C, 24 h} \quad \text{COOH}$$

1b \quad 2b (79%)

The reaction of 1b (247.5 mg, 1.00 mmol), zinc powder (69.0 mg, 1.05 mmol), LiOAc (66.2 mg, 1.00 mmol), and CO$_2$ (1 atm balloon) in 5 mL of THF afforded 167.9 mg of 2b$^6,7a$ (79%), eluent: petroleum ether/ethyl acetate = 5/1→ dichloromethane / methanol = 20/1) as a white solid: m.p. 75-76 °C (petroleum ether/ethyl acetate) (Lit.$^7a$ m.p.: 74.5 °C; Lit.$^6$ m.p. 76-77 °C, petroleum ether/ethyl acetate): $^1$H NMR (300 MHz, CDCl$_3$) δ 10.60 (bs, 1 H, COOH), 8.05-7.95 (m, 1 H, ArH) 7.86-7.70 (m, 2 H, ArH), 7.50-7.28 (m, 4 H, ArH), 5.59 (s, 1 H, one proton of CH$_2$=), 5.33 (s, 1 H, one proton of CH$_2$=), 3.53 (s, 2 H, CH$_2$); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 177.4, 140.3, 139.4, 133.7, 130.8, 128.3, 127.8, 126.1, 125.7, 125.4, 125.3, 125.2, 120.3, 43.3; MS (m/z) 212 (M$,^+$, 27.78), 152 (100); IR (neat, cm$^{-1}$) 3500-2200(board), 1704, 1440, 1409, 1320, 1295, 1268, 1189, 1169, 1009. 2-naphthylpropene was formed in 23% yield as a main by-product as judged by $^1$H NMR.

3. Synthesis of 3-(4-Tolyl)-3-butenoic Acid (2c, mbky-11-022):

$$\text{Br} \quad \text{Zn powder (1.05 equiv.)} \quad \text{LiOAc (1.0 equiv.)} \quad \text{CO}_2(\text{balloon}) \quad \text{THF, 20}^\circ\text{C, 24 h} \quad \text{COOH}$$

1c \quad 2c (80%)

The reaction of 1c (211.2 mg, 1.00 mmol), zinc powder (68.7 mg, 1.05 mmol), LiOAc (66.6 mg, 1.01 mmol), and CO$_2$ (1 atm balloon) in 5 mL of THF afforded
140.3 mg of \(2c^{6,7a}\) (80%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 20/1) as a white solid: m.p. 111-112 \(^\circ\)C (petroleum ether/ethyl acetate) (Lit.\(^{7a}\) m.p.: 106-107 \(^\circ\)C; Lit.\(^{6}\) m.p. 112-113 \(^\circ\)C, petroleum ether/ethyl acetate): \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 10.41 (bs, 1 H, COOH), 7.32 (d, \(J = 8.1\) Hz, 2 H, ArH), 7.13 (d, \(J = 7.8\) Hz, 2 H, ArH), 5.54 (s, 1 H, one proton of \(\text{CH}_2=\)), 5.20 (s, 1 H, one proton of \(\text{CH}_2=\)), 3.52 (s, 2 H, \(\text{CH}_2\)), 2.33 (s, 3 H, \(\text{CH}_3\)); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 177.6, 139.9, 137.8, 136.5, 129.1, 125.6, 115.9, 40.8, 21.0; MS (m/z) 176 (M\(^+\), 91 (100)); IR (neat, cm\(^{-1}\)) 3600-2200(broad), 1687, 1631, 1513, 1418, 1345, 1304, 1226, 1120.

**Synthesis of 3-(4-Tolyl)-3-butenoic Acid in the Absence of LiOAc (2c, mbky-12-127):**

\[
\begin{align*}
\text{1c} & \quad \xrightarrow{\text{Zn powder (1.05 equiv.)}} \quad \text{CO}_2 \text{ (balloon)} \quad \text{THF, 20 °C, 24 h} \quad \text{2c (61%)}
\end{align*}
\]

The reaction of \(1c\) (211.4 mg, 1.00 mmol), zinc powder (68.5 mg, 1.05 mmol), and \(\text{CO}_2\) (1 atm balloon) in 5 mL of THF afforded 107.3 mg of \(2c^{6,7a}\) (61%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 20/1) as a white solid: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.06 (bs, 1 H, COOH), 7.32 (d, \(J = 8.4\) Hz, 2 H, ArH), 7.13 (d, \(J = 8.4\) Hz, 2 H, ArH), 5.54 (s, 1 H, one proton of \(\text{CH}_2=\)), 5.20 (s, 1 H, one proton of \(\text{CH}_2=\)), 3.52 (s, 2 H, \(\text{CH}_2\)), 2.33 (s, 3 H, \(\text{CH}_3\)).

**4. Synthesis of 3-Benzyl-3-butenoic Acid (2d, mbky-10-185):**

\[
\begin{align*}
\text{1d} & \quad \xrightarrow{\text{Zn powder (1.05 equiv.) LiOAc (1.0 equiv.)}} \quad \text{CO}_2 \text{ (balloon)} \quad \text{THF, 20 °C, 24 h} \quad \text{2d (80%)}
\end{align*}
\]

The reaction of \(1d\) (211.1 mg, 1.00 mmol), zinc powder (68.8 mg, 1.00 mmol), LiOAc (65.7 mg, 1.00 mmol) and \(\text{CO}_2\) (1 atm balloon) in 5 mL of THF afforded 140.2 mg of \(2d^{6}\) (80%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 20/1) as a colorless oil: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 9.80 (bs, 1 H, COOH), 7.40-7.10 (m, 5 H, ArH), 5.04 (s, 1 H, one proton of \(\text{CH}_2=\)), 5.00 (s, 1 H, one proton of \(\text{CH}_2=\)), 3.48 (s, 2 H, \(\text{CH}_2\)), 3.02 (s, 2 H, \(\text{CH}_2\)); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 177.7, 141.2, 138.5, 129.1, 128.4, 126.4, 116.3, 42.6, 40.7; MS (m/z) 176 (M\(^+\), 70.81), 91 (100); IR (neat, cm\(^{-1}\)) 3700-2200(board), 1689, 1652, 1603, 1494, 1452, 1430, 1407, 1332, 1294, 1253, 1223, 1191, 1177, 1074, 1027. 2-methyl-1-phenyl-2-propene
was formed in 15% yield as a main by-product as judged by \textsuperscript{1}H NMR.

5. Synthesis of 3-Hexyl-3-butenoic Acid (2e, mbky-10-178):

The reaction of 1e (205.3 mg, 1.00 mmol), zinc powder (68.9 mg, 1.05 mmol), LiOAc (66.0 mg, 1.00 mmol), and CO\textsubscript{2} (1 atm balloon) in 5 mL of THF afforded 141.7 mg of 2e\textsuperscript{6} (83%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 20/1) as a colorless oil: \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 10.26 (bs, 1 H, COOH), 4.96 (s, 1 H, one proton of CH\textsubscript{2}=), 4.93 (s, 1 H, one proton of CH\textsubscript{2}=), 3.08 (s, 2 H, CH\textsubscript{2}CO), 2.12 (t, \( J = 7.5 \) Hz, 2 H, CH\textsubscript{2}), 1.55-1.16 (m, 8 H, 4 \( \times \) CH\textsubscript{2}), 0.88 (t, \( J = 6.8 \) Hz, 3 H, CH\textsubscript{3}); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \( \delta \) 178.3, 142.0, 114.0, 41.7, 35.9, 31.7, 28.9, 27.3, 22.6, 14.1; MS (m/z) 170 (M\textsuperscript{+}, 1.20), 110 (100); IR (neat, cm\textsuperscript{-1}) 2957, 2928, 2858, 2673, 1709, 1649, 1459, 1408, 1293, 1216, 1157.

Synthesis of 3-Hexyl-3-butenoic Acid in the Absence of LiOAc (2e, mbky-12-126):

The reaction of 1e (205.4 mg, 1.00 mmol), zinc powder (68.6 mg, 1.05 mmol), and CO\textsubscript{2} (1 atm balloon) in 5 mL of THF afforded 115.7 mg of 2e\textsuperscript{6} (68%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 20/1) as a colorless oil: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 9.81 (bs, 1 H, COOH), 4.96 (s, 1 H, one proton of CH\textsubscript{2}=), 4.93 (s, 1 H, one proton of CH\textsubscript{2}=), 3.08 (s, 2 H, CH\textsubscript{2}CO), 2.12 (t, \( J = 7.6 \) Hz, 2 H, CH\textsubscript{2}), 1.50-1.38 (m, 2 H, CH\textsubscript{2}), 1.37-1.30 (m, 6 H, 3 \( \times \) CH\textsubscript{2}), 0.88 (t, \( J = 6.4 \) Hz, 3 H, CH\textsubscript{3}).


The reaction of 1f (221.3 mg, 1.00 mmol), zinc powder (69.0 mg, 1.05 mmol),
LiOAc (66.2 mg, 1.00 mmol), and CO₂ (1 atm balloon) in 5 mL of THF afforded 91.9 mg of 2f₇b (49%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 20/1) as an oil: ¹H NMR (300 MHz, DMSO-D₆) δ 12.42 (bs, 1 H, COOH), 7.48-7.28 (m, 5 H, ArH), 5.57 (s, 1 H, one proton of CH=), 5.54 (s, 1 H, one proton of CH₂=), 3.23 (s, 2 H, CH₂); ¹³C NMR (75 MHz, DMSO-D₆) δ 171.2, 131.3, 128.8, 128.7, 125.4, 124.5, 122.2, 89.5, 88.9, 42.1; MS (m/z) 186 (100); IR (neat, cm⁻¹) 3700-2300 (board), 2211, 1709, 1611, 1490, 1442, 1411, 1298, 1224, 1177, 1158, 1070, 1026. (3-methyl-3-buten-1-yn-1-yl)benzene was formed in 37% yield as a main by-product as judged by ¹H NMR.

7. Synthesis of 3-Methylene-4-nonynoic Acid (2g, mbky-11-018):

The reaction of 1g (201.3 mg, 1.00 mmol), zinc powder (68.4 mg, 1.05 mmol), LiOAc (66.2 mg, 1.00 mmol), and CO₂ (1 atm balloon) in 5 mL of THF afforded 107.7 mg of 2g₇b (65%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 20/1) as an oil: ¹H NMR (300 MHz, CDCl₃) δ 10.84 (bs, 1 H, COOH), 5.46 (s, 1 H, one proton of CH=), 5.33 (s, 1 H, one proton of CH₂=), 3.20 (s, 2 H, =CCH₂), 2.30 (t, J = 6.9 Hz, 2 H, CH₂), 1.57-1.32 (m, 4 H, 2 × CH₂), 0.91 (t, J = 7.2 Hz, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 176.7, 123.9, 123.8, 91.5, 79.6, 42.6, 30.6, 21.9, 18.9, 13.6; MS (m/z) 166 (M⁺, 12.22), 91 (100); IR (neat, cm⁻¹) 2958, 2933, 2873, 2224, 1712, 1614, 1459, 1410, 1327, 1292, 1266, 1220, 1164. 2-methyl-1-octen-3-yne was formed in 13% yield as a main by-product as judged by ¹H NMR.

8. Synthesis of 3-(2-Fluorophenyl)-3-butenoic Acid (2h, mbky-10-183):

The reaction of 1h (215.1 mg, 1.00 mmol), zinc powder (68.7 mg, 1.00 mmol), LiOAc (66.2 mg, 1.00 mmol), and CO₂ (1 atm balloon) in 5 mL of THF afforded 140.2 mg of 2h (78%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 20/1) as an oil: ¹H NMR (300 MHz, CDCl₃) δ 9.31 (bs, 1 H, COOH),
7.38-7.15 (m, 2 H, ArH), 7.12-6.95 (m, 2 H, ArH), 5.45 (s, 1 H, one proton of CH=),
5.38 (s, 1 H, one proton of CH2=), 3.54 (s, 2 H, CH2); 13C NMR (75 MHz, CDCl3) δ
177.7, 159.7 (d, J = 246.2 Hz), 136.7, 129.9 (d, J = 3.6 Hz), 129.3 (d, J = 8.1 Hz),
d, J = 13.1 Hz), 124.1 (d, J = 2.9 Hz), 120.7 (d, J = 2.7 Hz), 115.7 (d, J = 23.0 Hz),
41.2; 19F NMR (282 MHz, CDCl3) δ -115.2; MS (m/z) 180 (M+, 100); IR (neat, cm-1)
3700-2300(board), 1708, 1633, 1612, 1573, 1488, 1450, 1410, 1294, 1254,
1215, 1090, 1033. HRMS (EI) calcd. for C10H9FO2 (M+): 180.0587; Found: 180.0591.

9. Synthesis of 3-(3-Fluorophenyl)-3-butenolic Acid (2i, mbky-10-177):

\[
\text{Zn powder (1.05 equiv.)} \quad \text{LiOAc (1.0 equiv.)} \quad \text{CO}_2 \text{ (balloon)} \quad \text{THF, 20 °C, 24 h}
\]

\[
\begin{array}{c}
\text{Br} \\
\text{F}
\end{array}
\rightarrow
\begin{array}{c}
\text{COOH}
\end{array}
\]

The reaction of 1i (215.3 mg, 1.00 mmol), zinc powder (68.3 mg, 1.00 mmol),
LiOAc (66.0 mg, 1.00 mmol), and CO2 (1 atm balloon) in 5 mL of THF afforded
132.5 mg of 2i (74%, eluent: petroleum ether/ethyl acetate = 5/1 →
dichloromethane / methanol = 20/1) as an oil: 1H NMR (300 MHz, CDCl3) δ 9.15 (bs, 1 H, COOH), 7.34-7.22 (m, 1 H, ArH), 7.22-7.08 (m, 1 H, ArH), 7.02-6.92 (m, 1 H, ArH), 5.60 (s, 1 H, one proton of CH=), 5.30 (s, 1 H, one proton of CH2=), 3.53 (s, 2 H, CH2); 13C NMR (75 MHz, CDCl3) δ 177.7, 162.8 (d, J = 243.8 Hz), 141.7 (d, J =
3.3 Hz), 114.7 (d, J = 20.9 Hz), 112.8 (d, J = 21.9 Hz), 40.7; 19F NMR (282 MHz, CDCl3) δ -113.5; MS (m/z) 180 (M+, 100); IR (neat, cm-1) 3800-2300(board), 1697,
1610, 1579, 1486, 1442, 1342, 1305, 1269, 1236, 1216, 1168. 2-(3-fluorophenyl)propene was formed in 13% yield as a main by-product as judged by 1H NMR.

10. Synthesis of 3-(4-Fluorophenyl)-3-butenolic Acid (2j, mbky-10-176):

\[
\text{Zn powder (1.05 equiv.)} \quad \text{LiOAc (1.0 equiv.)} \quad \text{CO}_2 \text{ (balloon)} \quad \text{THF, 20 °C, 24 h}
\]

\[
\begin{array}{c}
\text{Br} \\
\text{F}
\end{array}
\rightarrow
\begin{array}{c}
\text{COOH}
\end{array}
\]

The reaction of 1j (215.0 mg, 1.00 mmol), zinc powder (69.0 mg, 1.00 mmol),
LiOAc (65.5 mg, 0.99 mmol), and CO2 (1 atm balloon) in 5 mL of THF afforded
149.5 mg of 2j (83%, eluent: petroleum ether/ethyl acetate = 5/1 →
dichloromethane / methanol = 20/1) as a white solid: m.p. 65-66 °C (petroleum ether/ethanol acetate; Lit. 6 m.p.: 66-68 °C, petroleum ether/ethanol acetate; Lit. 7d m.p.: 67 °C): 1H NMR (300 MHz, CDCl3) δ 10.47 (bs, 1 H, COOH), 7.45-7.33 (m, 2 H, ArH), 7.07-6.96 (m, 2 H, ArH), 5.51 (s, 1 H, one proton of CH2=), 5.23 (s, 1 H, one proton of CH2=), 3.51 (s, 2 H, CH2); 13C NMR (75 MHz, CDCl3) δ 177.7, 162.5 (d, J = 245.7 Hz), 139.1, 135.5 (d, J = 3.2 Hz), 127.4 (d, J = 8.6 Hz), 116.8, 115.3 (d, J = 21.2 Hz), 41.0; 19F NMR (282 MHz, CDCl3) δ -114.8; MS (m/z) 180 (M+, 99.40), 109 (100); IR (neat, cm⁻¹) 3800-2300 (board), 1697, 1631, 1601, 1509, 1413, 1340, 1300, 1223, 1163, 1110, 1100, 1014. 2-(4-fluorophenyl)propene was formed in 12% yield as a main by-product as judged by 1H NMR.

**Synthesis of 3-(4-Fluorophenyl)-3-butenolic Acid in the Absence of LiOAc (2j, mbky-12-117):**

![Synthesis of 3-(4-Fluorophenyl)-3-butenolic Acid in the Absence of LiOAc (2j, mbky-12-117)](image)

The reaction of 1j (215.2 mg, 1.00 mmol), zinc powder (68.7 mg, 1.00 mmol), and CO2 (1 atm balloon) in 5 mL of THF afforded 81.6 mg of 2j (45%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 20/1) as a yellow solid: 1H NMR (400 MHz, CDCl3) δ 10.24 (bs, 1 H, COOH), 7.44-7.36 (m, 2 H, ArH), 7.07-6.94 (m, 2 H, ArH), 5.50 (s, 1 H, one proton of CH2=), 5.23 (s, 1 H, one proton of CH2=), 3.51 (s, 2 H, CH2).

**11. Synthesis of 3-(3-Chlorophenyl)-3-butenolic Acid (2k, mbky-10-192):**

![Synthesis of 3-(3-Chlorophenyl)-3-butenolic Acid (2k, mbky-10-192)](image)

The reaction of 1k (231.6 mg, 1.00 mmol), zinc powder (68.5 mg, 1.00 mmol), LiOAc (66.3 mg, 1.00 mmol), and CO2 (1 atm balloon) in 5 mL of THF afforded 143.4 mg of 2k (73%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 20/1) as a yellow oil: 1H NMR (300 MHz, CDCl3) δ 10.22 (bs, 1 H, COOH), 7.41 (s, 1 H, ArH), 7.33-7.18 (m, 3 H, ArH), 5.57 (s, 1 H, one proton of CH2=), 5.30 (s, 1 H, one proton of CH2=), 3.51 (s, 2 H, CH2); 13C NMR (75 MHz, CDCl3) δ 177.2, 141.4, 139.1, 134.5, 129.7, 128.0, 126.0, 123.9, 118.2, 40.7; MS (m/z)
198 (M+(37Cl), 14.65), 196 (M+(35Cl), 46.93), 115 (100); IR (neat, cm⁻¹) 3800-2300 (board), 1707, 1629, 1563, 1478, 1410, 1293, 1221, 1170, 1117, 1079; HRMS (EI) calcd. for C₁₀H₉₆ClO₂ (M⁺): 196.0291; Found: 196.0290.

2-(3-chlorophenyl)propene was formed in 19% yield as a main by-product as judged by ¹H NMR.

12. Synthesis of 3-(4-Chlorophenyl)-3-butenoic Acid (2l, mbky-11-021):

![Chemical Structure]

The reaction of 1l (231.7 mg, 1.00 mmol), zinc powder (68.6 mg, 1.00 mmol), LiOAc (66.4 mg, 1.01 mmol), and CO₂ (1 atm balloon) in 5 mL of THF afforded 143.4 mg of 2l⁶ (73%), eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 20/1) as a white solid: m.p. 122-123 °C (petroleum ether/ ethyl acetate) (Lit.⁶ m.p.: 123-124 °C, petroleum ether/ ethyl acetate): ¹H NMR (300 MHz, CDCl₃) δ 9.02 (bs, 1 H, COOH), 7.42-7.22 (m, 4 H, ArH), 5.55 (s, 1 H, one proton of CH₂=), 5.27 (s, 1 H, one proton of CH₂=), 3.51 (s, 2 H, CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 177.2, 139.1, 137.9, 133.8, 128.6, 127.1, 117.4, 40.8; MS (m/z) 198 M⁺ ((37Cl), 18.79), 196 M⁺ ((35Cl), 58.28), 115 (100); IR (neat, cm⁻¹) 3700-2200 (board), 1688, 1633, 1593, 1492, 1418, 1348, 1310, 1227, 1103, 1089, 1011. 2-(4-chlorophenyl)propene was formed in 20% yield as a main by-product as judged by ¹H NMR.

13. Synthesis of 3-(4-Trifluoromethylphenyl)-3-butenoic Acid (2m, mbky-10-194):

![Chemical Structure]

The reaction of 1m (265.5 mg, 1.00 mmol), zinc powder (69.0 mg, 1.00 mmol), LiOAc (66.0 mg, 1.00 mmol), and CO₂ (1 atm balloon) in 5 mL of THF afforded 163.7 mg of 2m⁶ (71%), eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 20/1) as a white solid: sublimation observed at 100-101 °C, m.p. 105-106 °C (petroleum ether/ ethyl acetate)(Lit.⁶: sublimation observed at 100-101 °C,
m.p. 105-106 °C, petroleum ether/ethyl acetate): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 10.08 (bs, 1 H, COOH), 7.58 (d, $J = 8.4$ Hz, 2 H, ArH), 7.51 (d, $J = 8.4$ Hz, 2 H, ArH), 5.63 (s, 1 H, one proton of CH$_2$=), 5.36 (s, 1 H, one proton of CH$_2$=), 3.55 (s, 2 H, CH$_2$); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 177.4, 143.0, 139.2, 129.9 (q, $J = 32.4$ Hz), 126.1, 125.4 (q, $J = 4.0$ Hz), 124.1 (q, $J = 269.9$ Hz), 119.0, 40.7; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -63.2; MS (m/z) 230 (M$^+$, 62.02), 160 (100); IR (neat, cm$^{-1}$) 3700-2200 (board), 1692, 1635, 1618, 1406, 1319, 1226, 1167, 1117, 1064, 1015. 2-(4-trifluoromethyl)propene was formed in 13% yield as a main by-product as judged by $^1$H NMR.

14. Synthesis of 3-[4-(Ethoxycarbonyl)phenyl]-3-butenolic Acid (2n, mbky-11-020):

\[
\text{COOC}_{\text{Et}} \quad \text{Zn powder (1.05 equiv.)} \quad \text{LiOAc (1.0 equiv.)} \quad \text{CO$_2$ (balloon)} \quad \text{THF, 20 °C, 24 h} \quad \text{COOC}_{\text{Et}}
\]

1n

2n (55%)

The reaction of 1n (269.7 mg, 1.00 mmol), zinc powder (69.0 mg, 1.00 mmol), LiOAc (66.0 mg, 1.00 mmol), and CO$_2$ (1 atm balloon) in 5 mL of THF afforded 128.8 mg of 2n$^6$ (55%), eluent: petroleum ether/ethyl acetate = 10/1 $\rightarrow$ dichloromethane/methanol = 30/1) as a white solid: m.p. 88-90 °C (petroleum ether/ethyl acetate) (Lit.$^6$: m.p. 88-90 °C, petroleum ether/ethyl acetate): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.31 (bs, 1 H, COOH), 8.00 (d, $J = 8.4$ Hz, 2 H, ArH), 7.48 (d, $J = 8.4$ Hz, 2 H, ArH), 5.66 (s, 1 H, one proton of CH$_2$=), 5.35 (s, 1 H, one proton of CH$_2$=), 4.37 (q, $J = 7.1$ Hz, 2 H, OCH$_2$), 3.56 (s, 2 H, CH$_2$), 1.38 (t, $J = 7.2$ Hz, 3 H, CH$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 176.9, 166.3, 143.8, 139.5, 129.7, 125.7, 118.7, 61.0, 40.6, 14.3; MS (m/z) 234 (M$^+$, 32.73), 189 (100); IR (neat, cm$^{-1}$) 3800-2300 (board), 1704, 1685, 1627, 1606, 1404, 1366, 1314, 1277, 1221, 1201, 1184, 1126, 1111, 1097, 1019. 2-[4-(ethoxycarbonyl)phenyl]propene was formed in 25% yield as a main by-product as judged by $^1$H NMR.

15. Synthesis of 3-(3-Cyanophenyl)-3-butenolic Acid (2o, mbky-11-009):

\[
\text{CN} \quad \text{Zn powder (1.05 equiv.)} \quad \text{LiOAc (1.0 equiv.)} \quad \text{CO$_2$ (balloon)} \quad \text{DMF, 20 °C, 24 h} \quad \text{COOH}
\]

1o

2o (55%)
The reaction of 1o (222.3 mg, 1.00 mmol), zinc powder (68.6 mg, 1.05 mmol), LiOAc (66.2 mg, 1.00 mmol), and CO₂ (1 atm balloon) in 5 mL of DMF afforded 102.7 mg of 2o (55%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 20/1) as a yellow solid: m.p. 81-82 °C (petroleum ether/ethyl acetate) (Lit.⁶: m.p. 81-82 °C, petroleum ether/ethyl acetate): ¹H NMR (300 MHz, CDCl₃) δ 10.03 (bs, 1 H, COOH), 7.70 (s, 1 H, ArH), 7.65 (d, J = 7.8 Hz, 1 H, ArH), 7.57 (d, J = 7.5 Hz, 1 H, ArH), 7.44 (t, J = 7.8 Hz, 1 H, ArH), 5.61 (s, 1 H, one proton of CH₂=), 5.38 (s, 1 H, one proton of CH₂=), 3.55 (s, 2 H, CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 176.8, 140.7, 138.4, 131.2, 129.1, 129.3, 119.2, 118.6, 112.6, 40.4; MS (m/z) 187 (M⁺, 44.39), 117 (100); IR (neat, cm⁻¹) 3750-2300 (board), 2229, 1695, 1634, 1486, 1415, 1399, 1341, 1294, 1276, 1223. 2-(3-cyanophenyl)propene was formed in 9% yield as a main by-product as judged by ¹H NMR.

16. Synthesis of 3-[4-(2-methyl-1,3-dioxolan-2-yl)phenyl]-3-butenoic Acid (2p, mbky-10-199):

\[
\begin{align*}
\text{Zn powder (1.05 equiv.,} \\
\text{LiOAc (1.0 equiv.,} \\
\text{CO₂ (balloon),} \\
\text{THF, 20 °C, 24 h,} \\
\text{1p} \rightarrow \text{2p (71%)}
\end{align*}
\]

The reaction of 1p (283.7 mg, 1.00 mmol), zinc powder (68.2 mg, 0.99 mmol), LiOAc (65.7 mg, 1.00 mmol), and CO₂ (1 atm balloon) in 5 mL of THF afforded 175.7 mg of 2p (71%, eluent: petroleum ether/ethyl acetate = 5/1 → dichloromethane / methanol = 20/1) as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 9.80 (bs, 1 H, COOH), 7.44 (d, J = 8.7 Hz, 2 H, ArH), 7.40 (d, J = 8.7 Hz, 2 H, ArH), 5.60 (s, 1 H, one proton of CH₂=), 5.26 (s, 1 H, one proton of CH₂=), 4.10-3.96 (m, 2 H, OCH₂), 3.85-3.70 (m, 2 H, OCH₂), 3.54 (s, 2 H, CH₂CO), 1.65 (s, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 177.3, 142.9, 139.7, 138.8, 125.5, 125.4, 116.9, 108.7, 64.4, 40.8, 27.5; MS (m/z) 248 (M⁺, 1.83), 233 (100); IR (neat, cm⁻¹) 2957, 2925, 2890, 2853, 1696, 1628, 1422, 1372, 1290, 1254, 1234, 1192, 1174, 1100, 1078, 1039, 1015. 2-[4-(2-methyl-1,3-dioxolan-2-yl)phenyl]propene was formed in 20% yield as a main by-product as judged by ¹H NMR.

Carboxylation of Commercially Available Allylic Bromides with CO₂ Followed by Benzyl Esterification (Scheme 3).

The benzyl esters in this session were characterized by comparing with the
authentic samples prepared previously in this group.  

1. Synthesis of Benzyl 2-methyl-3-butenoate (3q, mbky-11-117):

Typical Procedure II: To an oven-dried 25 mL Schlenk tube equipped with a magnetic stirring bar were added zinc powder (68.7 mg, 1.05 mmol), LiOAc (66.2 mg, 1.00 mmol), 1q (TCI, purity: 83%, 163.0 mg, 1.00 mmol), and 5 mL of THF under an argon atmosphere. The mixture was then frozen with a liquid nitrogen bath and the argon inside was completely replaced by a balloon with CO2. The Schlenk tube was then allowed to stand until the mixture thawed with the CO2 balloon and was stirred at 20 °C for 24 h. The mixture was quenched with 10 mL of 3 M aq. HCl and the aqueous layer was extracted with ethyl acetate (10 mL × 5). The combined organic layer was washed with 30 mL of brine, dried over anhydrous Na2SO4, filtrated and concentrated to afford the crude acid product in a 100 mL flask. DMAP (12.3 mg, 0.10 mmol), DCM (5 mL) and BnOH (0.11 mL, 1.10 mmol, d = 1.049) were added sequentially into this flask, which was followed by cooling with a bath of ice-water and the addition of a solution of DCC (216.6 mg, 1.05 mmol) in 1 mL of DCM dropwise. Then the resulting mixture was allowed to warm up to room temperature and react for additional 10 hours. DCM (30 mL) was added into the suspension and the resulting mixture was filtered through a short pad of silica gel (300-400 mesh), eluted with DCM (5 mL × 3). The combined organic layer was washed sequentially with 30 mL of 1 M aq HCl, 30 mL of brine, and concentrated. The crude product was purified by column chromatography on silica gel to afford 112.0 mg of 3q6 (59%, eluent: petroleum ether/ethyl acetate = 100/1) as a colorless oil. 1H NMR (400 MHz, CDCl3) δ 7.40-7.29 (m, 5 H, ArH), 5.94 (ddd, J1 = 17.2 Hz, J2 = 10.0 Hz, J3 = 7.6 Hz, 1 H, =CH), 5.18-5.09 (m, 4 H, CH2Ph + CH2=), 3.26-3.13 (m, 1 H, CHCO), 1.29 (d, J = 6.8 Hz, 3 H, CH3); 13C NMR (100 MHz, CDCl3) δ 174.3, 137.0, 135.9, 128.5, 128.1, 128.0, 116.0, 66.3, 43.7, 16.7.

The following compounds were prepared according to this Typical Procedure II.

2. Synthesis of Benzyl 2,2-dimethylbut-3-enoate (3r, mbky-12-050):
The reaction of 1r (Alfa-Aesar, purity: 90%, 165.6 mg, 1.00 mmol), zinc powder (68.8 mg, 1.05 mmol), LiOAc (66.0 mg, 1.00 mmol), and CO₂ (1 atm balloon) in 5 mL of THF afforded the crude acid product. The esterification reaction of the acid, BnOH (0.11 mL, 1.10 mmol, d = 1.049), DMAP (12.6 mg, 0.10 mmol), and DCC (216.3 mg, 1.05 mmol) in 6 mL of DCM afforded 118.9 mg of 3r₆ (58%, eluent: petroleum ether/ethyl acetate = 100/1) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.27 (m, 5 H, ArH), 6.05 (dd, J₁ = 17.0 Hz, J₂ = 10.5 Hz, 1 H, =CH), 5.13-5.05 (m, 4 H, CH₂ + CH₂=), 1.33 (s, 6 H, 2×CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 176.2, 142.4, 136.2, 128.5, 128.0, 127.7, 113.0, 66.3, 44.9, 24.6.

3. Synthesis of Benzyl 2-cyclohexene-1-carboxylate (3s, mbky-12-014):

The reaction of 1s (Acros, purity: 95%, 169.7 mg, 1.00 mmol), zinc powder (68.7 mg, 1.05 mmol), LiOAc (66.2 mg, 1.00 mmol), and CO₂ (1 atm balloon) in 5 mL of THF afforded the crude acid product. The esterification reaction of the acid, BnOH (0.11 mL, 1.10 mmol, d = 1.049), DMAP (12.6 mg, 0.10 mmol), and DCC (216.6 mg, 1.05 mmol) in 6 mL of DCM afforded 119.6 mg of 3s₆ (55%, eluent: petroleum ether/ethyl acetate = 100/1) as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 7.41-7.27 (m, 5 H, ArH), 5.90-5.73 (m, 2 H, CH=CH), 5.14 (s, 2 H, CH₂), 3.20-3.10 (m, 1 H, CHCO), 2.13-1.70 (m, 5 H, protons of cyclohexenyl), 1.66-1.50 (m, 1 H, proton of cyclohexenyl); ¹³C NMR (75 MHz, CDCl₃) δ 174.4, 136.1, 129.8, 128.5, 128.1, 128.0, 124.1, 66.2, 41.1, 25.2, 24.6, 20.7.

Synthesis of Benzyl 2-cyclohexene-1-carboxylate using DMF as solvent (3s, mbky-12-095):
The reaction of 1s (Acros, purity: 95%, 169.7 mg, 1.00 mmol), zinc powder (68.9 mg, 1.05 mmol), LiOAc (66.4 mg, 1.00 mmol), and CO₂ (1 atm balloon) in 5 mL of DMF afforded the crude acid product. The esterification reaction of the acid, BnOH (0.11 mL, 1.10 mmol, d = 1.049), DMAP (12.4 mg, 0.10 mmol), and DCC (216.7 mg, 1.05 mmol) in 6 mL of DCM afforded 124.2 mg of 3s⁶ (57%, eluent: petroleum ether/ethyl acetate = 100/1) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.23 (m, 5 H, ArH), 5.82-5.68 (m, 2 H, CH=CH), 5.06 (s, 2 H, CH₂), 3.12-3.04 (m, 1 H, CHCO), 2.05-1.65 (m, 5 H, protons of cyclohexenyl), 1.57-1.45 (m, 1 H, proton of cyclohexenyl).

References
mbky-11-054 H
Oct 10 2014
SOLVENT: cdc13
NA = 8
F1 = 399.753052 MHz

2b
mtky-11-022 C
spect, CDCl₃
Tus Apr 15 04:49:20 2014
NA = 5000
F1 = 75.475255 MHz

2c

[Chemical structure diagram]
mbky-10-185 C
spec, CDC3,
Mon Apr 14 21:28:30 2014
NA = 3900
F1 = 75.475296 MHz

\[ \text{COOH} \]

2d
mbky-11-019 H
Sat May 31 00:01:34 2014
SOLVENT: DMSO
NA = 6
F1 = 300.130005 MHz

Ph-CH=CH

COOH

2f

1.00
0.99

0.70

12 10 8 6 4 2 0
0 PPM
mbly-11-018 H
spec, CDCl3,
Wec Apr 23 12:09:53 2014
NA = 6
F1 = 300.131865 MHz

\[ ^n\text{Bu} \equiv \text{COOH} \]

2g
mbky-10-183 C
spect, CDCl₃,
Sun Apr 20 17:29:48 2014
NA = 1500
F1 = 75475298 MHz

![Chemical Structure](image)

2h
mbky-10-176C
spect. CDCl3
Sat Mar 29 03:28:06 2014
NA = 7031
F1 = 75.475296 MHz

2j

\[
\text{\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{image.png}
\caption{Diagram of molecular structure and spectrum data.}
\end{figure}}
\]
mbky-10-176 F
spect. CDCl3,
Sat Mar 29 14:38:19 2014
NA = 16
F1 = 282.376129 MHz

2j
mbky-10-192 C
spect, CDCl3.
Wed Apr 16 09:45 2014
NA = 300C
F1 = 75.473296 MHz

Cl

\[ \text{COOH} \]

2ξ
mbly-11-021 C
spect. CDCl3,
Fri Apr 18 10:10:52 2014
NA = 3000
F1 = 75.475296 MHz

Cl

COOH

2l
mbky-10-194 H
spect, CDCl3,
Fri Apr 18 08:40:47 2014
NA = 6
F1 = 303.131866 MHz

[Diagram of molecule with spectral data]
nrbky-10-194 C
spect, CDC33,
F1 Apr 18 08:3:44 2014
NA = 221
F1 = 76.475296 MHz

CF₃

COOH

2m
mbky-11-020 C
spect, CDCl3,
Sat Apr 19 13:35:25 2014
NA = 800
F1 = 75.475296 MHz

COOEt

COOH

2n
mbky-11-009 C
spec, CDCl3,
Sun Apr 20 22:26:06 2014
NA = 800
F1 = 7.476296 MHz

2o

CN

COOH
mbky-12-050 H
Oct 4 2014
SOLVENT: ccd3
NA = 8
F1 = 399.753052 MHz

\[
\begin{align*}
\text{COOBn} \\
3r
\end{align*}
\]
S61

mbky-12-014 H,  
15:06:24  
SOLVENT: CDCl3  
NA = 6  
F1 = 300.130005 MHz

COOBn

3s

PPM