Supporting Information

General Information
All $^1$H NMR and $^{13}$C NMR spectra were recorded on a JEOL ECS-400 (400 MHz for $^1$H, 100 MHz for $^{13}$C) or a Bruker Avance III HD (500 MHz for $^1$H, 125 MHz for $^{13}$C, with a CryoProbe) instrument in CDCl$_3$ with tetramethylsilane as an internal standard otherwise mentioned. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), integration. Infrared spectra (IR) were obtained on a Nicolet 380 FT-IR spectrometer and absorptions are reported in reciprocal centimeters. Mass spectra (MS) were obtained on a Bruker MicroTOF-QIII (ESI).

Materials or Methods.
All manipulations were performed under a dry nitrogen atmosphere by use of standard Schlenk techniques or nitrogen atmosphere in an mBRAUN Labmaster 130 glovebox unless otherwise noted. Nitrogen was purified by being passed through a Dryclean column (4 A molecular sieves, Nikka Seiko Co.) and a Gasclean CC-XR column (Nikka Seiko Co.). Carbon dioxide (purity: >99.995%) was purchased from Taiyo Nippon Sanso Co. and used without further purification. THF and toluene (dehydrated, stabilizer-free) were obtained from Kanato Kagaku Co. and purified by use of a MBraun SPS-800 solvent purification system. iBu$_3$Al(TMP)Li and NHC-copper complex (IMes)CuCl were also prepared according to literature methods. All other solvents and reagents were purified when necessary using standard procedures. Silica gel column chromatography was performed with Silica Gel 60N (spherical, neutral, 0.040-0.050 mm, Kanto Kagaku Co.).

Typical Procedures for the Formal C–H Carboxylation of Allylic Compounds. Typical Procedure (A), One-pot Synthesis of 3-Butenoic Acids; for the synthesis of 3a (Table 1, entry 5)

**Methyl 2-phenoxy-3-butenoate (3a)**: To a solution of lithium 2,2,6,6-tetramethylpiperidide (151.8 mg, 1.0 mmol, 97%) in THF (3.0 mL) placed in a 30-mL round bottomed flask was cooled to -78 °C, and iBu$_3$Al (1.0 mL 1.0 M in hexane, 1.0 mmol) was slowly added. The reaction mixture was stirred for 30 min at 0 °C, affording a yellow solution of the aluminum ate species (iBu$_3$Al(TMP)Li). A solution of allyl phenyl ether (1a, 67.2 mg, 0.5 mmol) in THF (2.0 mL) was added into the prepared solution of iBu$_3$Al(TMP)Li at -78 °C and the resulting mixture was stirred at room temperature for 3 hrs. Then, to this solution was added catalytic amount of (IMes)CuOrBu (22.0 mg, 0.05 mmol, 10 mol%) in THF (2.0 mL) at -78 °C. The flask was evacuated and gaseous CO$_2$ stored in balloon was quickly introduced in it. The same operation was repeated for several times. After the mixture was stirred at 0 °C for 2 hrs, it was hydrolyzed with 10% aqueous solution of HCl at 0 °C. Organic compounds were extracted by ethyl acetate (10 mL, 3 times). The combined organic layers were washed with brine and dried over anhydrous MgSO$_4$ and concentrated in vacuo. The obtained product was treated with TMSCHN$_2$ in Et$_2$O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane/AcOEt = 9/1 to 6/1), compound 3a (87.6 mg, 0.46 mmol) was obtained in 91% yield as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 3.78 (s, 3H; OCH$_3$), 5.16 (d, $^3$J$_{HH}$ = 5.5 Hz, 1H; OCH), 5.41 (d,

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Typical Procedures for the Formal C–H Carboxylation and Sequential Isomerization of Allylic Compounds. Typical Procedure (B), One-pot Synthesis of 2-Butenoic Acids; for the synthesis of 4a (Table 3, 4a)

Methyl 2-phenyloxy-(Z)-2-butenoate (4a): To a solution of lithium 2,2,6,6-tetramethylpiperidide (151.8 mg, 1.0 mmol, 97%) in THF (3.0 mL) placed in a 30-mL round bottomed flask was cooled to -78 °C, and iBu₃Al (1.0 mL 1.0 M in hexane, 1.0 mmol) was slowly added. The reaction mixture was stirred for 30 min at 0 °C, affording a yellow solution of the aluminum ate species (iBu₃Al(TMP)Li). A solution of allyl phenyl ether (1a, 67.2 mg, 0.5 mmol) in THF (2.0 mL) was added into the prepared solution of iBu₃Al(TMP)Li at -78 °C and the resulting mixture was stirred at room temperature for 3 hrs. Then, to this solution were added (IMes)CuO₃Bu (0.05 mmol, 10 mol%) in THF (2.0 mL) at -78 °C. The flask was evacuated and gaseous CO₂ stored in balloon was quickly introduced in it. The same operation was repeated for several times. After the mixture was stirred at 0 °C for 2 hrs, then, DBU (7.8 μL, 0.05 mmol) was added into the reaction mixture. After stirring the reaction mixture for 24 hrs at room temperature, it was hydrolyzed with 10% aqueous solution of HCl at 0 °C. Organic compounds were extracted by ethyl acetate (10 mL, 3 times). The combined organic layers were washed with brine and dried over anhydrous MgSO₄ and concentrated in vacuo. The obtained product was treated with TMSCHN₂ in Et₂O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane/AcOEt = 6/1), compound 4a (87.5 mg, 0.46 mmol) was obtained in 91% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 1.78 (d, ³JHH = 7.3 Hz, 3H; CHCH₃), 3.71 (s, 3H; OCH₃), 6.72 (q, ³JHH = 7.3 Hz, 1H; CHCH₃), 6.90-6.93 (m, 2H; aryl), 6.99-7.03 (m, 1H; aryl), 7.26-7.30 (m, 2H; aryl); ¹³C[¹H] NMR (101 MHz, CDCl₃, 25 °C, TMS); δ = 11.6, 52.3, 115.0, 122.2, 127.7, 129.7, 141.9, 157.3, 163.7; IR (neat): v = 2953, 1733, 1661, 1596, 1491, 1456, 1437, 1381, 1322, 1275, 1216, 1166, 1134, 1067, 1025, 1012 cm⁻¹; HRMS (ESI) calcd for C₁₁H₁₂NaO₃ 215.0684 ([M+Na]⁺), found 215.0686.

Spectral Data of Products and Experimental Details

~3-Butenoic acid esters (Table 2)~

Methyl 2-(4-tert-butylphenoxy)-3-butenoate (3b, a new compound): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1b (95.1 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuO₃Bu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with
he obtained carboxylic acid was

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\begin{align*}
\text{IR (neat): } &\nu = 2961, 2904, 2869, 1761, 1741, 1608, 1513, 1436, 1364, 1239, 1187, 1167, 1016 \text{ cm}^{-1}; \\
\text{HRMS (ESI) calcd for C}_{15}H_{20}NaO_3 &271.1305 ([M+Na]^+), \text{ found 271.1304.}
\end{align*}
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Methyl 2-(4-benzylphenoxy)-3-butenoate (3c, a new compound): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1c (112.1 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBuAl(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN₂ in Et₂O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), the compound 3c (119.9 mg, 0.43 mmol) was obtained in 85% yield as a colorless oil.

1H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 3.77 (s, 3H; OCH₃), 3.92 (s, 2H; CaH₃CH₂), 5.11 (d, J_HH = 5.5 Hz, 1H; OCH), 5.39 (d, J_HH = 10.5 Hz, 1H; CH=CH₂H₃), 5.59 (d, J_HH = 17.0 Hz, 1H; CH=CH₂H₃), 6.03 (ddd, J_HH = 5.5, 10.5, 17.0 Hz, 1H; CH=CH₂H₃), 6.82-6.86 (m, 2H; aryl), 7.07-7.11 (m, 2H; aryl), 7.15-7.21 (m, 3H; aryl), 7.28-7.29 (m, 2H; aryl); 13C{¹H} NMR (101 MHz, CDCl₃, 25 °C, TMS): δ = 41.2, 52.7, 77.8, 115.6, 119.5, 126.2, 128.6, 129.0, 130.1, 131.9, 134.7, 141.4, 155.8, 170.4; IR (neat): ν = 3027, 2657, 2919, 1737, 1609, 1585, 1509, 1494, 1453, 1438, 1298, 1266, 1237, 1181, 1113, 1062, 1009 cm⁻¹; HRMS (ESI) calcd for C₁₈H₂₉NaO₃ 305.1153 ([M+Na]^+), found 305.1160.

Methyl 2-(2,3-dihydro-1H-inden-5-yloxy)-3-butenoate (3d, a new compound): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1d (94.1 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBuAl(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN₂ in Et₂O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), the compound 3d (104.5 mg, 0.45 mmol) was
obtained in 90% yield as a colorless oil.

\[^1\text{H}~\text{NMR}~(400\text{ MHz, CDCl}_3, 25\degree\text{C}, \text{TMS}):~\delta = 2.02-2.10~(\text{m, 2H; CH}_2\text{CH}_2\text{CH}_2),~2.81-2.88~(\text{m, 4H; CH}_2\text{CH}_2\text{CH}_2),~3.78~(\text{s, 3H; OCH}_3),~5.12~(\text{d, }^3\text{J}_{\text{HH}} = 5.5\text{ Hz, 1H; OCH}),~5.39~(\text{d, }^3\text{J}_{\text{HH}} = 10.5\text{ Hz, 1H; CH=CH-})~\text{a(Ha),}~5.60~(\text{d, }^3\text{J}_{\text{HH}} = 17.4\text{ Hz, 1H; CH=CH(Hb)},~6.05~(\text{ddd, }^3\text{J}_{\text{HH}} = 5.5, 10.5, 17.4\text{ Hz, 1H; CH=CH(Hb),}~6.70-6.71~(\text{m, 1H; aryl}),~6.79-6.80~(\text{m, 1H; aryl}),~7.09-7.11~(\text{m, 1H; aryl}); ~^{13}\text{C}[^1\text{H}]~\text{NMR}~(101\text{ MHz, CDCl}_3, 25\degree\text{C}, \text{TMS}):~\delta = 25.9, 32.1, 33.2, 52.7, 78.1, 111.8, 113.5, 119.3, 125.0, 132.1, 137.7, 146.0, 156.3, 170.6; ~\text{IR (neat): } \nu = 2952, 2845, 1760, 1739, 1609, 1586, 1489, 1436, 1270, 1246, 1195, 1147, 1099, 1084, 1059, 1017\text{ cm}^{-1}; ~\text{HRMS (ESI) calcd for C}_{14}\text{H}_{18}\text{NaO}_3~255.0992~([M+Na]^+),~\text{found}~255.0993.\]

**Methyl 2-naphthoxy-3-butenoate (3e, a new compound):** According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1e (92.1 mg, 0.50 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN₂ in Et₂O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), the compound 3e (96.8 mg, 0.40 mmol) was obtained in 80% yield as a colorless oil.

\[^1\text{H}~\text{NMR}~(400\text{ MHz, CDCl}_3, 25\degree\text{C}, \text{TMS}):~\delta = 3.79~(\text{s, 3H; OCH}_3),~5.31~(\text{d, }^3\text{J}_{\text{HH}} = 5.9\text{ Hz, 1H; OCH}),~5.44~(\text{d, }^3\text{J}_{\text{HH}} = 10.5\text{ Hz, 1H; CH=CHH(a)}),~5.66~(\text{d, }^3\text{J}_{\text{HH}} = 17.4\text{ Hz, 1H; CH=CHH(b)}),~6.11~(\text{ddd, }^3\text{J}_{\text{HH}} = 5.9, 10.5, 17.4\text{ Hz, 1H; CH=CHH(b)}),~7.086-7.093~(\text{m, 1H; aryl}),~7.23-7.26~(\text{m, 1H; aryl}),~7.33-7.37~(\text{m, 1H; aryl}),~7.41-7.45~(\text{m, 1H; aryl}),~7.69-7.71~(\text{m, 1H; aryl}),~7.76-7.78~(\text{m, 2H; aryl}); ~^{13}\text{C}[^1\text{H}]~\text{NMR}~(101\text{ MHz, CDCl}_3, 25\degree\text{C}, \text{TMS}):~\delta = 52.8, 77.7, 108.3, 119.0, 119.7, 124.3, 126.6, 127.1, 127.8, 129.6, 129.9, 131.7, 134.3, 155.2, 170.3; ~\text{IR (neat): } \nu = 2951, 1732, 1627, 1598, 1510, 1469, 1444, 1434, 1390, 1365, 1297, 1273, 1254, 1215, 1187, 1121, 1055, 1012\text{ cm}^{-1}; ~\text{HRMS (ESI) calcd for C}_{15}\text{H}_{16}\text{NaO}_3~265.0835~([M+Na]^+),~\text{found}~265.0835.\]

**Methyl 2-[(3-dimethylamino)phenoxy]-3-butenoate (3f, a new compound):** According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1f (89.0 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN₂ in Et₂O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), the compound 3f (88.2 mg, 0.38 mmol) was obtained in 75% yield as a colorless oil.

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he obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN₂. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN₂ in Et₂O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), the compound 3g (94.1 mg, 0.39 mmol) was obtained in 79% yield as a colorless oil.

Methyl 2-[(4-methylthio)phenoxy]-3-butoxenate (3g): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1g (90.0 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMPr)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN₂ in Et₂O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), the compound 3g (94.1 mg, 0.39 mmol) was obtained in 79% yield as a colorless oil.

Methyl 2-[(4-tert-butylidimethylsilyloxy)phenoxy]-3-butoxenate (3h, a new compound): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1h (132.1 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMPr)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN₂ in Et₂O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), the compound 3h (140.3 mg, 0.44 mmol) was obtained in 87% yield as a colorless oil.

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**1H NMR (400 MHz, CDCl₃, 25 °C, TMS):** δ = 2.92 (s, 6H; N(CH₃)₂), 3.78 (s, 3H; OCH₃), 5.17 (d, 3J_HH = 5.5 Hz, 1H; OCH₃), 5.40 (d, 3J_HH = 10.5 Hz, 1H; CH=CH₂CH₃), 5.60 (d, 3J_HH = 17.0 Hz, 1H; CH=CH₂CH₃), 6.04 (dd, 3J_HH = 5.5, 10.5, 17.0 Hz, 1H; CH=CH₂CH₃, 6.21-6.23 (m, 1H; aryl), 6.35-6.40 (m, 2H; aryl), 7.09-7.13 (m, 1H; aryl); 13C[1H] NMR (101 MHz, CDCl₃, 25 °C, TMS): δ = 40.6, 52.7, 77.6, 100.7, 102.3, 106.8, 119.4, 129.9, 132.1, 152.1, 158.5, 170.6; IR (neat): ν = 2952, 2806, 1759, 1593, 1574, 1493, 1436, 1275, 1235, 1205, 1178, 1135, 1063, 1012 cm⁻¹; HRMS (ESI) calcd for C₁₃H₁₃NO₃ 236.1281 ([M+H]+), found 236.1289.
he obtained carboxylic acid was converted to the corresponding methyl ester by treatment with 1M HCl solution, taken out in a colorless oil by using Al(TMP)Li - TMSCHN3 in THF solution. After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), the compound 3i (95.6 mg, 0.43 mmol) was obtained in 86% yield as a colorless oil.

1H NMR (400 MHz, CDCl3, 25 °C, TMS): δ = 3.76 (s, 3H; OCH3), 3.78 (s, 3H; OCH3), 5.06 (d, J= 5.6 Hz, 1H; OCH), 5.40 (d, J= 10.5 Hz, 1H; CH=CH/Hb), 5.59 (d, J= 17.0 Hz, 1H; CH=CH/Ha), 6.04 (ddd, J= 5.6, 10.5, 17.0 Hz, 1H; CH=CH/Ha), 6.80-6.89 (m, 4H; doublet of doublets, J= 5.5, 10.4 Hz, 1H; CH=CH/Ha), 6.89 (d, J= 3.76 Hz), 127.1 (C{CH=CH}Si 271.6 Hz), 129.2 (C{CH=CH}Si 273.5 Hz), 131.0, 131.1, 134.8, 135.4, 137.1, 150.0, 154.0, 154.8, 156.6, 170.5; 13C{1H} NMR (101 MHz, CDCl3, 25 °C, TMS): δ = 52.7, 55.8, 78.8, 114.8, 117.0, 119.5, 132.1, 151.5, 154.8, 170.5; IR (neat): ν = 2954, 2836, 1759, 1508, 1464, 1440, 1228, 1181, 1133, 1109, 1036 cm⁻¹; HRMS (ESI) calcd for C17H24NaO4Si 345.1502 ([M+Na]+), found 345.1502.

F3C

MeO

O

AcO

Ha

Hb

Methyl 2-(4-trifluoromethylenophenoxy)-3-butenoate (3j, a new compound): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1j (101.1 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu3Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN2 in Et2O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 9:1), the compound 3j (115.8 mg, 0.45 mmol) was obtained in 89% yield as a colorless oil.

1H NMR (500 MHz, CDCl3, 25 °C, TMS): δ = 3.79 (s, 3H; OCH3), 5.20 (d, J= 5.5 Hz, 1H; OCH), 5.44 (d, J= 10.4 Hz, 1H; CH=CH/Hb), 5.61 (d, J= 17.1 Hz, 1H; CH=CH/Ha), 6.05 (ddd, J= 5.5, 10.4, 17.1 Hz, 1H; CH=CH/Ha), 6.85-6.99 (m, 4H; doublet of doublets, J= 5.5, 10.4 Hz, 1H; CH=CH/Ha), 127.1 (JCF = 32.7 Hz), 127.4 (JCF = 27.1 Hz), 127.1 (JCF = 3.6 Hz), 131.1, 159.7, 169.6; IR (neat): ν = 2957, 1760, 1615, 1593, 1518, 1482, 1438, 1424, 1331, 1250, 1208, 1164, 1114, 1068, 1011 cm⁻¹;
Methyl 2-(4-fluorophenoxy)-3-butoenate (3k, a new compound): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1k (76.0 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu3Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOEtBu (22.0 mg, 0.050 mmol) in THF (1.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN2 in Et2O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), the compound 3k (56.8 mg, 0.27 mmol) was obtained in 54% yield as a colorless oil.

1H NMR (400 MHz, CDCl3, 25 °C, TMS): δ = 3.78 (s, 3H; OCH3), 5.08 (d, 3JHH = 5.5 Hz, 1H; OCH), 5.41 (d, 3JHH = 10.5 Hz, 1H; CH=CH2Hc), 5.59 (d, 3JHH = 17.4 Hz, 1H; CH=CH2Hb), 6.03 (ddd, 3JHH = 5.5, 10.5, 17.4 Hz, 1H; CH=CH2Hb), 6.83-6.87 (m, 2H; aryl), 7.21-7.25 (m, 2H; aryl); 13C{1H} NMR (101 MHz, CDCl3, 25 °C, TMS): δ = 52.7, 78.5, 116.1 (JCF = 23.0 Hz), 117.0 (JCF = 7.7 Hz), 119.7, 131.7, 153.5, 158.0 (JCF = 239.6 Hz), 170.1; IR (neat): ν = 2956, 1759, 1506, 1437, 1268, 1204, 1134, 1098, 1066, 1017 cm⁻¹; HRMS (ESI) calcd for C11H11FNaO3 233.0584 (M⁺), found 233.0583.

Methyl 2-(4-chlorophenoxy)-3-butoenate (3l, a new compound): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1l (127.5 mg, 0.75 mmol, colorless oil) with 2.0 equivalent of iBu3Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOEtBu (22.0 mg, 0.050 mmol) in THF (1.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN2 in Et2O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), the compound 3l (82.7 mg, 0.37 mmol) was obtained in 73% yield as a colorless oil.

1H NMR (400 MHz, CDCl3, 25 °C, TMS): δ = 3.78 (s, 3H; OCH3), 5.11 (d, 3JHH = 5.5 Hz, 1H; OCH), 5.42 (d, 3JHH = 10.5 Hz, 1H; CH=CH2Hc), 5.59 (d, 3JHH = 17.4 Hz, 1H; CH=CH2Hb), 6.03 (ddd, 3JHH = 5.5, 10.5, 17.4 Hz, 1H; CH=CH2Hb), 6.83-6.87 (m, 2H; aryl), 7.21-7.25 (m, 2H; aryl); 13C{1H} NMR (101 MHz, CDCl3, 25 °C, TMS): δ = 52.8, 78.0, 116.9, 119.8, 127.0, 129.6, 131.4, 155.9, 169.9; IR (neat): ν = 2954, 1759, 1595, 1584, 1491, 1437, 1279, 1237, 1206, 1174, 1135, 1092, 1065, 1008 cm⁻¹; HRMS (ESI) calcd for C11H11ClNaO3 249.0289 ([M+Na]⁺), found 249.0282.
Methyl 2-(4-bromophenoxy)-3-butenoate (3m, a new compound): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1m (106.5 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu3Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN2 in Et2O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 9:1 to 8:1), the compound 3m (113.9 mg, 0.42 mmol) was obtained in 84% yield as a colorless oil.

1H NMR (400 MHz, CDCl3, 25 °C, TMS): δ = 3.78 (s, 3H; OCH3), 5.11 (d, 3JHH = 5.5 Hz, 1H; OCH), 5.42 (d, 3JHH = 10.5 Hz, 1H; CH=CHCH2), 5.59 (d, 3JHH = 17.4 Hz, 1H; CH=CHCH2), 6.03 (ddd, 3JHH = 5.5, 10.5, 17.4 Hz, 1H; CH2=CHCH2), 6.78-6.82 (m, 2H; aryl), 7.36-7.40 (m, 2H; aryl); 13C{1H} NMR (101 MHz, CDCl3, 25 °C, TMS): δ = 52.8, 77.8, 114.3, 117.4, 119.9, 131.4, 132.6, 156.4, 169.9; IR (neat): ν = 2953, 1759, 1589, 1580, 1488, 1436, 1278, 1237, 1206, 1175, 1134, 1071, 1005 cm−1; HRMS (ESI) calcd for C13H11BrNaO3 292.9786 ([M+Na]+), found 292.9779.

Methyl 2-(4-iodophenoxy)-3-butenoate (3n, a new compound): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1n (130.0 mg, 0.50 mmol, colorless oil) with 2.0 equivalent of iBu3Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (1.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN2 in Et2O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), the compound 3n (130.4 mg, 0.41 mmol) was obtained in 82% yield as a colorless oil.

1H NMR (400 MHz, CDCl3, 25 °C, TMS): δ = 3.78 (s, 3H; OCH3), 5.11 (d, 3JHH = 5.5 Hz, 1H; OCH), 5.42 (d, 3JHH = 10.5 Hz, 1H; CH=CHCH2), 5.59 (d, 3JHH = 17.4 Hz, 1H; CH=CHCH2), 6.03 (ddd, 3JHH = 5.5, 10.5, 17.4 Hz, 1H; CH2=CHCH2), 6.68-6.71 (m, 2H; aryl), 7.54-7.58 (m, 2H; aryl); 13C{1H} NMR (101 MHz, CDCl3, 25 °C, TMS): δ = 52.8, 77.7, 84.4, 117.9, 119.9, 131.4, 138.5, 157.2, 169.8; IR (neat): ν = 2952, 1759, 1503, 1484, 1435, 1276, 1230, 1205, 1177, 1134, 1057, 1001 cm−1; HRMS (ESI) calcd for C13H11I2NaO3 340.9650 ([M+Na]+), found 340.9642.
Methyl 2-(2-bromo-4-methylphenoxy)-3-butenoate (3o, a new compound): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1o (118.5 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu3Al(TMPLi) in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN2 in Et2O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 9:1 to 8:1), the compound 3o (114.1 mg, 0.40 mmol) was obtained in 80% yield as a colorless oil.

1H NMR (400 MHz, CDCl3, 25 °C, TMS): δ = 2.27 (s, 3H; CH3), 3.78 (s, 3H; OCH3), 5.12 (d, 3JHH = 5.5 Hz, 1H; OCH), 5.42 (d, 3JHH = 10.5 Hz, 1H; CH=CH2Hb), 5.69 (d, 3JHH = 17.3 Hz, 1H; CH=CH2Hb), 6.07 (ddd, 3JHH = 5.5, 10.5, 17.3 Hz, 1H; CH=CH2Hb), 6.71 (d, 3JHH = 8.2 Hz, 1H; OCCH), 7.00 (dd, 3JHH = 8.2 Hz, 4JHH = 1.8 Hz, 1H; CH2CCH=CH), 7.38 (d, 3JHH = 1.8 Hz, 1H; CH2CCH=CH), 13C{1H} NMR (101 MHz, CDCl3, 25 °C, TMS): δ = 20.4, 52.8, 79.0, 113.1, 115.5, 119.8, 128.9, 131.4, 133.3, 134.2, 151.9, 170.0; IR (neat): ν = 2953, 1760, 1741, 1494, 1436, 1284, 1248, 1204, 1178, 1159, 1129, 1049, 1016 cm⁻¹; HRMS (ESI) calcd for C12H13BrNaO3 306.9940 ([M+Na]⁺), found 306.9927.

Methyl 2-[2-(2H-benzotriazol-2-yl)-4-methylphenoxy]-3-butenoate (3p, a new compound): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1p (132.8 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu3Al(TMPLi) in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN2 in Et2O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 4:1), the compound 3p (121.3 mg, 0.38 mmol) was obtained in 75% yield as an orange oil.

1H NMR (400 MHz, CDCl3, 25 °C, TMS): δ = 2.38 (s, 3H; CH3), 3.68 (s, 3H; OCH3), 5.12 (d, 3JHH = 5.5 Hz, 1H; OCH), 5.28 (d, 3JHH = 10.5 Hz, 1H; CH=CH2Hb), 5.46 (d, 3JHH = 17.4 Hz, 1H; CH=CH2Hb), 5.93 (ddd, 3JHH = 5.5, 10.5, 17.4 Hz, 1H; CH=CH2Hb), 6.98-7.01 (m, 1H; aryl), 7.23-7.25 (m, 1H; aryl), 7.41-7.45 (m, 2H; aryl), 7.58-7.59 (m, 1H; aryl), 7.94-7.98 (m, 2H; aryl); 13C{1H} NMR (101 MHz, CDCl3, 25 °C, TMS): δ = 20.6, 52.6, 80.0, 117.4, 118.5, 119.7, 126.9, 128.0, 131.2, 131.4, 131.5, 132.8, 144.9, 149.1, 169.8; IR
He obtained carboxylic acid was converted to the corresponding

Methyl 2-(4-bromophenoxy)-4-phenyl-3-butenoate (3q, a new compound): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1q (144.6 mg, 0.5 mmol, white powder) with 2.0 equivalent of iBu3Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.1 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN2 in Et2O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 7:1), the compound 3q (121.5 mg, 0.35 mmol) was obtained in 70% yield as a colorless oil.

\(^1\)H NMR (400 MHz, CDCl3, 25 °C, TMS): δ = 3.69 (s, 3H; OCH3), 4.93 (d, \(^3\)JHH = 9.5 Hz, 1H; OCHCH), 5.41 (dd, \(^3\)JHH = 5.9, 9.5 Hz, 1H; OCHCH) 6.45 (d, \(^3\)JHH = 5.9 Hz, 1H; OCHCH=CH), 6.84-6.87 (m, 2H; aryl), 7.25-7.36 (m, 5H; aryl), 7.38-7.42 (m, 2H; aryl); \(^1^3\)C\[^1\]H NMR (101 MHz, CDCl3, 25 °C, TMS): δ = 18.3, 52.7, 80.6, 114.2, 116.8, 117.3, 132.4, 139.0, 156.3, 169.7; IR (neat): ν = 2951, 1737, 1667, 1587, 1485, 1454, 1434, 1310, 1235, 1196, 1165, 1070, 1027, 1007 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{18}\)H\(_{17}\)Na\(_3\)O\(_3\) 346.1168 ([M+Na\(^+\)], found 346.1170.

\[\text{Br} \sim \text{O} \text{-} \text{Ph} \sim \text{CH} \sim \text{O} \sim \text{Me}\]

Methyl 2-(4-bromophenoxy)-3-methyl-3-butenoate (3r, a new compound): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1r (113.5 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu3Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN2 in Et2O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 9:1 to 8:1), the compound 3r (92.7 mg, 0.33 mmol) was obtained in 65% yield as a colorless oil.

\(^1\)H NMR (400 MHz, CDCl3, 25 °C, TMS): δ = 1.85 (s, 3H; CH\(_3\)), 3.78 (s, 3H; OCH\(_3\)), 5.03 (s, 1H), 5.16 (s, 1H), 5.27 (s, 1H), 6.79-6.81 (m, 2H; aryl), 7.36-7.38 (m, 2H; aryl); \(^1^3\)C\[^1\]H NMR (101 MHz, CDCl3, 25 °C, TMS): δ = 18.3, 52.7, 80.6, 114.2, 116.8, 117.3, 132.4, 139.0, 156.3, 169.7; IR (neat): ν = 2955, 1760, 1586, 1482, 1269, 1236, 1200, 1181, 1130, 1051, 1006 cm\(^{-1}\); HRMS (ESI) calcd for C\(_{12}\)H\(_{13}\)BrNa\(_3\)O\(_3\) 306.9940 ([M+Na\(^+\)], found 306.9945.
Methyl 2-phenoxy-3-nonynoate (3s, a new compound): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1s (101.0 mg, 0.5 mmol, white powder) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN₂ in Et₂O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 8:1), the compound 3s (102.8 mg, 0.40 mmol) was obtained in 79% yield as a colorless oil.

1H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 0.87-2.24 (m, 11H), 3.85 (s, 3H; OCH₃), 5.32-5.33 (m, 1H; OCH), 6.99-7.03 (m, 3H; aryl), 7.27-7.31 (m, 2H; aryl); 13C{¹H} NMR (101 MHz, CDCl₃, 25 °C, TMS): δ = 14.1, 18.9, 22.3, 27.9, 31.1, 53.3, 67.7, 73.1, 89.9, 116.0, 122.3, 129.6, 156.8, 167.7; IR (neat): ν = 2956, 2932, 2861, 1748, 1598, 1590, 1494, 1457, 1436, 1328, 1288, 1223, 1174, 1080, 1059 cm⁻¹; HRMS (ESI) calcd for C_{16}H_{20}NaO₃ 283.1310 ([M+Na⁺], found 283.1305.

Methyl 2-[(diisopropylamino)carbonyloxy]-3-butenoate (3t, a new compound): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1t (92.6 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. The obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN₂ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 4:1), the compound 3t (110.7 mg, 0.46 mmol) was obtained in 91% yield as a colorless oil.

1H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 1.25 (br, 12H; N(CH(CH₃)₂)₂), 3.76 (s, 3H; OCH₃), 3.87-4.05 (m, 2H; N(CH(CH₃)₂)₂), 5.32-5.36 (m, 1H; CH=CH₂), 5.48-5.53 (m, 2H), 5.94-6.03 (m, 1H; CH=CH₂); 13C{¹H} NMR (101 MHz, CDCl₃, 25 °C, TMS): δ = 20.6, 20.6, 21.4, 21.7, 45.9, 46.9, 52.4, 73.6, 119.1, 131.2, 154.4, 170.0; IR (neat): ν = 2971, 2936, 1762, 1701, 1645, 1438, 1370, 1308, 1265, 1212, 1136, 1080, 1049 cm⁻¹; HRMS (ESI) calcd for C_{18}H_{22}NaNO₄ 266.1363 ([M+Na⁺], found 266.1363.

Methyl 2-[(diisopropylamino)carbonyloxy]-2-methyl-3-butenoate (3u, a new compound): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 1u (100.0 mg, 0.5 mmol, colorless oil, ...
oil) with 2.0 equivalent of iBu$_3$Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. The obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN$_2$ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 4:1), the compound 3u (114.5 mg, 0.45 mmol) was obtained in 89% yield as a colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 1.22$-1.27 (br, 12H; N(CH(CH$_3$)$_2$)$_2$), 1.69 (s, 3H; CCH$_3$), 3.75 (s, 3H; OCH$_3$), 3.80-4.04 (m, 2H; N(CH(CH$_3$)$_2$)$_2$), 5.25 (d, $^3$J$_{HH}$ = 11.0 Hz, 1H; CH=CH$_3$H$_0$), 5.36 (d, $^3$J$_{HH}$ = 17.7 Hz, 1H; CH=CH$_3$H$_0$), 6.27 (dd, $^3$J$_{HH}$ = 11.0, 17.7 Hz, 1H; CH=CH$_3$H$_0$); $^{13}$C$^1$H NMR (101 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 20.6, 21.6, 23.6, 45.7, 46.7, 52.5, 79.6, 115.2, 138.0, 154.0, 172.4$; IR (neat): $\nu = 2971, 1750, 1701, 1436, 1369, 1308, 1267, 1212, 1132, 1048$ cm$^{-1}$; HRMS (ESI) calcd for C$_{13}$H$_{22}$NaNO$_4$ 280.1519 ([M+Na]$^+$), found 280.1524.

~2-Butenoic acid esters (Table 3)~

![结构式](image)

**Methyl 2-[4-tert-butylyphenoxyl-(Z)-2-butenoate (4b):** According to the typical procedure B, in a 30-mL round bottomed flask, the reaction of 1b (95.0 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu$_3$Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. Then, DBU (8.0 μL, 0.050 mmol) was added in the reaction mixture and stirred for 24 hrs at room temperature. After quenching by 1N HClaq solution, organic compounds were extracted by EtOAc (10 mL$^*$3) and combined organic layer was dried over MgSO$_4$. Yellow crude mixture was obtained after removal of the solvent. The obtained mixture mainly including carboxylic acid product was converted to the methyl ester by treatment with TMSCHN$_2$ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), compound 4b (108.0 mg, 0.44 mmol) was obtained in 87% yield as a colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 1.29$ (s, 9H, C(CH$_3$)$_3$), 1.77 (d, $^3$J$_{HH}$ = 7.3 Hz, 3H; CHCH$_3$), 3.71 (s, 3H; OCH$_3$), 6.69 (q, $^3$J$_{HH}$ = 7.3 Hz, 1H; CHCH$_3$), 6.81-6.84 (m, 2H; aryl), 7.27-7.29 (m, 2H; aryl); $^{13}$C$^1$H NMR (125 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 11.7, 31.6, 34.3, 52.2, 114.4, 126.5, 127.5, 142.0, 144.9, 155.0, 163.8$; IR (neujol): $\nu = 2953, 1731, 1661, 1605, 1586, 1509, 1471, 1366, 1324, 1272, 1228, 1176, 1140, 1065, 1014$ cm$^{-1}$; HRMS (ESI) calcd for C$_{15}$H$_{20}$NaO$_3$ 271.1305 ([M+Na]$^+$), found 271.1303.

S12
Methyl 2-[4-benzylphenoxy]-2-butenoate (4c, a new compound): According to the typical procedure B, in a 30-mL round bottomed flask, the reaction of 1c (112.0 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMPh)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. Then, DBU (7.9 µL, 0.050 mmol) was added in the reaction mixture and stirred for 24 hrs at room temperature. After quenching by 1N HClq solution, organic compounds were extracted by EtOAc (10 mL*3) and combined organic layer was dried over MgSO₄. Yellow crude mixture was obtained after removal of the solvent. The obtained mixture mainly including carboxylic acid product was obtained after removal of the solvent. The obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN₂ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), compound 4c (117.2 mg, 0.42 mmol) was obtained in 83% yield as a colorless oil.

1H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ = 1.76 (d, 3JHH = 7.3 Hz, 3H; CHCH₃), 3.70 (s, 3H; OCH₃), 3.92 (s, 2H; CH₂CH₂), 6.68 (q, 3JHH = 7.3 Hz, 1H; CHCH₃), 6.81-6.83 (m, 2H; aryl), 7.07-7.09 (m, 2H; aryl), 7.17-7.20 (m, 3H; aryl), 7.25-7.29 (m, 2H; aryl); 13C{¹H} NMR (125 MHz, CDCl₃, 25 °C, TMS): δ = 11.7, 41.2, 52.3, 115.0, 126.2, 127.6, 128.6, 129.0, 130.1, 134.9, 141.4, 142.0, 155.7, 163.7; IR (neat): ν = 3028, 2951, 2916, 1732, 1660, 1506, 1453, 1436, 1380, 1326, 1275, 1220, 1169, 1133, 1068, 1015 cm⁻¹; HRMS (ESI) calcd for C₁₆H₁₉NaO₃ 305.1153 ([M+Na⁺), found 305.1184.

Methyl 2-(2,3-dihydro-1H-inden-5-yloxy)-(Z)-2-butenoate (4d, a new compound): According to the typical procedure B, in a 30-mL round bottomed flask, the reaction of 1d (82.5 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMPh)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. Then, DBU (7.8 µL, 0.050 mmol) was added in the reaction mixture and stirred for 24 hrs at room temperature. After quenching by 1N HClq solution, organic compounds were extracted by EtOAc (10 mL*3) and combined organic layer was dried over MgSO₄. Yellow crude mixture was obtained after removal of the solvent. The obtained mixture mainly including carboxylic acid product was converted to the corresponding methyl ester by treatment with TMSCHN₂ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), compound 4d (99.9 mg, 0.43 mmol) was obtained in 86% yield as a colorless oil.

1H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 1.78 (d, 3JHH = 6.9 Hz, 3H; CHCH₃), 2.03-2.10 (m, 2H; CH₂CH₂), 2.81-2.88 (m, 4H; CH₂CH₂), 3.71 (s, 3H; OCH₃), 6.65-6.71 (m, 2H), 6.77-6.78 (m, 1H; aryl), 7.08-7.10 (m, 1H; aryl); 13C{¹H} NMR (101 MHz, CDCl₃, 25 °C, TMS): δ = 11.6, 25.9, 32.1, 33.2, 52.2, 111.0, 112.8, 124.9, 127.4, 137.9, 142.1, 146.0, 156.1, 163.9; IR (neat): ν = 2951, 2846, 1733, 1660, 1611, 1590,
Methyl 2-naphtoxy-(Z)-2-butenoate (4e, a new compound): According to the typical procedure B, in a 30-mL round bottomed flask, the reaction of 1e (92.1 mg, 0.50 mmol, colorless oil) with 2.0 equivalent of iBu$_3$Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. Then, DBU (7.8 µL, 0.050 mmol) was added in the reaction mixture and stirred for 24 hrs at room temperature. After quenching by 1N HClaq solution, organic compounds were extracted by EtOAc (10 mL*3) and combined organic layer was dried over MgSO$_4$. Yellow crude mixture was obtained after removal of the solvent. The obtained mixture mainly including carboxylic acid product was converted to the corresponding methyl ester by treatment with TMSCHN$_2$ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), compound 4e (99.3 mg, 0.41 mmol) was obtained in 82% yield as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): $\delta$ = 1.81 (d, $^3$J$_{HH}$ = 6.9 Hz, 3H; CHCH$_3$), 3.71 (s, 3H; OCH$_3$), 6.81 (q, $^3$J$_{HH}$ = 6.9 Hz, 1H; CHCH$_3$), 7.10-7.11 (m, 1H; aryl), 7.25-7.28 (m, 1H; aryl), 7.34-7.38 (m, 1H; aryl), 7.41-7.45 (m, 1H; aryl), 7.68-7.70 (m, 1H; aryl), 7.78-7.81 (m, 2H; aryl); $^{13}$C $^1$H NMR (101 MHz, CDCl$_3$, 25 °C, TMS): $\delta$ = 11.7, 52.4, 108.8, 117.8, 124.3, 126.7, 127.0, 127.8, 128.1, 129.8, 130.0, 134.4, 141.9, 155.2, 163.8; IR (neat): $\nu$ = 3045, 2978, 2889, 1660, 1587, 1574, 1508, 1396, 1259, 1169, 1143, 1074, 1046, 1028, 1011 cm$^{-1}$; HRMS (ESI) calcd for C$_{18}$H$_{14}$NaO$_3$ 265.0835 ([M+Na]$^+$), found 265.0835.

Methyl 2-[3-dimethylaminophenoxy]-(Z)-2-butenoate (4f, a new compound): According to the typical procedure B, in a 30-mL round bottomed flask, the reaction of 1f (88.9 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu$_3$Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.1 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. Then, DBU (7.8 µL, 0.050 mmol) was added in the reaction mixture and stirred for 24 hrs at room temperature. After quenching by 1N HClaq solution, organic compounds were extracted by EtOAc (10 mL*3) and combined organic layer was dried over MgSO$_4$. Yellow crude mixture was obtained after removal of the solvent. The obtained mixture mainly including carboxylic acid product was converted to the corresponding methyl ester by treatment with TMSCHN$_2$ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 4:1), compound 4f (90.6 mg, 0.39 mmol) was obtained in 77% yield as an orange oil.

$^1$H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): $\delta$ = 1.77 (d, $^3$J$_{HH}$ = 7.3 Hz, 3H; CHCH$_3$), 2.92 (s, 6H; N(CH$_3$)$_2$).
3.70 (s, 3H; OCH₃), 6.18-6.21 (m, 1H; aryl), 6.32-6.33 (m, 1H; aryl), 6.37-6.40 (m, 1H; aryl), 6.67 (q, J_HH = 7.3 Hz, 1H; CHCH₃), 7.07-7.11 (m, 1H; aryl); \(^{13}\)C{\(^{1}\)H} NMR (101 MHz, CDCl₃, 25 °C, TMS): \(\delta = 11.6, 40.6, 52.3, 99.7, 102.3, 106.8, 127.4, 129.9, 141.9, 152.1, 158.3, 164.0\); IR (neat): \(\nu = 2951, 1733, 1660, 1614, 1574, 1503, 1438, 1380, 1330, 1272, 1231, 1191, 1170, 1146, 1069, 1021 \text{ cm}^{-1}\); HRMS (ESI) calcd for C₁₃H₁₈NO₃ 236.1281 ([M+H]⁺), found 236.1287.

\[\text{MeS} \to \text{O} \to \text{COOCH₃}\]

**Methyl 2-[(4-methylthio)phenoxy]-(Z)-2-butenoate (4g, a new compound):** According to the typical procedure B, in a 30-mL round bottomed flask, the reaction of 1g (90.1 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (iMes)CuOEtBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. Then, DBU (8.0 \(\mu\)L, 0.05 mmol) was added in the reaction mixture and stirred for 24 hrs at room temperature. After quenching by 1N HClaq solution, organic compounds were extracted by EtOAc (10 mL*3) and combined organic layer was dried over MgSO₄. Yellow crude mixture was obtained after removal of the solvent. The obtained mixture mainly including carboxylic acid product was converted to the corresponding methyl ester by treatment with TMSCHN₂ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), compound 4g (94.2 mg, 0.40 mmol) was obtained in 79% yield as a colorless oil.

\(^{1}\)H NMR (500 MHz, CDCl₃, 25 °C, TMS): \(\delta = 1.77\) (d, \(J_{HH} = 7.3\) Hz, 3H; OCH₃), 3.71 (s, 3H; OCH₃), 6.71 (q, \(J_{HH} = 7.3\) Hz, 1H; CHCH₃), 6.84-6.87 (m, 2H; aryl), 7.22-7.25 (m, 2H; aryl); \(^{13}\)C{\(^{1}\)H} NMR (125 MHz, CDCl₃, 25 °C, TMS): \(\delta = 11.6, 17.7, 52.3, 115.7, 127.8, 129.8, 130.9, 141.9, 155.7, 163.6\); IR (neat): \(\nu = 2988, 2951, 2920, 1732, 1661, 1592, 1489, 1437, 1380, 1323, 1274, 1223, 1170, 1134, 1096, 1067, 1012 \text{ cm}^{-1}\); HRMS (ESI) calcd for C₁₂H₁₄NaO₃S 261.0556 ([M+Na]⁺), found 261.0556.

\[\text{TBDMSO} \to \text{O} \to \text{COOCH₃}\]

**Methyl 2-[(4-tert-butyldimethylsilyloxy)phenoxy]-(Z)-2-butenoate (4h, a new compound):** According to the typical procedure B, in a 30-mL round bottomed flask, the reaction of 1h (132.3 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (iMes)CuOEtBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. Then, DBU (7.9 \(\mu\)L, 0.05 mmol) was added in the reaction mixture and stirred for 24 hrs at room temperature. After quenching by 1N HClaq solution, organic compounds were extracted by EtOAc (10 mL*3) and combined organic layer was dried over MgSO₄. Yellow crude mixture was obtained after removal of the solvent. The obtained mixture mainly including carboxylic acid product was converted to the corresponding methyl ester by treatment with TMSCHN₂ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), compound 4h (132.2 mg, 0.41 mmol)
was obtained in 82% yield as a colorless oil.

\[ ^1H\text{ NMR (400 MHz, CDCl}_3, 25^\circ\text{C, TMS): } \delta = 0.16 \text{ (s, 6H; Si(CH}_3)_2), 0.97 \text{ (s, 9H; Si(C(CH}_3)_3)), 1.77 \text{ (d, } ^3\text{J}_{HH} = 7.3 \text{ Hz, 3H; CHCH}_3), 3.70 \text{ (s, 3H; OCH}_3), 6.65 \text{ (q, } ^3\text{J}_{HH} = 7.3 \text{ Hz, 1H; CHCH}_3), 6.72-6.78 \text{ (m, 4H; aryl);} \]

\[ ^13\text{C} [^1H] \text{ NMR (101 MHz, CDCl}_3, 25^\circ\text{C, TMS): } \delta = -4.4, 11.6, 18.3, 25.8, 52.2, 115.8, 120.8, 127.2, 142.4, 150.6, 151.7, 163.9; \text{ IR (neat): } \nu = 2955, 2930, 2858, 1736, 1661, 1502, 1437, 1325, 1263, 1206, 1132, 1068, 1011 \text{ cm}^{-1}; \text{ HRMS (ESI) calcd for } C_{19}H_{36}NaO_3Si 345.1493 ([M+Na]^+), \text{ found 345.1493.} \]

![Diagram](image)

**Methyl 2-(4-methoxyphenoxy)-(Z)-2-butoenoate (4i, a new compound):** According to the typical procedure B, in a 30-mL round bottomed flask, the reaction of 1i (82.5 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (Mes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. Then, DBU (8.0 μL, 0.05 mmol) was added in the reaction mixture and stirred for 24 hrs at room temperature. After quenching by 1N HClaq solution, organic compounds were extracted by EtOAc (10 mL*3) and combined organic layer was dried over MgSO₄. Yellow crude mixture was obtained after removal of the solvent. The obtained mixture mainly including carboxylic acid product was converted to the corresponding methyl ester by treatment with TMSCHN₂ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), compound 4i (86.7 mg, 0.39 mmol) was obtained in 78% yield as a colorless oil.

\[ ^1H\text{ NMR (400 MHz, CDCl}_3, 25^\circ\text{C, TMS): } \delta = 1.78 \text{ (d, } ^3\text{J}_{HH} = 7.3 \text{ Hz, 3H; CHCH}_3), 3.70 \text{ (s, 3H; OCH}_3), 3.75 \text{ (s, 3H; OCH}_3), 6.66 \text{ (q, } ^3\text{J}_{HH} = 7.3 \text{ Hz, 1H; CHCH}_3), 6.80-6.86 \text{ (m, 4H; aryl);} \]

\[ ^13\text{C} [^1H] \text{ NMR (101 MHz, CDCl}_3, 25^\circ\text{C, TMS): } \delta = 11.5, 52.2, 55.7, 114.7, 115.9, 127.2, 142.3, 151.3, 154.8, 163.8; \text{ IR (neat): } \nu = 2999, 2953, 2836, 1732, 1660, 1505, 1438, 1381, 1326, 1274, 1243, 1208, 1134, 1104, 1069, 1036, 1014 \text{ cm}^{-1}; \text{ HRMS (ESI) calcd for } C_{12}H_{28}NaO_3Si 223.0970 ([M+H]^+), \text{ found 223.0963.} \]

![Diagram](image)

**Methyl 2-(4-trifluoromethylphenoxy)-(Z)-2-butoenoate (4j, a new compound):** According to the typical procedure B, in a 30-mL round bottomed flask, the reaction of 1j (101.0 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (Mes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. Then, DBU (8.0 μL, 0.05 mmol) was added in the reaction mixture and stirred for 24 hrs at room temperature. After quenching by 1N HClaq solution, organic compounds were extracted by EtOAc (10 mL*3) and combined organic layer was dried over MgSO₄. Yellow crude mixture was obtained after removal of the solvent. The obtained mixture mainly including carboxylic acid product was converted to the corresponding methyl ester by treatment with TMSCHN₂ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the
purification by silica gel column chromatography (hexane:AcOEt = 6:1), compound 4j (98.9 mg, 0.38 mmol) was obtained in 76% yield as a colorless oil.

1H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 1.78 (d, 3JHH = 6.9 Hz, 3H; CHCH₃), 3.73 (s, 3H; OCH₃), 6.78 (q, 3JHH = 6.9 Hz, 1H; CHCH₃), 6.97-6.99 (m, 2H; aryl), 7.54-7.56 (m, 2H; aryl); 13C{1H} NMR (101 MHz, CDCl₃, 25 °C, TMS): δ = 11.7, 52.4, 115.1, 124.4 (JC = 271.3 Hz), 124.5 (JC = 32.6 Hz), 127.3 (JC = 3.8 Hz), 128.6, 141.3, 159.7, 163.1; IR (neat): ν = 2956, 1735, 1664, 1614, 1514, 1439, 1382, 1329, 1277, 1236, 1164, 1123, 1108, 1063, 1012 cm⁻¹; HRMS (ESI) calcld for C₁₂H₁₁F₂NaO₃ 283.0558 ([M+Na]⁺), found 281.0551.

Methyl 2-(4-fluorophenoxy)-(Z)-2-butoenate (4k, a new compound) According to the typical procedure B, in a 30-mL round bottomed flask, the reaction of 1k (76.0 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.1 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. Then, DBU (8.0 µL, 0.050 mmol) was added in the reaction mixture and stirred for 24 hrs at room temperature. After quenching by 1N HClaq solution, organic compounds were extracted by EtOAc (10 mL*3) and combined organic layer was dried over MgSO₄. Yellow crude mixture was obtained after removal of the solvent. The obtained mixture mainly including carboxylic acid product was converted to the corresponding methyl ester by treatment with TMSCHN₂ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), compound 4k (54.7 mg, 0.26 mmol) was obtained in 52% yield as a colorless oil.

1H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ = 1.78 (d, 3JHH = 7.3 Hz, 3H; CHCH₃), 3.71 (s, 3H; OCH₃), 6.70 (q, 3JHH = 7.0 Hz, 1H; CHCH₃), 6.84-6.87 (m, 2H; aryl), 6.96-6.98 (m, 2H; aryl); 13C{1H} NMR (101 MHz, CDCl₃, 25 °C, TMS): δ = 11.6, 52.3, 116.1 (JC = 10.0 Hz), 116.2 (JC = 5.5 Hz), 127.7, 142.2, 153.4, 158.2 (JC = 239.8 Hz), 163.5; IR (neat): ν = 2956, 1736, 1660, 1610, 1511, 1420, 1379, 1278, 1160, 1110, 1101, 1053 cm⁻¹; HRMS (ESI) calcld for C₁₁H₁₁FNaO₅ 233.0584 ([M+Na]⁺), found 233.0588.

Methyl 2-(4-chlorophenoxy)-(Z)-2-butoenate (4l, a new compound) According to the typical procedure B, in a 30-mL round bottomed flask, the reaction of 1l (84.2 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.1 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. Then, DBU (8.0 µL, 0.050 mmol) was added in the reaction mixture and stirred for 24 hrs at room temperature. After quenching by 1N HClaq solution, organic compounds were extracted by EtOAc (10 mL*3) and combined organic layer was dried over MgSO₄. Yellow crude mixture was obtained after removal of the solvent. The obtained mixture
mainly including carboxylic acid product was converted to the corresponding methyl ester by treatment with TMSCHN₂ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), compound 4l (81.6 mg, 0.36 mmol) was obtained in 72% yield as a colorless oil.

1H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ = 1.77 (d, 3JHH = 7.0 Hz, 3H; CHCH₃), 3.71 (s, 3H; OCH₃), 6.72 (q, 3JHH = 7.0 Hz, 1H; CHCH₃), 6.82-6.86 (m, 2H; aryl), 7.22 - 7.25 (m, 2H; aryl); 13C{¹H} NMR (125 MHz, CDCl₃, 25 °C, TMS): δ = 11.6, 52.3, 116.4, 127.3, 128.0, 129.7, 141.8, 156.0, 163.4; IR (neat): ν = 2953, 1732, 1661, 1594, 1487, 1437, 1380, 1322, 1275, 1225, 1192, 1164, 1135, 1091, 1068, 1010 cm⁻¹; HRMS (ESI) calcd for C₁₆H₁₆ClNaO₃ 249.0289 ([M+Na]^+), found 249.0289.

![Structure of 2-(4-bromophenoxy)-(Z)-2-butenoate](image)

**Methyl 2-(4-bromophenoxy)-(Z)-2-butenoate (4m, a new compound)** According to the typical procedure B, in a 30-mL round bottomed flask, the reaction of 1m (106.2 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.1 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. Then, DBU (8.0 µL, 0.050 mmol) was added in the reaction mixture and stirred for 24 hrs at room temperature. After quenching by 1N HClaq solution, organic compounds were extracted by EtOAc (10 mL*3) and combined organic layer was dried over MgSO₄. Yellow crude mixture was obtained after removal of the solvent. The obtained mixture mainly including carboxylic acid product was converted to the corresponding methyl ester by treatment with TMSCHN₂ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), compound 4m (108.4 mg, 0.40 mmol) was obtained in 80% yield as a colorless oil.

1H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 1.77 (d, 3JHH = 7.3 Hz, 3H; CHCH₃), 3.72 (s, 3H; OCH₃), 6.73 (q, 3JHH = 7.3 Hz, 1H; CHCH₃), 6.78-6.81 (m, 2H; aryl), 7.36 - 7.40 (m, 2H; aryl); 13C{¹H} NMR (101 MHz, CDCl₃, 25 °C, TMS): δ = 11.6, 52.4, 114.6, 116.9, 128.1, 132.6, 141.7, 156.4, 163.3; IR (neat): ν = 2952, 1732, 1661, 1588, 1484, 1437, 1380, 1322, 1275, 1225, 1165, 1135, 1066, 1007 cm⁻¹; HRMS (ESI) calcd for C₁₃H₁₁BrNaO₃ 292.9786 ([M+Na]^+), found 292.9791.

![Structure of 2-(4-iodophenoxy)-(Z)-2-butenoate](image)

**Methyl 2-(4-iodophenoxy)-(Z)-2-butenoate (4n, a new compound)** According to the typical procedure B, in a 30-mL round bottomed flask, the reaction of 1n (144.5 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. Then, DBU (8.0 µL, 0.05 mmol) was added in the reaction mixture and stirred for 24 hrs at room temperature. After quenching by 1N HClaq solution, organic compounds were extracted by EtOAc (10 mL*3) and combined organic layer was
dried over MgSO₄. Yellow crude mixture was obtained after removal of the solvent. The obtained mixture mainly including carboxylic acid product was converted to the corresponding methyl ester by treatment with TMSCHN₂ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), compound 4n (123.3 mg, 0.39 mmol) was obtained in 78% yield as a colorless oil.

1H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 1.77 (d, 3J_HH = 7.3 Hz, 3H; CHCH₃), 3.71 (s, 3H; OCH₃), 6.62-6.71 (m, 2H; aryl), 6.73 (d, 3J_HH = 7.3 Hz, 1H; CHCH₃), 7.54-7.58 (m, 2H; aryl); 13C{1H} NMR (101 MHz, CDCl₃, 25 °C, TMS): δ = 11.7, 52.4, 84.7, 117.4, 128.2, 138.6, 141.5, 157.3, 163.3; IR (neat): ν = 2951, 1732, 1661, 1582, 1480, 1436, 1379, 123.3, 1169, 1134, 1096, 1068, 1057, 1005 cm⁻¹; HRMS (ESI) calcd for C₁₁H₁₁NαO₃ 340.9650 ([M+Na⁺]), found 340.9654.

![Methyl 2-(2-bromo-4-methylphenoxy)-(Z)-2-butenoate (4o, a new compound)](image)

**Methyl 2-(2-bromo-4-methylphenoxy)-(Z)-2-butenoate (4o, a new compound)** According to the typical procedure B, in a 30-mL round bottomed flask, the reaction of 1o (113.6 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (Mes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. Then, DBU (7.8 µL, 0.050 mmol) was added in the reaction mixture and stirred for 24 hrs at room temperature. After quenching by 1N HClaq solution, organic compounds were extracted by EtOAc (10 mL*3) and combined organic layer was dried over MgSO₄. Yellow crude mixture was obtained after removal of the solvent. The obtained mixture mainly including carboxylic acid product was converted to the corresponding methyl ester by treatment with TMSCHN₂ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), compound 4o (111.2 mg, 0.39 mmol) was obtained in 78% yield as a colorless oil.

1H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 1.77 (d, 3J_HH = 7.3 Hz, 3H; CHCH₃), 2.27 (s, 3H; CCH₂), 3.71 (s, 3H; OCH₃), 6.60 (d, 3J_HH = 8.2 Hz, 1H; OCH₂), 6.73 (q, 3J_HH = 7.3 Hz, 1H; CHCH₃), 6.97 (dd, 3J_HH = 8.2 Hz, 4J_HH = 1.4 Hz, 1H; CH₂(CCH=CH), 7.40 (d, 4J_HH = 1.4 Hz, 1H; CH₂CCH=CBr; 13C{1H} NMR (101 MHz, CDCl₃, 25 °C, TMS): δ = 11.7, 20.4, 52.4, 111.3, 114.0, 127.9, 128.9, 133.2, 134.2, 142.1, 151.8, 163.3; IR (neat): ν = 2952, 2922, 1734, 1661, 1602, 1490, 1436, 1380, 1322, 1275, 1240, 1209, 1191, 1133, 1071, 1046, 1011 cm⁻¹; HRMS (ESI) calcd for C₁₂H₁₃BrNaO₃ 306.9940 ([M+Na⁺]), found 306.9942.
Methyl 2-[2-(2H-benzotriazol-2-yl)-4-methylphenoxy]-(Z)-2-butenoate (4p, a new compound) According to the typical procedure B, in a 30-mL round bottomed flask, the reaction of 1p (132.7 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (lMes)CuOBU (22.1 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. Then, DBU (7.8 µL, 0.050 mmol) was added in the reaction mixture and stirred for 24 hrs at room temperature. After quenching by 1N HClaq solution, organic compounds were extracted by EtOAc (10 mL*3) and combined organic layer was dried over MgSO₄. Yellow crude mixture was obtained after removal of the solvent. The obtained mixture mainly including carboxylic acid product was converted to the corresponding methyl ester by treatment with TMSCHN₂ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 3:1), compound 4p (129.3 mg, 0.40 mmol) was obtained in 80% yield as a colorless oil.

**1H NMR (400 MHz, CDCl₃, 25 °C, TMS):** δ = 1.77 (d, 3J₉H = 7.3 Hz, 3H; CHCH₃), 3.72 (s, 3H; OCH₃), 6.73 (q, 3J₉H = 7.3 Hz, 1H; CHCH₃), 6.65 (q, 3J₉H = 7.3 Hz, 1H; CHCH₃), 6.85-6.87 (m, 1H; aryl), 7.19-7.22 (m, 1H; aryl), 7.40-7.44 (m, 2H; aryl), 7.55-7.56 (m, 1H; aryl), 7.95-7.99 (m, 2H; aryl); 13C{1H} NMR (101 MHz, CDCl₃, 25 °C, TMS): δ = 11.8, 20.5, 52.3, 115.4, 118.6, 126.8, 127.9, 128.2, 130.1, 131.4, 132.4, 142.1, 145.0, 149.1, 163.1; IR (neat): ν = 2952, 1732, 1661, 1509, 1437, 1321, 1276, 1233, 1145, 1076, 1063 cm⁻¹; HRMS (ESI) calcd for C₁₀H₁₇Na₃N₃O₅ 346.1168 ([M+Na⁺]), found 346.1169.

Benzeneacetic acid, α-ethyl, methyl ester (6a): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 5a (59.0 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (lMes)CuOBU (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN₂ in Et₂O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 9:1 to 6:1), the compound 6a (74.9 mg, 0.43 mmol) was obtained in 85% yield as a colorless oil.

**1H NMR (500 MHz, CDCl₃, 25 °C, TMS):** δ = 3.69 (s, 3H; OCH₃), 4.31 (d, 3J₉H = 7.9 Hz, 1H; CCH.CO), 5.13 (dd, 3J₉H = 1.2 Hz, 3J₉H = 17.1 Hz, 1H; CH=CH₂H₆), 5.20 (dd, 3J₉H = 1.2 Hz, 3J₉H = 10.4 Hz, 1H; CH=CH₂H₆), 6.20 (ddd, 3J₉H = 7.9, 10.4, 17.0 Hz, 1H; CH=CH₂H₆), 7.23-7.33 (m, 5H; aryl); 13C{1H} NMR
(125 MHz, CDCl₃, 25 °C, TMS): δ = 52.4, 55.8, 117.6, 127.5, 128.1, 128.9, 135.8, 138.1, 172.9.

Benzeneacetic acid, α-ethylidyne-4-methoxy, methyl ester (6b): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 5b (74.0 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.1 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. After treatment with 1N HCl solution, the obtained carboxylic acid was converted to the corresponding methyl ester by treatment with TMSCHN₂ in Et₂O/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 7:1), the compound 6b (81.5 mg, 0.40 mmol) was obtained in 84% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 3.70 (s, 3H; OCH₃), 3.79 (s, 3H; OCH₃), 4.27 (d, 3JHH = 7.8 Hz, 1H; CCHCO), 5.12 (d, 3JHH = 17.4 Hz, 1H; CH=CH₂H₃), 5.20 (d, 3JHH = 10.1 Hz, 1H; CH=CH₂H₃), 6.19 (ddd, 3JHH = 7.8, 10.1, 17.4 Hz, 1H; CH=CH₂H₃), 6.85-6.89 (m, 2H; aryl), 7.20-7.23 (m, 2H; aryl); ¹³C{¹H} NMR (101 MHz, CDCl₃, 25 °C, TMS): δ = 52.3, 54.9, 55.4, 114.2, 117.4, 129.2, 130.2, 136.0, 159.0, 173.2; IR (neat): ν = 3001, 2953, 2837, 1736, 1611, 1512, 1464, 1436, 1302, 1251, 1199, 1180, 1159, 1034 cm⁻¹; HRMS (ESI) calcd for C₁₂H₁₂NaO₃ 229.0841 ([M+Na]+), found 229.0845.

Benzeneacetic acid, α-ethylidyne, methyl ester, (E)- (7a)²: According to the typical procedure B, in a 30-mL round bottomed flask, the reaction of 5a (59.1 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOrBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. Then, DBU (77 µL, 0.5 mmol) was added in the reaction mixture and stirred for 24 hrs at room temperature. After quenching by 1N HClaq solution, organic compounds were extracted by EtOAc (10 mL*3) and combined organic layer was dried over MgSO₄. Yellow crude mixture was obtained after removal of the solvent. The obtained mixture mainly including carboxylic acid product was converted to the corresponding methyl ester by treatment with TMSCHN₂ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 6:1), compound 7a (72.2 mg, 0.41 mmol) was obtained in 82% yield as a colorless oil.

¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ = 1.73-1.75 (m, 3H; CHCH₃), 3.73 (s, 3H; OCH₃), 7.16-7.40 (m, 6H; aryl); ¹³C{¹H} NMR (125 MHz, CDCl₃, 25 °C, TMS): 15.6, 52.1, 127.5, 128.2, 129.9, 134.9, 135.2, 140.3, 167.8.

Benzeneacetic acid, 4-ethoxy-α-ethylidene, methyl ester, (E)- (7b, a new compound): According to the typical procedure B, in a 30-mL round bottomed flask, the reaction of 5b (74.1 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOtBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 2 hrs at 0 °C. Then, DBU (77 µL, 0.5 mmol) was added in the reaction mixture and stirred for 24 hrs at room temperature. After quenching by 1N HClaq solution, organic compounds were extracted by EtOAc (10 mL*3) and combined organic layer was dried over MgSO₄. Yellow crude mixture was obtained after removal of the solvent. The obtained mixture mainly including carboxylic acid product was converted to the corresponding methyl ester by treatment with TMSCHN₂ in toluene/MeOH (ca. ratio = 4:1, total 5.0 mL). After the purification by silica gel column chromatography (hexane:AcOEt = 9:1 to 6:1), compound 7b (81.5 mg, 0.40 mmol) was obtained in 79% yield as a colorless oil.

1H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 1.74-1.76 (m, 3H; CHC₃H₃), 3.73 (s, 3H; OCH₃), 3.83 (s, 3H; OCH₃), 6.89-6.93 (m, 2H; aryl), 7.09-7.17 (m, 3H; aryl).

13C{¹H} NMR (101 MHz, CDCl₃, 25 °C, TMS): δ = 15.6, 52.1, 55.3, 113.6, 127.4, 131.1, 134.3, 140.0, 158.9, 168.1; IR (neat): ν = 3001, 2953, 2838, 1736, 1611, 1512, 1464, 1435, 1302, 1179, 1159, 1035 cm⁻¹; HRMS (ESI) calcd for C₁₂H₁₄NaO₃ 229.0841 ([M+Na]+), found 229.0845.

Benzeneacetic acid, 4-[[bis(1-methylethyl)amino]carbonyl]- (9): According to the typical procedure A, in a 30-mL round bottomed flask, the reaction of 8 (132.0 mg, 0.5 mmol, colorless oil) with 2.0 equivalent of iBu₃Al(TMP)Li in THF solution was carried out for 3 hrs at room temperature. The carboxylation was carried out by using (IMes)CuOtBu (22.0 mg, 0.050 mmol) in THF (2.0 mL) for 20 hrs at room temperature. After treatment with 1N HCl solution, the obtained carboxylic acid was purified by silica gel column chromatography (hexane:AcOEt = 4:1 to 2:1), the compound 9 (80.1 mg, 0.26 mmol) was obtained in 52% yield as a white powder.

1H NMR (500 MHz, Acetone-d₆, 25 °C, TMS): δ = 1.33 (br, 12H; N(CH(CH₃)₂)₂), 3.81 (br, 1H; OH), 3.66 (s, 2H; CH₂-COOH), 3.71 (br, 2H; N(CH(CH₃)₂)₂), 7.26-7.28 (m, 2H; aryl), 7.35-7.37 (m, 2H; aryl); 13C{¹H} NMR (125 MHz, CDCl₃, 25 °C, TMS): δ = 20.8, 41.4, 46.4, 51.3, 126.0, 129.4, 135.1, 136.7, 171.9, 174.3.

X: parts per Million: Proton
X: parts per Million: Proton
X: parts per Million: Carbon13
\[ X \text{: parts per Million : Carbon}^{13} \]
X : parts per Million : 1H