Gold/Silver-Catalyzed Controllable Regioselective Vinylcarbene Insertion into O-H Bonds

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General Information

All of the reactions were carried out in flame-dried tubes under argon atmosphere. Solvents were dried prior to use. For column chromatography, 200-300 mesh silica gel was used. $^1$H NMR were recorded on Bruker 300 MHz, 400 MHz or 500 MHz spectrometer and $^{13}$C NMR were recorded on Bruker 75 MHz, 100 MHz or 125MHz spectrometer in CDCl$_3$. HRMS were performed on Agilent 6540 Q-TOF mass spectrometer (ESI). Melting points were determined on a SGW X-4B melting point apparatus. 2-pyridones and AgSbF$_6$ were commercial available. The gold catalysts$^{[1]}$ and diazo compounds$^{[2]}$ were prepared according to the literature procedures.

General procedure for table 2

To a schlenk tube was added Xantphos(AuCl)$_2$ (26 mg, 0.025 mmol), AgSbF$_6$ (17.1 mg, 0.05 mmol), 1 (0.6 mmol) and dry CH$_2$Cl$_2$ (2.5 mL) under argon atmosphere, the mixture was stirred at room temperature for 30 min; then a solution of 2 (0.5 mmol) in dry CH$_2$Cl$_2$ (2.5 mL) was added via syringe pump over 30 min at 40 °C. The resulting mixture was stirred at 40 °C for another 4 h. The mixture was concentrated under vacuum; the crude residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:50-1:10) to afford product 3.

methyl (E)-4-phenyl-2-(pyridin-2-yloxy)but-3-enoate (3a):

Yellow oil (122 mg, 91 %).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.13 – 8.10 (m, 1H), 7.66 – 7.60 (m, 1H), 7.44 (d, $J =$
7.4 Hz, 2H), 7.38 – 7.26 (m, 3H), 6.97– 6.89 (m, 6.5 Hz, 3H), 6.43 (dd, \(J = 16.0, 6.7\) Hz, 1H), 5.93 (d, \(J = 6.7\) Hz, 1H), 3.78 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.75, 162.09, 146.62, 138.99, 135.96, 134.45, 128.66, 128.35, 126.84, 122.29, 117.64, 111.24, 74.28, 52.50. HRMS (ESI) calcd. for C\(_{16}\)H\(_{16}\)NO\(_3\) [M+H]\(^+\): 270.1125, found: 270.1128.

**ethyl (E)-4-phenyl-2-(pyridin-2-yloxy)but-3-enoate (3b):**

Yellow oil (127 mg, 90 %). 

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.11 (d, \(J = 4.7\) Hz, 1H), 7.63 (t, \(J = 7.7\) Hz, 1H), 7.44 (d, \(J = 7.5\) Hz, 2H), 7.37 – 7.27 (m, 3H), 6.98– 6.88 (m, 3H), 6.43 (dd, \(J = 15.9, 6.6\) Hz, 1H), 5.90 (d, \(J = 6.6\) Hz, 1H), 4.24 (q, \(J = 6.9\) Hz, 2H), 1.26 (t, \(J = 6.9\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.25, 162.14, 146.56, 138.94, 136.05, 134.30, 128.65, 128.30, 126.83, 122.43, 117.60, 111.23, 74.45, 61.42, 14.15. HRMS (ESI) calcd. for C\(_{17}\)H\(_{18}\)NO\(_3\) [M+H]\(^+\): 284.1281, found: 284.1285.

**benzyl (E)-4-phenyl-2-(pyridin-2-yloxy)but-3-enoate (3c):**

Yellow oil (150 mg, 87 %). 

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.04 (s, 1H), 7.62 (t, \(J = 8.0\) Hz, 1H), 7.42 (d, \(J = 8.0\) Hz, 2H), 7.38 – 7.27 (m, 8H), 6.96 – 6.87 (m, 3H), 6.44 (dd, \(J = 16.0, 8.0\) Hz, 1H), 5.93 (d, \(J = 8.0\) Hz, 1H), 5.23 (q, \(J = 24.0\) Hz, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.17, 162.06, 146.56, 138.97, 135.97, 135.65, 134.61, 128.67, 128.50, 128.36, 128.21, 128.11, 126.86, 122.18, 117.65, 111.18, 74.53, 66.86. HRMS (ESI) calcd. for C\(_{22}\)H\(_{20}\)NO\(_3\) [M+H]\(^+\): 346.1438, found: 346.1440.
**tert-butyl (E)-4-phenyl-2-(pyridin-2-yloxy)but-3-enoate (3d):**

A white solid (134 mg, 86 %), mp: 103-105 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.13 – 8.09 (m, 1H), 7.62 (t, $J = 8.0$ Hz, 1H), 7.44 (d, $J = 4.0$ Hz, 2H), 7.38 – 7.27 (m, 3H), 6.96 – 6.85 (m, 3H), 6.42 (dd, $J = 16.0$, 8.0 Hz, 1H), 5.77 (d, $J = 8.0$ Hz, 1H), 1.44 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.23, 162.25, 146.46, 138.86, 136.35, 133.87, 128.63, 128.16, 126.80, 122.87, 117.45, 111.19, 81.95, 74.84, 27.98. HRMS (ESI) calcd. for C$_{19}$H$_{22}$NO$_3$ [M+H]$^+$: 312.1594, found: 312.1596.

**methyl (E)-2-(pyridin-2-yloxy)-4-(p-tolyl)but-3-enoate (3e):**

Yellow oil (113 mg, 80 %).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.13 – 8.09 (m, 1H), 7.62 (t, $J = 8.0$ Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 6.95 – 6.86 (m, 3H), 6.37 (dd, $J = 16.0$, 4.0 Hz, 1H), 5.90 (d, $J = 8.0$ Hz, 1H), 3.77 (s, 3H), 2.35 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.87, 146.62, 138.96, 138.31, 137.19, 134.51, 133.17, 129.35, 126.76, 121.17, 117.60, 111.25, 74.44, 52.47, 21.30. HRMS (ESI) calcd. for C$_{17}$H$_{18}$NO$_3$ [M+H]$^+$: 284.1281, found: 284.1282.
**methyl (E)-4-(4-chlorophenyl)-2-(pyridin-2-yloxy)but-3-enoate (3f):**

Yellow oil (127 mg, 84 %).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 – 8.09 (m, 1H), 7.63 (t, $J$ = 8.0 Hz, 1H), 7.38 – 7.28 (m, 4H), 6.96 – 6.84 (m, 3H), 6.40 (dd, $J$ = 16.0, 8.0 Hz, 1H), 5.93 (d, $J$ = 4.0 Hz, 1H), 3.78 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.57, 161.98, 146.63, 139.05, 134.46, 134.02, 133.02, 128.85, 128.04, 122.97, 117.73, 111.20, 74.04, 52.57. HRMS (ESI) calcd. for C$_{16}$H$_{15}$ClNO$_3$ [M+H]$^+$: 304.0735, found: 304.0738.

**methyl (E)-4-(2-bromophenyl)-2-(pyridin-2-yloxy)but-3-enoate (3g):**

Yellow oil (150 mg, 86 %).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.14 – 8.09 (m, 1H), 7.66 – 7.53 (m, 3H), 7.32 – 7.26 (m, 2H), 7.13 (t, $J$ = 8.0 Hz, 1H), 6.98 – 6.88 (m, 2H), 6.38 (dd, $J$ = 16.0, 8.0 Hz, 1H), 5.99 (d, $J$ = 8.0 Hz, 1H), 3.79 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.51, 161.98, 146.62, 139.05, 135.85, 133.17, 133.07, 129.58, 127.59, 127.25, 125.22, 124.04, 117.74, 111.29, 74.13, 52.61. HRMS (ESI) calcd. for C$_{16}$H$_{15}$BrNO$_3$ [M+H]$^+$: 348.0230, found: 348.0234.
methyl (E)-2-(pyridin-2-yloxy)-4-(m-tolyl)but-3-enoate (3h):

Yellow oil (115 mg, 81 %).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.13 – 8.09 (m, 1H), 7.66 – 7.59 (m, 1H), 7.26 – 7.19 (m, 3H), 7.12 – 7.07 (m, 1H), 6.96 – 6.85 (m, 3H), 6.86 (d, $J = 8.0$ Hz, 1H), 6.40 (dd, $J = 20.0$, 8.0 Hz, 1H), 5.93 – 5.89 (m, 1H), 3.77 (s, 3H), 2.35 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.78, 162.06, 146.61, 138.96, 138.22, 135.90, 134.57, 129.13, 128.54, 127.51, 124.01, 122.07, 117.60, 111.25, 74.33, 52.47, 21.39. HRMS (ESI) calcd. for C$_{17}$H$_{18}$NO$_3$ [M+H]$^+$: 284.1281, found: 284.1282.

methyl (E)-4-(4-cyanophenyl)-2-(pyridin-2-yloxy)but-3-enoate (3i):

Colorless oil (110 mg, 75 %).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.13 – 8.09 (m, 1H), 7.69 – 7.60 (m, 3H), 7.54 – 7.49 (m, 2H), 6.99 – 6.91 (m, 3H), 6.56 (dd, $J = 24.0$, 8.0 Hz, 1H), 6.01 (dd, $J = 8.0$, 4.0 Hz, 1H), 3.79 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.13, 161.82, 146.62, 140.44, 139.15, 132.49, 131.99, 127.29, 126.40, 118.79, 117.89, 111.53, 111.16, 73.59, 52.66. HRMS (ESI) calcd. for C$_{17}$H$_{15}$N$_2$O$_3$ [M+H]$^+$: 295.1077, found: 295.1081.

methyl (E)-2-((5-methylpyridin-2-yl)oxy)-4-phenylbut-3-enoate (3j):

Yellow oil (114 mg, 81 %).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 (s, 1H), 7.47 – 7.41 (m, 3H), 7.37 – 7.26 m, 3H), 6.92 (d, $J = 16.0$ Hz, 1H), 6.85 (d, $J = 8.0$ Hz, 1H), 6.43 (dd, $J = 16.0$, 8.0 Hz, 1H), 5.89 (d, $J = 4.0$ Hz, 1H), 3.77 (s, 3H), 2.24 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ
170.91, 160.35, 146.03, 140.04, 136.00, 134.33, 128.64, 128.30, 126.82, 126.64, 122.43, 110.55, 74.25, 52.47, 17.47. HRMS (ESI) calcd. for C$_{17}$H$_{18}$NO$_3$ [M+H]$^+$: 284.1281, found: 284.1282.

**methyl (E)-2-((5-bromopyridin-2-yl)oxy)-4-phenylbut-3-enoate (3k):**

Yellow oil (155 mg, 89 %).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.15 – 8.09 (m, 1H), 7.67 – 7.53 (m, 3H), 7.33 – 7.26 (m, 2H), 7.13 (t, $J=8.0$ Hz, 1H), 6.98 – 6.88 (m, 2H), 6.38 (dd, $J=16.0$, 8.0 Hz, 1H), 5.99 (d, $J=8.0$ Hz, 1H), 3.79 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.30, 160.95, 147.26, 141.60, 135.79, 134.79, 128.67, 128.45, 126.83, 121.79, 112.86, 112.76, 74.69, 52.56. HRMS (ESI) calcd. for C$_{16}$H$_{15}$BrNO$_3$ [M+H]$^+$: 348.0230, found: 348.0234.

![Structure of methyl (E)-2-((5-bromopyridin-2-yl)oxy)-4-phenylbut-3-enoate (3k)](image)

**methyl (E)-2-((5-chloropyridin-2-yl)oxy)-4-phenylbut-3-enoate (3l):**

Yellow oil (128 mg, 84 %).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, $J=4.0$ Hz, 1H), 7.58 (dd, $J=12.0$, 4.0 Hz, 1H), 7.46 – 7.27 (m, 5H), 6.95 – 6.88 (m, 2H), 6.39 (dd, $J=16.0$, 4.0 Hz, 1H), 5.87 (d, $J=4.0$ Hz, 1H), 3.77 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.36, 160.55, 144.94, 139.00, 135.80, 134.78, 128.69, 128.47, 126.84, 125.10, 121.82, 112.25, 74.75, 52.57. HRMS (ESI) calcd. for C$_{16}$H$_{15}$ClNO$_3$ [M+H]$^+$: 304.0735, found: 304.0738.

![Structure of methyl (E)-2-((5-chloropyridin-2-yl)oxy)-4-phenylbut-3-enoate (3l)](image)
methyl (E)-2-((4-methylpyridin-2-yl)oxy)-4-phenylbut-3-enoate (3m):

Yellow oil (109 mg, 77 %).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, $J = 4.0$ Hz, 1H), 7.43 (d, $J = 8.0$ Hz, 2H), 7.37 – 7.26 (m, 3H), 6.91 (d, $J = 16.0$ Hz, 1H), 6.77 – 6.72 (m, 2H), 6.41 (dd, $J = 16.0$, 8.0 Hz, 1H), 5.92 (d, $J = 8.0$ Hz, 1H), 3.76 (s, 3H), 2.31 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.83, 162.42, 150.41, 146.12, 136.02, 134.29, 128.64, 128.29, 126.82, 122.46, 119.19, 111.28, 74.19, 52.44, 20.96. HRMS (ESI) calcd. for C$_{17}$H$_{18}$NO$_3$ [M+H]$^+$: 284.1281, found: 284.1284.

methyl (E)-2-((3-chloropyridin-2-yl)oxy)-4-phenylbut-3-enoate (3n):

Yellow oil (102 mg, 67 %).

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.13 – 8.09 (m, 1H), 7.65 – 7.59 (m, 1H), 7.43 – 7.37 (m, 2H), 7.02 (t, $J = 8.0$ Hz, 2H), 6.96 – 6.85 (m, 3H), 6.34 (dd, $J = 16.0$, 8.0 Hz, 1H), 5.92 (d, $J = 8.0$ Hz, 1H), 3.77 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 170.83, 162.42, 150.41, 146.12, 136.02, 134.29, 128.64, 128.29, 126.82, 122.46, 119.19, 111.28, 74.19, 52.44, 20.96. HRMS (ESI) calcd. for C$_{16}$H$_{15}$ClNO$_3$ [M+H]$^+$: 304.0735, found: 304.0738.
methyl (E)-2-((6-methylpyridin-2-yl)oxy)-4-phenylbut-3-enoate (3o):

Yellow oil (108 mg, 76%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 – 7.40 (m, 3H), 7.36 – 7.23 (m, 3H), 6.92 (d, $J$ = 20.0 Hz, 1H), 6.73 (t, $J$ = 8.0 Hz, 2H), 6.41 (dd, $J$ = 16.0, 8.0 Hz, 1H), 5.89 (dd, $J$ = 12.0, 4.0 Hz, 1H), 3.76 (s, 3H), 2.39 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.98, 161.39, 155.86, 139.20, 136.03, 134.43, 128.64, 128.30, 126.83, 122.47, 116.63, 107.62, 63.73, 52.32, 23.97. HRMS (ESI) calcd. for C$_{17}$H$_{18}$NO$_3$ [M+H]$^+$: 284.1281, found: 284.1278.

methyl (E)-4-phenyl-2-(pyridin-2-yloxy)pent-3-enoate (3p):

A white solid (118 mg, 83%), mp: 81-83 °C.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.15 – 8.09 (m, 1H), 7.65 – 7.58 (m, 1H), 7.49 – 7.43 (m, 2H), 7.38 – 7.28 (m, 3H), 6.94 – 6.87 (m, 2H), 6.12 (d, $J$ = 12.0 Hz, 1H), 6.00 (d, $J$ = 12.0 Hz, 1H), 3.76 (s, 3H), 2.29 (d, $J$ = 1.2 Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 171.20, 162.31, 146.60, 142.35, 142.17, 138.89, 128.34, 127.85, 126.03, 120.80, 117.47, 111.23, 71.70, 52.35, 17.04. HRMS (ESI) calcd. for C$_{17}$H$_{18}$NO$_3$ [M+H]$^+$: 284.1281, found: 284.1282.

methyl (E)-4-phenyl-2-(pyridin-2-ylthio)but-3-enoate (3q):

Yellow oil (76.0 mg, 53%).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.44 (d, $J = 4.0$ Hz, 1H), 7.53 – 7.46 (m, 1H), 7.37 (d, $J = 12.0$ Hz, 2H), 7.33 – 7.19 (m, 4H), 7.02 (dd, $J = 8.0$, 4.0 Hz, 1H), 6.74 (d, $J = 16.0$ Hz, 1H), 6.38 (dd, $J = 16.0$, 8.0 Hz, 1H), 5.41 (d, $J = 8.0$ Hz, 1H), 3.78 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.57, 161.98, 146.63, 139.05, 134.46, 134.02, 133.02, 128.85, 128.04, 122.97, 117.73, 111.20, 74.04, 52.57. HRMS (ESI) calcd. for C$_{16}$H$_{16}$NO$_2$S [M+H]$^+$: 286.0896, found: 286.0899.

**General procedure for table 3**

To a schlenk tube was added AgSbF$_6$ (17.1 mg, 0.05 mmol), 1 (0.6 mmol) and dry CH$_2$Cl$_2$ (2.5 mL) under argon atmosphere, then a solution of 2 (0.5 mmol) in dry CH$_2$Cl$_2$ (2.5 mL) was added via syringe pump over 30 min at 40 °C. The resulting mixture was stirred at 40 °C for another 4 h. The mixture was concentrated under vacuum; the crude residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:60-1:10) to afford product 4.

**methyl (E)-4-(pyridin-2-yloxy)-4-(p-tolyl)but-2-enoate (4a):**

Colorless oil (112 mg, 83 %).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (dd, $J = 4.8$, 1.4 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.45 (d, $J = 7.1$ Hz, 2H), 7.39 – 7.28 (m, 3H), 7.16 (dd, $J = 15.7$, 4.8 Hz, 1H), 6.89 – 6.81 (m, 3H), 6.12 (dd, $J = 15.7$, 1.7 Hz, 1H), 3.72 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 166.75, 162.27, 146.81, 146.77, 138.92, 138.41, 128.70, 128.29, 127.39, 120.58, 117.36, 111.50, 74.62, 51.68. HRMS (ESI) calcd. for C$_{16}$H$_{16}$NO$_3$ [M+H]$^+$:
methyl (E)-4-(pyridin-2-yloxy)-4-(p-tolyl)but-2-enoate (4b):

Colorless oil (110 mg, 78 %).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (dd, $J = 5.0$, 1.3 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.20 – 7.12 (m, 3H), 6.83 (ddd, $J = 17.5$, 9.0, 4.4 Hz, 3H), 6.10 (dd, $J = 15.7$, 1.7 Hz, 1H), 3.71 (s, 3H), 2.33 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 166.79, 162.34, 146.99, 146.77, 138.87, 138.14, 135.40, 129.38, 127.41, 120.41, 117.28, 111.51, 74.52, 51.64, 21.21. HRMS (ESI) calcd. for C$_{17}$H$_{18}$NO$_3$ [M+H]$^+$: 284.1281, found: 284.1284.

methyl (E)-4-(4-chlorophenyl)-4-(pyridin-2-yloxy)but-2-enoate (4c):

Colorless oil (105 mg, 69 %).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.09 (dd, $J = 4.9$, 1.5 Hz, 1H), 7.63 – 7.54 (m, 1H), 7.38 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 8.5$ Hz, 2H), 7.11 (dd, $J = 15.7$, 4.7 Hz, 1H), 6.90 – 6.85 (m, 1H), 6.84 – 6.76 (m, 2H), 6.12 (dd, $J = 15.7$, 1.6 Hz, 1H), 3.73 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 166.61, 162.02, 146.75, 146.20, 139.02, 137.03, 134.10, 128.88, 128.79, 120.95, 117.54, 111.45, 73.88, 51.75. HRMS (ESI) calcd. for C$_{16}$H$_{15}$ClNO$_3$ [M+H]$^+$: 304.0735, found: 304.0738.
methyl (E)-4-(2-bromophenyl)-4-(pyridin-2-yloxy)but-2-enoate (4d):
A white solid (101 mg, 58 %), mp: 74-76 °C.
$^1$H NMR (400 MHz, CDCl$_3$) δ 8.11 (d, $J = 4.9$ Hz, 1H), 7.63 – 7.54 (m, 2H), 7.51 (d, $J = 7.8$ Hz, 1H), 7.30 (t, $J = 7.8$ Hz, 1H), 7.22 – 7.10 (m, 3H), 6.90 – 6.81 (m, 2H), 6.14 (d, $J = 14.8$ Hz, 1H), 3.72 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 166.70, 161.90, 147.05, 145.11, 138.92, 138.06, 132.92, 129.56, 128.52, 127.87, 122.78, 121.05, 117.52, 111.13, 73.70, 51.71. HRMS (ESI) calcd. for C$_{16}$H$_{15}$BrNO$_3$ [M+H]$^+$: 348.0230, found: 348.0227.

tert-butyl (E)-4-phenyl-4-(pyridin-2-yloxy)but-2-enoate (4e):
Colorless oil (132 mg, 85 %).
$^1$H NMR (400 MHz, CDCl$_3$) δ 8.13 – 8.08 (m, 1H), 7.61 – 7.53 (m, 1H), 7.45 (d, $J = 7.3$ Hz, 2H), 7.40 – 7.28 (m, 3H), 7.05 (dd, $J = 15.6$, 4.8 Hz, 1H), 6.88 – 6.80 (m, 3H), 6.02 (dd, $J = 15.6$, 1.5 Hz, 1H), 1.46 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 165.62, 162.33, 146.79, 145.24, 138.87, 138.74, 128.65, 128.17, 127.38, 122.86, 117.28, 111.53, 80.60, 74.67, 28.10. HRMS (ESI) calcd. for C$_{19}$H$_{22}$NO$_3$ [M+H]$^+$: 312.1594, found: 312.1598.

dert-butyl (E)-4-(4-methoxyphenyl)-4-(pyridin-2-yloxy)but-2-enoate (4f):
A white solid (128 mg, 75 %), mp: 90-92 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.10 (d, $J = 4.3$ Hz, 1H), 7.60 (t, $J = 7.7$ Hz, 1H), 7.38 (d, $J = 8.6$ Hz, 2H), 6.93 – 6.81 (m, 5H), 6.27 (dd, $J = 15.9$, 6.8 Hz, 1H), 5.73 (d, $J = 6.8$ Hz, 1H), 3.82 (s, 3H), 1.44 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 169.43, 162.33, 159.62, 146.44, 138.80, 133.67, 129.01, 128.05, 120.51, 117.37, 113.99, 111.17, 81.81, 75.09, 55.32, 27.96. HRMS (ESI) calcd. for C$_{20}$H$_{24}$NO$_4$ [M+H]$^+$: 342.1700, found: 342.1703.

tert-butyl (E)-4-(4-chlorophenyl)-4-(pyridin-2-yloxy)but-2-enoate (4g):

Colorless oil (111 mg, 64 %).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.09 (d, $J = 4.5$ Hz, 1H), 7.63 – 7.54 (m, 1H), 7.39 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.00 (dd, $J = 15.6$, 4.8 Hz, 1H), 6.90 – 6.77 (m, 3H), 6.01 (d, $J = 15.6$ Hz, 1H), 1.46 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 165.47, 162.09, 146.76, 144.66, 138.96, 137.34, 133.96, 128.82, 128.77, 123.24, 117.45, 111.48, 80.74, 73.94, 28.09. HRMS (ESI) calcd. for C$_{19}$H$_{21}$ClNO$_3$ [M+H]$^+$: 346.1204, found: 346.1207.

tert-butyl (E)-4-((5-methylpyridin-2-yl)oxy)-4-phenylbut-2-enoate (4h):

A white solid (132 mg, 81 %), mp: 92-94 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.90 (s, 1H), 7.44 (d, $J = 7.2$ Hz, 2H), 7.37 (dd, $J = 17.4$, 9.2 Hz, 3H), 7.30 (d, $J = 7.2$ Hz, 1H), 7.04 (dd, $J = 15.6$, 4.8 Hz, 1H), 6.75 (dd, $J = 11.0$, 6.6 Hz, 2H), 6.01 (d, $J = 15.6$ Hz, 1H), 2.22 (s, 3H), 1.46 (s, 9H). $^{13}$C NMR
(125 MHz, CDCl₃) δ 165.65, 160.60, 146.21, 145.41, 139.89, 138.92, 128.62, 128.09, 127.34, 126.23, 122.80, 110.86, 80.54, 74.66, 28.10, 17.42. HRMS (ESI) calcd. for C₂₀H₂₄NO₃ [M+H]⁺: 326.1751, found: 326.1755.

tert-butyl (E)-4-((5-methylpyridin-2-yl)oxy)-4-(_p_-tolyl)but-2-enoate (4i):
Colorless oil (141 mg, 83 %).

¹H NMR (400 MHz, CDCl₃) δ 7.90 (s, 1H), 7.40 – 7.35 (m, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.03 (dd, J = 15.6, 4.8 Hz, 1H), 6.75 – 6.69 (m, 2H), 5.99 (dd, J = 15.6, 1.6 Hz, 1H), 2.33 (s, 3H), 2.21 (s, 3H), 1.45 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 165.69, 160.65, 146.20, 145.58, 139.85, 137.92, 135.89, 129.31, 127.35, 126.14, 122.61, 110.87, 80.48, 74.55, 28.10, 21.21, 17.43. HRMS (ESI) calcd. for C₂₁H₂₆NO₃ [M+H]⁺: 340.1907, found: 340.1904.

A white solid (103 mg, 53 %), mp: 134-136 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.14 (s, 1H), 7.70 – 7.59 (m, 1H), 7.46 – 7.28 (m, 5H), 7.01 (dd, J = 15.6, 4.9 Hz, 1H), 6.73 (dd, J = 12.8, 6.7 Hz, 2H), 6.00 (d, J = 15.6 Hz, 1H), 1.46 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 165.48, 161.17, 147.43, 144.62, 141.44, 138.30, 128.70, 128.36, 127.39, 123.15, 113.11, 112.25, 80.71, 75.40, 28.10. HRMS (ESI) calcd. for C₁₉H₂₁BrNO₃ [M+H]⁺: 390.0699, found: 390.0695.
**tert-butyl (E)-4-((4-methylpyridin-2-yl)oxy)-4-(p-tolyl)but-2-enoate (4k):**

A yellow solid (127 mg, 75 %), mp: 78-80 °C.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.95 (d, \(J = 5.2\) Hz, 1H), 7.33 (d, \(J = 8.1\) Hz, 2H), 7.16 (d, \(J = 8.1\) Hz, 2H), 7.03 (dd, \(J = 15.6, 4.7\) Hz, 1H), 6.77 (dd, \(J = 4.7, 1.6\) Hz, 1H), 6.70 – 6.65 (m, 1H), 6.65 – 6.61 (m, 1H), 5.99 (dd, \(J = 15.6, 1.7\) Hz, 1H), 2.33 (s, 3H), 2.28 (s, 3H), 1.45 (s, 9H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 165.67, 162.74, 150.16, 146.30, 145.55, 137.90, 135.91, 129.31, 127.35, 122.64, 118.75, 111.60, 80.46, 74.46, 28.11, 21.20, 20.90. HRMS (ESI) calcd. for C\(_{21}\)H\(_{26}\)NO\(_3\) [M+H]\(^+\): 340.1907, found: 340.1904.

**tert-butyl (E)-4-((6-methylpyridin-2-yl)oxy)-4-(p-tolyl)but-2-enoate (4l):**

Colorless oil (100 mg, 59 %).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42 (t, \(J = 7.7\) Hz, 1H), 7.35 (d, \(J = 7.9\) Hz, 2H), 7.16 (d, \(J = 7.9\) Hz, 2H), 7.03 (dd, \(J = 15.6, 4.8\) Hz, 1H), 6.81 (d, \(J = 4.8\) Hz, 1H), 6.68 (d, \(J = 7.2\) Hz, 1H), 6.57 (d, \(J = 8.2\) Hz, 1H), 6.02 (dd, \(J = 15.6, 1.0\) Hz, 1H), 2.39 (s, 3H), 2.33 (s, 3H), 1.46 (s, 9H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 165.78, 161.75, 156.09, 145.67, 138.97, 137.87, 135.97, 129.25, 127.57, 122.66, 116.18, 107.84, 80.46, 74.22, 28.11, 24.13, 21.22. HRMS (ESI) calcd. for C\(_{21}\)H\(_{26}\)NO\(_3\) [M+H]\(^+\): 340.1907, found: 340.1904.
Yellow oil (52 mg, 54%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.14 (d, $J = 4.8$ Hz, 1H), 7.60 (t, $J = 7.6$ Hz, 1H), 7.13 (dt, $J = 16.0$, 4.1 Hz, 1H), 6.94 – 6.86 (m, 1H), 6.80 (d, $J = 8.3$ Hz, 1H), 6.14 (d, $J = 16.0$ Hz, 1H), 5.04 (d, $J = 2.0$ Hz, 2H), 3.75 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 166.65, 162.79, 146.80, 143.40, 138.85, 121.13, 117.28, 111.15, 63.82, 51.64. HRMS (ESI) calcd. for C$_{10}$H$_{12}$NO$_3$ [M+H]$^+$: 194.0812, found: 194.0815.

Control experiments for Scheme 2

Scheme 2 - a:

To a schlenk tube was added AgSbF$_6$ (3.4 mg, 0.01 mmol), 3a (27 mg, 0.1 mmol) and dry CH$_2$Cl$_2$ (2.5 mL) under argon atmosphere. The resulting mixture was stirred at 40 °C for 4 h. The mixture was concentrated under vacuum and purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:20) to recovered 3a (25.5 mg).

To a schlenk tube was added Xantphos(AuCl)$_2$ (5.2 mg, 0.005 mmol), AgSbF$_6$ (3.4 mg, 0.01 mmol), 4a (27 mg, 0.1 mmol) and dry CH$_2$Cl$_2$ (2 mL) under argon atmosphere; the resulting solution was stirred at 40 °C for 4 h. The mixture was concentrated under vacuum and purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:15) to recovered 4a (26 mg).

Scheme 2 - b:
To a schlenk tube was added Xantphos(AuCl)$_2$ (26 mg, 0.025 mmol), AgSbF$_6$ (17.1 mg, 0.05 mmol), 1a (57 mg, 0.6 mmol) and dry CH$_2$Cl$_2$ (2.5 mL) under argon atmosphere, the mixture was stirred at room temperature for 30 min; then a solution of 5 (88 mg, 0.5 mmol) in dry CH$_2$Cl$_2$ (2.5 mL) was added via syringe pump over 30 min at 40 °C. The resulting mixture was stirred at 40 °C for another 4 h. The mixture was concentrated under vacuum; the crude residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:15) to give 6a (112 mg, yield: 92%) as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.12 (d, $J$ = 4.7 Hz, 1H), 7.66 – 7.55 (m, 3H), 7.45 – 7.3 (m, 3H), 6.91 (dd, $J$ = 14.2, 7.4 Hz, 2H), 6.23 (s, 1H), 3.71 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.89, 162.35, 146.62, 138.94, 135.15, 128.97, 128.74, 127.70, 117.63, 111.34, 75.58, 52.41. HRMS (ESI) calcd. for C$_{14}$H$_{14}$NO$_3$ [M+H]$^+$: 244.0968, found: 244.0965.

To a schlenk tube was added AgSbF$_6$ (17.1 mg, 0.05 mmol), 1a (57 mg, 0.6 mmol) and dry CH$_2$Cl$_2$ (2.5 mL) under argon atmosphere, then a solution of 5 (0.5 mmol) in dry CH$_2$Cl$_2$ (2.5 mL) was added via syringe pump over 30 min at 40 °C. The resulting mixture was stirred at 40 °C for another 4 h. The mixture was concentrated under vacuum; the crude residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:15) to afford product 6a (109 mg, yield: 90%) as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.12 (d, $J$ = 4.7 Hz, 1H), 7.66 – 7.55 (m, 3H), 7.45 – 7.3 (m, 3H), 6.91 (dd, $J$ = 14.2, 7.4 Hz, 2H), 6.23 (s, 1H), 3.71 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.89, 162.35, 146.62, 138.94, 135.15, 128.97, 128.74, 127.70, 117.63, 111.34, 75.58, 52.41. HRMS (ESI) calcd. for C$_{14}$H$_{14}$NO$_3$ [M+H]$^+$: 244.0968, found: 244.0965.
Carbene insertion into O-H bonds of benzyl alcohols for Scheme 3

General procedure for gold-catalyzed O-H insertion of benzyl alcohols:

To a schlenk tube was added Xantphos(AuCl)$_2$ (26 mg, 0.025 mmol), AgSbF$_6$ (17.1 mg, 0.05 mmol), 7 (0.6 mmol) and dry CH$_2$Cl$_2$ (2.5 mL) under argon atmosphere, the mixture was stirred at room temperature for 30 min. The reaction was cooled to 0 °C and a solution of 2a (101 mg, 0.5 mmol) in dry CH$_2$Cl$_2$ (2.5 mL) was added via syringe pump over 30 min at 0 °C. The resulting mixture was stirred at 0 °C for 6 h. The mixture was concentrated under vacuum; the crude residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:30-1:20) to afford product 8.

General procedure B for silver-catalyzed O-H insertion of benzyl alcohols:

To a schlenk tube was added AgSbF$_6$ (17.1 mg, 0.05 mmol), 7 (0.6 mmol) and dry CH$_2$Cl$_2$ (2.5 mL) under argon atmosphere at 0 °C, then a solution of 2a (101 mg, 0.5 mmol) in dry CH$_2$Cl$_2$ (2.5 mL) was added via syringe pump over 30 min at 0 °C. The resulting mixture was stirred at 0 °C for 6 h. The mixture was concentrated under vacuum; the crude residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:20-1:15) to afford product 9.

methyl (E)-2-(benzyloxy)-4-phenylbut-3-enoate (8a)$^{[3]}$:

Yellow oil (95 mg, 67 %).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.46 – 7.21 (m, 10H), 6.77 (d, $J = 16.0$ Hz, 1H), 6.25 (dd, $J = 16.0$, 6.9 Hz, 1H), 4.75 – 4.55 (m, 3H), 3.78 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 171.14, 137.15, 135.91, 134.44, 128.64, 128.52, 128.29, 128.07, 127.99,
126.77, 123.71, 78.58, 71.33, 52.37.

**methyl (E)-2-((4-bromobenzyl)oxy)-4-phenylbut-3-enoate (8b):**

Yellow oil (105 mg, 58%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J = 7.9$ Hz, 2H), 7.40 (d, $J = 7.6$ Hz, 2H), 7.36 – 7.23 (m, 5H), 6.75 (d, $J = 15.9$ Hz, 1H), 6.24 (dd, $J = 15.9$, 7.0 Hz, 1H), 4.66 – 4.54 (m, 3H), 3.78 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 170.93, 136.26, 135.80, 134.65, 131.64, 129.64, 128.67, 128.39, 126.79, 123.46, 121.90, 78.79, 70.56, 52.41. HRMS (ESI) calcd. for C$_{18}$H$_{18}$BrO$_3$ [M+H]$^+$: 361.0434, found: 361.0438.

**methyl (E)-4-(benzyloxy)-4-phenylbut-2-enoate (9a):**

Yellow oil (96 mg, 68%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 – 7.24 (m, 10H), 7.01 (dd, $J = 15.6$, 5.2 Hz, 1H), 6.15 (d, $J = 15.6$ Hz, 1H), 4.98 (d, $J = 5.2$ Hz, 1H), 4.49 (q, $J = 12.1$ Hz, 2H), 3.71 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 166.83, 147.78, 138.91, 137.87, 128.83, 128.47, 128.39, 127.76, 127.65, 127.30, 120.49, 79.72, 70.39, 51.66.

**methyl (E)-4-((4-bromobenzyl)oxy)-4-phenylbut-2-enoate (9b):**
Yellow oil (116 mg, 64 %).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (d, $J = 8.1$ Hz, 2H), 7.41 – 7.28 (m, 5H), 7.19 (d, $J = 8.1$ Hz, 2H), 6.99 (dd, $J = 15.6$, 5.2 Hz, 1H), 6.13 (d, $J = 15.6$ Hz, 1H), 4.96 (d, $J = 5.1$ Hz, 1H), 4.43 (q, $J = 12.1$ Hz, 2H), 3.72 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 166.72, 147.45, 138.65, 136.90, 131.57, 129.24, 128.88, 128.50, 127.25, 121.61, 120.59, 79.94, 69.65, 51.69. HRMS (ESI) calcd. for C$_{18}$H$_{18}$BrO$_3$ [M+H]$^+$: 361.0434, found: 361.0438.

**X-ray structure of 3d and 4h**

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC 1445771, 3d) and (CCDC 1523822, 4h). The data can be obtained free of charge via the internet at www.ccdc.cam.ac.uk/data_request/cif.
References:


$\text{3b}$
$3k$
4d
4k
$d_{1}$ (ppm)

\begin{align*}
20.90 & \quad 21.20 & \quad 28.11 & \quad 74.46 & \quad 76.79 & \quad 77.04 & \quad 77.29 & \quad 80.46 \\
111.60 & \quad 118.75 & \quad 122.64 & \quad 127.35 & \quad 129.31 & \quad 135.91 & \quad 137.90 & \quad 145.55 & \quad 146.30 & \quad 150.16
\end{align*}

4k

$Me$

$O$

$CO_2Bu$

$Me$
$\text{Ph}^+\text{OBn} \rightarrow \text{CO}_2\text{Me}$

9a