Supporting Information

Gold-Catalyzed Intermolecular Carboalkoxylation of Alkenes

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I. General Information.

Unless otherwise noted, all reagents and catalysts were obtained commercially and used without further purification. Diethyl ether (Et₂O) was distilled from CaH₂ and toluene was distilled from sodium sand. Unless otherwise noted, all reaction mixtures were stirred with a magnetic stir bar in flame-dried glassware under a positive pressure of dry argon.

Chromatography: Analytical thin layer chromatography (TLC) was performed and phosphomolybdic acid stain. Technical grade solvents were employed, which were distilled prior to use. Concentration under reduced pressure was performed by rotary evaporation at 38 ℃ at the appropriate pressure. Yields refer to chromatographically purified and spectroscopically pure compounds, unless stated otherwise.

Nuclear magnetic resonance spectra: ¹H and ¹³C spectra were recorded on INOVA-400MHz spectrometer. Chemical shifts (δ) are reported in ppm. ¹H NMR spectra were referenced to CDCl₃ (7.26 ppm) and ¹³C NMR spectra were referenced to CDCl₃ (77.0 ppm). All ¹³C spectra were measured with complete proton decoupling. Peak multiplicities are designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad; and J coupling constant in Hz.

Mass spectroscopy: The molecular weights were measured on electrospray ionization of mass spectrometry (ESI /MS).
II. Synthesis and characterization data for substates 2b-2e.

General procedures for 2b-2e. Aryl aldehyde (1.0 equiv.) and trimethoxymethane (TMOF; 4.0 equiv.) were mixed, mixtures were stirred with a magnetic stir in one-necked bottle. Then 4-toluene sulfonic acid (p-TsOH; 0.08 equiv.) was put in the one-necked bottle as catalyst. The reaction mixture was then heated to reflux for appropriate time while stirring. Aryl aldehyde was consumed (as observed by TLC), appropriate NaHCO₃ was put in the one-necked bottle and stirred for 10 minutes, and the reaction mixture was filtered through a pad of silica and then concentrated. The crude products were used directly.

\[
\begin{align*}
\text{(2b)} & \\
\text{1H NMR (400 MHz, CDCl₃) } & \delta 7.53-7.52 (m, 1 H), 7.21-7.14 (m, 3 H), 5.45 (s, 1 H), 3.31 (s, 6 H), 2.36 (s, 3 H); \text{ MS: } m/z 166.10 (M⁺), 135.10 \text{ (bs), 91.05.}
\end{align*}
\]

\[
\begin{align*}
\text{(2c)} & \\
\text{1H NMR (400 MHz, CDCl₃) } & \delta 7.27-7.24 (m, 3 H), 7.14-7.12 (m, 1 H), 5.35 (s, 1 H), 3.33 (s, 6 H), 2.44 (s, 3 H); \text{ }^{13}\text{C NMR (100 MHz, CDCl₃)}
\end{align*}
\]
δ 137.9, 137.8, 129.1, 128.0, 127.2, 123.7, 103.3, 52.7, 21.4; **MS: m/z**
166.05 (M⁺), 135.05 (bs), 91.05.

(2d)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.33-7.27 (m, 2 H), 7.20-7.14 (m, 2 H), 5.35 (s, 1 H), 3.29 (s, 6 H), 2.33 (s, 3 H); **MS: m/z** 166.10 (M⁺), 135.10 (bs), 91.05.

(2e)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.36-7.33 (m, 2 H), 6.99-6.94 (m, 2 H), 5.29 (s, 1 H), 3.23 (s, 6 H); **MS: m/z** 170.00 (M⁺), 139.05 (bs), 109.05.

The acetals list below are obtained commercially and used without further purification: 1-(dimethoxymethyl)-4-nitrobenzene, 4-bromobenzaldehyde dimethyl acetal, Benzaldehyde dimethyl acetal; 1,1-dimethoxyhexane, 4-methoxybenzaldehyde dimethyl acetal.
III. Gold-catalyzed intermolecular carboalkoxylation of alkenes.

General Procedures for gold-catalyzed intermolecular carboalkoxylation of alkenes. The mixture of PicAuCl$_2$ (0.05 mmol, 5 mol %), AgNTf$_2$ (0.1 mmol, 10 mol %) was stirred in toluene (2.0 ml) for 2 minutes, and then the solution of alkenes (1.0 mmol) and acetals (1.5 mmol) in toluene (2.0 ml) was added. The system was stirred at 50 ºC (or room temperature) and stopped until the starting material completely consumed. The system was filtered through a short column of silica gel and flushed by ethyl ether. The concentrated crude product was purified by flash silica-gel column chromatography using petroleum ether and ethyl ether as eluent.

$^1$H NMR (400 MHz, CDCl$_3$), cis: $\delta$ 7.37-7.25 (m, 10 H), 4.06-4.03 (t, $J$ = 7.2 Hz, 2 H), 3.14 (s, 6 H), 2.47-2.40 (m, $J$ = 6.0 Hz, 1 H), 1.86-1.80 (m, $J$ = 6.8 Hz, 1 H), 7.36-7.22 (m, 20 H, cis / anti), anti: $\delta$ 4.45-4.40 (m, $J$ = 2.4 Hz, 2 H), 3.25 (s, 6 H), 2.00-1.97 (q, $J$ = 2.4 Hz, 1.6 Hz, 2 H); $^{13}$C
NMR (100 MHz, CDCl₃, cis / anti) δ 142.3, 141.6, 128.3, 127.6, 127.4, 126.8, 126.5, 80.8, 80.0, 56.7, 56.3, 47.6, 46.1; HRMS (ESI): exact mass calculated for C₁₇H₂₀NaO₂[M+Na]⁺, 279.1356; found 279.1344.

1H NMR (400 MHz, CDCl₃), cis: δ 7.39-7.08 (m, 9 H), 4.21-4.16 (m, J = 4.4 Hz, 2 H), 3.16 (s, 3 H), 3.12 (s, 3 H), 2.36 (m, 1 H), 2.06 (s, 3 H), 1.86-1.83 (m, 1 H), anti: δ 7.37-7.11 (m, 9 H), 4.77-4.74 (q, J = 6.4 Hz, 2.8 Hz, 1 H), 4.49-4.46 (q, J = 6.0 Hz, 3.6 Hz, 1 H), 3.28 (s, 3 H), 3.27 (s, 3 H), 2.35 (s, 3 H), 1.90-1.85 (m, J = 9.6 Hz, 3.2 Hz, 2 H); 13C NMR (125 MHz, CDCl₃), cis: δ 141.7, 139.7, 135.6, 130.3, 128.4, 127.8, 127.1, 127.0, 126.3, 126.0, 81.3, 56.4, 45.2, 18.6; 13C NMR (100 MHz, CDCl₃), anti: δ 142.5, 140.4, 135.3, 130.3, 128.3, 127.4, 126.8, 126.5, 126.1, 125.4, 80.1, 56.9, 46.6, 19.0; HRMS (ESI): exact mass calculated for C₁₈H₂₂NaO₂ [M+Na]⁺, 293.1512; found 293.1501.

1H NMR (400 MHz, CDCl₃) δ 7.37-7.05 (m, 18 H, cis / anti), cis: δ 4.08-4.04 (t, J = 7.2 Hz, 1 H), 4.01-3.98 (t, J = 6.8 Hz, 1 H), 3.15 (s, 3 H),
3.14 (s, 3 H), 2.44-2.40 (m, J = 6.0 Hz, 1 H), 2.33 (s, 3 H), 1.85-1.80 (m, J = 6.8 Hz, 1 H), **anti:** δ 7.33-7.07 (m, 9 H), 4.43-4.37 (m, J = 6.8 Hz, 2 H), 3.27 (s, 6 H), 2.34 (s, 3 H), 1.99-1.96 (t, J = 6.8 Hz, 2 H); **13C NMR (100 MHz, CDCl₃), cis:** δ 142.3, 141.7, 138.0, 128.4, 128.2, 127.5, 126.9, 123.9, 80.9, 56.4, 46.0, 21.4, **anti:** δ 142.3, 142.2, 138.0, 128.4, 128.3, 128.2, 127.5, 127.2, 126.6, 123.7, 80.0, 56.8, 47.6, 21.4; **HRMS (ESI):** exact mass calculated for C₁₈H₂₂NaO₂ [M+Na]⁺, 293.1512; found 293.1500.

\[\text{(3d)}\]

**¹H NMR (400 MHz, CDCl₃)** δ 7.28-7.05 (m, 18 H, cis / anti), **cis:** δ 3.99-3.92 (t, J = 6.8 Hz, 2 H), 3.06 (s, 3 H), 3.05 (s, 3 H), 2.37-2.33 (m, J = 6.8 Hz, 1 H), 2.27 (s, 3 H), 1.76-1.72 (m, J = 6.4 Hz, 1 H), **anti:** δ 7.28-7.06 (m, 9 H), 4.34-4.27 (m, J = 6.4 Hz, 2 H), 3.18 (s, 3 H), 3.17 (s, 3 H), 2.26 (s, 3 H), 1.92-1.89 (t, J = 6.4 Hz, 2 H); **¹³C NMR (125 MHz, CDCl₃), cis:** δ 141.8, 139.2, 137.2, 129.1, 128.4, 127.6, 127.4, 126.6, 80.7, 80.1, 56.7, 56.4, 46.1, 21.1; **¹³C NMR (100 MHz, CDCl₃), anti:** δ 142.3, 139.1, 137.1, 129.1, 128.4, 127.5, 126.7, 126.6, 80.1, 79.8, 56.8, 56.6, 47.4, 21.1; **HRMS (ESI):** exact mass calculated for C₁₈H₂₂NaO₂ [M+Na]⁺, 293.1512; found 293.1504.
\( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.48-7.13 (m, 18 H, cis / anti), cis: \( \delta \) 4.05-4.00 (q, J = 6.4 Hz, 2 H), 3.14 (s, 3 H), 3.13 (s, 3 H), 2.44-2.37 (m, J = 8.0 Hz, 1 H), 1.82-1.75 (m, J = 6.4 Hz, 1 H), anti: \( \delta \) 7.46-7.17 (m, 9 H), 4.41-4.37 (q, J = 6.0 Hz, 2 H), 3.25 (s, 3 H), 3.24 (s, 3 H), 1.95-1.91 (t, J = 6.8 Hz, 2 H); \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)), cis: \( \delta \) 141.4, 140.7, 131.5, 128.4, 128.2, 127.5, 126.5, 121.4, 80.6, 80.2, 56.7, 56.3, 46.0, anti: \( \delta \) 142.1, 141.4, 131.5, 128.4, 128.3, 127.6, 126.6, 121.2, 79.9, 79.5, 56.9, 56.8, 47.5; HRMS (ESI): exact mass calculated for C\(_{17}\)H\(_{19}\)BrNaO\(_2\) [M+Na]\(^+\), 357.0461; found 357.0444.

\( ^1\)H NMR (400 MHz, CDCl\(_3\)), cis: \( \delta \) 7.37-7.02 (m, 9 H), 4.06-3.99 (m, J = 7.2 Hz, 2 H), 3.13 (s, 6 H), 2.44-2.40 (m, J = 6.0 Hz, 1 H), 1.81-1.77 (m, J = 6.8 Hz, 1 H), anti: \( \delta \) 7.36-6.99 (m, 9 H), 4.41-4.38 (t, J = 6.8 Hz, 2 H), 3.24 (s, 3 H), 3.13 (s, 3 H), 1.96-1.93 (t, J = 6.4 Hz, 2 H); \( ^{13}\)C NMR (125 MHz, CDCl\(_3\)), cis: \( \delta \) 163.3, 161.4, 141.5, 137.4, 128.5, 127.8, 126.8, 126.6, 115.3, 80.8, 80.3, 56.3, 46.1, anti: \( \delta \) 163.2, 161.2, 142.2, 138.1, 128.4, 128.2, 127.6, 126.6, 115.3, 80.0, 79.4, 56.8, 47.6; HRMS (ESI):
exact mass calculated for C$_{17}$H$_{19}$FNaO$_2$ [M+Na]$^+$, 297.1261; found 297.1247.

$^{1}$H NMR (400 MHz, CDCl$_3$, cis / anti) $\delta$ 7.36-7.12 (m, 14 H), 6.90-6.81 (m, 4 H), 4.39-4.14 (m, 2 H), 4.04-4.00 (t, J = 7.2 Hz, 2 H), 3.81 (s, 3 H), 3.78 (s, 3 H), 3.24 (s, 3 H), 3.22 (s, 3 H), 3.11 (s, 3 H), 3.10 (s, 3 H), 2.47-2.39 (m, J = 8.0 Hz, 6.0 Hz, 1 H), 2.01-1.96 (m, 2 H), 1.84-1.77 (m, J = 6.4 Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$, cis / anti) $\delta$ 159.1, 159.0, 142.3, 141.7, 134.2, 133.6, 128.8, 128.6, 128.4, 128.1, 127.8, 127.6, 126.8, 126.6, 114.3, 113.8, 80.9, 80.4, 80.1, 79.5, 56.7, 56.5, 56.4, 56.1, 47.3, 46.0; HRMS (ESI): exact mass calculated for C$_{18}$H$_{22}$NaO$_3$ [M+Na]$^+$, 309.1461; found 309.1454.

$^{1}$H NMR (400 MHz, CDCl$_3$, cis / anti) $\delta$ 8.23-8.19 (m, J = 9.2 Hz, 4 H), 7.50-7.26 (m, 14 H), 4.61-4.58 (t, J = 6.0 Hz, 1 H), 4.47-4.44 (t, J = 6.4 Hz, 1 H), 4.18-4.14 (t, J = 6.8 Hz, 1 H), 4.06-4.03 (t, J = 6.8 Hz, 1 H), 3.31 (s, 3 H), 3.28 (s, 3 H), 3.17 (s, 3 H), 3.14 (s, 3 H), 2.46-2.39 (m, J =
6.4 Hz, 1 H), 1.92-1.90 (t, J = 2.8 Hz, 2 H), 1.85-1.70 (m, J = 6.4 Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$, cis / anti) δ 150.3, 149.6, 141.8, 141.0, 130.4, 129.8, 128.5, 128.5, 127.9, 127.6, 127.4, 127.1, 126.8, 126.4, 124.3, 123.7, 80.5, 80.1, 79.6, 79.4, 57.3, 56.8, 56.3, 47.6, 45.9; HRMS (ESI): exact mass calculated for C$_{17}$H$_{19}$NNaO$_4$ [M+Na]$^+$, 324.1206; found 324.1191.

cis anti

$^1$H NMR (400 MHz, CDCl$_3$), cis: δ 7.38-7.26 (m, 5 H), 4.29-4.25 (t, J = 6.8 Hz, 1 H), 3.23 (s, 3 H), 3.17 (s, 3 H), 3.00-2.97 (m, J = 5.6 Hz, 1 H), 2.16-2.09 (m, J = 6.8 Hz, 1 H), 1.72-1.66 (m, J = 6.0 Hz, 1 H), 1.47-1.44 (m, 2 H), 1.31-1.26 (m, 6 H), 0.90-0.85 (t, 3 H), anti: δ 7.38-7.26 (m, 5 H), 4.35-4.31 (q, J = 6.8 Hz, 3.2 Hz, 1 H), 3.48-3.47 (m, J = 3.6 Hz, 1 H), 3.38 (s, 3 H), 3.23 (s, 3 H), 1.81-1.77 (m, J = 3.2 Hz, 2 H), 1.54-1.47 (m, 2 H), 1.40-1.28 (m, 6 H), 0.87-0.86 (m, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$), cis: δ 142.0, 128.4, 127.6, 127.0, 81.2, 77.6, 56.5, 56.0, 42.0, 33.0, 32.0, 24.4, 22.6, 14.0, anti: δ 142.8, 128.4, 127.4, 126.4, 80.3, 77.4, 57.0, 56.7, 45.0, 33.8, 32.1, 24.6, 22.6, 13.9; HRMS (ESI): exact mass calculated for C$_{16}$H$_{26}$O$_2$ [(M)$^+$] 273.1825; found 273.1814.
1H NMR (400 MHz, CDCl₃, cis / anti) δ 7.35-7.16 (m, 18 H), 4.44-4.39 (q, J = 7.2 Hz, 2 H), 4.12-4.08 (t, J = 7.2 Hz, 1 H), 4.01-3.98 (t, J = 7.2 Hz, 1 H), 3.25 (s, 6 H), 3.15 (s, 3 H), 3.13 (s, 3 H), 2.46-2.43 (t, J = 6.4 Hz, 1 H), 1.99-1.96 (t, J = 6.4 Hz, 2 H), 1.86-1.82 (t, J = 6.8 Hz, 1 H), 1.32 (s, 9 H), 1.30 (s, 9 H); 13C NMR (100 MHz, CDCl₃, cis / anti), δ 150.4, 150.2, 142.3, 141.7, 139.2, 138.4, 128.3, 128.3, 127.6, 127.4, 126.9, 126.5, 126.2, 125.2, 80.9, 80.5, 80.0, 79.7, 56.7, 56.3, 47.6, 45.9, 34.5, 31.3; HRMS (ESI): exact mass calculated for C₂₁H₂₈NaO₂ [M+Na]⁺, 335.1982; found 335.1965.

1H NMR (400 MHz, CDCl₃), cis: δ 7.38-6.91 (m, 8 H), 4.19-4.15 (m, J = 3.2 Hz, 2 H), 3.15 (s, 3 H), 3.10 (s, 3 H), 2.39-2.32 (m, J = 5.2 Hz, 1 H), 2.27 (s, 3 H), 2.04 (s, 3 H), 1.85-1.78 (m, J = 6.4 Hz, 1 H), anti: δ 7.24-6.87 (m, 8 H), 4.65-4.62 (q, J = 3.6 Hz, 1 H), 4.40-4.36 (q, J = 4.0 Hz, 1 H), 3.20 (s, 3 H), 3.18 (s, 3 H), 2.24 (s, 3 H), 2.18 (s, 3 H), 1.83-1.79 (m, J = 3.2 Hz, 2 H); 13C NMR (125 MHz, CDCl₃), cis: δ 141.7, 136.6, 135.5, 131.1, 128.4, 127.7, 127.0, 126.0, 81.3, 56.4, 56.2,
45.3, 21.0, 18.5, **anti**: δ 142.5, 137.3, 136.5, 135.2, 131.2, 128.3, 127.4, 126.8, 126.5, 125.7, 80.3, 56.9, 56.7, 46.6, 20.9, 18.9; **HRMS (ESI)**: exact mass calculated for C$_{19}$H$_{24}$NaO$_2$ [M+Na]$^+$, 307.1669; found 307.1674.

![Diagram](3l)

$^1$H NMR (400 MHz, CDCl$_3$, cis / anti) δ 7.44-7.11 (m, 20 H), 4.35-4.33 (q, J = 6.0 Hz, 2.0 Hz, 1 H), 3.81-3.78 (q, J = 5.6 Hz, 2.8 Hz, 1 H), 3.13 (s, 3 H), 3.08 (s, 3 H), 3.05 (s, 3 H), 2.95 (s, 3 H), 2.36-2.25 (m, 2 H), 2.05-2.02 (m, 2 H), 1.66 (s, 3 H), 1.49 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$, cis / anti) δ 145.7, 144.5, 143.3, 142.9, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.2, 127.1, 126.9, 126.7, 126.4, 126.1, 80.6, 80.1, 78.8, 78.4, 56.1, 51.7, 50.5, 50.0, 23.8, 22.9.

![Diagram](3m)

$^1$H NMR (400 MHz, CDCl$_3$, cis / anti) δ 7.36-7.24 (m, 10 H), 4.45-4.42 (q, J = 8.0 Hz, 3.2 Hz, 1 H), 4.40-4.37 (q, J = 3.6 Hz, 1 H), 3.33 (s, 3 H), 3.32 (s, 3 H), 3.19 (s, 3 H), 3.17 (s, 3 H), 2.30-2.25 (q, J = 7.6 Hz, 2 H), 2.24-2.18 (m, 2 H), 2.16-2.10 (m, 2 H), 2.09-1.98 (q, 2 H), 1.47 (s, 3 H),
1.42 (s, 3 H), 1.19-1.18 (t, 3 H), 1.11-1.10 (t, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$, cis / anti) δ 143.1, 143.0, 128.3, 127.4, 127.3, 126.7, 126.5, 87.9, 87.2, 81.2, 80.5, 80.1, 80.0, 73.3, 72.4, 56.5, 56.2, 51.2, 50.9, 49.4, 48.7, 29.7, 26.8, 14.2, 14.0, 12.4, 12.3; HRMS (ESI): exact mass calculated for C$_{16}$H$_{22}$NaO$_2$ [M+Na]$^+$, 269.1512; found 269.1514.

$^{1}$H NMR (400 MHz, CDCl$_3$) δ 7.35-7.24 (m, 5 H), 5.38 (s, 1 H), 4.26-4.23 (t, J = 6.0 Hz, 1 H), 3.21 (s, 3 H), 2.49-2.43 (q, J = 8.0 Hz, 1 H), 2.22-2.19 (q, J = 8.8 Hz, 5.6 Hz, 1 H), 1.95-1.88 (m, 4 H), 1.60-1.50 (m, 4 H); $^{13}$C NMR (100 MHz, CDCl$_3$), δ 142.4, 134.3, 128.2, 127.4, 126.6, 123.6, 82.6, 56.7, 46.9, 28.7, 25.3, 22.9, 22.3.

IV. Acid-catalyzed intermolecular carboalkoxylation of alkenes.

General Procedures for Lewis acid and Proton acid-catalyzed intermolecular carboalkoxylation of alkenes. The solution of alkenes (1.0 mmol) and acetals (1.5 mmol) in toluene (2.0 ml) was added into a
solution of lewis acid (TMSOTf) or proton acid (CF$_3$SO$_3$H) in toluene (2.0 ml) under argon atmosphere. The system was stirred at room temperature and stopped until the starting material completely consumed. The system was filtered through a short column of silica gel and flushed by ethyl ether. The concentrated crude product was purified by flash silica-gel column chromatography using petroleum ether and ethyl ether as eluent.
V. Copies of $^1$H NMR, $^{13}$C NMR spectra.
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