Supporting Information

The first palladium-catalyzed 1,4-addition of terminal alkenes to acrylate esters

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1 General Information Methods.

All manipulations were performed under an air atmosphere unless otherwise statement. Column chromatography was performed on silica gel (300–400 mesh). NMR spectra were obtained using a Bruker Avance 500 spectrometer (1H at 500 MHz and 13C at 125 MHz). Chemical shifts for 1H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (CDCl3: δ 7.26 ppm). Chemical shifts for 13C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (CDCl3: δ 77.0 ppm). High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with APCI or ECI ionization source.

Materials. Unless stated otherwise, commercial reagents were used without further purification. All reagents were weighed and handled in air at room temperature.

2 General Experimental Procedure

The reaction mixture of alkenes 1 (0.5 mmol), acrylate esters 2 (0.75 mmol), PdCl2 (6 mol%), and PhCl (2 mL) in a 15 mL sealed tube was stirred at 110 °C for 72 h, and monitored periodically by TLC. Upon completion, the reaction mixture was diluted with water (30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with water and brine, dried over Na2SO4 and filtered. The solvent was removed under vacuum. The residue was purified by flash column chromatography to afford (E)-alkenyl esters.
3 Characterization of the Compounds

\((E)-\)Ethyl 5-phenylpent-4-enoate (3aa)

\[
\begin{align*}
\text{Yellowish oil; }^{1}H \text{ NMR (500 MHz, CDCl}_3\text{)} & \delta 7.35-7.33 (m, 2H), \\
& 7.31-7.28 (m, 2H), 7.22-7.19 (m, 1H), 6.44 (d, J = 15.8 Hz, 1H), 6.22 (dt, J = 15.8, \\
& 6.6 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 2.57-2.53 (m, 2H), 2.51-2.46 (m, 2H), 1.26 (t, J \\
& = 7.1 Hz, 3H); ^{13}C \text{ NMR (125 MHz, CDCl}_3\text{)} & \delta 173.0, 137.3, 130.9, 128.5, 127.1, \\
& 126.0, 60.4, 34.0, 28.3, 14.2; \text{ ESI HRMS exact mass calcd for (C}_{13}\text{H}_{16}\text{O}_2\text{Na})^+ \\
& \text{requires m/z 227.10480, found m/z 227.10374.}
\end{align*}
\]

The NMR data was in good agreement with that reported in the literature.1

\((E)-\)Methyl 5-phenylpent-4-enoate (3ab)

\[
\begin{align*}
\text{Yellow oil; }^{1}H \text{ NMR (500 MHz, CDCl}_3\text{)} & \delta 7.34 (d, J = 7.4 Hz, 2H), \\
& 7.31-7.28 (m, 2H), 7.22 (d, J = 7.2 Hz, 1H), 6.44 (d, J = 15.9 Hz, 1H), 6.21 (dt, J = \\
& 15.8, 6.5 Hz, 1H), 3.70 (s, 3H), 2.57-2.53 (m, 2H), 2.51-2.48 (m, 2H); ^{13}C \text{ NMR (125} \\
& \text{MHz, CDCl}_3\text{)} & \delta 173.4, 137.3, 131.0, 128.5, 128.4, 127.1, 126.0, 51.6, 33.8, 28.2; \text{ ESI} \\
& \text{HRMS exact mass calcd for (C}_{12}\text{H}_{15}\text{O}_2\text{)}^+ \text{ requires m/z 191.10720, found m/z} \\
& 191.10664.
\end{align*}
\]

The NMR data was in good agreement with that reported in the literature.2

\((E)-\)Butyl 5-phenylpent-4-enoate (3ac)

\[
\begin{align*}
\text{Yellow oil; }^{1}H \text{ NMR (500 MHz, CDCl}_3\text{)} & \delta 7.34 (d, J = 7.3 Hz, 2H), \\
& 7.31-7.28 (m, 2H), 7.22-7.20 (m, 1H), 6.44 (d, J = 15.9 Hz, 1H), 6.22 (dt, J = 15.8, \\
& 6.6 Hz, 1H), 4.11 (t, J = 6.7 Hz, 2H), 2.57-2.53 (m, 2H), 2.52-2.47 (m, 2H), 1.65-1.59 \\
& (m, 2H), 1.43-1.35 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C \text{ NMR (125 MHz, CDCl}_3\text{)} & \delta \\
& 173.0, 137.3, 130.9, 128.4, 127.1, 126.0, 64.3, 34.0, 30.6, 28.3, 19.1, 13.6; \text{ APCI}
\end{align*}
\]

S3
HRMS exact mass calcd for \((C_{15}H_{21}O_2)^+\) requires \(m/z\) 233.15415, found \(m/z\) 233.15385.

\((E)\)-Isobutyl 5-phenylpent-4-enoate (3ad)

\[
\begin{align*}
\text{Yellowish oil; } ^1H \text{ NMR (500 MHz, CDCl}_3) & \delta 7.36-7.34 (m, 2H), 7.32-7.29 (m, 2H), 7.23-7.20 (m, 1H), 6.45 (d, } J = 15.9 \text{ Hz, 1H), 6.23 (dt, } J = 15.8, 6.5 \text{ Hz, 1H), 3.90 (d, } J = 6.7 \text{ Hz, 2H), 2.59-2.54 (m, 2H), 2.53-2.49 (m, 2H), 1.97-1.92 (m, 1H), 0.95 (s, 3H), 0.94 (s, 3H); }^{13C} \text{ NMR (125 MHz, CDCl}_3) & \delta 173.0, 137.3, 130.9, 128.4, 127.1, 127.0, 126.0, 70.5, 34.0, 28.3, 27.7, 19.0; \text{ APCI HRMS exact mass calcd for } (C_{15}H_{21}O_2)^+ \text{ requires } m/z \, 233.15415, \text{ found } m/z \, 233.15387.
\end{align*}
\]

\((E)\)-Tert-butyl 5-phenylpent-4-enoate (3ae)

\[
\begin{align*}
\text{Yellow oil; } ^1H \text{ NMR (500 MHz, CDCl}_3) & \delta 7.33 (d, } J = 7.0 \text{ Hz, 2H), 7.31-7.28 (m, 3H), 6.42 (d, } J = 15.9 \text{ Hz, 1H), 6.21 (dt, } J = 15.8, 6.7 \text{ Hz, 1H), 2.52-2.48 (m, 2H), 2.41-2.38 (m, 2H), 1.45 (s, 9H); }^{13C} \text{ NMR (125 MHz, CDCl}_3) & \delta 172.4, 139.7, 130.7, 128.8, 128.5, 127.0, 126.0, 80.3, 35.2, 29.7, 28.1; \text{ APCI HRMS exact mass calcd for } (C_{15}H_{21}O_2)^+ \text{ requires } m/z \, 233.15415, \text{ found } m/z \, 233.15297.
\end{align*}
\]

\((E)\)-Isobutyl 5-(o-tolyl)pent-4-enoate (3bd)

\[
\begin{align*}
\text{Yellow oil; } ^1H \text{ NMR (500 MHz, CDCl}_3) & \delta 7.40 (d, } J = 5.7 \text{ Hz, 1H), 7.18-7.13 (m, 3H), 6.65 (d, } J = 15.7 \text{ Hz, 1H), 6.10 (dt, } J = 15.5, 6.6 \text{ Hz, 1H), 3.90 (d, } J = 6.7 \text{ Hz, 2H), 2.61-2.57 (m, 2H), 2.55-2.51 (m, 2H), 2.34 (s, 3H), 1.98-1.91 (m, 1H), 0.96 (s, 3H), 0.95 (s, 3H); }^{13C} \text{ NMR (125 MHz, CDCl}_3) & \delta 173.0, 136.5, 135.0, 130.1, 129.8, 128.8, 127.0, 126.0, 125.5, 70.5, 34.2, 28.6, 27.7, 19.7, 19.1; \text{ APCI HRMS exact mass calcd for } (C_{16}H_{23}O_2)^+ \text{ requires } m/z \, 247.16980, \text{ found } m/z \, 247.16870.
\end{align*}
\]
(E)-Methyl 5-(p-tolyl)pent-4-enoate (3ca)

Yellowish oil; \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.23 (d, \(J = 8.0\) Hz, 2H), 7.10 (d, \(J = 7.9\) Hz, 2H), 6.40 (d, \(J = 15.9\) Hz, 1H), 6.15 (dt, \(J = 15.8, 6.6\) Hz, 1H), 4.15 (q, \(J = 7.1\) Hz, 2H), 2.56-2.49 (m, 2H), 2.49-2.45 (m, 2H), 2.33 (s, 3H), 1.26 (t, \(J = 7.2\) Hz, 3H); \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta\) 173.1, 136.9, 134.6, 130.7, 129.2, 127.4, 125.9, 60.4, 34.1, 28.3, 21.1, 14.3; APCI HRMS exact mass calcd for \((C_{14}H_{19}O_2)^+\) requires m/z 219.13850, found m/z 219.13763.

(E)-Ethyl 5-(4-bromophenyl)pent-4-enoate (3da)

Yellow oil; \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.41 (d, \(J = 1.9\) Hz, 1H), 7.40 (d, \(J = 1.8\) Hz, 1H), 7.20 (d, \(J = 2.0\) Hz, 1H), 7.18 (d, \(J = 1.7\) Hz, 1H), 6.36 (d, \(J = 15.9\) Hz, 1H), 6.20 (dt, \(J = 15.8, 6.4\) Hz, 1H), 4.14 (q, \(J = 7.1\) Hz, 2H), 2.54-2.50 (m, 2H), 2.49-2.45 (m, 2H), 1.25 (t, \(J = 7.1\) Hz, 3H); \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta\) 172.9, 136.3, 131.6, 129.8, 129.4, 127.6, 120.8, 60.4, 33.9, 28.3, 14.3; APCI HRMS exact mass calcd for \((C_{13}H_{16}O_2Br)^+\) requires m/z 283.03337, found m/z 283.03040.

(E)-Isobutyl 5-(4-fluorophenyl)pent-4-enoate (3ed)

Yellow oil; \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.30-7.26 (m, 2H), 6.99-6.94 (m, 2H), 6.39 (d, \(J = 15.9\) Hz, 1H), 6.12 (dt, \(J = 15.8, 6.4\) Hz, 1H), 3.87 (d, \(J = 6.6\) Hz, 2H), 2.55-2.47 (m, 4H), 1.96-1.88 (m, 1H), 0.93 (s, 3H), 0.92 (s, 3H); \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \(\delta\) 173.0, 163.0 and 161.0, 133.5, 129.7, 128.2, 127.5, 127.4, 115.4 and 115.2, 70.6, 34.0, 28.2, 27.7, 19.0; APCI HRMS exact mass calcd for \((C_{15}H_{20}O_2F)^+\) requires m/z 251.14473, found m/z 251.14366.
(E)-Methyl 5-phenylhex-4-enoate (3fb)

\[
\begin{align*}
\text{Yellow oil; } ^1H \text{ NMR (500 MHz, CDCl}_3) \delta & \ 7.39 \ (d, J = 7.5 \text{ Hz, } 2\text{H}), \\
7.34-7.31 \ (m, \ 2\text{H}), \ 7.25 \ (d, J = 7.4 \text{ Hz, } 1\text{H}), \ 5.78-5.72 \ (m, \ 1\text{H}), \ 3.71 \ (s, \ 3\text{H}), \ 2.57-\ 2.54 \ (m, \ 2\text{H}), \ 2.50-2.47 \ (m, \ 2\text{H}), \ 2.08 \ (s, \ 3\text{H}); \\
^{13}C \text{ NMR (125 MHz, CDCl}_3) \delta & \ 173.5, \ 143.5, \ 136.2, \ 128.1, \ 126.7, \ 125.9, \ 125.6, \ 51.5, \ 33.8, \ 24.2, \ 15.7; \text{ ESI HRMS exact mass calcd for (C}_{13}H_{17}O_2)^+ requires m/z 205.12285, found m/z 205.12259.\
\end{align*}
\]

(E)-Isobutyl 5-phenylhex-4-enoate (3fd)

\[
\begin{align*}
\text{Yellow oil; } ^1H \text{ NMR (500 MHz, CDCl}_3) \delta & \ 7.38-7.35 \ (m, \ 2\text{H}), \\
7.32-7.29 \ (m, \ 2\text{H}), \ 7.24-7.21 \ (m, \ 1\text{H}), \ 5.76-5.72 \ (m, \ 1\text{H}), \ 3.88 \ (d, J = 6.7 \text{ Hz, } 2\text{H}), \\
2.57-2.52 \ (m, \ 2\text{H}), \ 2.49-2.45 \ (m, \ 2\text{H}), \ 2.06 \ (s, \ 3\text{H}), \ 1.95-1.91 \ (m, \ 1\text{H}), \ 0.94 \ (s, \ 3\text{H}), \\
0.93 \ (s, \ 3\text{H}); \text{ APCI HRMS exact mass calcd for (C}_{16}H_{23}O_2)^+ requires m/z 247.16980, found m/z 247.16943.\
\end{align*}
\]

(E)-Isobutyl 5-(4-chlorophenyl)hex-4-enoate (3gd)

\[
\begin{align*}
\text{Yellow oil; } ^1H \text{ NMR (500 MHz, CDCl}_3) \delta & \ 7.30-7.26 \ (m, \ 4\text{H}), \\
5.75-5.72 \ (m, \ 1\text{H}), \ 3.89 \ (d, J = 6.7 \text{ Hz, } 2\text{H}), \ 2.55-2.52 \ (m, \ 2\text{H}), \ 2.50-2.47 \ (m, \ 2\text{H}), \\
2.36-2.30 \ (m, \ 1\text{H}), \ 2.04 \ (s, \ 3\text{H}), \ 0.95 \ (s, \ 3\text{H}), \ 0.94 \ (s, \ 3\text{H}); \text{ APCI HRMS exact mass calcd for (C}_{16}H_{22}O_2Cl)^+ requires m/z 281.13083, found m/z 281.13016.\
\end{align*}
\]

(Z)-Methyl 4-(3,3-dimethylbicyclo[2.2.1]heptan-2-ylidene)butanoate (3ib)

\[
\begin{align*}
\text{Yellow oil; } ^1H \text{ NMR (500 MHz, CDCl}_3) \delta & \ 5.77-5.71 \ (m, \ 1\text{H}), \ 3.73 \ (s,} \]
3H), 3.29-3.28 (m, 1H), 2.34-2.29 (m, 1H), 2.04-1.96 (m, 2H), 1.78-1.73 (m, 1H), 1.73-1.67 (m, 2H), 1.67-1.63 (m, 1H), 1.47-1.40 (m, 1H), 1.33-1.29 (m, 1H), 1.25-1.23 (m, 1H), 1.21-1.16 (m, 1H), 1.07 (s, 3H), 1.04 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 171.5, 168.2, 117.0, 51.3, 47.7, 43.2, 42.6, 37.4, 28.4, 28.3, 28.1, 25.3, 23.6; APCI HRMS exact mass calcd for (C$_{14}$H$_{23}$O$_2$)$^+$ requires m/z 223.16980, found m/z 233.16942.

D-(E)-Ethyl 5-phenylpent-4-enoate (3aa-d)

Yellow oil; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.34 (d, J = 7.3 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 2.53 (d, J = 6.4 Hz, 1H), 2.48 (dd, J = 11.3, 4.5 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H).
4 References


5 Copies of $^1$H NMR and $^{13}$C NMR Spectra of Products
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