Supporting Information

Acid-Promoted Olefination of Ketones by Iron(III) Porphyrin Complex
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Experimental Section

General Considerations. All reactions were carried out in oven-dried glassware using standard Schlenk techniques. Toluene was distilled under nitrogen from sodium benzophenone ketyl. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as supplied. All other solvents were of liquid chromatography grade quality, purchased from Fisher Scientific and used as supplied. Ketones were purchased from Acros Organics or Aldrich Chemical Co. and used without further purification. Triphenylphosphine and Fe(TPP)Cl were supplied by Strem Chemical Co. EDA and t-BDA were obtained from Aldrich Chemical Co. Proton and carbon nuclear magnetic resonance spectra (\(^1\)H NMR and \(^{13}\)C NMR) were recorded on a Varian Mercury 300 spectrometer and referenced with respect to internal TMS standard or residual solvent. GC/GC-MS spectroscopy was carried out on a Hewlett Packard G1800B GCD system. High-resolution mass spectroscopy was performed by the Mass Spectrometry Center located in the Chemistry Department of the University of Tennessee on a VG Analytical hybrid high performance ZAB-EQ (B-E-Q geometry) instrument using electron impact (EI) ionization technique with a 70 eV electron beam. Thin layer chromatography was carried out on E. Merck Silica Gel 60 F-254 TLC plates.

General Procedures for Olefination Reaction. Fe(TPP)Cl (1.5 mol %) and triphenylphosphine (1.2 equivalents) were placed in an oven-dried, resealable Schlenk tube. The tube was capped with a Teflon screwcap, evacuated, and backfilled with nitrogen. The screwcap was replaced with a rubber septum, and ketone (0.5 mmol, 1.0 equivalent) was added via syringe, followed by solvent (2 mL) and EDA (1.2 equivalents) or t-BDA (1.4 equivalents). The tube was purged with nitrogen for 2 min and its contents were stirred at constant temperature in an oil bath. After the reaction was finished, the resulting mixture was cooled to room
temperature and concentrated. The residue was purified by flash chromatography (silica gel) to afford the product.

**Ethyl 3-phenyl-2-butenoate (1)** was synthesized from acetophenone. **E isomer:** \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.46-7.49 (m, 2H), 7.35-7.39 (m, 3H), 6.13 (q, 1H, \(J = 1.5\) Hz), 4.22 (q, 2H, \(J = 7.2\) Hz), 2.58 (d, 3H, \(J = 1.5\) Hz), 1.32 (t, 3H, \(J = 7.2\) Hz); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 166.9, 155.5, 142.2, 128.9, 128.5, 126.3, 117.1, 59.8, 17.9, 14.3. **Z isomer:** \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.30-7.38 (m, 2H), 7.19-7.22 (m, 3H), 5.91 (q, 1H, \(J = 1.5\) Hz), 3.99 (q, 2H, \(J = 7.2\) Hz), 2.18 (d, 3H, \(J = 1.5\) Hz), 1.08 (t, 3H, \(J = 7.2\) Hz); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 165.9, 155.4, 140.8, 127.9, 127.7, 126.8, 117.7, 59.7, 27.1, 13.9. HRMS-EI ([M⁺]): calcd for C\(_{12}\)H\(_{14}\)O\(_2\), 190.0994; found 190.0990.

**Ethyl 3-(4-chlorophenyl)-2-butenoate (2)** was synthesized from 4-chloroacetophenone. **E isomer:** \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.40 (d, 2H, \(J = 8.4\) Hz), 7.33 (d, 2H, \(J = 8.4\) Hz), 6.11 (q, 1H, \(J = 1.5\) Hz), 4.21 (q, 2H, \(J = 7.2\) Hz), 2.54 (d, 3H, \(J = 1.5\) Hz), 1.31 (t, 3H, \(J = 7.2\) Hz); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 166.5, 153.9, 140.4, 134.8, 128.6, 127.5, 117.4, 59.8, 17.7. **Z isomer:** \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.31 (d, 2H, \(J = 8.4\) Hz), 7.14 (d, 2H, \(J = 8.4\) Hz), 5.91 (q, 1H, \(J = 1.5\) Hz), 4.01 (q, 2H, \(J = 7.2\) Hz), 2.14 (d, 3H, \(J = 1.5\) Hz), 1.12 (t, 3H, \(J = 7.2\) Hz); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 165.5, 154.2, 139.0, 133.5, 128.2, 128.0, 118.1, 59.8, 26.9, 13.9. HRMS-EI ([M⁺]): calcd for C\(_{12}\)H\(_{13}\)ClO\(_2\), 224.0604; found 224.0600.

**Ethyl 3-(4-nitrophenyl)-2-butenoate (3)** was synthesized from 4-nitroacetophenone. **E isomer:** \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.23 (d, 2H, \(J = 8.4\) Hz), 7.62 (d, 2H, \(J = 8.4\) Hz), 6.19 (s, 1H), 4.24 (q, 2H, \(J = 7.2\) Hz), 2.60 (s, 3H), 1.34 (t, 3H, \(J = 7.2\) Hz); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 166.0, 152.6, 148.5, 147.8, 127.2, 123.7, 120.1, 60.2, 17.8, 14.2. **Z isomer:** \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.22 (d, 2H, \(J = 8.4\) Hz), 7.36 (d, 2H, \(J = 8.4\) Hz), 6.01 (q, 1H, \(J = 1.5\) Hz), 4.01 (q, 2H, \(J = 7.2\) Hz), 2.20 (d, 3H, \(J = 1.5\) Hz), 1.12 (t, 3H, \(J = 7.2\) Hz); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 165.0, 153.3, 148.0, 147.0, 127.7, 123.2, 119.2, 60.0, 26.7, 13.9. HRMS-EI ([M⁺]): calcd for C\(_{12}\)H\(_{13}\)NO\(_4\), 235.0845; found 235.0839.

**Ethyl 3-methyl-5-phenyl-2,4-pentadieneoate (4)** was synthesized from trans-4-phenyl-3-buten-2-one. **ZE isomer:** \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.43 (d, 1H, \(J = 16.2\) Hz), 7.52-7.55 (m, 2H), 7.24-7.36 (m, 3H), 6.90 (d, 1H, \(J = 16.2\) Hz), 5.75 (s, 1H), 4.19 (q, 2H, \(J = 7.2\) Hz), 2.11 (d, 3H, \(J = 1.2\) Hz), 1.30 (t, 3H, \(J = 7.2\) Hz); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 166.4, 150.7, 136.6, 135.2, 128.6, 127.3, 125.8, 117.6, 59.7, 20.8, 14.3. **EE isomer:** \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.45-7.48 (m, 2H), 7.26-7.38 (m, 3H), 6.94 (d, 1H, \(J = 16.2\) Hz), 6.81 (d, 1H, \(J = 16.2\) Hz).
Hz), 5.91 (s, 1H), 4.19 (q, 2H, J = 7.2 Hz), 2.41 (d, 3H, J = 1.5 Hz), 1.31 (t, 3H, J = 7.2 Hz); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$: 167.0, 152.0, 134.0, 131.9, 128.7, 128.6, 127.0, 119.8, 59.8, 14.3, 13.7. HRMS-EI ([M$^+$]): calcd for C$_{14}$H$_{16}$O$_2$, 216.1150; found 216.1158.

**Ethyl 3-methyl-decenoate (5)** was synthesized from 2-nonanone. **Z isomer:** $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 5.64 (q, 1H, J = 1.2 Hz), 4.13 (q, 2H, J = 7.2 Hz), 2.61 (m, 2H), 1.88 (d, 3H, J = 1.2 Hz), 1.24-1.48 (m, 13H), 0.88 (t, 3H, J = 7.2 Hz); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$: 166.4, 160.9, 115.9, 59.4, 33.4, 31.8, 29.7, 29.2, 28.7, 25.2, 22.6, 14.3, 14.1. **E isomer:** $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 5.66 (q, 1H, J = 1.5 Hz), 4.14 (q, 2H, J = 7.2 Hz), 2.15 (d, 3H, J = 1.5 Hz), 2.13 (m, 2H), 1.26-1.49 (m, 13H), 0.88 (t, 3H, J = 6.9 Hz); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$: 166.9, 160.5, 115.3, 59.4, 40.9, 31.7, 29.1, 27.4, 22.6, 18.7, 14.3, 14.1. HRMS-EI ([M$^+$]): calcd for C$_{13}$H$_{24}$O$_2$, 212.1776; found 212.1786.

**Ethyl cyclohexylideneacetate (6)** was synthesized from cyclohexanone. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 5.55 (s, 1H), 4.09 (q, 2H, J = 7.2 Hz), 2.78 (m, 2H), 2.14 (m, 2H), 1.57 (m, 6H), 1.22 (t, 3H, J = 7.2 Hz). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$: 166.8, 163.4, 112.9, 59.4, 37.9, 29.7, 28.5, 27.7, 26.2, 14.2. HRMS-EI ([M$^+$]): calcd for C$_{10}$H$_{16}$O$_2$, 168.1150; found 168.1149.

**Ethyl 4-methylcyclohexylideneacetate (7)** was synthesized from 4-methylcyclohexanone. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 5.61 (s, 1H), 4.13 (q, 2H, J = 7.2 Hz), 3.71-3.79 (m, 1H), 2.12-2.30 (m, 2H), 1.82-2.00 (m, 2H), 1.56-1.70 (m, 1H), 1.27 (t, 3H, J = 7.2 Hz), 1.05-1.19 (m, 2H), 0.91 (d, 3H, J = 7.2 Hz). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$: 166.8, 163.1, 113.0, 59.4, 37.3, 36.4, 35.7, 28.9, 21.6, 14.2. HRMS-EI ([M$^+$]): calcd for C$_{11}$H$_{18}$O$_2$, 182.1307; found 182.1307.

**Ethyl 4-phenylcyclohexylideneacetate (8)** was synthesized from 4-phenylcyclohexanone. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 7.25-7.30 (m, 2H), 7.15-7.20 (m, 3H), 5.68 (s, 1H), 4.15 (q, 2H, J = 7.2 Hz), 3.96-4.01 (m, 1H), 2.73-2.82 (m, 1H), 2.32-2.41 (m, 2H), 1.97-2.08 (m, 3H), 1.58-1.70 (m, 2H), 1.28 (t, 3H, J = 7.2 Hz). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$: 166.6, 161.7, 145.9, 128.3, 126.7, 126.1, 113.6, 59.4, 43.9, 37.6, 35.4, 34.7, 29.3, 14.2. HRMS-EI ([M$^+$]): calcd for C$_{16}$H$_{20}$O$_2$, 244.1463; found 244.1469.

**Ethyl cyclopentylideneacetate (9)** was synthesized from cyclopentanone. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$: 5.80 (m, 1H), 4.15 (q, 2H, J = 7.2 Hz), 2.77 (t, 2H, J = 7.2 Hz), 2.44 (t, 2H, J = 7.2 Hz), 1.6-1.8 (m, 4H), 1.28 (t, 3H, J = 7.2 Hz). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$: 169.1, 166.9, 111.6, 59.4, 35.9, 32.6, 26.4, 25.4, 14.3. HRMS-EI ([M$^+$]): calcd for C$_{9}$H$_{14}$O$_2$, 154.0994; found 154.0991.
Ethyl cycloheptylideneacetate (10)\textsuperscript{10} was synthesized from cycloheptanone. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 5.67 (m, 1H), 4.13 (q, 2H, \(J = 7.2\) Hz), 2.87 (t, 2H, \(J = 6.0\) Hz), 2.37 (t, 2H, \(J = 6.0\) Hz), 1.66 (m, 4H), 1.54 (m, 4H), 1.27 (t, 3H, \(J = 7.2\) Hz). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta\) 166.7, 166.6, 115.5, 59.3, 38.9, 32.0, 29.8, 28.9, 28.0, 26.5, 14.3. HRMS-EI ([M\textsuperscript{+}]): calcd for C\textsubscript{11}H\textsubscript{18}O\textsubscript{2}, 182.1307; found 182.1303.

tert-Butyl 3-(4-nitrophenyl)-2-butenoate (13) was synthesized from 4-nitroacetophenone. \textit{E} isomer: \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 8.22 (d, 2H, \(J = 8.4\) Hz), 7.61 (d, 2H, \(J = 8.4\) Hz), 6.11 (q, 1H, \(J = 1.5\) Hz), 2.56 (d, 3H, \(J = 1.5\) Hz), 1.53 (s, 9H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta\) 165.5, 151.1, 148.9, 147.7, 127.2, 123.7, 122.0, 80.7, 28.1, 17.6. \textit{Z} isomer: \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 8.22 (d, 2H, \(J = 8.4\) Hz), 7.35 (d, 2H, \(J = 8.4\) Hz), 5.92 (q, 1H, \(J = 1.5\) Hz), 2.15 (d, 3H, \(J = 1.5\) Hz), 1.28 (s, 9H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta\) 164.5, 151.0, 148.4, 147.0, 127.8, 123.3, 121.3, 80.5, 27.7, 26.5. HRMS-EI ([M-C\textsubscript{4}H\textsubscript{9}O\textsuperscript{+}]): calcd for C\textsubscript{10}H\textsubscript{8}NO\textsubscript{3}, 190.0504; found 190.0502.

tert-Butyl 3-methyl-5-phenyl-2,4-pentadieneoate (14) was synthesized from \textit{trans}-4-phenyl-3-buten-2-one. \textit{ZE} isomer: \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 8.38 (d, 1H, \(J = 16.2\) Hz), 7.53-7.56 (m, 2H), 7.25-7.37 (m, 3H), 6.89 (d, 1H, \(J = 16.2\) Hz), 5.68 (q, 1H, \(J = 0.9\) Hz), 2.09 (d, 3H, \(J = 0.9\) Hz), 1.52 (s, 9H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta\) 165.9, 149.3, 136.8, 134.8, 128.6, 128.5, 127.3, 125.9, 119.8, 79.9, 28.3, 20.9. \textit{EE} isomer: \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 7.44-7.47 (m, 2H), 7.24-7.37 (m, 3H), 6.90 (d, 1H, \(J = 16.2\) Hz), 6.79 (d, 1H, \(J = 16.2\) Hz), 5.85 (s, 1H), 2.37 (d, 3H, \(J = 0.9\) Hz), 1.51 (s, 9H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta\) 166.6, 150.7, 136.4, 133.4, 132.1, 128.7, 128.4, 126.9, 121.8, 79.9, 28.3, 13.5. HRMS-EI ([M\textsuperscript{+}]): calcd for C\textsubscript{16}H\textsubscript{20}O\textsubscript{2}, 244.1463; found 244.1471.

tert-Butyl 4-phenylcyclohexylideneacetate (15) was synthesized from 4-phenylcyclohexanone. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 7.26-7.31 (m, 2H), 7.15-7.20 (m, 3H), 5.61 (s, 1H), 3.92-3.97 (m, 1H), 2.71-2.82 (m, 1H), 2.30-2.38 (m, 2H), 1.94-2.07 (m, 3H), 1.58-1.70 (m, 2H), 1.49 (s, 9H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta\) 166.2, 160.1, 146.0, 128.3, 126.7, 126.1, 115.3, 79.6, 44.0, 37.5, 35.5, 34.7, 29.1, 28.2. HRMS-EI ([M-C\textsubscript{4}H\textsubscript{9}O\textsuperscript{+}]): calcd for C\textsubscript{14}H\textsubscript{15}O, 199.1123; found 199.1110.
References