Supporting Information for

Phosphoramidites are Efficient, Green Organocatalysts for the Michael Reaction.
Mechanistic Insights into the Phosphorus-Catalyzed Michael Reaction of Alkynones and
Implications for Asymmetric Catalysis.

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Substrates and catalysts used in the asymmetric catalysis experiments, analytical data for all new
compounds, and some experimental procedures (12 pages).

Figure S1. Chiral compounds used to investigate the catalytic asymmetric Michael reaction. (a) Starting materials; (b) catalysts.¹

Experimental Procedures

Starting materials were prepared by literature procedures.² In cases where the E and Z isomers were separated, the reported elemental analysis is of one of the pure isomers.

(-)-Menthyl 2-cyano-5-methylhexanoate. DCC (8.67 g, 42.0 mmol) in CH_2Cl_2 (30 mL) was added dropwise to a solution of 2-cyano-5-methylhexanoic acid (5.93 g, 38.2 mmol), DMAP (1.40 g, 11.46 mmol) and (-)-menthol (5.97 g, 38.20 mmol) in CH_2Cl_2 (160 mL) at 0 °C. The mixture was stirred at 0 °C during 20 min, at RT 1 day and filtered through Celite 545. The solvent was

removed by a rotary evaporator under reduced pressure. The resulting oil was purified by flash chromatography (eluant: 1% EtOAc in petroleum ether) to give the title compound (80% yield) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 4.76 (dt, 4.4 Hz, 11.0 Hz, 0.5H), 4.75 (dt, 4.4 Hz, 11.0 Hz, 0.5H), 3.47 (t, 6.9 Hz, 0.5H), 3.46 (t, 7.0 Hz, 0.5H), 2.05-1.83 (m, 4H), 1.78-1.68 (m, 2H), 1.64-1.57 (m, 1H), 1.55-1.43 (m, 2H), 1.41-1.34 (m, 2H), 1.12-1.00 (m, 2H), 0.99-0.83 (m, 13), 0.78 (d, 7.0 Hz, 1.5H), 0.77 (d, 7.0 Hz, 1.5H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 166.0 (2), 116.9 (2), 77.3, 46.9 (2), 38.3, 38.2, 35.9, 35.8, 34.2, 31.6, 28.2, 28.1, 27.8, 26.4, 26.3, 23.4, 22.6, 22.4, 22.1, 20.9, 16.3. IR (neat): 2245, 1741 cm^{-1} . Calcd for $\text{C}_{18}\text{H}_{31}\text{NO}_2$: C, 73.67; H, 10.65. Found: C, 73.39; H, 10.72.

(–)-Menthyl 2-cyano-4-phenylbutanoate. The same procedure was used starting with 2-cyano-4-phenylbutyric acid. The resulting oil was purified by flash chromatography (eluant: 5% EtOAc in petroleum ether) to give the title compound (94% yield) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.35-7.30 (m, 2H), 7.27-7.19 (m, 3H), 4.77 (dt, 4.4 Hz, 11.0 Hz, 0.5H), 4.76 (dt, 4.4 Hz, 11.0 Hz, 0.5H), 3.43 (dd, 6.5 Hz, 7.8 Hz, 0.5H), 3.42 (dd, 6.2 Hz, 8.2 Hz, 0.5H), 2.91-2.75 (m, 2H), 2.30-2.20 (m, 2H), 2.03-1.95 (m, 1H), 1.93-1.82 (m, 1H), 1.74-1.67 (m, 2H), 1.53-1.43 (m, 2H), 1.11-1.00 (m, 2H), 0.93 (d, 6.4 Hz, 1.5H), 0.92 (d, 6.6 Hz, 1.5H), 0.91 (d, 7.1 Hz, 1.5H), 0.90 (d, 7.1 Hz, 1.5H), 0.92-0.86 (m, 1H), 0.77 (d, 7.0 Hz, 1.5H), 0.76 (d, 7.0 Hz, 1.5H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 165.8, 139.5, 129.0, 128.8, 127.0, 116.6, 77.9, 47.0, 46.9, 40.7, 40.6, 37.2, 37.1, 34.2, 32.8, 31.6, 31.5, 26.4, 23.4, 22.0, 20.8, 16.3. IR (neat): 2245, 1734 cm^{-1} .

(–)-Menthyl 1-indanone-2-carboxylate. In a 50 mL flask fitted with a 10 cm tube, a stirred mixture of methyl 1-indanone-2-carboxylate (479 mg, 2.52 mmol) and (–)-menthol (472 mg, 3.02 mmol) in toluene (18 mL) was heated so the toluene refluxed halfway up the tube (120-130 °C, oil bath temperature), over 6.5 h. After being cooled to room temperature, the reaction mixture was directly concentrated under reduce pressure, and the resulting oil was purified by flash chromatography (eluant: 5% EtOAc in petroleum ether) to give the title compound (de = 68%, 99%

yield) as a pink oil. ^1H NMR (400 MHz, CDCl_3): δ 7.77 (dd, 0.8 Hz, 7.7 Hz, 0.84H), 7.66-7.60 (m, 1H), 7.52 (dd, 0.8 Hz, 7.7 Hz, 0.84H), 7.48-7.43 (m, 0.16H), 7.42-7.37 (m, 1.16H), 4.88 (dt, 4.4 Hz, 11.0 Hz, 0.16H), 4.76 (dt, 4.4 Hz, 10.8 Hz, 0.84H), 3.70 (dd, 4.0 Hz, 8.2 Hz, 0.84H), 3.58-3.50 (m, 1.16H), 3.40-3.34 (m, 1H), 2.18-2.09 (m, 0.84H), 2.09-2.00 (m, 1H), 1.96-1.86 (m, 0.16H), 1.78-1.64 (m, 2H), 1.54-1.41 (m, 2H), 1.15-0.98 (m, 2H), 0.95-0.87 (m, 6.52H), 0.81 (d, 7.0 Hz, 0.48H), 0.78 (d, 7.1 Hz, 0.48H), 0.75 (d, 7.1 Hz, 2.52H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 199.9, 199.8, 169.0, 168.9, 153.9, 153.8, 143.4, 135.6, 135.5, 129.4, 128.0, 127.0, 126.8, 124.8, 120.8, 76.0, 75.9, 74.2, 74.1, 53.9, 53.7, 47.1, 47.0, 40.9, 40.8, 34.5, 34.4, 31.6, 30.6, 30.5, 26.3, 25.9, 23.5, 23.2, 22.2, 21.1, 21.0, 16.5, 16.1. IR (neat): 1712, 1645, 1627, 1573 cm^{-1} . Calcd for $\text{C}_{20}\text{H}_{26}\text{O}_3$: C, 76.40; H, 8.33. Found: C, 76.35; H, 8.51.

Typical Procedure for Michael Reaction. See main body of paper.

Ethyl 5-oxo-2-cyano-2-(2-phenylethyl)-3-hexenoate. The resulting oil was purified by flash chromatography (eluant: 20% EtOAc in petroleum ether) to give the title compound (E/Z = 30/70, 83% yield) as a colorless oil. E isomer: ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.18 (m, 5H), 6.70 (d, 15.8 Hz, 1H), 6.61 (d, 15.8 Hz, 1H), 4.26 (q, 7.1 Hz, 2H), 2.81 (ddd, 5.6 Hz, 11.3 Hz, 13.7 Hz, 1H), 2.75 (ddd, 5.4 Hz, 11.5 Hz, 13.5 Hz, 1H), 2.45 (ddd, 5.5 Hz, 11.3 Hz, 13.7 Hz, 1H), 2.30 (s, 3H), 2.20 (ddd, 5.6 Hz, 11.3 Hz, 13.5 Hz, 1H), 1.33 (t, 7.1 Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 196.5, 166.3, 139.1, 138.5, 132.3, 128.9, 128.6, 126.9, 116.4, 64.0, 52.1, 39.2, 31.7, 28.8, 14.1. IR (neat): 2249, 1745, 1705, 1685 cm^{-1} . Z isomer: ^1H NMR (400 MHz, CDCl_3): δ 7.33-7.18 (m, 5H), 6.48 (d, 11.2 Hz, 1H), 5.95 (d, 11.2 Hz, 1H), 4.30 (dq, 15.6 Hz, 7.1 Hz, 1H), 4.28 (dq, 15.6 Hz, 7.1 Hz, 1H), 2.91 (ddd, 5.6 Hz, 11.6 Hz, 13.6 Hz, 1H), 2.79 (ddd, 5.6 Hz, 11.5 Hz, 13.6 Hz, 1H), 2.46-2.29 (m, 2H), 2.31 (s, 3H), 1.36 (t, 7.1 Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 197.7, 167.2, 139.5, 137.6, 131.2, 128.8, 128.5, 126.8, 117.0, 63.1, 48.0, 41.4, 31.5, 31.2, 14.2. IR (neat): 2245, 1740, 1701, 1618 cm^{-1} .

Ethyl 5-oxo-2-cyano-2-(3-methylbutyl)-3-hexenoate. The resulting oil was purified by flash chromatography (eluant: 5% EtOAc in petroleum ether) to give the title compound (E/Z = 30/70, 89% yield) as a colorless oil. E isomer: ^1H NMR (400 MHz, CDCl_3): δ 6.69 (d, 15.7 Hz, 1H), 6.58 (d, 15.7 Hz, 1H), 4.30 (q, 7.1 Hz, 2H), 2.27 (s, 3H), 2.13 (ddd, 4.8 Hz, 12.5 Hz, 13.4 Hz, 1H), 1.89 (dt, 4.8 Hz, 12.5 Hz, 1H), 1.64-1.54 (m, 1H), 1.42-1.22 (m, 2H), 1.34 (t, 7.1 Hz, 3H), 0.91 (d, 6.8 Hz, 3H), 0.90 (d, 6.6 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, CDCl_3): δ 196.4, 166.5, 138.7, 132.0, 116.5, 63.6, 52.0, 35.8, 33.8, 28.7, 27.8, 22.2, 13.9. IR (neat): 2250, 1747, 1685, 1628 cm^{-1} . Z isomer: ^1H NMR (400 MHz, CDCl_3): δ 6.43 (d, 11.2 Hz, 1H), 5.89 (d, 11.2 Hz, 1H), 4.27 (q, 7.1 Hz, 2H), 2.27 (s, 3H), 2.10-1.95 (m, 2H), 1.62-1.34 (m, 3H), 1.33 (t, 7.1 Hz, 3H), 0.89 (d, 6.6 Hz, 3H), 0.88 (d, 6.2 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, CDCl_3): δ 197.5, 167.3, 137.9, 130.8, 117.1, 62.7, 47.8, 37.8, 33.6, 31.0, 27.9, 22.3, 14.0. IR (neat): 2245, 1745, 1701, 1618 cm^{-1} . Calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_3$: C, 66.91; H, 8.42. Found: C, 66.91; H, 8.64.

8-Methyl-3-nonen-2-one-5,5-dicarbonitrile. The resulting oil was purified by flash chromatography (eluant: 10% EtOAc in petroleum ether) to give the title compound (E/Z = 75/25, 75% yield) as a colorless oil. E isomer: ^1H NMR (400 MHz, CDCl_3): δ 6.68 (d, 15.5 Hz, 1H), 6.55 (d, 15.5 Hz, 1H), 2.36 (s, 3H), 2.09 (dt, 8.2 Hz, 4.6 Hz, 2H), 1.72-1.62 (m, 1H), 1.56-1.50 (m, 2H), 0.96 (d, 6.6 Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 195.2, 134.1, 133.1, 113.0, 38.6, 37.0, 33.8, 29.1, 27.5, 22.1. IR (neat): 2249, 1711, 1689, 1630 cm^{-1} . Calcd for $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}$: C, 70.56; H, 7.90. Found: C, 70.63; H, 8.15. Z isomer: ^1H NMR (400 MHz, CDCl_3): δ 6.57 (d, 11.1 Hz, 1H), 5.86 (d, 11.1 Hz, 1H), 2.38 (s, 3H), 2.25-2.21 (m, 2H), 1.72-1.58 (m, 3H), 0.97 (d, 6.4 Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 196.6, 133.1, 132.7, 113.5, 38.0, 35.6, 33.8, 31.2, 27.5, 22.1. IR (neat): 2246, 1704, 1621 cm^{-1} .

Diethyl 4-cyano-4-(3-methylbutyl)-2-pentenedioate. The resulting oil was purified by flash chromatography (eluant: 5% EtOAc in petroleum ether) to give the title compound (E/Z = 75/25, 89% yield) as a colorless oil. E isomer: ^1H NMR (400 MHz, CDCl_3): δ 6.85 (d, 15.7 Hz, 1H),

6.33 (d, 15.7 Hz, 1H), 4.30 (q, 7.2 Hz, 2H), 4.23 (q, 7.1 Hz, 2H), 2.12 (ddd, 4.8 Hz, 12.7 Hz, 13.4 Hz, 1H), 1.89 (dt, 4.8 Hz, 12.7 Hz, 1H), 1.64-1.54 (m, 1H), 1.43-1.22 (m, 2H), 1.34 (t, 7.1 Hz, 3H), 1.32 (t, 7.1 Hz, 3H), 0.91 (d, 6.6 Hz, 6H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 166.3, 164.9, 140.3, 124.7, 116.4, 63.5, 61.0, 51.9, 35.6, 33.7, 27.7, 22.2, 22.1, 14.1, 13.9. IR (neat): 2245, 1747, 1726, 1655 cm^{-1} . Calcd for $\text{C}_{15}\text{H}_{23}\text{NO}_4$: C, 64.03; H, 8.24. Found: C, 63.88; H, 8.44. Z isomer: ^1H NMR (400 MHz, CDCl_3): δ 6.13 (d, 11.4 Hz, 1H), 6.07 (d, 11.4 Hz, 1H), 4.33-4.24 (m, 2H), 4.23 (q, 7.1 Hz, 2H), 2.17-2.04 (m, 2H), 1.65-1.55 (m, 1H), 1.52-1.29 (m, 8H), 0.93 (d, 6.6 Hz, 3H), 0.92 (d, 6.6 Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.4, 164.4, 139.7, 125.6, 117.2, 62.8, 61.1, 47.8, 37.6, 33.6, 27.9, 22.3, 14.0, 13.9. IR (neat): 2245, 1747, 1719, 1645 cm^{-1} .

Triethyl 4-phenyl-1-butene-1,3,3-tricarboxylate. The resulting oil was purified by flash chromatography (eluant: 5% EtOAc in petroleum ether) to give the title compound (E/Z = 85/15, 79% yield) as a colorless oil. Mixture of E and Z isomers: ^1H NMR (400 MHz, CDCl_3): δ 7.28-7.19 (m, 3H), 7.23 (d, 16.5 Hz, 0.85H), 7.12-7.05 (m, 2H), 6.70 (d, 12.4 Hz, 0.15H), 6.03 (d, 12.4 Hz, 0.15H), 5.93 (d, 16.5 Hz, 0.85H), 4.21 (q, 7.1 Hz, 3.4H), 4.20 (q, 7.1 Hz, 1.7H), 4.18 (q, 7.2 Hz, 0.6H), 4.18 (q, 7.2 Hz, 0.3H), 3.64 (s, 0.3H), 3.41 (s, 1.7H), 1.30 (t, 7.2 Hz, 0.45H), 1.29 (t, 7.1 Hz, 2.55H), 1.23 (t, 7.1 Hz, 5.1H), 1.22 (t, 7.2 Hz, 0.9H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 169.1 (E), 169.0, 165.8 (E), 165.7, 144.7, 144.4 (E), 136.1, 135.0 (E), 130.3, 130.2 (E), 128.5 (E), 128.2, 127.4 (E), 127.2, 123.1 (E), 121.5, 62.2 (E), 62.1, 61.1 (E), 60.9 (E), 60.7, 60.6, 42.2 (E), 41.1, 14.4, 14.1. IR (neat): 3460, 1732, 1651 cm^{-1} . Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_6$: C, 65.50; H, 6.94. Found: C, 65.64; H, 7.12.

Ethyl 5-oxo-2-cyano-5-phenyl-2-(3-methylbutyl)-3-pentenoate. The resulting oil was purified by flash chromatography (eluant: 5% EtOAc in petroleum ether) to give the title compound (E/Z = 65/35, 79% yield) as a colorless oil. E isomer: ^1H NMR (400 MHz, CDCl_3): δ 8.05-7.98 (m, 2H), 7.65-7.56 (m, 3H), 7.42 (d, 15.3 Hz, 1H), 6.95 (d, 15.3 Hz, 1H), 4.31 (q, 7.1 Hz, 2H), 2.19 (ddd, 4.8 Hz, 12.5 Hz, 13.4 Hz, 1H), 1.95 (dt, 4.6 Hz, 13.4 Hz, 1H), 1.66-1.56 (m, 1H), 1.46-1.26

(m, 2H), 1.32 (t, 7.1 Hz, 3H), 0.92 (d, 6.6 Hz, 3H), 0.91 (d, 6.6 Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 188.6, 166.6, 140.2, 137.0, 133.8, 129.0, 127.8, 117.0, 63.8, 52.8, 35.9, 34.1, 28.0, 22.4 (2), 14.2. IR (neat): 2249, 1745, 1678 cm^{-1} . Calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_3$: C, 72.82; H, 7.40. Found: C, 72.69; H, 7.45. Z isomer: ^1H NMR (400 MHz, CDCl_3): δ 8.00-7.95 (m, 2H), 7.62-7.56 (m, 1H), 7.50-7.44 (m, 2H), 7.16 (d, 11.4 Hz, 1H), 6.20 (d, 11.4 Hz, 1H), 4.29 (q, 7.1 Hz, 2H), 2.21-2.09 (m, 2H), 1.66-1.56 (m, 1H), 1.56-1.46 (m, 1H), 1.45-1.35 (m, 1H), 1.32 (t, 7.1 Hz, 3H), 0.94 (d, 6.6 Hz, 3H), 0.93 (d, 6.6 Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 190.1, 167.5, 139.4, 137.0, 133.8, 128.9, 128.4, 117.3, 62.9, 48.5, 37.9, 33.8, 28.0, 22.5 (2), 14.2. IR (neat): 2244, 1733, 1664 cm^{-1} .

Ethyl 5-oxo-2-cyano-2-(3-methylbutyl)-3-ethyl-3-hexenoate. The resulting oil was purified by flash chromatography (eluant: 20% EtOAc in petroleum ether) to give the title compound (E/Z = 60/40 or 40/60, 87% yield) as a colorless oil. Isomer 1: ^1H NMR (400 MHz, CDCl_3): δ 6.51 (s, 1H), 4.28 (q, 7.1 Hz, 1H), 4.27 (q, 7.1 Hz, 1H), 2.59 (q, 7.5 Hz, 2H), 2.29 (s, 3H), 2.20-2.10 (m, 1H), 1.98-1.90 (m, 1H), 1.66-1.56 (m, 1H), 1.32 (t, 7.1 Hz, 3H), 1.32-1.28 (m, 2H), 1.08 (t, 7.5 Hz, 3H), 0.93 (d, 6.6 Hz, 3H), 0.92 (d, 6.6 Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 197.6, 166.7, 153.9, 125.8, 117.7, 63.6, 56.7, 34.2, 33.7, 32.6, 28.2, 23.3, 22.6, 22.5, 14.2, 14.1. IR (neat): 2242, 1747, 1697, 1612 cm^{-1} . Calcd for $\text{C}_{16}\text{H}_{25}\text{NO}_3$: C, 68.79; H, 9.02. Found: C, 68.47; H, 9.19. Isomer 2: ^1H NMR (400 MHz, CDCl_3): δ 6.23 (t, 1.5 Hz, 1H), 4.24 (q, 7.1 Hz, 1H), 4.23 (q, 7.1 Hz, 1H), 2.54 (ddq, 1.5 Hz, 17.4 Hz, 7.2 Hz, 1H), 2.42 (ddq, 1.5 Hz, 17.4 Hz, 7.2 Hz, 1H), 2.29 (dt, 4.5 Hz, 13.6 Hz, 1H), 2.23 (s, 3H), 2.17 (ddd, 4.4 Hz, 12.4 Hz, 13.6 Hz, 1H), 1.64-1.43 (m, 2H), 1.30 (t, 7.1 Hz, 3H), 1.21 (t, 7.2 Hz, 3H), 1.20-1.13 (m, 1H), 0.91 (d, 6.6 Hz, 3H), 0.90 (d, 6.4 Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 197.9, 166.2, 153.3, 124.6, 118.3, 62.7, 53.8, 34.5, 33.7, 31.6, 31.5, 28.2, 22.5, 14.0, 12.7. IR (neat): 2235, 1749, 1693, 1612 cm^{-1} .

Ethyl 5-oxo-2-cyano-3-phenyl-2-(3-methylbutyl)-3-hexenoate. The resulting oil was purified by flash chromatography (eluant: 20% EtOAc in petroleum ether) to give the title compound (E/Z = 78/22 or 22/78, 77% yield) as a colorless oil. Mixture of E and Z isomers: ^1H NMR (400 MHz,

CDCl_3): δ 7.44-7.34 (m, 3H), 7.15-7.11 (m, 2H), 6.60 (s, 0.78H), 6.39 (s, 0.22H), 4.31 (dq, 1.6 Hz, 7.1 Hz, 0.44H), 4.22 (q, 7.1 Hz, 1.56H), 2.31 (s, 0.66H), 2.11 (ddd, 4.5 Hz, 12.4 Hz, 13.4 Hz, 0.78H), 1.97-1.92 (m, 0.22H), 1.92 (ddd, 4.2 Hz, 12.8 Hz, 13.4 Hz, 0.78H). 1.80 (s, 2.34H), 1.64-1.54 (m, 1H), 1.52-1.43 (m, 1H), 1.38 (t, 7.1 Hz, 0.66H), 1.35-1.22 (m, 1.22H), 1.26 (t, 7.1 Hz, 2.34H), 0.91 (d, 6.6 Hz, 2.34H), 0.90 (d, 6.6 Hz, 2.34H), 0.70 (d, 6.4 Hz, 0.66H), 0.68 (d, 6.3 Hz, 0.66H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 198.8 (E), 198.0, 167.4, 166.0 (E), 149.8, 146.5 (E), 138.8, 134.6 (E), 131.8, 131.2, 128.6, 128.5, 128.1, 128.0, 118.0, 117.3 (E), 63.3, 62.7, 60.3, 56.3, 51.1, 35.2, 34.0, 33.0, 31.3, 30.6, 27.9, 27.7, 22.3 (2), 22.1, 22.0, 21.0, 14.1, 13.9, 13.8. IR (neat): 2242, 1747, 1697, 1612 cm^{-1} . Calcd for $\text{C}_{20}\text{H}_{25}\text{NO}_3$: C, 73.37; H, 7.70. Found: C, 73.54; H, 7.85.

Ethyl 2-Cyano-2-(3-oxobutyl)-5-methylhexanoate. The resulting oil was purified by flash chromatography (eluant: 15% EtOAc in petroleum ether) to give the title compound (96% yield) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 4.28 (q, 7.1 Hz, 2H), 2.72 (ddd, 5.0 Hz, 10.6 Hz, 17.9 Hz, 1H), 2.54 (ddd, 5.3 Hz, 10.6 Hz, 17.9 Hz, 1H), 2.20 (ddd, 5.3 Hz, 10.6 Hz, 14.2 Hz, 1H), 2.18 (s, 3H), 2.08 (ddd, 5.0 Hz, 10.7 Hz, 14.2 Hz, 1H), 1.93 (ddd, 4.6 Hz, 12.5 Hz, 13.3 Hz, 1H), 1.78 (dt, 4.4 Hz, 13.0 Hz, 1H), 1.57 (m, 1H), 1.46 (ddt, 4.5 Hz, 6.6 Hz, 12.4 Hz, 1H), 1.34 (t, 7.1 Hz, 3H), 1.19 (ddt, 4.6 Hz, 6.6 Hz, 12.6 Hz, 1H), 0.91 (d, 6.6 Hz, 3H), 0.90 (d, 6.6 Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 206.0, 168.9, 119.1, 63.0, 49.2, 39.4, 35.7, 34.3, 30.9, 30.2, 28.1, 22.5, 22.4, 14.3. IR (neat): 2243, 1793, 1710 cm^{-1} . Calcd for $\text{C}_{14}\text{H}_{23}\text{NO}_3$: C, 66.37; H, 9.15. Found: C, 66.29; H, 9.46.

1-Ethyl 5-methyl 2-cyano-2-(3-methylbutyl)pentanedioate. The resulting oil was purified by flash chromatography (eluant: 10% EtOAc in petroleum ether) to give the title compound (99% yield) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 4.28 (q, 7.1 Hz, 2H), 3.70 (s, 3H), 2.59 (ddd, 5.4 Hz, 10.9 Hz, 16.4 Hz, 1H), 2.40 (ddd, 5.5 Hz, 11.1 Hz, 16.3 Hz, 1H), 2.26 (ddd, 5.4 Hz, 10.9 Hz, 14.0 Hz, 1H), 2.16 (ddd, 5.5 Hz, 11.2 Hz, 14.1 Hz, 1H), 1.94 (dt, 4.6 Hz, 12.6 Hz, 1H),

1.79 (dt, 4.6 Hz, 12.6 Hz, 1H), 1.57 (m, 1H), 1.47 (dddd, 4.6 Hz, 6.6 Hz, 11.2 Hz, 12.6 Hz, 1H), 1.34 (t, 7.1 Hz, 3H), 1.21 (dddd, 4.6 Hz, 6.6 Hz, 11.3 Hz, 12.7 Hz, 1H), 0.92 (d, 6.6 Hz, 3H), 0.91 (d, 6.6 Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 172.2, 168.7, 118.9, 63.0, 52.1, 49.2, 35.6, 34.2, 32.2, 30.2, 28.1, 22.4, 14.3. IR (neat): 2242, 1734 cm^{-1} . Calcd for $\text{C}_{14}\text{H}_{23}\text{NO}_4$: C, 62.43; H, 8.61. Found: C, 62.13; H, 8.86.

Dimethyl 8-methyl-2-nonanone-5,5-dicarboxylate. The resulting oil was purified by flash chromatography (eluant: 10% EtOAc in petroleum ether) to give the title compound (81% yield) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 3.72 (s, 6H), 2.45-2.41 (m, 2H), 2.15-2.10 (m, 2H), 2.14 (s, 3H), 1.88-1.84 (m, 2H), 1.56-1.48 (m, 1H), 1.06-1.00 (m, 2H), 0.87 (d, 6.6 Hz, 6H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 207.5, 172.2, 57.0, 52.6, 38.9, 33.1, 31.7, 31.1, 28.4, 26.7, 22.6. IR (neat): 1735 cm^{-1} . Calcd for $\text{C}_{14}\text{H}_{24}\text{O}_5$: C, 61.74; H, 8.88. Found: C, 62.00; H, 9.09.

Ethyl 4-nitrobutyrate.³ HMPT (3.3 mL, 19 mmol) was added to a solution of ethyl acrylate (20 mL, 185 mmol) in nitromethane (200 mL) at 0 °C. The mixture was stirred for 1 h. HMPT and nitromethane were removed by a rotary evaporator under reduced pressure. The resulting oil was purified by Kugelrohr distillation to give the title compound (17 g, 105 mmol, 57% yield) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 4.49 (t, 6.8 Hz, 2H), 4.16 (q, 7.1 Hz, 2H), 2.47 (t, 6.8 Hz, 2H), 2.32 (p, 6.8 Hz, 2H), 1.27 (t, 7.1 Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (50 MHz, CDCl_3): δ 172.0, 74.5, 60.9, 30.6, 22.5, 14.2. IR (neat): 1734, 1554 cm^{-1} .

(-)-Menthyl 5-oxo-2-cyano-2-(3-methylbutyl)-3-hexenoate. E isomer: ^1H NMR (400 MHz, CDCl_3): δ 6.70 (d, 15.7 Hz, 0.5H), 6.69 (d, 15.7 Hz, 0.5H), 6.58 (d, 15.9 Hz, 0.5H), 6.57 (d, 15.9 Hz, 0.5H), 4.75 (dt, 4.4 Hz, 11.0 Hz, 0.5H), 4.75 (dt, 4.4 Hz, 11.0 Hz, 0.5H), 2.32 (s, 3H), 2.17-2.08 (m, 1H), 2.2-1.94 (m, 1H), 1.92-1.78 (m, 1.5H), 1.75-1.67 (m, 1.5H), 1.60-1.57 (m, 1H), 1.55-1.45 (m, 2H), 1.44-1.33 (m, 1H), 1.32-1.21 (m, 1H), 1.12-1.00 (m, 2H), 0.94-0.88 (m, 14H), 0.76 (d, 7.0 Hz, 1.5H), 0.74 (d, 7.0 Hz, 1.5H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 196.6, 166.1, 139.2,

139.1, 132.0, 116.7, 78.5, 52.5, 46.9, 46.8, 40.5, 40.4, 36.0, 34.1, 34.0, 28.8, 28.7, 28.1, 28.0, 26.4, 23.4, 23.3, 22.4, 22.0, 20.9, 20.8, 16.3, 16.2. IR (neat): 2249, 1739, 1708, 1686, 1627 cm^{-1} . Z isomer: ^1H NMR (400 MHz, CDCl_3): δ 6.44 (d, 11.4 Hz, 0.5H), 6.43 (d, 11.2 Hz, 0.5H), 5.92 (d, 11.2 Hz, 0.5H), 5.90 (d, 11.4 Hz, 0.5H), 4.71 (dt, 4.2 Hz, 10.8 Hz, 0.5H), 4.70 (dt, 4.2 Hz, 10.8 Hz, 0.5H), 2.29 (s, 1.5H), 2.28 (s, 1.5H), 2.24-1.97 (m, 3.5H) 1.90-1.82 (m, 0.5H), 1.74-1.66 (m, 2H), 1.54-1.35 (m, 6H), 1.26-1.16 (m, 0.5H), 1.12-1.00 (m, 0.5H), 0.96-0.84 (m, 13H), 0.78 (d, 6.2 Hz, 1.5H), 0.76 (d, 6.2 Hz, 1.5H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 197.3, 197.2, 166.9, 166.7, 138.1, 137.8, 131.2, 131.1, 117.4, 117.3, 77.8, 48.5, 48.4, 47.1, 47.0, 40.5, 40.3, 38.0, 34.3, 33.9, 31.7, 31.6, 31.2, 28.2, 26.1, 25.9, 23.2, 23.1, 22.5, 22.2, 21.1, 21.0, 16.1, 15.9. Calcd for $\text{C}_{22}\text{H}_{35}\text{NO}_3$: C, 73.09; H, 9.76. Found: C, 73.07; H, 9.98.

(-)-Menthyl 5-oxo-2-cyano-2-(2-phenylethyl)-3-hexenoate. E isomer: ^1H NMR (400 MHz, CDCl_3): δ 7.34-7.16 (m, 5H), 6.73 (d, 15.9 Hz, 0.5H), 6.69- (d, 15.9 Hz, 0.5H), 6.60 (d, 15.9 Hz, 0.5H), 6.60 (d, 15.9 Hz, 0.5H), 4.79 (dt, 4.6 Hz, 10.8 Hz, 0.5H), 4.77 (dt, 4.6 Hz, 10.8 Hz, 0.5H), 2.85-2.68 (m, 2H), 2.48-2.38 (m, 1H), 2.29 (s, 3H), 2.24-2.13 (m, 1H), 2.02-1.95 (m, 1H), 1.92-1.80 (m, 1H), 1.76-1.67 (m, 2H), 1.58-1.46 (m, 2H), 1.14-1.02 (m, 2H), 0.94-0.88 (m, 7H), 0.79 (d, 7.1 Hz, 1.5H), 0.74 (d, 7.1 Hz, 1.5H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 196.5, 196.4, 165.8, 139.3, 139.2, 138.7, 138.6, 132.3, 128.9, 128.6, 127.0, 116.4, 78.7, 52.4, 52.2, 46.9, 46.8, 40.5, 40.4, 39.2, 34.1, 31.7, 31.6, 28.7, 26.5, 26.4, 23.4, 23.3, 22.1, 20.9, 16.3, 16.2. IR (neat): 3029, 2245, 1739, 1706, 1681, 1627 cm^{-1} . Z isomer: ^1H NMR (400 MHz, CDCl_3): δ 7.34-7.28 (m, 2H), 7.27-7.17 (m, 3H), 6.46 (d, 11.2 Hz, 1H), 5.96 (d, 11.2 Hz, 0.5H), 5.95 (d, 11.2 Hz, 0.5H), 4.79-4.71 (m, 1H), 2.95-2.75 (m, 2.5H), 2.44-2.34 (m, 2H), 2.31 (s, 1.5H), 2.30 (s, 1.5H), 2.26-2.14 (m, 1H), 2.08-2.01 (m, 0.5H), 1.89-1.83 (m, 0.5H), 1.76-1.66 (m, 2.5H), 1.60-1.52 (m, 2.5H), 1.26-1.16 (m, 0.5H), 1.12-1.00 (m, 1H), 0.95 (d, 7.1 Hz, 1.5H), 0.94 (d, 6.4 Hz, 1.5H), 0.91 (d, 6.6 Hz, 1.5H), 0.90 (d, 7.0 Hz, 1.5H), 0.83 (d, 7.0 Hz, 1.5H), 0.75 (d, 7.0 Hz, 1.5H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 197.4, 197.3, 166.6, 166.4, 139.8, 139.7, 137.6, 137.4, 131.3, 131.2, 128.9, 128.7, 128.6, 126.8, 117.1, 117.0, 78.0, 77.8, 48.5, 48.4, 47.1, 47.0, 41.5, 41.3, 40.5, 40.3, 34.3, 34.2, 31.7, 31.6,

31.3, 31.2, 26.2, 25.9, 23.2, 23.1, 22.2, 21.1, 21.0, 16.1, 15.9. IR (neat): 2959, 2245, 1738, 1722, 1696 cm^{-1} .

(-)-Menthyl 2-(3-oxo-1-butenyl)-1-indanone-2-carboxylate. Mixture of E and Z isomers (E/Z = 40/60), 2 diastereomers for each: ^1H NMR (400 MHz, CDCl_3): δ 7.81-7.75 (m, 1H), 7.69-7.59 (m, 1H), 7.54-7.50 (m, 0.4H), 4.47-7.34 (m, 1.6H), 7.32 (d, 16.7 Hz, 0.2H), 7.29 (d, 16.5 Hz, 0.2H), 6.66 (d, 11.5 Hz, 0.3H), 6.65 (d, 11.5 Hz, 0.3H), 6.45 (d, 11.5 Hz, 0.3H), 6.44 (d, 11.5 Hz, 0.3H), 6.11 (d, 16.5 Hz, 0.2H), 6.10 (d, 16.5 Hz, 0.2H), 4.72 (dt, 4.6 Hz, 11.0 Hz, 0.2H), 4.71 (dt, 4.6 Hz, 11.0 Hz, 0.2H), 4.56 (dt, 4.4 Hz, 11.0 Hz, 0.3H), 4.53 (dt, 4.4 Hz, 11.0 Hz, 0.3H), 4.06 (d, 7.4 Hz, 0.3H), 3.97 (d, 7.4 Hz, 0.3H), 3.86 (d, 7.2 Hz, 0.2H), 3.84 (d, 7.2 Hz, 0.2H), 3.37 (d, 7.2 Hz, 0.2H), 3.36 (d, 7.2 Hz, 0.2H), 3.16 (d, 7.2 Hz, 0.3H), 3.08 (d, 7.2 Hz, 0.3H), 2.25 (s, 1.2H), 2.20 (s, 1.8H), 2.02-1.88 (m, 1H), 1.71-1.52 (m, 3H), 1.50-1.30 (m, 1.6H), 1.22-1.13 (m, 0.6H), 1.02-0.74 (m, 2.8H), 0.89 (d, 6.6 Hz, 0.6H), 0.88 (d, 6.6 Hz, 0.6H), 0.85 (d, 6.6 Hz, 0.9H), 0.84 (d, 7.0 Hz, 0.6H), 0.83 (d, 6.6 Hz, 0.9H), 0.81 (d, 7.0 Hz, 0.6H), 0.77 (d, 7.0 Hz, 0.9H), 0.71 (d, 7.0 Hz, 0.6H), 0.70 (d, 7.0 Hz, 0.6H), 0.68 (d, 7.0 Hz, 0.9H), 0.62 (d, 7.0 Hz, 0.9H), 0.58 (d, 7.0 Hz, 0.9H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 200.3, 200.2, 198.7, 198.5, 198.4, 198.3, 198.0, 197.9, 169.2, 168.9, 168.6, 168.3, 153.6, 152.9, 152.6, 152.4, 143.8, 143.5, 143.0, 142.9, 136.1, 136.0, 135.6, 135.4, 135.2, 134.1, 134.0, 131.4, 131.3, 128.7, 128.6, 128.5, 128.4, 127.8, 127.7, 126.6, 126.5, 126.0, 125.9, 125.7, 125.6, 124.7, 124.6, 77.1, 77.0, 76.7, 76.6, 63.9, 63.6, 63.3, 63.2, 47.0, 46.9, 41.2, 40.1, 40.4, 40.3, 40.2, 34.3, 34.2, 31.6, 31.5, 31.3, 27.1, 27.0, 26.3, 25.8, 23.5, 23.3, 23.1, 13.0, 22.1, 21.0, 20.9, 20.8, 16.3, 16.2, 15.9, 15.8. IR (neat): 1747, 1723, 1717, 1679, 1616, 1593 cm^{-1} . Calcd for $\text{C}_{24}\text{H}_{30}\text{O}_4$: C, 75.36; H, 7.91. Found: C, 75.03; H, 7.80.

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