Supporting Information for:

**Cyanoesterification of 1,2-Dienes: Synthesis and Transformations of
Highly Functionalized α -Cyanomethylacrylate Esters**

Yoshiaki Nakao,* Yasuhiro Hirata, and Tamejiro Hiyama*

Department of Material Chemistry, Graduate School of Engineering,

Kyoto University, Kyoto 615-8510 Japan

General. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere or in a dry box under a nitrogen atmosphere. Flush column chromatography was performed using Kanto Chemical silica gel (spherical, 40–50 μ m). Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F₂₅₄ (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline KMnO₄ solution followed by heating.

Apparatus. Proton and carbon nuclear magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded on a Varian Mercury 400 (¹H NMR, 400 MHz; ¹³C NMR, 101 MHz) spectrometer with solvent resonance as the internal standard (¹H NMR, CHCl₃ at 7.26 ppm; ¹³C NMR, CDCl₃ at 77.0 ppm). ¹H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, br = broad, m = multiplet), coupling constants (Hz), and integration. Melting points were determined using a YANAKO MP-500D. IR spectra recorded on a Shimadzu FT-IR 8400 spectrometer are reported in cm⁻¹. Mass spectra (EI) were obtained with a JEOL JMS-700 spectrometer. GC analysis was performed on a Shimadzu GC 2010 equipped with a DB-5 column (30 m x 0.53 mm, pressure = 31.7 kPa, detector = FID, 290 °C) with helium gas as a carrier. Preparative recycling gel permeation chromatography (GPC) and recycling silica gel chromatography were performed with a JAI LC-908 chromatograph equipped with JAIGEL-1H and -2H (chloroform as an eluent) or COSMOSIL 5SL-II (hexane–ethyl acetate as an eluent), respectively.

Chemicals. Unless otherwise noted, commercially available reagents were used without purification. Toluene was distilled from sodium/benzophenone ketyl. 1,2-Dienes were prepared according to the literature procedures.¹

Nickel-catalyzed cyanoesterification of 1,2-dienes. A general procedure. To a stirred mixture of ethyl cyanoformate (119 mg, 1.2 mmol) and a 1,2-diene (1.0 mmol) in a vial was added a solution of Ni(cod)₂ (28 mg, 0.10 mmol) and PMe₂Ph (27 mg, 0.20 mmol) in toluene (2.0 mL) in a dry box. The vial was taken outside the dry box and heated at 50 °C for the time specified in Tables 1 and 2. The resulting mixture was filtered through a silica gel pad, concentrated in vacuo, and purified by flash silica gel column chromatography to give the corresponding cyanoesterification products in yields listed in Tables 1 and 2.

Ethyl 2-(1-cyano-3-phenylprop-1-yl)acrylate (3aa). A colorless oil, *R_f* 0.28 (hexane–ethyl acetate = 5:1). ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.28 (m, 3H), 7.25–7.19 (m, 2H), 6.47 (s, 1H), 6.07 (s, 1H), 4.29–4.18 (m, 2H), 3.81–3.74 (m, 1H), 2.95–2.86 (m, 1H), 2.83–2.73 (m, 1H), 2.20–2.09 (m, 1H), 2.07–1.96 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 164.5, 139.6, 135.6, 128.6, 128.4, 127.9, 126.5, 119.6, 61.6, 34.3, 33.12, 33.10, 14.1; IR (neat) 2982, 2934, 2243, 1714, 1632, 1454, 1259, 1140, 1028, 960, 816, 750, 700 cm⁻¹; Anal. Calcd for C₁₅H₁₇NO₂; C, 74.05; H, 7.04. Found: C, 74.12; H, 7.11.

Ethyl (Z)-(2-cyanomethyl)-5-phenyl-2-pentenoate [(Z)-4aa]. A colorless oil, *R_f* 0.18 (hexane–ethyl acetate = 5:1). ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.27 (m, 2H), 7.24–7.18 (m, 3H), 6.45 (tt, *J* = 7.6, 1.3 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.31 (d, *J* = 1.3 Hz, 2H), 2.95 (q, *J* = 7.6 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 164.8, 147.1, 140.7, 128.5, 128.4, 126.2, 121.7, 117.2, 61.1, 34.9, 31.2, 22.6, 14.1; IR (neat) 2981, 2936, 2253, 1720, 1647, 1454, 1383, 1217, 1107, 1028, 750, 700 cm⁻¹; Anal. Calcd for C₁₅H₁₇NO₂; C, 74.05; H, 7.04. Found: C, 73.75; H, 7.19.

Ethyl (E)-(2-cyanomethyl)-5-phenyl-2-pentenoate [(E)-4aa]. A colorless oil, *R_f* 0.18 (hexane–ethyl acetate = 5:1). ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.27 (m, 2H), 7.27–7.16 (m, 3H), 7.08 (t, *J* = 7.7 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.24 (s, 2H), 2.83 (t, *J* = 7.7 Hz, 2H), 2.60 (q, *J* = 7.7 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 165.1, 146.2, 140.1, 128.6, 128.2, 126.4, 122.8, 116.9, 61.4, 34.1, 31.0, 14.9, 14.1; IR (neat) 2982, 2251, 1709, 1653, 1454, 1373, 1288, 1213, 1103, 748, 700 cm⁻¹; Anal. Calcd for C₁₅H₁₇NO₂; C, 74.05; H, 7.04. Found: C, 74.32; H, 7.25.

Ethyl 2-(1-cyanoheptan-1-yl)acrylate (3ab). A colorless oil, R_f 0.43 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 6.44 (s, 1H), 6.04 (s, 1H), 4.32–4.19 (m, 2H), 3.83–3.75 (m, 1H), 1.85–1.62 (m, 2H), 1.60–1.22 (m, 11H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.7, 135.9, 127.6, 120.0, 61.6, 33.5, 32.8, 31.4, 28.5, 26.9, 22.5, 14.1, 14.0; IR (neat) 2930, 2860, 2243, 1720, 1632, 1468, 1254, 1151, 1026, 959, 816 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{21}\text{NO}_2$; C, 69.92; H, 9.48. Found: C, 70.19; H, 9.35.

Ethyl (Z)-(2-cyanomethyl)-2-nonenolate [(Z)-4ab]. A colorless oil, R_f 0.38 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 6.41 (tt, J = 7.5, 1.3 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.34 (d, J = 1.3 Hz, 2H), 2.60 (q, J = 7.5 Hz, 2H), 1.50–1.40 (m, 2H), 1.37–1.22 (m, 9H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 165.1, 148.7, 120.9, 117.4, 61.0, 31.5, 29.7, 29.0, 28.9, 22.7, 22.5, 14.1, 14.0; IR (neat) 2928, 2255, 1724, 1647, 1466, 1383, 1213, 1142, 1096, 1024, 860 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{21}\text{NO}_2$: M^+ , 223.1572. Found: m/z 223.1575.

Ethyl 2-[cyano(cyclohexyl)methyl]acrylate (3ac). A colorless oil, R_f 0.43 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 6.47 (s, 1H), 5.99 (d, J = 0.8 Hz, 1H), 4.31–4.17 (m, 2H), 3.77 (dd, J = 4.9, 0.8 Hz, 1H), 1.86–1.61 (m, 6H), 1.32 (t, J = 7.1 Hz, 3H), 1.30–1.02 (m, 5H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.9, 134.5, 128.4, 119.1, 61.5, 40.1, 39.2, 31.6, 28.4, 26.0, 25.73, 25.69, 14.1; IR (neat) 2931, 2855, 2241, 1717, 1632, 1450, 1266, 1151, 1024, 959, 816 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_2$; C, 70.56; H, 8.65. Found: C, 70.48; H, 8.59.

Ethyl (Z)-(2-cyanomethyl)-4-cyclohexyl-2-butenolate [(Z)-4ac]. A colorless oil, R_f 0.33 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 6.19 (d, J = 9.7 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.32 (s, 2H), 3.18–3.06 (m, 1H), 1.78–1.62 (m, 5H), 1.33 (t, J = 7.1 Hz, 3H), 1.38–1.04 (m, 5H); ^{13}C NMR (101 MHz, CDCl_3) δ 165.0, 153.3, 119.2, 117.4, 61.0, 38.2, 32.2, 25.7, 25.4, 22.7, 14.1; IR (neat) 2928, 2853, 2253, 1722, 1643, 1448, 1217, 1153, 1097, 1022, 978 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_2$; C, 70.56; H, 8.65. Found: C, 70.68; H, 8.57.

Ethyl 2-[1-cyano-2,2-dimethylprop-1-yl]acrylate (3ad). A colorless oil, R_f 0.40 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 6.53 (s, 1H), 6.00 (s, 1H), 4.24 (q, $J = 7.1$ Hz, 2H), 3.94 (s, 1H), 1.31 (t, $J = 7.1$ Hz, 3H), 1.03 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 165.7, 134.7, 129.5, 119.9, 61.7, 43.0, 35.1, 26.9, 14.1; IR (neat) 2970, 2241, 1720, 1628, 1465, 1371, 1263, 1182, 1142, 1022, 961, 814 cm^{-1} ; Anal. Calcd for $\text{C}_{11}\text{H}_{17}\text{NO}_2$; C, 67.66; H, 8.78. Found: C, 67.61; H, 8.59.

Ethyl 2-[1-cyano-3-(2-tetrahydro-2H-pyranoxy)prop-1-yl]acrylate (3ae, mixture of diastereomers). A colorless oil, R_f 0.33 (hexane–ethyl acetate = 2:1). ^1H NMR (400 MHz, CDCl_3) δ 6.46 (s, 1H), 6.04 (s, 1H), 4.60 (t, $J = 3.2$ Hz, 1H), 4.26 (q, $J = 7.1$ Hz, 2H), 4.05–3.96 (m, 1H), 3.95–3.78 (m, 2H), 3.59–3.46 (m, 2H), 2.18–2.08 (m, 1H), 2.05–1.94 (m, 1H), 1.90–1.46 (m, 6H), 1.32 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.5, 135.6, 128.1, 128.0, 119.61, 119.56, 99.1, 98.3, 64.0, 63.5, 62.3, 62.0, 61.5, 32.7, 32.6, 30.83, 30.80, 30.4, 30.3, 25.3, 19.3, 19.1, 14.1; IR (neat) 2943, 2871, 2243, 1720, 1632, 1369, 1261, 1202, 1136, 1036, 968, 870, 816 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_4$; C, 62.90; H, 7.92. Found: C, 63.19; H, 8.21.

Ethyl (Z)-2-(cyanomethyl)-5-(2-tetrahydro-2H-pyranoxy)-2-pentenoate [(Z)-4ae]. A colorless oil, R_f 0.25 (hexane–ethyl acetate = 2:1). ^1H NMR (400 MHz, CDCl_3) δ 6.54 (t, $J = 7.0$ Hz, 1H), 4.60 (t, $J = 3.5$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 3.89–3.80 (m, 2H), 3.56–3.46 (m, 2H), 3.36 (d, $J = 1.3$ Hz, 2H), 2.88–2.84 (m, 2H), 1.88–1.45 (m, 6H), 1.32 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.9, 145.4, 122.3, 117.2, 98.8, 65.9, 62.3, 61.2, 30.5, 30.3, 25.4, 22.7, 19.5, 14.1; IR (neat) 2945, 2253, 1720, 1649, 1383, 1215, 1121, 1034, 986, 870, 814 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_4$; M^+ , 267.1471. Found: m/z 267.1467.

Ethyl 2-[1-cyano-3-(tert-butyldimethylsilyloxy)prop-1-yl]acrylate (3af). A colorless oil, R_f 0.38 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 6.45 (s, 1H), 6.02 (s, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 4.01 (dd, $J = 9.6, 4.7$ Hz, 1H), 3.84–3.71 (m, 2H), 2.09–1.98 (m, 1H), 1.93–1.83 (m, 1H), 1.32 (t, $J = 7.1$ Hz, 3H), 0.90 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.5, 135.8, 128.0, 119.7, 61.5, 59.6, 35.5, 30.3, 25.8, 18.2, 14.1, –5.5, –5.6; IR (neat) 2930, 2858, 2243, 1720, 1632, 1472, 1258, 1150, 1111, 951, 835, 777 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{27}\text{NO}_3\text{Si}$; C, 60.57; H, 8.59.

9.15. Found: C, 60.52; H, 8.93.

Ethyl (Z)-2-(cyanomethyl)-5-(tert-butyldimethylsilyloxy)-2-pentenoate

[(Z)-4af]. A colorless oil, R_f 0.23 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 6.52 (tt, $J = 7.0, 1.3$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 3.72 (t, $J = 6.2$ Hz, 2H), 3.35 (d, $J = 1.4$ Hz, 2H), 2.84 (dt, $J = 7.0, 6.2$ Hz, 2H), 1.32 (t, $J = 7.1$ Hz, 3H), 0.88 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.9, 145.4, 122.1, 117.2, 61.7, 61.1, 33.2, 25.8, 22.7, 18.2, 14.1, -5.4 ; IR (neat) 2957, 2858, 2255, 1724, 1472, 1385, 1215, 1099, 837, 777 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{27}\text{NO}_3\text{Si}$; C, 60.57; H, 9.15. Found: C, 60.65; H, 9.01.

Ethyl 2-(1,4-dicyanobut-1-yl)acrylate (3ag).

A colorless oil, R_f 0.20 (hexane–ethyl acetate = 2:1). ^1H NMR (400 MHz, CDCl_3) δ 6.49 (s, 1H), 6.08 (s, 1H), 4.19–4.32 (m, 2H), 3.85 (dd, $J = 7.4, 4.7$ Hz, 1H), 2.43 (t, $J = 6.7$ Hz, 2H), 2.04–1.74 (m, 4H), 1.32 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.3, 134.9, 128.3, 119.0, 118.6, 61.8, 33.0, 31.4, 22.7, 16.6, 14.0; IR (neat) 2984, 2245, 1715, 1632, 1421, 1258, 1146, 1024, 964, 816 cm^{-1} ; Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_2$; C, 64.06; H, 6.84. Found: C, 63.90; H, 6.86.

Ethyl (Z)-2-(cyanomethyl)-6-cyano-2-hexenoate [(Z)-4ag].

A colorless oil, R_f 0.14 (hexane–ethyl acetate = 2:1). ^1H NMR (400 MHz, CDCl_3) δ 6.36 (tt, $J = 7.7, 1.4$ Hz, 1H), 4.26 (q, $J = 7.1$ Hz, 2H), 3.37 (d, $J = 1.3$ Hz, 2H), 2.76 (q, $J = 7.7$ Hz, 2H), 2.39 (t, $J = 7.1$ Hz, 2H), 1.84 (tt, $J = 7.7, 7.1$ Hz, 2H), 1.33 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.5, 144.6, 123.2, 119.1, 117.0, 61.4, 28.4, 24.6, 22.6, 16.8, 14.1; IR (neat) 2984, 2247, 1713, 1651, 1416, 1244, 1123, 1028 cm^{-1} ; Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_2$; C, 64.06; H, 6.84. Found: C, 64.19; H, 6.88.

Ethyl 2-(1-cyano-5-N-phthaloylpent-1-yl)acrylate (3ah).

A colorless oil, R_f 0.21 (hexane–ethyl acetate = 3:1). ^1H NMR (400 MHz, CDCl_3) δ 7.82–7.71 (m, 2H), 7.70–7.60 (m, 2H), 6.38 (s, 1H), 5.98 (s, 1H), 4.19 (q, $J = 7.1$ Hz, 2H), 3.75 (dd, $J = 8.8, 4.9$ Hz, 1H), 3.65 (t, $J = 7.0$ Hz, 2H), 1.87–1.37 (m, 6H), 1.26 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.1, 164.3, 135.4, 133.8, 131.8, 127.6, 123.0, 119.5, 61.4, 37.1, 33.2, 31.9, 27.6, 23.9, 13.9; IR (neat) 2939, 2866, 2243, 1771,

1713, 1633, 1396, 1371, 1259, 1152, 1047 cm^{-1} ; Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_4$; C, 67.05; H, 5.92. Found: C, 67.14; H, 6.01.

4ah (*Z:E* = 90:10)

Ethyl 2-(cyanomethyl)-7-*N*-phthaloyl-2-heptenoate [4ah, a mixture of stereoisomers (*Z:E* = 90:10)]. A colorless oil, R_f 0.10 (hexane–ethyl acetate = 3:1).

^1H NMR (400 MHz, CDCl_3) δ 7.85–7.77 (m, 2H), 7.73–7.65 (m, 2H), 6.98 (t, J = 7.5 Hz, 0.10H), 6.35 (t, J = 7.5 Hz, 0.90H), 4.22 (q, J = 7.1 Hz, 1.80H), 4.09 (q, J = 7.1 Hz, 0.20H), 3.58 (t, J = 7.1 Hz, 2H), 3.38 (s, 0.20H), 3.32 (d, J = 1.3 Hz, 1.80H), 2.64 (dt, J = 7.7, 7.5 Hz, 1.80H), 2.33 (dt, J = 7.7, 7.5 Hz, 0.20H), 1.76–1.64 (m, 2H), 1.58–1.42 (m, 2H), 1.29 (t, J = 7.1 Hz, 2.70H), 1.23 (t, J = 7.1 Hz, 0.30H); ^{13}C NMR [for (*Z*)-4ah, 101 MHz, CDCl_3] δ 168.3, 164.8, 147.4, 133.8, 132.0, 123.1, 121.5, 117.2, 61.1, 37.5, 29.0, 28.2, 26.1, 22.6, 14.1; IR (neat) 2939, 2864, 2253, 1773, 1715, 1396, 1375, 1215, 721 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_4$: M^+ , 340.1423. Found: m/z 340.1429.

3ba

Benzyl 2-(1-cyano-3-phenylprop-1-yl)acrylate (3ba). A colorless oil, R_f 0.23

(hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.44–7.14 (m, 10H), 6.51 (s, 1H), 6.11 (d, J = 1.0 Hz, 1H), 5.24 (d, J = 12.3 Hz, 1H), 5.19 (d, J = 12.3 Hz, 1H), 3.79 (ddd, J = 9.5, 4.8, 1.0 Hz, 1H), 2.94–2.83 (m, 1H), 2.82–2.70 (m, 1H), 2.20–2.08 (m, 1H), 2.06–1.94 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.3, 139.5, 135.4, 135.2, 128.7, 128.6, 128.5, 128.4, 128.3, 126.5, 119.5, 67.3, 34.2, 33.3, 33.1; IR (neat) 3030, 2932, 2243, 1720, 1631, 1497, 1454, 1259, 1136, 961, 750, 698 cm^{-1} ; Anal. Calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_2$; C, 78.66; H, 6.27. Found: C, 78.96; H, 6.44.

4ba

Benzyl (2-cyanomethyl)-5-phenyl-2-pentenoate [4ba, a mixture of stereoisomers (*Z:E* = 91:9)]. A colorless oil, R_f 0.13 (hexane–ethyl acetate = 5:1).

^1H NMR (400 MHz, CDCl_3) δ 7.32–6.96 (m, 10.09H), 7.37 (tt, J = 7.5, 1.3 Hz, 0.91H), 5.12 (s, 0.18H), 5.10 (s, 1.82H), 3.23 (d, J = 1.3 Hz, 1.82H), 3.14 (s, 0.18H), 2.82 (td, J = 8.1, 7.5 Hz, 1.82H), 2.70 (t, J = 7.7 Hz, 0.18H), 2.64 (t, J = 8.1 Hz, 1.82H), 2.49 (q, J = 7.7 Hz, 0.18H); ^{13}C NMR [for (*Z*)-4ba, 101 MHz, CDCl_3] δ 164.6, 147.7, 140.6, 135.2, 128.7, 128.6, 128.5, 128.4, 128.3, 126.1, 121.4, 117.2, 67.0, 34.8, 31.3, 22.6; IR (neat) 3028, 2930, 2253, 1707, 1497, 1454, 1215, 1113, 750, 698 cm^{-1} ; Anal. Calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_2$; C, 78.66; H, 6.27. Found: C, 78.64; H, 6.35.

Ethyl 2-(2-cyanoprop-2-yl)acrylate (3ai). A colorless oil, R_f 0.30 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 6.36 (s, 1H), 5.96 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.65 (s, 6H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.4, 140.6, 126.1, 123.4, 61.3, 35.6, 26.7, 14.1; IR (neat) 2986, 2238, 1720, 1624, 1466, 1367, 1313, 1213, 1111, 1024, 964, 814 cm^{-1} ; Anal. Calcd for $\text{C}_9\text{H}_{13}\text{NO}_2$; C, 64.65; H, 7.84. Found: C, 64.38; H, 7.84.

Ethyl 2-(cyanomethyl)-3-methyl-2-butenate (4ai). A colorless oil, R_f 0.28 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 4.24 (q, J = 7.1 Hz, 2H), 3.38 (s, 2H), 2.20 (s, 3H), 1.99 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.0, 153.3, 117.6, 116.9, 60.9, 23.9, 23.5, 18.2, 14.2; IR (neat) 2984, 2249, 1715, 1639, 1371, 1283, 1205, 1078, 1020 cm^{-1} ; Anal. Calcd for $\text{C}_9\text{H}_{13}\text{NO}_2$; C, 64.65; H, 7.84. Found: C, 64.71; H, 8.12.

Ethyl (Z)-2-(1-cyanopent-1-yl)-2-heptenoate (3aj). A colorless oil, R_f 0.35 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 6.39 (t, J = 7.5 Hz, 1H), 4.31–4.18 (m, 2H), 3.72 (dd, J = 8.8, 5.6 Hz, 1H), 2.62–2.46 (m, 2H), 1.80–1.60 (m, 2H), 1.56–1.24 (m, 8H), 1.32 (t, J = 7.1 Hz, 3H), 0.91 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 165.5, 146.4, 126.9, 120.5, 61.0, 35.2, 33.1, 31.1, 29.4, 29.0, 22.4, 22.0, 14.2, 13.8, 13.7; IR (neat) 2959, 2862, 2241, 1722, 1641, 1466, 1383, 1229, 1148 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{25}\text{NO}_2$; C, 71.67; H, 10.02. Found: C, 71.39; H, 9.85.

Benzoylcyanation of 5-phenyl-1,2-pentadiene. To a stirred mixture of benzyol cyanide (131 mg, 1.0 mmol) and 5-phenyl-1,2-pentadiene (288 mg, 2.0 mmol) in a vial was added a solution of $\text{Ni}(\text{cod})_2$ (28 mg, 0.10 mmol) and PMePh_2 (40 mg, 0.20 mmol) in toluene (2.0 mL) in a dry box. The vial was taken outside the dry box and heated at 70 °C for 60 h. The resulting mixture was filtered through a silica gel pad, concentrated in vacuo, and purified by flash silica gel column chromatography followed by preparative GPC to give 3-benzoyl-2-(2-phenylethyl)-3-butenenitrile (**11**, 129 mg, 47%) as a colorless oil, R_f 0.25 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.76–7.68 (m, 2H), 7.63–7.56 (m, 1H), 7.52–7.43 (m, 2H), 7.36–7.27 (m, 2H), 7.25–7.17 (m, 3H), 6.42 (s, 1H), 5.60 (s, 1H), 4.12 (dd, J = 9.3, 4.2 Hz, 1H), 3.00–2.90 (m, 1H), 2.88–2.78 (m, 1H), 2.19–1.96 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 194.7, 142.4, 139.6, 136.6, 133.0, 129.5, 129.0, 128.6, 128.5, 128.4, 126.5, 119.8, 34.1, 33.4, 33.3; IR

(neat) 3028, 2928, 2241, 1659, 1597, 1448, 1263, 984, 752, 698 cm^{-1} ; Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{NO}$; C, 82.88; H, 6.22. Found: C, 82.74; H, 6.28.

1,4-Addition of *n*-BuCu·BF₃ to **3ai.** A 1.6 M solution of *n*-BuLi in hexane (10 mL, 16 mmol) was added dropwise to a suspension of CuI (3.0 g, 16 mmol) in diethyl ether (24 mL) at $-40\text{ }^{\circ}\text{C}$. To this was added dropwise BF₃·Et₂O (2.0 mL, 16 mmol) and **3ai** (0.67 g, 4.0 mmol) sequentially at $-70\text{ }^{\circ}\text{C}$. The resulting mixture was stirred at the same temperature for 2 h and then at rt for 5 h. The reaction was quenched by a saturated NH₄Cl aqueous solution, and the aqueous layer was extracted with diethyl ether for three times. The combined organic layers were washed with water for six times followed by brine and dried over anhydrous MgSO₄. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel to give ethyl 2-(2-cyanoprop-2-yl)heptanoate (**12a**, 0.74 g, 82%) as a colorless oil, *R*_f 0.24 (hexane–ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 4.19 (q, *J* = 7.1 Hz, 2H), 2.38 (dd, *J* = 11.9, 3.3 Hz, 1H), 1.90–1.77 (m, 1H), 1.70–1.58 (m, 1H), 1.40 (s, 3H), 1.38 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.36–1.18 (m, 6H), 0.87 (t, *J* = 5.7 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.3, 123.5, 60.8, 53.6, 34.5, 31.4, 28.7, 27.2, 26.0, 24.0, 22.3, 14.2, 13.9; IR (neat) 2957, 2235, 1734, 1466, 1375, 1258, 1178, 1144, 1026 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{23}\text{NO}_2$; C, 62.29; H, 10.29. Found: C, 62.32; H, 10.04.

1,4-Addition of diethyl malonate to **3ai.** A solution of sodium malonate was prepared by treatment of diethyl malonate (34 mg, 0.21 mmol) with NaH (6.2 mg, 0.26 mmol) at $0\text{ }^{\circ}\text{C}$ in THF (0.4 mL). This was added to a solution of **3ai** (33 mg, 0.20 mmol) in THF (0.4 mL) at $0\text{ }^{\circ}\text{C}$, and the resulting mixture was stirred at rt for 1 h. The reaction mixture was quenched by a few drops of water and was filtered through a pad of anhydrous MgSO₄. The residue was purified by flash chromatography on silica gel to give triethyl 2,2-dimethylpentanenitrile-3,5,5-tricarboxylate (**12b**, 49 mg, 74%) as a colorless oil, *R*_f 0.13 (hexane–ethyl acetate = 5:1). ¹H NMR (400 MHz, CDCl₃) δ 4.28–4.10 (m, 6H), 3.27 (dd, *J* = 10.3, 4.9 Hz, 1H), 2.47 (dd, *J* = 10.9, 4.1 Hz, 1H), 2.38–2.23 (m, 2H), 1.44 (s, 3H), 1.39 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 171.2, 168.3, 122.7, 61.8, 61.7, 61.3, 51.0, 49.8, 34.4, 27.5, 25.5, 24.6, 14.1, 14.0, 13.9; IR (neat) 2984, 2237, 1732, 1468, 1447, 1371, 1246, 1177, 1038, 854 cm^{-1} ; Anal. Calcd for $\text{C}_{16}\text{H}_{25}\text{NO}_5$; C, 58.70; H, 7.70. Found: C, 58.68; H, 7.59.

γ -Lactam synthesis from 12a. NaBH₄ (189 mg, 5.0 mmol) was added portionwise to a solution of **12a** (113 mg, 0.5 mmol) and CoCl₂ (130 mg, 1.0 mmol) in EtOH (14 mL) at 0 °C. The resulting mixture was stirred at rt for 1.5 h and then at rt overnight. The reaction was quenched with a 1 M HCl aqueous solution and the mixture was stirred at rt for 0.5 h. After neutralization with a saturated NaHCO₃ aqueous solution, the mixture was extracted with diethyl ether. The combined organic layers were washed with water for three times followed by brine and dried over anhydrous MgSO₄. The residue was purified by flash chromatography on silica gel to give 2-butyl-3,3-dimethyl-2-pyrrolidone (**13**, 59 mg, 64%) as a white solid (mp 88.6–89.2 °C), R_f 0.13 (hexane–ethyl acetate = 5:1). ¹H NMR (400 MHz, CDCl₃) δ 6.31 (br s, 1H), 3.03 (d, J = 9.3 Hz, 1H), 2.95 (d, J = 9.3 Hz, 1H), 1.98 (t, J = 6.8 Hz, 1H), 1.68–1.50 (m, 2H), 1.48–1.22 (m, 6H), 1.15 (s, 3H), 0.99 (s, 3H), 0.88 (t, J = 6.6 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 180.3, 54.2, 51.5, 39.5, 32.1, 28.0, 27.2, 25.6, 22.5, 22.0, 14.1; IR (KBr) 3201, 3091, 2956, 2930, 2870, 1707, 1682, 1465, 1321, 1078, 797, 706, 581, 542 cm⁻¹; Anal. Calcd for C₁₁H₂₁NO; C, 72.08; H, 11.55. Found: C, 71.78; H, 11.47.

Carbocyanation of 4-octyne using 3aa. **3aa** (1.0 mmol) and 4-octyne (165 mg, 1.5 mmol) were added to a solution of Ni(cod)₂ (28 mg, 0.10 mmol) and P(4-CF₃-C₆H₄)₃ (92 mg, 0.20 mmol) in CH₃CN (2.0 mL) in a dry box. The vial was taken outside the dry box and heated at 80 °C for 8 h. The resulting mixture was filtered through a silica gel pad, concentrated in vacuo, and purified by flash silica gel column chromatography to give (2*Z*)-5-ethoxycarbonyl-8-phenyl-2,3-dipropylocta-2,5-dienenitrile [**14**, mixture of stereoisomers (5*E*:5*Z* = 83:17), 288 mg, 81%] as a colorless oil, R_f 0.41(hexane–ethyl acetate = 5:1). Stereoisomers were further separated by preparative recycling silica gel chromatography.

(5E)-14. ¹H NMR (400 MHz, CDCl₃) δ 7.35–7.15 (m, 5H), 6.99 (t, J = 7.5 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.47 (s, 2H), 2.77 (t, J = 7.5 Hz, 2H), 2.56 (q, J = 7.5 Hz, 2H), 2.17 (t, J = 7.3 Hz, 2H), 1.96 (t, J = 8.1 Hz, 2H), 1.56 (sext, J = 7.5 Hz, 2H), 1.40–1.25 (m, 5H), 0.93 (t, J = 7.3 Hz, 3H), 0.87 (t, J = 7.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.3, 156.3, 144.8, 140.7, 129.0, 128.5, 128.3, 126.2, 119.2, 111.2, 60.8, 34.7, 33.3, 32.4, 31.7, 30.6, 21.8, 21.6, 14.2, 13.5; IR (neat) 2963, 2206, 1713, 1643, 1454, 1277, 1120, 1053, 914, 765, 700 cm⁻¹; HRMS (EI) Calcd for C₂₃H₃₁NO₂: M⁺, 353.2355. Found: m/z 353.2364.

(5Z)-14. ^1H NMR (400 MHz, CDCl_3) δ 7.32–7.24 (m, 2H), 7.22–7.14 (m, 3H), 5.94 (t, J = 7.3 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.35 (s, 2H), 2.88–2.70 (m, 4H), 2.18 (t, J = 7.3 Hz, 2H), 2.00 (t, J = 7.9 Hz, 2H), 1.56 (sext, J = 7.5 Hz, 2H), 1.40–1.26 (m, 5H), 0.94 (t, J = 7.3 Hz, 3H), 0.87 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.0, 156.2, 143.7, 141.1, 128.8, 128.44, 128.36, 126.0, 119.1, 112.1, 60.5, 40.1, 35.2, 32.5, 31.7, 31.0, 21.7, 21.3, 14.2, 14.1, 13.5; IR (neat) 2963, 2206, 1713, 1643, 1454, 1277, 1200, 1053, 735, 700 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{23}\text{H}_{31}\text{NO}_2$: M^+ , 353.2355. Found: m/z 353.2357.

References

- (1) (a) Brandsma, L. *Synthesis of Acetylenes, Allenes and Cumulenes: Methods and Techniques*; Elsevier: New York, 2004. (b) Trost, B. M.; Pinkerton, A. B.; Seidel, M. *J. Am. Chem. Soc.* **2001**, *123*, 12466–12476.

5310-62-11-frc.11-14

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 5310-62-11-082-isomer

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

OBSERVE H1, 399.9480266 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 1 min, 42 sec

5310-62-11-082-frc.11-14

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

158 repetitions

OBSERVE C13, 100.5670136 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 6 min, 59 sec

(Z) 4ab

5315-62-11-088-frc.22-33

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

OBSERVE H1, 399.9480264 MHz

DATA PROCESSING

Line broadening 0.2 Hz

Ft size 65536

Total time 1 min, 42 sec

5315-62-11-088-frc.22-33-13C

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

294 repetitions

OBSERVE C13, 100.5670144 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 6 min, 54 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

OBSERVE H1, 399.9480275 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 1 min, 42 sec

4ah (Z:E = 90:10)

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

386 repetitions

OBSERVE C13, 100.5670190 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 6 min, 54 sec

4ah (Z:E = 90:10)

5624-62-13-0 -NP-frc.b

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

OBSERVE H1, 399.9480270 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 1 min, 42 sec

(5E)-14

(5E)-14

5624-62-13-0 -NP-irc.b

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

354 repetitions

OBSERVE C13, 100.5670144 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 6 min, 54 sec

5624-62-13-0 -NP-irc.a

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

OBSERVE H1, 399.9480268 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 1 min, 42 sec

(5Z)-14

5624-62-13-0 -NP-frc.a

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

190 repetitions

OBSERVE C13, 100.5670121 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 6 min, 54 sec