(Supporting Information)

Palladium-Catalyzed Hydrocarbonation and Hydroamination of 3,3-Dihexylcyclopropene with Pronucleophiles

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General. Spectroscopic measurements were carried out with the following instruments: JEOL JNM LA-300 (^1H and ^{13}C NMR), SHIMADZU FTIR-8200A (FT-IR), HITACHI M-2500s (HRMS). Carbon and nitrogen pronucleophiles were purchased from TOKYO CHEMICAL INDUSTRY CO., LTD or Aldrich. All 3,3-dihexylpropene was prepared following the reported procedure.¹

General procedure of the addition of the pronucleophiles 2 to 3,3-dihexylcyclopropene 1. To a mixture of $\text{Pd}(\text{PPh}_3)_4$ (8.6 mg, 0.0075 mmol), 1, 1'-bis(diphenylphosphino)ferrocene (dppf) (16.6 mg, 0.03 mmol) and pronucleophiles **2** (0.3 mmol) was added ethanol (2 ml) under Ar atmosphere in a Wheaton microreactor. The mixture was stirred at 60 °C for 10 minutes and then 3,3-dihexylcyclopropene (125.0 mg, 0.6 mmol) was added *via* syringe. After heating at 100 °C for 5-20 hours, the reaction mixture was filtered through a short florisil column using ethyl acetate as an eluent. Purification by silica column chromatography (hexane/ethyl acetate 19/1 as an eluent), and in certain cases, further purification by middle-pressure liquid chromatography (silica gel) using hexane/ethyl acetate 40/1 as an eluent, afforded the allylated products **3** in analytically pure form.

1. Rush, S.; Reinmuth, A.; Risse, W. *Macromolecules* 1997, 30, 7375.

Ethyl 2-cyano-5-hexyl-2-methyl-4-undecenoate (3a). IR (neat) 2957-2858, 1745, 1662, 1460, 1379, 1284, 1244, 1119, 1018, 858, 764, 725 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 0.86 (t, J = 6.4 Hz, 6H), 1.32-1.25 (m, 19H), 1.54 (s, 3H), 2.00-1.96 (m, 4H), 2.49 (dd, J = 7.1, 14.5 Hz, 1H), 2.62 (dd, J = 7.1, 14.5 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 5.12 (t, J = 7.1 Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 14.00, 14.07, 22.57, 22.61, 28.08, 28.33, 29.00, 29.43, 30.22, 31.72, 36.18, 36.93, 43.92, 62.61, 116.03, 120.07, 146.13, 169.30. Anal. Calcd for $\text{C}_{21}\text{H}_{37}\text{NO}_2$ (335.52): C, 75.17; H, 11.12; N, 4.17. Found: C, 75.18; H, 11.25; N, 4.25. HRMS (EI) Calcd for $\text{C}_{21}\text{H}_{37}\text{NO}_2$: m/z 335.2824. Found: m/z 335.2827.

2-Cyano-5-hexyl-2-methyl-4-undecenitrile (3b). IR (neat) 2957-2858, 2249, 1661, 1458, 1379, 1306, 1275, 1157, 1128, 752 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 0.87 (t, J = 6.4 Hz, 6H), 1.37-1.26 (m, 16H), 1.74 (s, 3H), 2.07-2.01 (m, 4H), 2.66 (d, J = 7.5 Hz, 2H), 5.21 (t, J = 7.3 Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 14.03, 22.58, 22.60, 23.99, 27.95, 28.32, 28.96, 29.42, 30.48, 31.67, 31.68, 31.84, 36.90, 37.05, 114.05, 116.26, 148.94. Anal. Calcd for $\text{C}_{19}\text{H}_{32}\text{N}_2$ (288.47): C, 79.11; H, 11.18; N, 9.71. Found: C, 79.17; H, 11.07; N, 9.68. HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{32}\text{N}_2$: m/z 288.2565. Found: m/z 288.2565.

2-Cyano-3-hexyl-2-methyl-3-vinylnonanenitrile (4). IR (neat) 3092-2858, 2361, 2341, 1653, 1466, 1416, 1376, 1178, 1121, 1005, 932, 725 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 0.87 (t, J = 5.1 Hz, 6H), 1.83-1.28 (m, 23H), 5.22 (d, J = 17.6 Hz, 1H), 5.43 (d, J = 11.0 Hz, 1H), 5.74 (dd, J = 11.0, 17.6 Hz, 6.4 Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 14.00, 20.82, 22.58, 23.80, 27.95, 30.01, 31.52, 32.84, 39.97, 47.21, 116.26, 119.41, 138.16. Anal. Calcd for $\text{C}_{19}\text{H}_{32}\text{N}_2$ (288.47): C, 79.11; H, 11.18; N, 9.71. Found: C, 79.42; H, 11.33; N, 9.32. HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{32}\text{N}_2$: m/z 288.2565. Found: m/z 288.2565.

Ethyl 2-cyano-5-hexyl-2-phenyl-4-undecenoate (3c). IR (neat) 3063-2856, 1745, 1495, 1450, 1367, 1296, 1230, 1095, 1036, 1005, 856, 764, 729 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 0.86 (t, J = 6.7 Hz, 6H), 1.25-1.20 (m, 19H), 2.02-1.92 (m, 4H), 2.82 (dd, J = 7.1, 14.5 Hz, 1H), 3.07 (dd, J = 7.1, 14.5 Hz, 1H), 4.30-4.11 (m, 2H), 5.06 (t, J = 7.1 Hz, 1H), 7.55-7.31 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) δ 13.82, 14.09, 22.62, 27.95, 28.23, 28.87, 29.44, 30.24, 31.71, 31.74, 36.57, 36.85, 54.31, 63.07, 116.17, 118.40, 126.20, 128.69, 128.96, 134.47, 146.23, 167.58. Anal. Calcd for $\text{C}_{26}\text{H}_{39}\text{NO}_2$ (397.59): C, 78.54; H, 9.89; N, 3.52. Found: C, 78.55; H, 10.16; N, 3.53. HRMS (EI) Calcd for $\text{C}_{26}\text{H}_{39}\text{NO}_2$: m/z 397.2981. Found: m/z 397.2975.

2-Cyano-5-hexyl-2-(3-hexyl-2-nonenyl)-4-undecenitrile (3d). IR (neat) 2957-2858, 1661, 1466, 1379, 1304, 1244, 1049, 849, 742, 723 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 0.82 (t, J = 6.5 Hz, 12H), 1.32-1.15 (m, 32H), 2.02-1.95 (m, 8H), 2.59 (d, J = 7.5 Hz, 4H), 5.18 (t, J = 7.4 Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 14.07, 22.62, 28.00, 28.34,

29.01, 29.46, 30.54, 31.71, 35.02, 36.94, 37.96, 114.31, 115.74, 148.50. Anal. Calcd for $C_{33}H_{58}N_2$ (482.83): C, 82.09; H, 12.11; N, 5.80. Found: C, 80.91; H, 11.93; N, 5.47. HRMS (EI) Calcd for $C_{33}H_{58}N_2$: m/z 482.4600. Found: m/z 482.4593.

Ethyl 2-acetyl-5-hexyl-2-(3-hexyl-2-nonenyl)-4-undecenoate(3e). IR (neat) 2957-2856, 1743, 1716, 1466, 1354, 1279, 1213, 1188, 1153, 1095, 1053, 1018, 889, 858, 725 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ 0.83-0.79 (m, 12H), 1.20-1.15 (m, 35H), 1.86 (t, $J = 7.3$ Hz, 8H), 2.06 (s, 3H), 2.57-2.42 (m, 4H), 4.10 (q, $J = 7.0$ Hz, 2H), 4.77 (t, $J = 7.1$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.10, 22.67, 26.79, 28.23, 28.36, 29.13, 29.36, 29.57, 30.27, 31.79, 31.82, 37.12, 61.16, 63.56, 117.29, 143.85, 172.18, 205.06. Anal. Calcd for $C_{36}H_{66}O_3$ (546.91): C, 79.06; H, 12.16. Found: C, 78.84; H, 12.23. HRMS (EI) Calcd for $C_{36}H_{66}O_3$: m/z 546.5012. Found: m/z 546.5012.

Ethyl 2-acetyl-5-hexyl-4-undecenoate (3f). IR (neat) 2957-2856, 1743, 1718, 1466, 1358, 1244, 1203, 1176, 1148, 1095, 1024, 858 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ 0.88-0.83 (m, 6H), 1.27-1.22 (m, 19H), 1.98-1.89 (m, 4H), 2.19 (s, 3H), 2.53 (t, $J = 7.3$ Hz, 2H), 3.39 (t, $J = 7.5$ Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 4.96 (t, $J = 7.1$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.10, 22.64, 26.61, 28.09, 28.37, 29.02, 29.14, 29.46, 30.04, 31.79, 36.83, 60.12, 61.28, 119.35, 143.23, 169.62, 203.19. Anal. Calcd for $C_{21}H_{38}O_3$ (338.52): C, 74.51; H, 11.31. Found: C, 73.97; H, 11.10. HRMS (EI) Calcd for $C_{21}H_{38}O_3$: m/z 338.2821. Found: m/z 338.2824.

***N*-(3-Hexyl-2-nonenyl)-*N*-tosylaniline (3g).** IR (neat) 3063-2856, 1597, 1493, 1456, 1352, 1165, 1094, 876, 814, 768, 719 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ 0.85-0.76 (m, 6H), 1.19-1.00 (m, 16H), 1.79-1.73 (m, 4H), 2.36 (s, 3H), 4.11-4.01 (m, 2H), 4.98 (t, $J = 7.0$ Hz, 1H), 6.96-6.94 (m, 2H), 7.21-7.16 (m, 5H), 7.44 (d, $J = 8.2$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.08, 21.51, 22.55, 27.66, 28.18, 28.71, 29.26, 29.94, 31.68, 36.44, 48.31, 118.62, 127.61, 127.70, 128.70, 128.99, 129.32, 135.92, 139.29, 143.14, 144.95. Anal. Calcd for $C_{28}H_{41}NO_2S$ (455.70): C, 73.80; H, 9.07; N, 3.07; S, 7.04. Found: C, 73.49; H, 9.01; N, 3.13; S, 7.01. HRMS (EI) Calcd for $C_{28}H_{41}NO_2S$: m/z 455.2858. Found: m/z 455.2856.

***N*-(3-Hexyl-2-nonenyl)phthalimide (3h).** IR (neat) 2955-2856, 1772, 1716, 1614, 1468, 1429, 1392, 1323, 1186, 1107, 1088, 949, 891, 860, 791, 719 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 0.85-0.80 (m, 6H), 1.28-1.21 (m, 16H), 1.95 (t, $J = 7.6$ Hz, 2H), 2.19 (t, $J = 7.2$ Hz, 2H), 4.27 (d, $J = 7.0$ Hz, 2H), 5.20 (t, $J = 6.8$ Hz, 1H), 7.83-7.66 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ 14.04, 14.10, 22.58, 22.65, 27.80, 28.55, 29.06, 29.48, 30.39, 31.68, 31.78, 35.64, 36.68, 117.64, 123.11, 132.30, 133.76, 145.23, 168.12. Anal. Calcd for $\text{C}_{23}\text{H}_{33}\text{NO}_2$ (355.51): C, 77.70; H, 9.36; N, 3.94. Found: C, 77.93; H, 9.57; N, 4.10. HRMS (EI) Calcd for $\text{C}_{23}\text{H}_{33}\text{NO}_2$: m/z 355.2511. Found: m/z 355.2512.

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