Supporting Information for:

A Dramatic Effect of Lewis Acid Catalyst on Nickel-catalyzed Carbocyanation of Alkynes

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General. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique or in a dry box under an argon atmosphere. Flash column chromatography was performed using Kanto Chemical silica gel (spherical, 40–50 μm). 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. Mass spectra were obtained with a JEOL JMS-700 (EI). GC analysis was performed on a Shimadzu GC 2014 equipped with an ENV-1 column (Kanto Chemical, 30 m x 0.25 mm, pressure = 31.7 kPa, detector = FID, 290 °C) with helium gas as a carrier.

Chemicals. Unless otherwise noted, commercially available reagents were used without purification. Anhydrous toluene purchased from Kanto Chemical was degassed by purging vigorously with argon for 20 min and further purified by passage through activated alumina under positive argon pressure as described by Grubbs et al.¹ 4-Cyanophenyl-[2-(tetrahydro-2*H*-pyranoxymethyl)phenyl]-dimethylsilane (**1c**),² 4-diphenylaminobenzonitrile (**1e**),³ 1-methyl-3-cyanoindole (**1i**),⁴ 1-(4-methoxyphenyl)-1-butyne (**2c**),⁵ dichlorobis(dimethylphenylphosphine)nickel(II),⁶ cyanomethylenecyclohexane (**4d**),⁷ 3,3-diphenyl-2-propenenitrile (**4e**),⁸ and 1-octynyl(trimethyl)silane (**2e**)⁹ were prepared according

to the respective literature procedure.

Nickel–LA-catalyzed arylocyanation of alkynes. A general procedure. An aryl cyanide (1.00 mmol), a Lewis acid (0.040 mmol), an alkyne (1.00 mmol), and C₁₂H₂₆ (internal standard, 56 mg, 0.33 mmol) were added sequentially to a solution of Ni(cod)₂ (2.8 mg, 0.010 mmol) and a ligand (0.020 mmol) in toluene (1.0 mL) in a dry box. The vial was taken outside the dry box and heated at 50 °C for the time specified Table 1. 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 arylocyanation products in yields listed in Table 1. The spectra of **3aa** and **3ba** agreed well with those reported by us previously.¹⁰

Table S1. Optimization of a combination of a ligand and Lewis acid for the nickel-catalyzed addition of **1a** across **2a**.

Reaction scheme: 4-methoxybenzonitrile (**1a**) + 2-butyne (**2a**) $\xrightarrow[\text{toluene, 50 °C, 24 h}]{\text{Ni(cod)}_2 \text{ (1 mol \%), ligand (2 mol \%), LA (4 mol \%)}}$ 2-cyano-2-(4-methoxyphenyl)-3-methylbut-3-ene (**3aa**)

ligand	Lewis acid ^a /GC yield of 3aa (%) ^b			
	BPh ₃	AlMe ₃	AlMe ₂ Cl	none
PMe ₃	31	60	88	1
P(<i>n</i> -Bu) ₃	39	63	41	<1
PPhMe ₂	78	95	>99	<1
PPh ₂ Me	92	92	98	<1
PPh ₂ Cy	79	95	50	<1
P(4-MeO-C ₆ H ₄) ₃	53	29	6	<1
Ph ₂ P(CH ₂) ₆ PPh ₂	60	72	66	<1

^a Other Lewis acids including AlMeCl₂, AlCl₃, Al(OR)₃ (R = Et, *i*-Pr, and Ph), AlPh₃, B(C₆F₅)₃, BEt₃, and BF₃•OEt₂ were ineffective. ^b GC yields estimated using dodecane as an internal standard.

(Z)-3-(4-[2-(2-Tetrahydro-2H-pyranoxymethyl)phenyl]dimethylsilylphenyl)-2-propyl-2-hexenenitrile (3ca). A colorless oil, R_f 0.35 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 7.54 (dd, $J = 7.5, 1.3$ Hz, 1H), 7.51–7.47 (m, 3H), 7.41 (td, $J = 7.5, 1.5$ Hz, 1H), 7.33–7.23 (m, 3H), 4.67 (d, $J = 12.1$ Hz, 1H), 4.48 (t, $J = 3.5$ Hz, 1H), 4.39 (d, $J = 12.1$ Hz, 1H), 3.84–3.74 (m, 1H), 3.49–3.39 (m, 1H), 2.49 (t, $J = 7.8$ Hz, 2H), 2.35 (t, $J =$

7.6 Hz, 2H), 1.83–1.40 (m, 8H), 1.30 (sext, $J = 7.5$ Hz, 2H), 1.01 (t, $J = 7.4$ Hz, 3H), 0.87 (t, $J = 7.4$ Hz, 3H), 0.61 (s, 3H), 0.60 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.6, 144.2, 140.6, 139.5, 135.7, 135.5, 134.0, 129.7, 128.5, 127.0, 126.8, 119.6, 111.5, 97.8, 68.8, 62.0, 35.6, 32.5, 30.4, 25.4, 21.7, 21.1, 19.3, 13.8, 13.5, –0.96, –1.11; IR (neat): 2959, 2872, 2361, 2210, 1458, 1437, 1389, 1350, 1258, 1202, 1119, 1078, 1028, 833, 814, 775, 756 cm^{-1} ; Anal. Calcd for $\text{C}_{29}\text{H}_{39}\text{NO}_2\text{Si}$; C, 75.44; H, 8.51. Found: C, 75.53; H, 8.69.

(Z)-3-(4-*N,N*-Dimethylaminophenyl)-2-propyl-2-hexenenitrile (3da). A colorless oil, R_f 0.61 (hexane–ethyl acetate = 2:1). ^1H NMR (400 MHz, CDCl_3) δ 7.26 (d, $J = 9.0$ Hz, 2H), 6.70 (d, $J = 9.0$ Hz, 2H), 2.98 (s, 6H), 2.49 (t, $J =$

7.7 Hz, 2H), 2.33 (t, $J = 7.7$ Hz, 2H), 1.66 (sext, $J = 7.5$ Hz, 2H), 1.32 (sext, $J = 7.5$ Hz, 2H), 1.01 (t, $J = 7.3$ Hz, 3H), 0.86 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.8, 150.5, 128.9, 127.3, 120.7, 111.6, 108.9, 40.2, 35.3, 32.7, 21.9, 21.4, 13.8, 13.5; IR (neat): 2961, 2932, 2872, 2205, 1611, 1524, 1454, 1445, 1360, 1229, 1202, 1167, 947, 820, 733 cm^{-1} ; Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2$; C, 79.64; H, 9.44. Found: C, 79.64; H, 9.50.

(Z)-3-(4-*N,N*-Diphenylaminophenyl)-2-propyl-2-hexenenitrile (3ea). A

colorless oil, R_f 0.24 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 7.32–7.00 (m, 14H), 2.49 (t, $J = 7.7$ Hz, 2H), 2.34 (t, $J = 7.6$ Hz, 2H), 1.67 (sext, $J = 7.5$ Hz, 2H), 1.35 (sext, $J = 7.5$ Hz, 2H), 1.01 (t, $J = 7.3$ Hz, 3H), 0.90 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.3, 148.1, 147.3, 133.1, 129.3, 128.7, 125.0, 123.4, 122.0, 120.1, 110.5, 35.5, 32.7, 21.8, 21.3, 13.9, 13.5; IR (neat): 2963, 2932, 2872, 2208, 1591, 1506, 1493, 1327, 1277, 839, 754, 696 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{27}\text{H}_{28}\text{N}_2$: M^+ , 380.2252. Found: m/z 380.2244.

(Z)-3-(4-Bromophenyl)-2-propyl-2-hexenenitrile (3fa). A colorless oil, R_f 0.53 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, J = 8.6 Hz, 2H), 7.18 (d, J = 8.6 Hz, 2H), 2.48 (t, J = 7.7 Hz, 2H), 2.35 (t, J = 7.6 Hz, 2H), 1.67 (sext, J = 7.5 Hz, 2H), 1.30 (sext, J = 7.5 Hz, 2H), 1.01 (t, J = 7.4 Hz, 3H), 0.87 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 157.5, 138.9, 131.7, 129.4, 122.8, 119.3, 112.3, 35.5, 32.4, 21.7, 21.0, 13.8, 13.5; IR (neat): 2963, 2932, 2872, 2210, 1587, 1487, 1458, 1393, 1381, 1101, 1072, 1011, 831, 785 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{18}\text{BrN}$: M^+ , 291.0622. Found: m/z 291.0628.

(Z)-3-(4-Chlorophenyl)-2-propyl-2-hexenenitrile (3ga). A colorless oil, R_f 0.48 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.6 Hz, 2H), 2.49 (t, J = 7.7 Hz, 2H), 2.35 (t, J = 7.6 Hz, 2H), 1.67 (sext, J = 7.5 Hz, 2H), 1.30 (sext, J = 7.5 Hz, 2H), 1.02 (t, J = 7.4 Hz, 3H), 0.87 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 157.5, 138.5, 134.6, 129.2, 128.7, 119.3, 112.3, 35.6, 32.4, 21.7, 21.0, 13.8, 13.5; IR (neat): 2963, 2932, 2874, 2210, 1593, 1491, 1458, 1092, 1015, 835 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{ClN}$; C, 72.71; H, 7.32. Found: C, 72.97; H, 7.59.

(Z)-3-(2,6-Dimethylphenyl)-2-propyl-2-hexenenitrile (3ha). A colorless oil, R_f 0.53 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.13 (dd, J = 8.5, 6.5 Hz, 1H), 7.06 (d, J = 7.3 Hz, 2H), 2.45–2.35 (m, 4H), 2.22 (s, 6H), 1.70 (sext, J = 7.4 Hz, 2H), 1.42–1.29 (m, 2H), 1.05 (t, J = 7.3 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.1, 139.5, 134.6, 127.9, 127.7, 118.7, 113.7, 36.2, 31.6, 21.6, 20.8, 19.8, 14.6, 13.6; IR (neat): 2963, 2932, 2872, 2212, 1464, 1379, 772 cm^{-1} ; Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{N}$; C, 84.59; H, 9.60. Found: C, 84.38; H, 9.71.

(Z)-3-(1-Methyl-3-indolyl)-2-propyl-2-hexenenitrile (3ia). A pale yellow solid, mp = 74.7–75.3 $^{\circ}\text{C}$, R_f 0.30 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, J = 7.9 Hz, 1H), 7.34 (d, J = 8.1 Hz, 1H), 7.30–7.23 (m, 2H), 7.17 (t, J = 7.5 Hz, 1H), 3.81 (s, 3H), 2.66 (t, J = 7.8 Hz, 2H), 2.41 (t, J = 7.6 Hz, 2H), 1.71 (sext, J = 7.5 Hz, 2H), 1.36 (sext, J = 7.6 Hz, 2H), 1.05 (t, J = 7.4 Hz, 3H), 0.87 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 152.4, 137.0, 129.0, 126.3, 122.0, 120.9, 120.2, 119.9, 114.3, 109.7, 109.4, 35.3, 33.0, 32.4, 22.0, 21.8, 13.9, 13.6; IR (KBr): 2961, 2870, 2201, 1614, 1605, 1537, 1477, 1466, 1385, 1331, 1244, 1134, 1105, 1090, 1015, 845, 741 cm^{-1} ; Anal. Calcd

3qb

A colorless solid, mp = 109.8–110.5 °C, R_f 0.34 (hexane–ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.46–7.30 (m, 6H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.58 (q, *J* = 7.5 Hz, 2H), 0.93 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 159.9, 159.8, 137.5, 135.0, 130.1,

(E)-3qb

pale yellow oil, R_f 0.26 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, J = 8.4 Hz, 2H), 7.03–6.97 (m, 4H), 6.70 (d, J = 8.8 Hz, 2H), 3.76 (s, 3H), 2.92 (q, J = 7.5 Hz, 2H), 1.06 (t, J = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.3, 158.2, 136.4, 134.3, 130.7, 129.9, 128.8, 125.7, 118.8, 113.8, 111.4, 55.2, 32.0, 12.6; IR (neat): 2972, 2936, 2212, 1607, 1510, 1489, 1092, 1034, 1015, 912, 826, 733 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{16}\text{ClNO}$: M^+ , 270.0932.

A pale yellow oil, R_f 0.26 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 9.0 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 3.83 (s, 3H), 2.42 (q, J = 7.5 Hz, 2H), 1.24 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 160.1, 154.9,

The chemical structure of (E)-3gc is shown, featuring a 4-chlorophenyl group, a cyano group (CN), and a trimethylsilyl group (Si(CH₃)₃). Curved arrows indicate nOe correlations between the aromatic proton (H) and the methyl group (CH₃) of the silyl group, and between the methyl group (CH₃) and the cyano group (CN).

colorless oil, R_f 0.14 (hexane–ethyl acetate = 30:1). ^1H NMR (400 MHz, CDCl_3) δ 7.39–7.33 (m, 4H), 2.31, (s, 3H), 0.39 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.1, 140.5, 134.9, 128.6, 128.1, 120.1, 111.2, 24.5, –0.2;

IR (neat): 2959, 2195, 1595, 1578, 1556, 1489, 1254, 1103, 1013, 845, 760, 673 cm^{-1} ; Anal. Calcd [as a mixture with (Z)-**3gc** and **3'gc**] for $\text{C}_{13}\text{H}_{16}\text{ClNSi}$; C, 62.50; H, 6.46. Found: C, 62.75; H, 6.52.

(Z)-3-(4-Chlorophenyl)-2-trimethylsilyl-2-butenenitrile [(Z)-3gc]. A colorless oil, R_f 0.14 (hexane–ethyl acetate = 30:1). ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 8.6 Hz, 2H), 2.46 (s, 3H), –0.01 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.7, 140.3, 134.7, 128.5, 128.1, 119.7, 113.0, 28.2, –0.2; IR (neat): 2959, 2899, 2197, 1599, 1576, 1485, 1435, 1254, 1105, 1090, 1015, 982, 845, 762, 698, 633, 554 cm^{-1} .

(E)-3-(4-Chlorophenyl)-3-trimethylsilyl-2-methylpropenenitrile (3'gc**).** A colorless solid, mp = 67.2–67.9 $^{\circ}\text{C}$, R_f 0.14 (hexane–ethyl acetate = 30:1). ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H), 2.19 (s, 3H), 0.16 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 161.9, 140.9, 132.9, 128.6, 127.7, 119.9, 118.3, 20.5, –0.2; IR (KBr): 2957, 2214, 1580, 1487, 1250, 1088, 1013, 908, 843, 800, 760, 521 cm^{-1} .

(E)-3-(4-Chlorophenyl)-3-(4-methoxyphenyl)-2-trimethylsilylacrylonitrile (3gd**).** A colorless oil, R_f 0.38 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.35–7.29 (m, 4H), 7.07 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 0.10 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.0, 160.6, 139.6, 135.7, 133.2, 130.8, 130.7, 128.3, 121.0, 113.5, 111.3, 55.4, 0.0; IR (neat): 2957, 2899, 2839, 2189, 1607, 1508, 1487, 1304, 1288, 1252, 1175, 1092, 1032, 1015, 845, 802, 760 cm^{-1} ; Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{ClNOSi}$; C, 66.74; H, 5.90. Found: C, 66.92; H, 5.86.

(Z)-3-(4-Chlorophenyl)-3-(4-methoxyphenyl)-2-trimethylsilylacrylonitrile [(Z)-3gd]. A colorless solid, mp = 98.7–99.6 $^{\circ}\text{C}$, R_f 0.35 (hexane–ethyl acetate = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 0.07 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.4, 160.8, 139.8, 135.3, 132.9, 131.0, 130.7, 128.3, 121.1, 113.5, 110.1, 55.4, –0.01; IR (KBr): 2961, 2191, 1601, 1572, 1543, 1508, 1489, 1306, 1252, 1182, 1167, 1092, 1028, 860, 837 cm^{-1} ; Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{ClNOSi}$; C, 66.74; H, 5.90. Found: C, 66.48; H, 5.97.

Nickel–LA-catalyzed arylocyanation of alkynes using dichlorobis(dimethylphenylphosphine)nickel(II) as a precatalyst. A solution of $(\text{PhMe}_2\text{P})_2\text{NiCl}_2$ (4.1 mg, 0.010 mmol) in toluene (1.0 mL), **2a** (110 mg, 1.00 mmol), a 1.0 M solution of AlMe_3 in hexane (0.040 mL, 0.040 mmol), and $\text{C}_{12}\text{H}_{26}$ (internal standard, 56 mg, 0.33 mmol) were added to **1a** (133 mg, 1.00 mmol) in a dry box. The vial was taken outside the dry box and heated at 50 °C for 19 h. The resulting mixture was filtered through a silica gel pad, concentrated in vacuo, and purified by flash silica gel column chromatography (hexane–ethyl acetate = 8:1) to give **3aa** (233 mg, 96%).

Nickel–LA-catalyzed alkenylcyanation of alkynes. A general procedure. An alkenyl cyanide (1.00 mmol), BPh_3 (19.4 mg, 0.080 mmol), an alkyne (1.2 mmol), and $\text{C}_{12}\text{H}_{26}$ (internal standard, 85 mg, 0.50 mmol) were added to a solution of $\text{Ni}(\text{cod})_2$ (5.5 mg, 0.020 mmol) and PMe_3 (3.0 mg, 0.040 mmol) in toluene (1.0 mL) in a dry box. The vial was taken outside the dry box and heated at 80 °C for the time specified Table 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 alkenylcyanation products in yields listed in Table 2.

(2Z,4E)-5-Phenyl-2,3-dipropyl-2,4-pentadienenitrile (5aa). A pale yellow oil,

R_f 0.13 (hexane–ethyl acetate = 30:1). ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, J = 7.1 Hz, 2H), 7.40–7.26 (m, 4H), 6.84 (d, J = 16.1 Hz, 1H), 2.46 (t, J = 8.0 Hz, 2H), 2.33 (t, J = 7.6 Hz, 2H), 1.66 (sext, J = 7.5 Hz, 2H), 1.53 (sext, J = 7.6 Hz,

2H) 1.02 (t, J = 7.5 Hz, 3H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 153.1, 136.2, 133.5, 128.8, 128.7, 127.1, 127.0, 119.1, 112.4, 32.2, 29.9, 22.6, 21.8, 14.3, 13.6; IR (neat): 2963, 2934, 2874, 2203, 1692, 1450, 962, 754, 692 cm^{-1} ; Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{N}$; C, 85.30; H, 8.84. Found: C, 85.54; H, 8.78.

(2Z,4Z)-2,3-dipropyl-2,4-heptadienenitrile [(Z)-5ba]. A colorless oil, R_f 0.15

(hexane–ethyl acetate = 30:1). ^1H NMR (400 MHz, CDCl_3) δ 5.89 (d, J = 11.7 Hz, 1H), 5.66 (dt, J = 11.7, 7.3 Hz, 1H), 2.25 (t, J = 7.6 Hz, 2H), 2.20 (t, J = 7.7 Hz, 2H), 2.13 (qdd, J = 7.5, 7.3, 1.8 Hz, 2H), 1.62 (sext, J = 7.4 Hz, 2H), 1.42 (sext, J = 7.5 Hz, 2H),

1.03 (t, J = 7.5 Hz, 3H), 0.98 (t, J = 7.3 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 154.7, 137.6, 126.8, 119.5, 111.5, 34.4, 31.8, 22.9, 21.9, 21.3, 14.1, 13.9, 13.7; IR (neat): 2964, 2934, 2874, 2208, 1458, 1379 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{21}\text{N}$: M^+ , 191.1674. Found: m/z 191.1677.

(2Z,4E)-2,3-dipropyl-2,4-heptadienenitrile [(E)-5ba]. A colorless oil, R_f 0.15 (hexane–ethyl acetate = 30:1). ^1H NMR (400 MHz, CDCl_3) δ 6.60 (dt, $J = 15.6$, 1.5 Hz, 1H), 6.07 (dt, $J = 15.6$, 6.7 Hz, 1H), 2.32 (t, $J = 8.0$ Hz, 2H), 2.28–2.19 (m, 4H), 1.61 (sext, $J = 7.5$ Hz, 2H), 1.44 (sext, $J = 7.6$ Hz, 2H), 1.07 (t, $J = 7.4$ Hz, 3H), 0.972 (t, $J = 7.3$ Hz, 3H), 0.966 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 153.4, 138.3, 128.0, 119.2, 109.8, 32.0, 30.1, 26.4, 22.7, 21.9, 14.4, 13.8, 13.5; IR (neat): 2964, 2934, 2874, 2205, 1638, 1570, 1462, 1381, 1088, 966 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{21}\text{N}$: M^+ , 191.1674. Found: m/z 191.1675.

(Z)-2,3-Dipropyl-4-cyclohexylidene-2-butenenitrile (5ca). A pale yellow oil, R_f 0.28 (hexane–ethyl acetate = 40:1). ^1H NMR (400 MHz, CDCl_3) δ 5.62 (s, 1H), 2.27–2.10 (m, 8H), 1.65–1.52 (m, 8H), 1.40 (sext, $J = 7.5$ Hz, 2H), 0.96 (t, $J = 7.4$ Hz, 3H), 0.90 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 155.3, 146.6, 121.0, 119.9, 111.1, 37.1, 34.7, 31.7, 30.6, 28.3, 27.1, 26.4, 21.8, 21.1, 14.0, 13.5; IR (neat): 2961, 2932, 2872, 2856, 2208, 1647, 1611, 1448, 1379, 1342, 1234, 1109, 1088, 833, 735 cm^{-1} ; Anal. Calcd for $\text{C}_{16}\text{H}_{25}\text{N}$; C, 83.06; H, 10.89. Found: C, 82.85; H, 10.71.

(Z)-5,5-Diphenyl-2,3-dipropyl-2,4-pentadienenitrile (5da). A colorless solid, mp = 58.1–58.7 $^{\circ}\text{C}$, R_f 0.25 (hexane–ethyl acetate = 20:1). ^1H NMR (400 MHz, CDCl_3) δ 7.40–7.16 (m, 10H), 6.83 (s, 1H), 2.20 (t, $J = 7.5$ Hz, 2H), 1.89 (t, $J = 7.8$ Hz, 2H), 1.54 (sext, $J = 7.5$ Hz, 2H), 1.32 (sext, $J = 7.5$ Hz, 2H), 0.91 (t, $J = 7.3$ Hz, 3H), 0.74 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 155.6, 146.8, 142.2, 139.8, 129.9, 128.2, 128.0, 126.6, 119.5, 113.6, 32.8, 31.8, 22.0, 21.7, 13.9, 13.5; IR (KBr): 2963, 2932, 2870, 2203, 1599, 1493, 1445, 1375, 870, 779, 762, 696 cm^{-1} ; Anal. Calcd for $\text{C}_{23}\text{H}_{25}\text{N}$; C, 87.57; H, 7.99. Found: C, 87.46; H, 8.04.

(2Z,4Z)-4-Cyano-5-phenyl-2,3-dipropyl-2,4-pentadienenitrile (5ea). A pale yellow oil, R_f 0.10 (hexane–ethyl acetate = 20:1). ^1H NMR (400 MHz, CDCl_3) δ 7.89–7.81 (m, 2H), 7.49–7.44 (m, 3H), 7.36 (s, 1H), 2.49 (t, $J = 7.8$ Hz, 2H), 2.36 (t, $J = 7.7$ Hz, 2H), 1.69 (sext, $J = 7.5$ Hz, 2H), 1.53 (sext, $J = 7.5$ Hz, 2H), 1.03 (t, $J = 7.3$ Hz, 3H), 0.98 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 152.0, 148.2, 132.4, 131.3, 129.4, 128.9, 118.1, 116.3, 114.7, 109.6, 33.0, 32.8, 21.7, 21.4, 13.9, 13.7; IR (neat): 2964, 2933, 2874, 2212, 1605, 1574, 1448, 1381, 1092, 935, 758, 691 cm^{-1} ; Anal. Calcd for

C₁₈H₂₀N₂; C, 81.78; H, 7.63. Found: C, 81.83; H, 7.66.

Conversion of 5aa to 3,4-dipropyl-1-phenylpyridine (6). To a solution of **5aa** (72 mg, 0.30 mmol) in toluene (15 mL) was added a 1.5 M solution of DIBAL-H in toluene (0.40 mL, 0.60 mmol) at 0 °C, and the resulting mixture was stirred at the same temperature for 15 min. The reaction was quenched with MeOH (0.150 mL) at 0 °C

and heated at 100 °C for 5 h in the open air. To the resulting mixture was added a slurry of SiO₂ (3.0 g) in water (0.90 mL), and the whole was stirred at rt for 45 min. Anhydrous MgSO₄ (0.50 g) and K₂CO₃ (0.50 g) were added, and the resulting mixture was further stirred for 90 min, filtered through a Celite pad, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (hexane–ethyl acetate = 35:1) to give **6** (44 mg, 61%) as a pale yellow oil, R_f 0.43 (hexane–ethyl acetate = 7:1). ¹H NMR (400 MHz, CDCl₃) δ 8.43 (s, 1H), 7.99–7.93 (m, 2H), 7.50 (s, 1H), 7.48–7.42 (m, 2H), 7.41–7.34 (m, 1H), 2.68–2.59 (m, 4H), 1.74–1.58 (m, 4H), 1.02 (t, *J* = 7.3 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 155.0, 150.3, 149.8, 139.6, 134.5, 128.6, 128.4, 126.7, 120.7, 34.1, 31.8, 24.1, 23.5, 14.11, 14.07; IR (neat): 2959, 2932, 2870, 1597, 1477, 1377, 777, 694 cm⁻¹; Anal. Calcd for C₁₇H₂₁N; C, 85.30; H, 8.84. Found: C, 85.51; H, 9.12.

Nickel–LA-catalyzed methylcyanation of 4-octyne (2a) with a 10 mmol scale.

Acetonitrile (**7a**, 0.41 g, 10.0 mmol), a 1.0 M solution of AlMe₃ in hexane (0.20 mL, 2.0 mmol), and **2a** (1.10 g, 10.0 mmol) were added sequentially to a solution of Ni(cod)₂ (138 mg, 0.50 mmol) and PPh₂(*t*-Bu) (0.24 g, 1.00 mmol) in toluene (10 mL) in a dry box.

After being stirred at 80 °C for 4 h, the resulting mixture was filtered through a silica gel pad, and concentrated in vacuo. The residue was distilled to give (*E*)-3-methyl-2-propyl-2-hexenenitrile (**8aa**, 1.1 g, 71%) as a pale yellow oil, bp 80 °C (20 mmHg), R_f 0.18 (hexane–ethyl acetate = 40:1). ¹H NMR (400 MHz, CDCl₃) δ 2.21–2.12 (m, 4H), 2.05 (s, 3H), 1.56 (sext, *J* = 7.5 Hz, 2H), 1.46 (sext, *J* = 7.5 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 155.3, 119.3, 109.7, 35.6, 31.5, 22.6, 21.9, 21.0, 14.1, 13.6; IR (neat): 2964, 2934, 2874, 2208, 1630, 1466, 1381, 1138, 1094, 741 cm⁻¹; Anal. Calcd for C₁₀H₁₇N; C, 79.41; H, 11.33. Found: C, 79.47; H, 11.47.

Nickel–LA-catalyzed alkylcyanation of 4-octyne (2a). A general procedure. An alkyl cyanide (1.00 mmol), a solution of an aluminum Lewis acid (0.20 mmol) in hexane, **2a** (1.00 mmol), and C₁₂H₂₆ (internal standard, 85 mg, 0.50 mmol) were added sequentially to a solution of Ni(cod)₂ (14 mg, 0.050 mmol) and a ligand (0.10 mmol) in toluene (1.0 mL) in a dry box. The vial was taken

outside the dry box and heated at 80 °C for the time specified in Table 3. 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 alkylcyanation products in yields listed in Table 3.

(E)-3-(²H₃)Methyl-2-propyl-2-hexenenitrile (8aa-*d*₃). A colorless oil, *R*_f 0.20 (hexane–ethyl acetate = 40:1). ¹H NMR (400 MHz, CDCl₃) δ 2.21–2.11 (m, 4H), 1.55 (sext, *J* = 7.5 Hz, 2H), 1.45 (sext, *J* = 7.5 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 155.2, 119.3, 109.7, 35.5, 31.5, 21.9, 21.0, 14.1, 13.6; IR (neat): 2963, 2934, 2874, 2208, 1624, 1466, 1381, 1090, 1042, 739 cm^{−1}; HRMS (EI) Calcd for C₁₀H₁₄D₃N: M⁺, 154.1549. Found: *m/z* 154.1557.

(Z)-3-(Trimethylsilyl)methyl-2-propyl-2-hexenenitrile (8ba). A pale yellow oil, *R*_f 0.18 (hexane–ethyl acetate = 50:1). ¹H NMR (400 MHz, CDCl₃) δ 2.16 (t, *J* = 7.5 Hz, 2H), 2.08 (t, *J* = 7.8 Hz, 2H), 2.02 (s, 2H), 1.56 (sext, *J* = 7.5 Hz, 2H), 1.44 (sext, *J* = 7.6 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.11 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 159.1, 120.4, 105.7, 35.7, 31.4, 28.8, 22.3, 21.6, 14.2, 13.6, −0.6; IR (neat): 2961, 2874, 2203, 1611, 1464, 1421, 1379, 1250, 1148, 1078, 853, 766, 694 cm^{−1}; Anal. Calcd for C₁₃H₂₅NSi: C, 69.88; H, 11.28. Found: C, 70.18; H, 11.17.

(Z)-3-Ethyl-2-propyl-2-hexenenitrile (8ca). A colorless oil, *R*_f 0.18 (hexane–ethyl acetate = 40:1). ¹H NMR (400 MHz, CDCl₃) δ 2.40 (q, *J* = 7.5 Hz, 2H), 2.17 (t, *J* = 7.3 Hz, 2H), 2.15 (t, *J* = 7.9 Hz, 2H), 1.57 (sext, *J* = 7.4 Hz, 2H), 1.43 (sext, *J* = 7.6 Hz, 2H), 1.09 (t, *J* = 7.6 Hz, 3H), 0.944 (t, *J* = 7.3 Hz, 3H), 0.940 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 161.1, 119.1, 109.2, 33.0, 31.5, 29.3, 21.9, 21.4, 14.3, 13.6, 13.2; IR (neat): 2964, 2936, 2874, 2208, 1624, 1464, 1379, 1138, 1057, 797, 741 cm^{−1}; Anal. Calcd for C₁₁H₁₉N: C, 79.94; H, 11.59. Found: C, 79.91; H, 11.71.

(E)-2-Propyl-2-hexenenitrile (9). A colorless oil, *R*_f 0.18 (hexane–ethyl acetate = 40:1). ¹H NMR (400 MHz, CDCl₃) δ 6.35 (t, *J* = 7.6 Hz, 1H), 2.17 (quint, *J* = 7.5 Hz, 4H), 1.58 (sext, *J* = 7.4 Hz, 2H), 1.46 (sext, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 147.9, 120.1, 114.8, 30.5, 30.4, 21.9, 21.4, 13.8, 13.5; IR (neat): 2963, 2934, 2874, 2216, 1634, 1460, 1381, 1067, 908 cm^{−1}; HRMS (EI) Calcd for C₉H₁₅N: M⁺, 137.1204. Found: *m/z* 137.1209.

(Z)-3-Methyl-2-trimethylsilyl-2-nonenenitrile (8ae). A colorless oil, R_f 0.15 (hexane–ethyl acetate = 30:1). ^1H NMR (400 MHz, CDCl_3) δ 2.25 (t, $J = 8.0$ Hz, 2H), 2.15 (s, 3H), 1.50–1.40 (m, 2H), 1.37–1.24 (m, 6H) 0.90 (t, $J = 6.9$ Hz, 3H), 0.28 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 174.2, 120.3, 108.7, 38.7, 31.7, 29.5, 28.4, 24.4, 22.6, 14.1, 0.08; IR (neat): 2957, 2930, 2858, 2197, 1583, 1466, 1377, 1254, 843, 762 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{25}\text{NSi}$; C, 69.88; H, 11.28. Found: C, 69.81; H, 11.42.

(E)-3-Methyl-2-trimethylsilyl-2-nonenenitrile [(E)-8ae]. A colorless oil, R_f 0.15 (hexane–ethyl acetate = 30:1). ^1H NMR (400 MHz, CDCl_3) δ 2.49 (t, $J = 7.8$ Hz, 2H), 1.97 (s, 3H), 1.55–1.46 (m, 2H), 1.39–1.26 (m, 6H) 0.89 (t, $J = 6.9$ Hz, 3H), 0.29 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 174.2, 120.0, 108.3, 41.0, 31.7, 29.1, 28.1, 22.63, 22.56, 14.2, –0.2; IR (neat): 2957, 2930, 2858, 2195, 1583, 1462, 1377, 1254, 843, 760 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{25}\text{NSi}$; C, 69.88; H, 11.28. Found: C, 69.98; H, 11.08.

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3ea

6427-77-03-143

fra##

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

3a

6808-77-05-083
03-143-fra

Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
Mercury-400BE "m400"

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
1024 repetitions
OBSERVE C13, 100.5670128 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 50 min, 47 sec

6426-77-03-169
fra

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

3fa

6426-77-03-159

fra

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

17516 repetitions

OBSERVE C13, 100.5670128 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 16 hr, 31 min, 56 sec

3fa

76.680
77.000
77.206
77.313

157.461
138.941
131.683
129.426
122.778
119.270
112.324

35.507
32.427
21.684
20.998
13.778
13.518

220 200 180 160 140 120 100 80 60 40 20 0 ppm

6726-77-05-015
frbGPCfra

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

6726-77-05-015
frbGPCfra

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
1024 repetitions

OBSERVE C13, 100.5670128 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 50 min, 47 sec

(E)-3gc

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Pulse Sequence: s2pul

6X06-69-07-164-E-13C

Pulse Sequence: s2pul

6906-69-07-145-fr.32-44

Pulse Sequence: s2pul

6906-69-07-145-fr.32-44-13C

Pulse Sequence: s2pul

6929-69-07-111-H-CN-13C

Pulse Sequence: s2pul