Supporting Information for:

Nickel/$AlMe_2Cl$-catalysed Carbocyanation of Alkynes Using Arylacetonitriles

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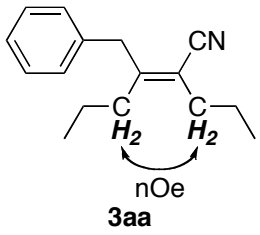
General. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique or in a dry box under an argon atmosphere. Flash column chromatography was performed using Kanto Chemical silica gel (spherical, 40–50 μm). Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F_{254} (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating.

Apparatus. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Varian Mercury 400 spectrometer with Me_4Si or solvent resonance as the internal standard (^{1}H NMR, Me_4Si at 0 ppm, $CHCl_3$ at 7.26 ppm, or C_6D_5H at 7.16 ppm; ^{13}C NMR, Me_4Si at 0 ppm, $CDCl_3$ at 77.0 ppm, or C_6D_5H at 128.0 ppm). ^{1}H 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. Assignment of the resonances observed in ^{1}H and ^{13}C NMR spectra was based on ^{1}H–^{1}H COSY, HMQC, and HMBC 2D NMR experiments. Infrared spectra (IR) recorded on a Shimadzu FTIR-8400 spectrometer are reported in cm^{-1}. Melting points (mp) were determined using a YANAKO MP-500D. Elemental analyses were performed by Elemental Analysis Center of Kyoto University. Chiral HPLC analyses were performed with a Shimadzu Prominence chromatograph. Optical rotations were measured on a JASCO DIP-360. High-resolution mass spectra were obtained with a JEOL JMS-700 (EI). X-ray crystal data were collected with a Bruker SMART APEX diffractometer [for (*Z*)-**3ac**]. Preparative recycling silica gel chromatography was performed with a JAI LC-908 chromatograph equipped with Nacalai Tesque 5SL-II (hexane–ethyl acetate as an eluent). 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 chemicals were distilled and degassed before use. $Ni(cod)_2$ was purchased from Strem and used without further purification. Anhydrous toluene was purchased from Kanto Chemical and 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] 2-Mes–C_6H_4–PCy_2,[2] 2-(2,4,6-*i*-Pr_3–C_6H_2)–C_6H_4–PCy_2,[3] 1,4-bis(trimethylsilyl)-2-butyne (**2b**),[4] pyrrolylaceonitrile (**1k**),[5] and (*S*)-α-phenylpropionitrile [(*S*)-**1n**] (using (*R*,*S*)-Josiphos as a ligand)[6] were prepared according to the respective literature procedure.

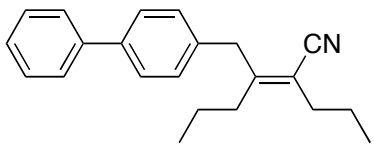
Nickel/$AlMe_2Cl$-catalyzed carbocyanation of alkynes using arylacetonitriles. *A general procedure*. To a stirred mixture of an arylacetonitrile (1.00 mmol), an alkyne (1.00 mmol), and tetradecane (internal standard, 99 mg, 0.50 mmol) in a vial was added a solution of $Ni(cod)_2$ (5.5 mg, 20 μmol), 2-Mes–C_6H_4–PCy_2 (15.7 mg, 40 μmol), and a 1.0 M solution of $AlMe_2Cl$ in hexane (80 μL, 80 μmol) in toluene (1.0 mL) in a dry box. The vial was taken outside the dry box and stirred at 35 °C

for the time specified in Table 1 and 2. The resulting mixture was filtered through a Florisil pad, concentrated *in vacuo*, and purified by flash column chromatography on silica gel to give the corresponding carbocyanation products in yields listed in Table 1 and 2. Regio- and/or stereoisomers were separated by preparative GPC or HPLC to obtain respective spectra.



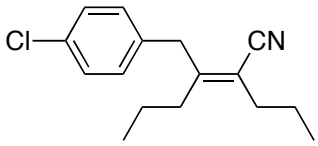
3aa

(*Z*)-3-Benzyl-2-propyl-2-hexenenitrile (3aa). A colorless oil, R_f 0.41 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (tt, *J* = 7.1, 1.5 Hz, 2H), 7.27–7.19 (m, 3H), 3.74 (s, 2H), 2.24 (t, *J* = 7.6 Hz, 2H), 2.04 (t, *J* = 8.0 Hz, 2H), 1.63 (sext, *J* = 7.5 Hz, 2H), 1.38 (sext, *J* = 7.6 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 137.8, 128.7, 128.6, 126.7, 119.6, 111.2, 42.0, 32.7, 31.6, 21.8, 21.3, 14.1, 13.5; IR (neat): 2963, 2932, 2872, 2206, 1624, 1603, 1495, 1454, 1381, 1086, 1030, 737, 702 cm^{-1}; Anal. Calcd for $C_{16}H_{21}N$: C, 84.53; H, 9.31. Found: C, 84.46; H, 9.39.



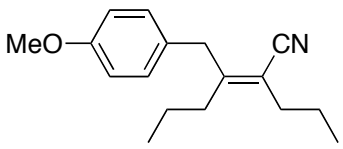
3ba

(*Z*)-3-(4-Biphenylmethyl)-2-propyl-2-hexenenitrile (3ba). A colorless oil, R_f 0.41 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.56 (m, 2H), 7.53 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34 (tt, *J* = 7.4, 1.5 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 3.78 (s, 2H), 2.26 (t, *J* = 7.6 Hz, 2H), 2.09 (t, *J* = 8.0 Hz, 2H), 1.65 (sext, *J* = 7.5 Hz, 2H), 1.42 (sext, *J* = 7.6 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 140.7, 139.6, 136.9, 129.1, 128.7, 127.3, 127.2, 126.9, 119.6, 111.3, 41.6, 32.7, 31.6, 21.7, 21.3, 14.1, 13.5; IR (neat): 3028, 2963, 2932, 2872, 2361, 2343, 2206, 1487, 1458, 1408, 1381, 1009, 910, 735, 698, 421 cm^{-1}; Anal. Calcd for $C_{22}H_{25}N$: C, 87.08; H, 8.30. Found: C, 87.34; H, 8.36.



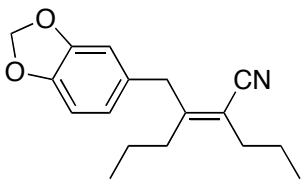
3ca

(*Z*)-3-[(4-Chlorophenyl)methyl]-2-propyl-2-hexenenitrile (3ca). A colorless oil, R_f 0.34 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dt, *J* = 8.6, 2.3 Hz, 2H), 7.14 (dt, *J* = 8.4, 2.1 Hz, 2H), 3.70 (s, 2H), 2.24 (t, *J* = 7.6 Hz, 2H), 2.03 (t, *J* = 7.9 Hz, 2H), 1.62 (sext, *J* = 7.5 Hz, 2H), 1.37 (sext, *J* = 7.6 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 136.3, 132.6, 130.0, 128.7, 119.4, 111.7, 41.2, 32.7, 31.6, 21.7, 21.3, 14.1, 13.4; IR (neat): 2963, 2932, 2872, 2341, 2208, 1624, 1491, 1466, 1408, 1381, 1092, 1016, 912, 800, 735 cm^{-1}; Anal. Calcd for $C_{16}H_{20}ClN$: C, 73.41, H, 7.70. Found: C, 73.62, H, 7.94.



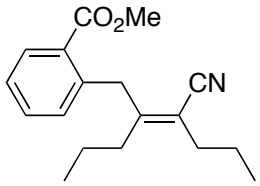
3da

(*Z*)-3-[(4-Methoxyphenyl)methyl]-2-propyl-2-hexenenitrile (3da). A colorless oil, R_f 0.13 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (dt, *J* = 8.8, 2.6 Hz, 2H), 6.83 (dt, *J* = 8.8, 2.6 Hz, 2H), 3.79 (s, 3H), 3.67 (s, 2H), 2.23 (t, *J* = 7.6 Hz, 2H), 2.03 (t, *J* = 8.0 Hz, 2H), 1.62 (sext, *J* = 7.5 Hz, 2H), 1.37 (sext, *J* = 7.6 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 158.2, 129.7, 129.6, 119.6, 113.9, 110.7, 55.1, 41.0, 32.5, 31.5, 21.6, 21.2, 14.0, 13.4; IR (neat): 2963, 2934, 2872, 2835, 2361, 2343, 2206, 1611, 1512, 1464, 1441, 1302, 1250, 1178, 1115, 1036, 816 cm^{-1}; Anal. Calcd for $C_{17}H_{23}NO$: C, 79.33; H, 9.01. Found: C, 79.50; H, 9.03.



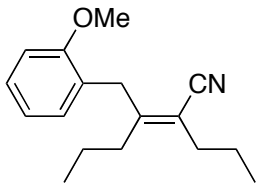
3ea

(*Z*)-3-[(3,4-Methylenedioxyphenyl)methyl]-2-propyl-2-hexenenitrile (3ea). A colorless oil, R_f 0.39 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, *J* = 7.9 Hz, 1H), 6.69 (d, *J* = 1.8 Hz, 1H), 6.66 (dd, *J* = 7.9, 1.6 Hz, 1H), 5.94 (s, 2H), 3.65 (s, 2H), 2.23 (t, *J* = 7.7 Hz, 2H), 2.04 (t, *J* = 7.9 Hz, 2H), 1.62 (sext, *J* = 7.5 Hz, 2H), 1.37 (sext, *J* = 7.6 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 147.8, 146.3, 131.4, 121.7, 119.5, 111.1, 108.9, 108.2, 100.9, 41.5, 32.5, 31.5, 21.7, 21.3, 14.1, 13.4; IR (neat): 2963, 2932, 2874, 2206, 1504, 1489, 1443, 1246, 1186, 1097, 1040, 928, 810, 773 cm^{-1}; Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80. Found: C, 75.45; H, 7.89.



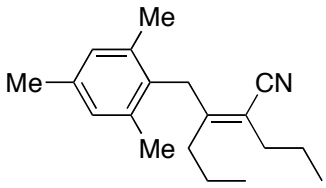
3fa

(*Z*)-3-[(2-Methoxycarbonylphenyl)methyl]-2-propyl-2-hexenenitrile (3fa). A yellow oil, R_f 0.31 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.44 (td, *J* = 7.6, 1.5 Hz, 1H), 7.33–7.22 (m, 2H), 4.22 (s, 2H), 3.91 (s, 3H), 2.26 (t, *J* = 7.6 Hz, 2H), 1.99 (t, *J* = 8.0 Hz, 2H), 1.64 (sext, *J* = 7.5 Hz, 2H), 1.33 (sext, *J* = 7.6 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H), 0.84 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 157.8, 139.0, 132.1, 130.8, 130.2, 130.1, 126.7, 119.5, 112.0, 52.2, 38.8, 33.0, 31.7, 21.8, 21.5, 14.1, 13.5; IR (neat): 2963, 2874, 2206, 1720, 1435, 1265, 1192, 1109, 1078, 739 cm^{-1}; Anal. Calcd for $C_{18}H_{23}NO_2$: C, 75.76; H, 8.12 Found: C, 75.82; H, 8.27.



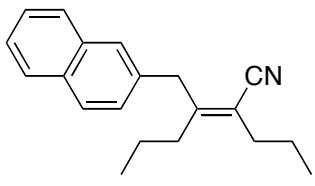
3ga

(*Z*)-3-[(2-Methoxyphenyl)methyl]-2-propyl-2-hexenenitrile (3ga). A colorless oil, R_f 0.30 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (td, *J* = 8.1, 1.8 Hz, 1H), 7.13 (dd, *J* = 7.3, 1.6 Hz, 1H), 6.89 (td, *J* = 7.5, 1.1 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 2H), 2.23 (t, *J* = 7.5 Hz, 2H), 2.02 (t, *J* = 8.0 Hz, 2H), 1.61 (sext, *J* = 7.5 Hz, 2H), 1.37 (sext, *J* = 7.6 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 157.5, 129.9, 127.9, 126.2, 120.4, 119.6, 110.9, 110.2, 55.1, 35.8, 32.6, 31.6, 21.7, 21.4, 14.1, 13.3; IR (neat): 2963, 2934, 2872, 2837, 2361, 2343, 2206, 1624, 1599, 1587, 1493, 1464, 1439, 1290, 1246, 1123, 1051, 1030, 754 cm^{-1}; Anal. Calcd for $C_{17}H_{23}NO$: C, 79.33; H, 9.01. Found: C, 79.21; H, 9.18.



3ha

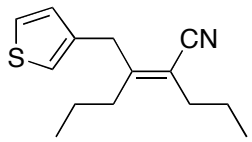
(*Z*)-2-Propyl-3-[(2,4,6-trimethylphenyl)methyl]-2-hexenenitrile (3ha). A colorless oil, R_f 0.37 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 2H), 3.82 (s, 2H), 2.27 (s, 6H), 2.26 (s, 3H), 2.22 (t, *J* = 7.7 Hz, 2H), 1.86 (t, *J* = 8.2 Hz, 2H), 1.62 (sext, *J* = 7.5 Hz, 2H), 1.22 (sext, *J* = 7.8 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.81 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 137.3, 136.1, 131.3, 129.2, 119.2, 110.0, 36.4, 32.4, 31.7, 22.1, 21.6, 20.8, 20.4, 14.3, 13.6; IR (neat): 2963, 2932, 2872, 2206, 1614, 1456, 1379, 912, 851, 735 cm^{-1}; Anal. Calcd for $C_{19}H_{27}N$: C, 84.70; H, 10.10 Found: C, 84.92; H, 10.23.



3ia

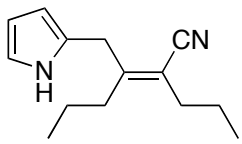
(*Z*)-3-(2-Naphthylmethyl)-2-propyl-2-hexenenitrile (3ia). A colorless oil, R_f 0.42 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.71 (m, 3H), 7.64 (s, 1H), 7.51–7.42 (m, 2H), 7.35 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.91 (s, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 2.07 (t, *J* = 8.0 Hz, 2H), 1.66 (sext, *J* = 7.5 Hz, 2H), 1.41 (sext, *J* = 7.6 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 135.3, 133.4,

132.3, 128.3, 127.6, 127.5, 127.2, 126.8, 126.1, 125.6, 119.6, 111.4, 42.1, 32.6, 31.6, 21.7, 21.3, 14.0, 13.4; IR (neat): 2963, 2932, 2872, 2206, 1624, 1601, 1508, 1458, 818, 756 cm^{-1}; Anal. Calcd for $C_{20}H_{23}N$: C, 86.59; H, 8.36. Found: C, 86.50; H, 8.58.



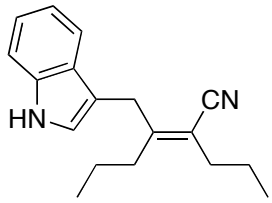
3ja

(*Z*)-2-Propyl-3-(3-thienylmethyl)-2-hexenenitrile (3ja). A colorless oil, R_f 0.46 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30–7.24 (m, 1H), 7.02 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.96 (d, *J* = 4.9 Hz, 1H), 3.73 (s, 2H), 2.23 (t, *J* = 7.7 Hz, 2H), 2.08 (t, *J* = 8.0 Hz, 2H), 1.61 (sext, *J* = 7.4 Hz, 2H), 1.38 (sext, *J* = 7.5 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 137.7, 127.9, 125.8, 121.7, 119.2, 110.9, 36.6, 32.8, 31.4, 21.6, 21.2, 14.0, 13.3; IR (neat): 2963, 2932, 2872, 2206, 1624, 1464, 1381, 1082, 787, 745 cm^{-1}; Anal. Calcd for $C_{14}H_{19}NS$: C, 72.05; H, 8.21. Found: C, 72.29; H, 8.11.



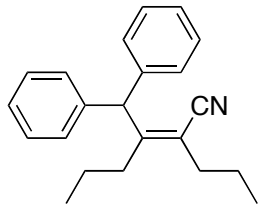
3ka

(*Z*)-2-Propyl-3-(2-pyrrolylmethyl)-2-hexenenitrile (3ka). A slightly brown oil, R_f 0.23 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (br s, 1H), 6.70 (ddd, *J* = 2.7, 1.5, 1.3 Hz, 1H), 6.12 (dd, *J* = 5.9, 2.7 Hz, 1H), 6.02–5.96 (m, 1H), 3.69 (s, 2H), 2.20 (t, *J* = 7.7 Hz, 2H), 2.13 (t, *J* = 7.9 Hz, 2H), 1.60 (sext, *J* = 7.5 Hz, 2H), 1.40 (sext, *J* = 7.6 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 127.5, 119.8, 117.5, 110.6, 108.4, 107.1, 34.4, 33.2, 31.5, 21.7, 21.2, 14.1, 13.5; IR (neat): 3373, 2963, 2932, 2872, 2208, 1624, 1566, 1466, 1381, 1121, 1094, 1026, 912, 883, 795, 716 cm^{-1}; Anal. Calcd for $C_{14}H_{20}N_2$: C, 77.73; H, 9.32. Found: C, 77.87; H, 9.07.



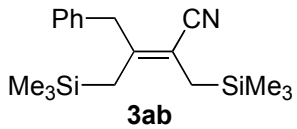
3la

(*Z*)-3-(3-Indolylmethyl)-2-propyl-2-hexenenitrile (3la). A slightly brown oil, R_f 0.24 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (br s, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.05 (s, 1H), 3.89 (s, 2H), 2.26 (t, *J* = 7.6 Hz, 2H), 2.12 (t, *J* = 7.9 Hz, 2H), 1.65 (sext, *J* = 7.4 Hz, 2H), 1.43 (sext, *J* = 7.6 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 136.0, 127.2, 122.4, 122.0, 119.6, 119.5, 118.8, 112.3, 111.0, 110.1, 32.9, 32.1, 31.8, 21.9, 21.6, 14.3, 13.7; IR (neat): 3414, 2963, 2932, 2872, 2206, 1620, 1456, 1433, 1339, 1232, 1094, 1011, 910, 737, 648 cm^{-1}; Anal. Calcd for $C_{18}H_{22}N_2$: C, 81.16; H, 8.32. Found: C, 81.07; H, 8.33.



3ma

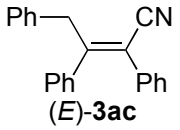
(*Z*)-3-(Diphenylmethyl)-2-propyl-2-hexenenitrile (3ma). A colorless oil, R_f 0.37 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.23 (m, 6H), 7.16 (d, *J* = 5.1 Hz, 4H), 5.70 (s, 1H), 2.28 (t, *J* = 7.7 Hz, 2H), 2.20 (t, *J* = 8.0 Hz, 2H), 1.68 (sext, *J* = 7.5 Hz, 2H), 1.01 (t, *J* = 7.3 Hz, 3H), 0.73–0.59 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 140.7, 129.1, 128.4, 126.9, 118.9, 113.1, 57.4, 33.5, 32.1, 22.7, 21.6, 14.6, 13.6; IR (neat): 2963, 2932, 2872, 2206, 1601, 1495, 1454, 1379, 1115, 1078, 1032, 910, 733, 698 cm^{-1}; Anal. Calcd for $C_{22}H_{25}N$: C, 87.08; H, 8.30. Found: C, 86.85; H, 8.43.



3ab

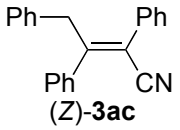
(*Z*)-3-Benzyl-4-trimethylsilyl-2-(trimethylsilyl)methyl-2-butenenitrile (3ab). A colorless oil, R_f 0.25 (hexane–ethyl acetate = 20:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (tt, *J* = 7.1, 1.3 Hz, 2H), 7.26–7.19 (m, 3H), 3.69 (s, 2H), 1.64 (s, 2H), 1.61 (s, 2H), 0.12 (s, 9H), 0.11 (s, 9H); ^{13}C NMR (101 MHz,

$CDCl_3$) δ 153.9, 138.4, 128.6, 128.4, 126.5, 121.0, 103.4, 43.7, 24.2, 21.4, –0.2, –0.9; IR (neat): 3063, 3028, 2955, 2899, 2203, 1603, 1495, 1454, 1437, 1418, 1250, 1219, 1173, 1142, 1084, 1030, 957, 847, 762, 727, 700, 610, 552 cm^{-1}; Anal. Calcd for $C_{18}H_{29}NSi_2$: C, 68.50; H, 9.26. Found: C, 68.73; H, 9.09.



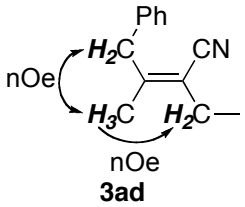
(*E*)-**3ac**

(*E*)-2,3,4-Triphenyl-2-butenenitrile [(*E*)-3ac]. A colorless solid, mp = 105.0–106.0 °C, R_f 0.23 (hexane–ethyl acetate = 20:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.26–7.11 (m, 13H), 6.95–6.89 (m, 2H), 4.27 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 137.5, 136.6, 133.4, 129.4, 128.7, 128.5, 128.4, 128.3, 128.14, 128.09, 126.7, 119.2, 112.8, 44.9; IR (KBr): 3439, 3057, 3028, 2915, 2218, 1966, 1954, 1896, 1881, 1821, 1805, 1755, 1599, 1575, 1493, 1454, 1441, 1431, 1219, 1184, 1107, 1069, 1030, 1001, 976, 945, 926, 910, 854, 833, 773, 750, 702, 677, 637, 600, 561, 517, 488, 461 cm^{-1}; Anal. Calcd for $C_{22}H_{17}N$: C, 89.46; H, 5.80. Found: C, 89.42; H, 5.74.



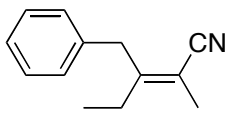
(*Z*)-**3ac**

(*Z*)-2,3,4-Triphenyl-2-butenenitrile [(Z)-3ac]. A yellow solid, mp = 103.5–104.3 °C, R_f 0.15 (hexane–ethyl acetate = 20:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.51–7.32 (m, 10H), 7.22–7.11 (m, 3H), 6.95 (d, *J* = 6.6 Hz, 2H), 3.96 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 138.7, 136.9, 134.0, 129.1, 129.0, 128.83, 128.80, 128.5, 128.4, 128.2, 128.0, 126.4, 119.0, 113.8, 40.0; IR (KBr): 3443, 3061, 3028, 2207, 1981, 1960, 1888, 1809, 1763, 1603, 1591, 1570, 1495, 1445, 1290, 1277, 1244, 1180, 1157, 1074, 1030, 999, 947, 920, 893, 791, 777, 766, 731, 708, 698, 567, 517, 490, 461, 446 cm^{-1}; Anal. Calcd for $C_{22}H_{17}N$: C, 89.46; H, 5.80. Found: C, 89.29; H, 5.84.



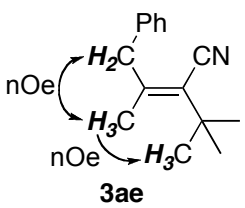
3ad

(*Z*)-2-Ethyl-3-methyl-4-phenyl-2-butenenitrile (3ad). A colorless oil, R_f 0.31 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.20 (m, 5H), 3.71 (s, 2H), 2.28 (q, *J* = 7.6 Hz, 2H), 1.73 (s, 3H), 1.17 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 137.7, 128.7, 128.6, 126.8, 119.3, 112.0, 44.4, 23.4, 17.6, 12.8; IR (neat): 3028, 2974, 2936, 2876, 2208, 1630, 1603, 1495, 1454, 1377, 752, 704 cm^{-1}; HRMS (EI) Calcd for $C_{13}H_{15}N$: M^+, 185.1204. Found: *m/z* 185.1199.



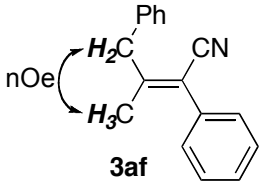
3'ad

(*Z*)-3-Benzyl-2-methyl-2-pentenenitrile (3'ad). A colorless oil, R_f 0.31 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.20 (m, 5H), 3.74 (s, 2H), 2.10 (q, *J* = 7.6 Hz, 2H), 1.96 (s, 3H), 0.95 (t, *J* = 7.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 137.5, 128.7, 128.5, 126.7, 120.2, 104.5, 41.7, 24.1, 16.1, 12.0; IR (neat): 3028, 2966, 2934, 2874, 2361, 2341, 2208, 1603, 1489, 1454, 1379, 912, 735, 702 cm^{-1}; HRMS (EI) Calcd for $C_{13}H_{15}N$: M^+, 185.1204. Found: *m/z* 185.1196.



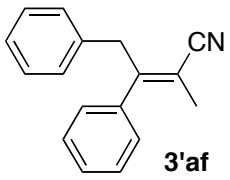
3ae

(*Z*)-2-*tert*-Butyl-3-methyl-4-phenyl-2-butenenitrile (3ae). A colorless oil, R_f 0.43 (hexane–ethyl acetate = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (tt, *J* = 7.1, 1.6 Hz, 2H), 7.27–7.19 (m, 3H), 3.76 (s, 2H), 1.91 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 137.8, 128.6, 128.5, 126.7, 120.4, 119.3, 46.5, 33.6, 30.6, 19.8; IR (neat): 2970, 2206, 1601, 1495, 1454, 1367, 914, 735, 700, 428 cm^{-1}; Anal. Calcd for $C_{15}H_{19}N$: C, 84.46; H, 8.98. Found: C, 84.55; H, 9.03.



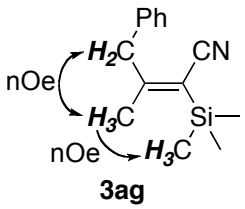
3af

(*Z*)-2,4-Diphenyl-3-methyl-2-butenenitrile (3af). A colorless oil, R_f 0.33 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.26 (m, 10H), 3.91 (s, 2H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 137.3, 133.8, 129.1, 128.73, 128.70, 128.5, 128.3, 126.9, 119.0, 111.6, 44.5, 19.2; IR (neat): 3061, 3028, 2210, 1601, 1493, 1447, 1375, 1076, 1030, 1005, 989, 912, 767, 750, 700 cm^{-1}; HRMS (EI) Calcd for $C_{17}H_{15}N$: M^+, 233.1204. Found: *m*/*z* 233.1214.



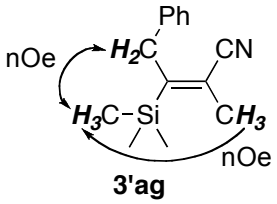
3'af

(*E*)-3,4-Diphenyl-2-methyl-2-butenenitrile (3'af). A colorless oil, R_f 0.33 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.26 (m, 3H), 7.23–7.14 (m, 3H), 7.07–7.02 (m, 2H), 6.96–6.90 (m, 2H), 4.04 (s, 2H), 1.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 137.4, 136.8, 128.7, 128.3, 128.2, 128.1, 127.6, 126.5, 119.9, 106.5, 44.5, 17.9; IR (neat): 3061, 3028, 2924, 2855, 2361, 2343, 2210, 1601, 1493, 1443, 1375, 1076, 1030, 1005, 912, 779, 766, 735, 702, 565 cm^{-1}; HRMS (EI) Calcd for $C_{17}H_{15}N$: M^+, 233.1204. Found: *m*/*z* 233.1195.



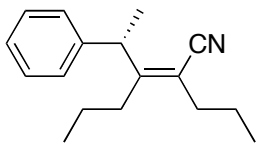
3ag

(*E*)-3-Methyl-4-phenyl-2-trimethylsilyl-2-butenenitrile (3ag). A colorless oil, R_f 0.42 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (tt, *J* = 7.2, 1.6 Hz, 2H), 7.28–7.20 (m, 3H), 3.82 (s, 2H), 1.88 (s, 3H), 0.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 137.5, 128.8, 128.7, 126.8, 120.4, 110.0, 46.7, 22.1, –0.4; IR (neat): 3029, 2959, 2901, 2193, 1582, 1495, 1454, 1375, 1254, 1028, 880, 845, 762, 745, 700, 633, 559 cm^{-1}; Anal. Calcd for $C_{14}H_{19}NSi$: C, 73.30; H, 8.35. Found: C, 73.56; H, 8.37.



3'ag

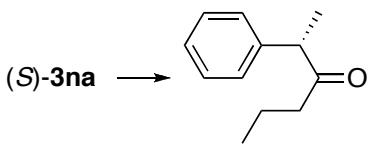
(*E*)-2-Methyl-4-phenyl-3-trimethylsilyl-2-butenenitrile (3'ag). A colorless oil, R_f 0.47 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.17 (m 3H), 7.11 (d, *J* = 7.0 Hz, 2H), 3.87 (s, 2H), 2.17 (s, 3H), 0.08 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 137.9, 128.8, 128.4, 126.5, 119.3, 118.8, 43.0, 20.5, –0.4; IR (neat): 3028, 2955, 2901, 2855, 2206, 1587, 1495, 1452, 1254, 1080, 1030, 843, 760, 739, 700 cm^{-1}; Anal. Calcd for $C_{14}H_{19}NSi$: C, 73.30; H, 8.35. Found: C, 73.56; H, 8.37.



(*S*)-**3na**

Nickel/AlMe$_2$Cl-catalyzed carbocyanation of 2a using (*S*)-1n (Eq. 2). To a solution of $Ni(cod)_2$ (55 mg, 0.2 mmol) and 2-(2,4,6-*i*-Pr_3–C_6H_2)–C_6H_4–PCy_2 (191 mg, 40 mmol) in toluene (1.0 mL) was added (*S*)-**1n** (131 mg, 1.00 mmol), a 1.0 M solution of $AlMe_2Cl$ in hexane (0.20 mL, 0.20 mmol), **2a** (0.55 g, 5.0 mmol), and tridecane (internal standard, 92 mg, 0.50 mmol) sequentially in a dry box. The vial was taken outside the dry box and heated at 80 °C for 0.5 h. GC analysis of the mixture showed the formation of hydrocyanation product **4**, styrene **5**, and hydrocinnnamonitrile **6** in 35%, 44%, and 3% yield, respectively. The mixture was filtered through a silica gel pad, concentrated *in vacuo*, and purified by flash column chromatography on silica gel followed by preparative HPLC to give (*S*)-(*Z*)-3-(1-phenylethyl)-2-propyl-2-hexenenitrile [(*S*)-**3na**] (54 mg, 22%) and (*S*)-**1n** (17 mg, 13%). (*S*)-**3na**: A colorless oil, R_f 0.27 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.20 (m, 5H), 4.46 (q, *J* = 7.1 Hz, 1H), 2.18 (t, *J* = 7.6 Hz, 2H), 1.91 (t, *J* = 8.2 Hz, 2H), 1.64 (sext, *J* = 7.5 Hz, 2H), 1.47 (d, *J* = 7.1 Hz, 3H), 1.27–1.09 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.91–0.73 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 141.6, 128.3, 127.4, 126.8, 119.3, 110.2, 45.6, 31.7, 30.9, 23.1, 21.5, 17.1, 14.6, 13.5; IR (neat): 2964, 2934, 2874, 2206, 1601, 1495, 1450, 1379, 1123, 1090, 1022, 912, 735, 700 cm^{-1}; Anal. Calcd for $C_{17}H_{23}N$: C, 84.59; H, 9.60.

Found: C, 84.78; H, 9.59. The enantiomeric excess (ee) was determined by HPLC analysis on a Daicel Chiralcel OB-H column with hexane, flow rate = 0.5 ml/min, detection at 254 nm. Retention times: 14.5 min [(*S*)-enantiomer], 17.2 min [(*R*)-enantiomer]. 41% ee. $[\alpha]_D^{30}$ –145.97 (*c* 1.055 in toluene). (*S*)-**1n**: The ee was determined by HPLC analysis on a Daicel Chiralcel OD-H column with hexane, flow rate = 0.5 ml/min, detection at 258 nm. Retention times: 37.4 min [(*S*)-enantiomer], 43.8 min [(*R*)-enantiomer]. 80% ee.



Ruthenium catalyzed oxidation of (*S*)-3na. To a solution of (*S*)-**3na** (42 mg, 0.18 mmol) in CCl_4–CH_3CN–H_2O (1.0:1.0:1.5, 1.4 mL) was added $NaIO_4$ (0.38 g, 1.6 mmol) and $RuCl_3 \bullet 3H_2O$ (2.1 mg, 7.9 μmol) at 0 °C, and the resulting mixture was stirred at rt for 5 h. Water was added, and the resulting aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, concentrated *in vacuo*, and purified by flash column chromatography on silica gel to give (*S*)-2-phenyl-3-hexanone (14 mg, 43%) as a pale yellow oil, R_f 0.20 (hexane–ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.30 (m, 2H), 7.28–7.19 (m, 3H), 3.75 (q, *J* = 7.0 Hz, 1H), 2.33 (t, *J* = 7.5 Hz, 2H), 1.58–1.47 (m, 2H), 1.40 (d, *J* = 7.0 Hz, 3H), 0.80 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.6, 140.6, 128.7, 127.7, 126.9, 53.0, 43.0, 17.6, 17.4, 13.7; IR (neat): 3028, 2964, 2932, 2874, 1713, 1601, 1493, 1452, 1373, 1130, 1070, 1015, 762, 700 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{16}O$: M^+, 176.1201. Found: *m*/*z* 176.1203. The ee was determined by HPLC analysis on a Daicel Chiralcel OD-H column with hexane, flow rate = 0.5 ml/min, detection at 254 nm. Retention times: 17.2 min [(*S*)-enantiomer], 18.8 min [(*R*)-enantiomer]. 38% ee. $[\alpha]_D^{30}$ +113.51 (*c* 0.555 in toluene) [lit.[7] $[\alpha]_D^{20}$ –234 (*c* 0.281 in toluene) for 91% ee of (*R*)-enantiomer].

X-ray structure report for (*Z*)-**3ac.**

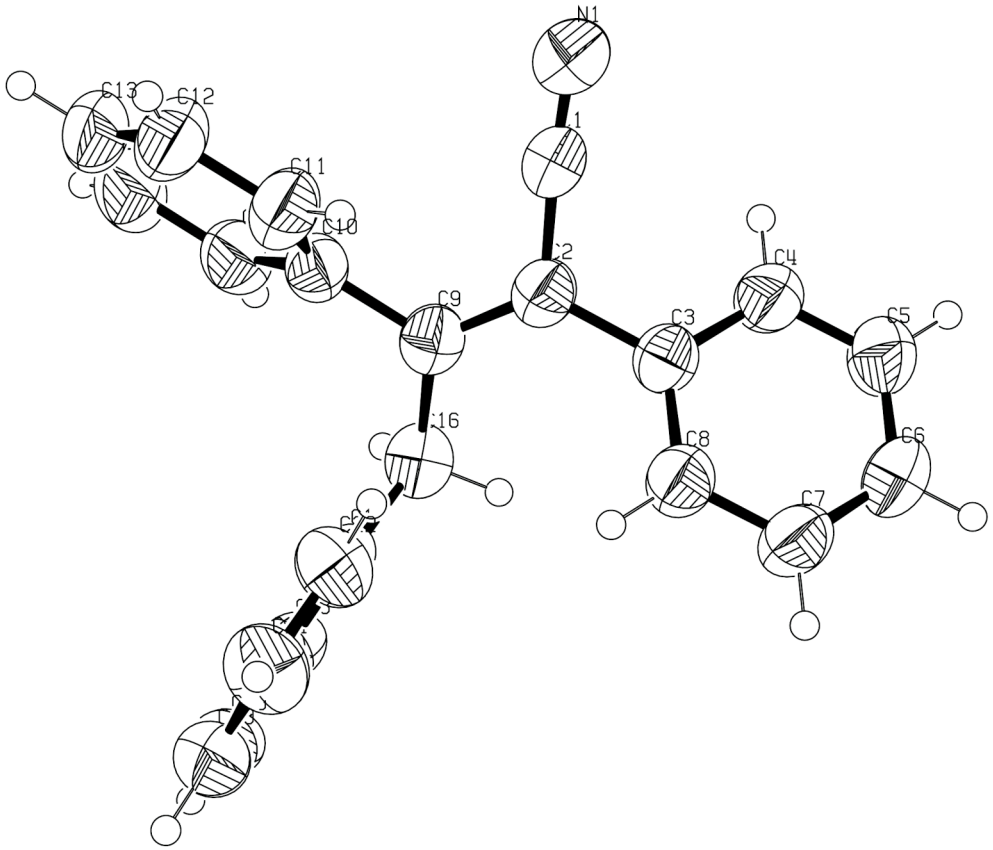


Table S1. Crystal data and structure refinement for (*Z*)-**3ac**.

Empirical formula	C22 H17 N	
Formula weight	295.37	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 16.1248(17) Å	a= 90°.
	b = 8.3530(8) Å	b= 101.290(2)°.
	c = 25.014(3) Å	g = 90°.
Volume	3303.9(6) $Å^3$	
Z	8	
Density (calculated)	1.188 Mg/m^3	
Absorption coefficient	0.069 mm^{-1}	

F(000)	1248
Crystal size	0.50 x 0.50 x 0.50 mm^3
Theta range for data collection	1.66 to 25.50°.
Index ranges	-9<=h<=19, -10<=k<=10, -30<=l<=28
Reflections collected	8599
Independent reflections	3059 [R(int) = 0.0278]
Completeness to theta = 25.50°	100.0 %
Absorption correction	Empirical
Max. and min. transmission	0.9665 and 0.9665
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3059 / 0 / 208
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0421, wR2 = 0.1091
R indices (all data)	R1 = 0.0541, wR2 = 0.1144
Largest diff. peak and hole	0.135 and -0.135 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (*Z*)-**3ac**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(2)	881(1)	5970(2)	814(1)	55(1)
C(3)	1392(1)	7286(2)	639(1)	55(1)
C(9)	1162(1)	4539(2)	1032(1)	55(1)
C(17)	2578(1)	3715(1)	1622(1)	54(1)
C(7)	2626(1)	8966(2)	779(1)	70(1)
C(1)	-15(1)	6301(2)	704(1)	64(1)
C(10)	591(1)	3420(2)	1246(1)	58(1)
C(18)	3249(1)	2652(2)	1699(1)	65(1)
C(16)	2053(1)	3969(2)	1057(1)	62(1)
C(11)	91(1)	3954(2)	1602(1)	71(1)
C(8)	2163(1)	7744(2)	950(1)	64(1)
C(6)	2319(1)	9774(2)	306(1)	69(1)
N(1)	-714(1)	6636(2)	588(1)	90(1)
C(22)	2443(1)	4567(2)	2068(1)	68(1)
C(15)	550(1)	1805(2)	1105(1)	75(1)
C(4)	1089(1)	8127(2)	164(1)	68(1)

C(5)	1549(1)	9363(2)	0(1)	75(1)
C(13)	-478(1)	1349(3)	1661(1)	99(1)
C(19)	3763(1)	2468(2)	2203(1)	78(1)
C(12)	-439(1)	2926(2)	1808(1)	87(1)
C(20)	3627(1)	3332(2)	2638(1)	79(1)
C(14)	10(1)	792(2)	1311(1)	97(1)
C(21)	2963(1)	4381(2)	2572(1)	80(1)

Table S3. Bond lengths [Å] and angles [°] for (*Z*)-**3ac**.

C(2)-C(9)	1.3548(18)
C(2)-C(1)	1.443(2)
C(2)-C(3)	1.4904(17)
C(3)-C(4)	1.3841(18)
C(3)-C(8)	1.3844(18)
C(9)-C(10)	1.4837(18)
C(9)-C(16)	1.5037(19)
C(17)-C(22)	1.3754(18)
C(17)-C(18)	1.3839(19)
C(17)-C(16)	1.5131(19)
C(7)-C(6)	1.368(2)
C(7)-C(8)	1.3805(19)
C(7)-H(7)	0.9300
C(1)-N(1)	1.1432(18)
C(10)-C(11)	1.388(2)
C(10)-C(15)	1.392(2)
C(18)-C(19)	1.376(2)
C(18)-H(18)	0.9300
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(11)-C(12)	1.380(2)
C(11)-H(11)	0.9300
C(8)-H(8)	0.9300
C(6)-C(5)	1.368(2)
C(6)-H(6)	0.9300

C(22)-C(21)	1.380(2)
C(22)-H(22)	0.9300
C(15)-C(14)	1.384(3)
C(15)-H(15)	0.9300
C(4)-C(5)	1.380(2)
C(4)-H(4)	0.9300
C(5)-H(5)	0.9300
C(13)-C(12)	1.366(3)
C(13)-C(14)	1.369(3)
C(13)-H(13)	0.9300
C(19)-C(20)	1.360(2)
C(19)-H(19)	0.9300
C(12)-H(12)	0.9300
C(20)-C(21)	1.368(2)
C(20)-H(20)	0.9300
C(14)-H(14)	0.9300
C(21)-H(21)	0.9300

C(9)-C(2)-C(1)	119.28(12)
C(9)-C(2)-C(3)	127.43(12)
C(1)-C(2)-C(3)	113.23(11)
C(4)-C(3)-C(8)	117.98(12)
C(4)-C(3)-C(2)	120.16(12)
C(8)-C(3)-C(2)	121.82(12)
C(2)-C(9)-C(10)	121.25(12)
C(2)-C(9)-C(16)	122.56(12)
C(10)-C(9)-C(16)	116.16(11)
C(22)-C(17)-C(18)	117.54(13)
C(22)-C(17)-C(16)	122.48(12)
C(18)-C(17)-C(16)	119.90(12)
C(6)-C(7)-C(8)	120.36(13)
C(6)-C(7)-H(7)	119.8
C(8)-C(7)-H(7)	119.8
N(1)-C(1)-C(2)	174.96(15)
C(11)-C(10)-C(15)	117.97(14)
C(11)-C(10)-C(9)	120.57(12)

C(15)-C(10)-C(9)	121.45(14)
C(19)-C(18)-C(17)	120.92(14)
C(19)-C(18)-H(18)	119.5
C(17)-C(18)-H(18)	119.5
C(9)-C(16)-C(17)	115.96(11)
C(9)-C(16)-H(16A)	108.3
C(17)-C(16)-H(16A)	108.3
C(9)-C(16)-H(16B)	108.3
C(17)-C(16)-H(16B)	108.3
H(16A)-C(16)-H(16B)	107.4
C(12)-C(11)-C(10)	121.35(16)
C(12)-C(11)-H(11)	119.3
C(10)-C(11)-H(11)	119.3
C(7)-C(8)-C(3)	120.77(13)
C(7)-C(8)-H(8)	119.6
C(3)-C(8)-H(8)	119.6
C(5)-C(6)-C(7)	119.65(14)
C(5)-C(6)-H(6)	120.2
C(7)-C(6)-H(6)	120.2
C(17)-C(22)-C(21)	121.29(14)
C(17)-C(22)-H(22)	119.4
C(21)-C(22)-H(22)	119.4
C(14)-C(15)-C(10)	120.03(17)
C(14)-C(15)-H(15)	120.0
C(10)-C(15)-H(15)	120.0
C(5)-C(4)-C(3)	120.89(13)
C(5)-C(4)-H(4)	119.6
C(3)-C(4)-H(4)	119.6
C(6)-C(5)-C(4)	120.29(14)
C(6)-C(5)-H(5)	119.9
C(4)-C(5)-H(5)	119.9
C(12)-C(13)-C(14)	119.90(17)
C(12)-C(13)-H(13)	120.1
C(14)-C(13)-H(13)	120.1
C(20)-C(19)-C(18)	120.81(15)
C(20)-C(19)-H(19)	119.6

C(18)-C(19)-H(19)	119.6
C(13)-C(12)-C(11)	119.90(19)
C(13)-C(12)-H(12)	120.1
C(11)-C(12)-H(12)	120.1
C(19)-C(20)-C(21)	119.21(15)
C(19)-C(20)-H(20)	120.4
C(21)-C(20)-H(20)	120.4
C(13)-C(14)-C(15)	120.84(17)
C(13)-C(14)-H(14)	119.6
C(15)-C(14)-H(14)	119.6
C(20)-C(21)-C(22)	120.23(15)
C(20)-C(21)-H(21)	119.9
C(22)-C(21)-H(21)	119.9

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (*Z*)-**3ac**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... \quad + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(2)	59(1)	54(1)	53(1)	-1(1)	12(1)	-8(1)
C(3)	59(1)	54(1)	53(1)	-1(1)	15(1)	-3(1)
C(9)	65(1)	52(1)	48(1)	-5(1)	10(1)	-8(1)
C(17)	55(1)	44(1)	64(1)	0(1)	19(1)	-6(1)
C(7)	65(1)	69(1)	74(1)	-3(1)	11(1)	-18(1)
C(1)	61(1)	56(1)	75(1)	9(1)	14(1)	-10(1)
C(10)	64(1)	52(1)	54(1)	3(1)	0(1)	-10(1)
C(18)	58(1)	54(1)	86(1)	-7(1)	21(1)	-3(1)
C(16)	72(1)	57(1)	60(1)	-5(1)	20(1)	0(1)
C(11)	78(1)	68(1)	68(1)	3(1)	16(1)	-20(1)
C(8)	68(1)	63(1)	58(1)	3(1)	7(1)	-10(1)
C(6)	76(1)	64(1)	74(1)	3(1)	29(1)	-15(1)
N(1)	65(1)	84(1)	122(1)	23(1)	21(1)	-5(1)
C(22)	75(1)	65(1)	63(1)	-1(1)	14(1)	13(1)
C(15)	80(1)	54(1)	83(1)	1(1)	-5(1)	-7(1)

C(4)	62(1)	75(1)	64(1)	11(1)	7(1)	-11(1)
C(5)	82(1)	79(1)	65(1)	19(1)	14(1)	-9(1)
C(13)	86(1)	91(1)	107(1)	41(1)	-10(1)	-36(1)
C(19)	58(1)	66(1)	105(1)	6(1)	7(1)	4(1)
C(12)	80(1)	101(1)	78(1)	20(1)	12(1)	-29(1)
C(20)	75(1)	75(1)	80(1)	11(1)	-2(1)	-7(1)
C(14)	103(1)	54(1)	117(2)	17(1)	-23(1)	-22(1)
C(21)	95(1)	81(1)	64(1)	-5(1)	12(1)	4(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for (*Z*)-**3ac**.

	x	y	z	U(eq)
H(7)	3150	9242	987	84
H(18)	3353	2053	1405	78
H(16A)	2341	4741	868	74
H(16B)	2031	2966	859	74
H(11)	113	5026	1704	85
H(8)	2371	7223	1277	76
H(6)	2632	10598	193	83
H(22)	1993	5282	2028	81
H(15)	885	1407	872	90
H(4)	567	7856	-47	81
H(5)	1336	9918	-319	90
H(13)	-836	655	1799	118
H(19)	4209	1744	2246	93
H(12)	-768	3307	2047	104
H(20)	3981	3211	2977	95
H(14)	-22	-281	1210	117
H(21)	2862	4972	2868	97

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