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# Nickel/Lewis Acid-Catalyzed Carbocyanation of Alkynes Using Acetonitrile and Substituted Acetonitriles

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Nickel/Lewis acid dual catalysis is found to effect the carbocyanation reaction of alkynes using acetonitrile and substituted acetonitriles to give a range of variously substituted acrylonitriles. The addition of propionitrile across alkynes is also demonstrated briefly to give the corresponding ethylcyanation products in good yields, whereas the reaction of butyronitrile gives significant amounts of hydrocyanation products due possibly to $\beta$-hydride elimination of a propylnickel intermediate. The reaction of optically active $\alpha$-phenylpropionitrile suggests a reaction mechanism that involves oxidative addition of a C–CN bond with retention of its absolute configuration.

Stereoselective construction of polysubstituted alkenes has been a major subject in organic synthesis.[1] To this end, we[2] and others[3] have demonstrated carbocyanation reaction[4] of alkynes catalyzed by nickel or palladium as a new entry to stereochemically well-defined and atom economical protocols for the synthesis of tri- or disubstituted acrylonitriles, versatile synthetic intermediates for polysubstituted alkenes. We have recently disclosed that a Lewis acid (LA) cocatalyst significantly improves the efficiency of the nickel-catalyzed carbocyanation of unsaturated bonds, and allows a wide variety of nitriles including aryl,[2d] alkenyl,[2d] alkynyl,[2e,2f] and allyl[2g] cyanides to participate in the reaction. We further anticipated carbocyanation using alkyl cyanides might be feasible under similar dual catalysis, because some alkyl cyanides were reported to undergo oxidative addition to nickel(0) through the activation of C($sp^3$)–CN $\sigma$-bonds.[5] In this paper, we report a full scope of the carbocyanation reaction of alkynes with acetonitrile under nickel/$AlMe_3$ dual catalysis. The reactions of propionitrile and butyronitrile with alkynes are also described briefly. Also demonstrated is the addition reaction of substituted acetonitriles such as aryl- and silylacetonitriles as well as protected amino- and hydroxyacetonitriles to give regio- and stereoselectively a wide variety of tri- and disubstituted acrylonitriles having allylic functional groups.[6]

## Results and Discussion

**Nickel/Lewis Acid-Catalyzed Carbocyanation of Alkynes Using Acetonitrile.** First, we investigated the reaction of acetonitrile (**1a**) with 4-octyne (**2a**) in the presence of a nickel/LA cooperative catalyst and found that $AlMe_3$, $AlMe_2Cl$, and $BPh_3$ were effective as a LA cocatalyst. After screening several combinations of catalysts and conditions, we found that the reaction of **1a** (10 mmol) with **2a** (10 mmol) proceeded in the presence of $Ni(cod)_2$ (5 mol %), $PPh_2(t\text{-Bu})$ (10 mol %), and $AlMe_3$ (20 mol %) in toluene at 80 °C to give the corresponding *cis*-methylcyanation product **3aa** in 71% yield after 4 h (Entry 1 of Table 1).[2d] Exclusive *cis*-addition of **1a** was unambiguously confirmed by NOE experiments. In the absence of the LA cocatalyst, the methylcyanation product was not observed in any detectable amount. Use of $CH_3CN$-$d_3$ as a nitrile substrate gave **3aa**-$d_3$ of 99% deuterium content, suggesting that the methyl group in **3aa** was fully derived from acetonitrile and definitely not from $AlMe_3$ (Entry 2). Under the same reaction conditions, 1,4-bis(trimethylsilyl)-2-butyne (**2b**) also underwent methylcyanation to give bis(silylmethyl)-substituted crotonitrile **3ab** in 91% yield (Entry 3). Partial isomerization of the initially formed *cis*-adduct was observed to give a 12:88 mixture of *E*/*Z* stereoisomers. Methylcyanation of unsymmetrical alkynes gave a single regioisomer but as a mixture of stereoisomers (Entries 4–9). Addition to 1-phenyl-1-propyne (**2c**) and 1-phenyl-1-butyne (**2d**) proceeded in the presence of a slightly modified catalyst with $PMe_3$ as a ligand in acetonitrile as a solvent to give methylcyanation products **3ac** and **3ad** in 53% and 49% yield, respectively (Entries 4 and 5). In the latter case, *E*/*Z* ratio remained constant throughout the reaction, implying a mechanism leading to *trans*-adduct (vide infra). Silyl-substituted acetylenes **2e**–**2h** also underwent the methylcyanation reaction in the presence of a Ni/$PPhCy_2$/$AlMe_2Cl$ catalyst (Entries 6–9). Functional groups such as ester, silyloxy, and internal double bond were compatible with the reaction conditions. Formation of formal *trans*-adducts was ascribed to isomerization of the initial *cis*-adducts based on variable *E*/*Z* ratios during the

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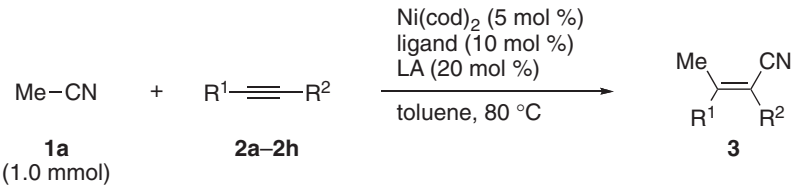
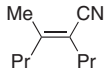
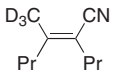
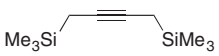
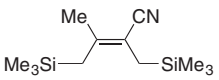
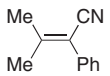
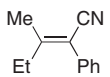
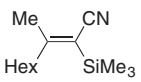
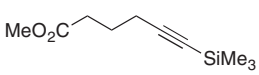
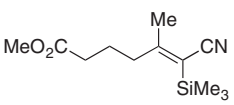
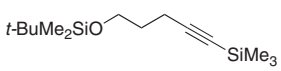
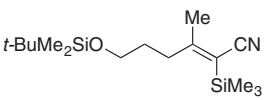
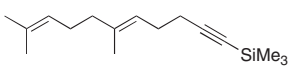
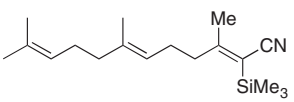
**Table 1.** Nickel/Lewis Acid-Catalyzed Carbocyanation of Alkynes with Acetonitrile




**1a** (1.0 mmol) **2a–2h** **3**

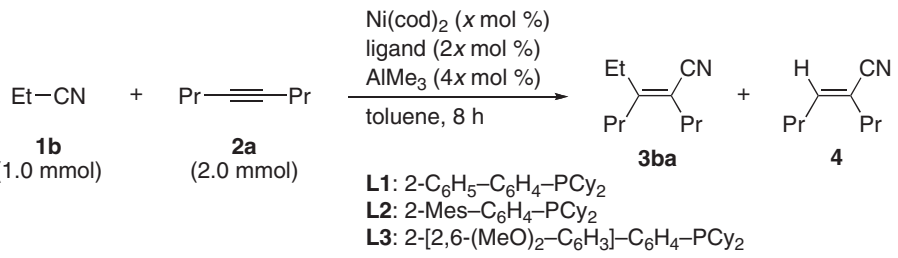
| Entry | Alkyne (mmol) | Cond.[a] | Time/h | Major product, yield/%,[b] $E/Z$ |
|---|---|---|---|---|
| 1[c] | Pr—≡—Pr **2a** (10.0) | A | 4 |  **3aa**, 71 |
| 2[d] | **2a** (1.0) | A | 5 |  **3aa**-$d_3$, 66[e] |
| 3 |  **2b** (1.0) | A | 10 |  **3ab**, 91, 12:88[f] |
| 4[g] | Me—≡—Ph **2c** (1.0) | B | 19 |  **3ac**, 53 |
| 5[g] | Et—≡—Ph **2d** (1.0) | B | 23 |  **3ad**, 49, 61:39[h] |
| 6[i] | Hex—≡—SiMe$_3$ **2e** (2.0) | C | 12 |  **3ae**, 74, 9:91[j] |
| 7[i] |  **2f** (2.0) | C | 21 |  **3af**, 38, 9:91 |
| 8[i] |  **2g** (2.0) | C | 24 |  **3ag**, 60, 25:75 |
| 9[i] |  **2h** (2.0) | C | 24 |  **3ah**, 63, 14:86 |

a) Conditions A, $PPh_2(t\text{-Bu})$ and $AlMe_3$; conditions B, $PMe_3$ and $AlMe_3$; conditions C, $PPhCy_2$ and $AlMe_2Cl$. b) Isolated yields. c) Reaction run in a 10 mmol scale. d) $d_3$-Acetonitrile was used. e) 99% Deuteration. f) $E/Z = 6{:}94$ at 6 h. g) Reaction run with 1.0 mL of acetonitrile as a solvent. h) $E/Z = 61{:}39$ at 8 h. i) Run with 10 mol % of $Ni(cod)_2$. j) $E/Z = 7{:}93$ at 3 h.

reaction (Entries 6–9). The isomerization may be induced by conjugate addition of a phosphorus ligand as a nucleophile. The presence of a LA catalyst, which could interact with the cyano group of the methylcyanation products, might further promote the isomerization. Indeed, exposure of an isolated sample of (*Z*)-**3ae** to the reaction conditions in the presence or absence of a LA catalyst revealed such promotion of the isomerization.

**Nickel/$AlMe_3$-Catalyzed Carbocyanation Reaction of Alkynes Using Propionitrile and Butyronitrile.** We then examined the reaction of propionitrile (**1b**) with **2a**. Under the optimal reaction conditions for the methylcyanation reaction, no trace amount of ethylcyanation product **3ba** was observed. Instead, hydrocyanation product **4** was obtained in 3% yield probably through $\beta$-hydride elimination from an ethylnickel

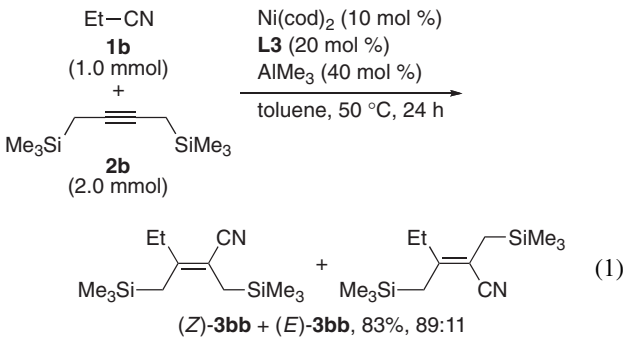
**Table 2.** Nickel/$AlMe_3$-Catalyzed Carbocyanation of 4-Octyne with Propionitrile (**1b**)[a)]



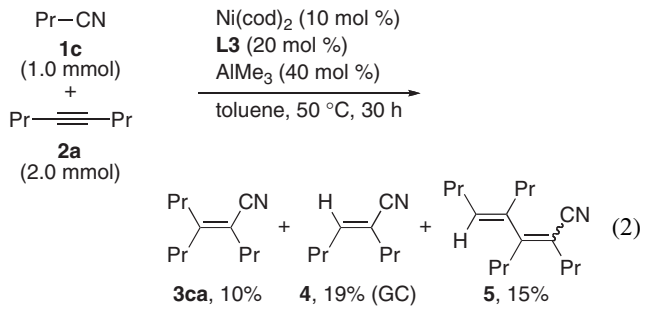

| Entry | Ligand | $x$/mol % | Temp/°C | Product, yield/%[b)] | |
|---|---|---|---|---|---|
| | | | | **3ba** | **4** |
| 1 | $PPh_2(t\text{-Bu})$ | 5 | 80 | 0 | 3 |
| 2 | $P(t\text{-Bu})_3$ | 5 | 80 | 11 | 5 |
| 3 | $PCy_3$ | 5 | 80 | 2 | 4 |
| 4 | **L1** | 5 | 80 | 21 | 1 |
| 5 | **L2** | 5 | 80 | 22 | 1 |
| 6 | **L3** | 5 | 80 | 39 | 1 |
| 7 | **L3** | 5 | 50 | 36 | 0 |
| 8 | **L3** | 10 | 50 | 78[c)] | 1 |

a) All the reaction was carried out using **1b** (1.0 mmol) and **2a** (2.0 mmol) in toluene (1.0 mL). b) Estimated by GC using dodecane as an internal standard. c) Isolated yield.

intermediate (Entry 1 of Table 2). To suppress the unproductive $\beta$-hydride elimination and to optimize reaction conditions for general alkylcyanation, we screened several ligands, especially focusing on bulky phosphines (Entries 2–6). Of the ligands examined, Buchwald's ligands[7] such as 2-Mes–$C_6H_4$–$PCy_2$ (**L2**)[7b] and 2-[2,6-$(MeO)_2$–$C_6H_3$]–$C_6H_4$–$PCy_2$ (**L3**)[7c] were found to be effective to give **3ba** in modest yields accompanied by small amounts of **4** (Entries 5 and 6). Use of $Ni(cod)_2$ (10 mol %) with **L3** as a ligand at 50 °C significantly improved yield of **3ba** up to 78%, and only a trace amount of **4** was detected by GC (Entry 8). The improvement may be attributed to lower reaction temperature and methoxy substituents in **L3** that can coordinate to the nickel center of the reaction intermediates to generate monophosphine nickel species. Indeed, monitoring the reaction mixture by $^{31}P$ NMR showed free **L3** in a significant amount (ca. 50%). Under the same conditions, ethylcyanation of **2b** also proceeded to give the corresponding adduct **3bb** in 83% yield, although partial isomerization of the *cis*-adduct was again observed (eq 1).



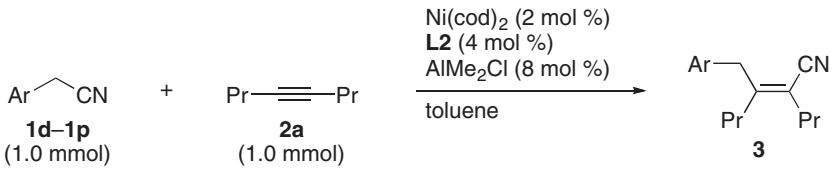

These results prompted us to examine the reaction of butyronitrile (**1c**) with **2a** under similar conditions. However, an expected propylcyanation product was obtained only in 10% yield, and by-products **4** and **5** were obtained as major components (eq 2).

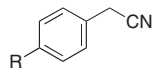
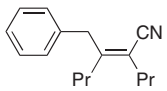
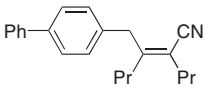
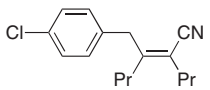
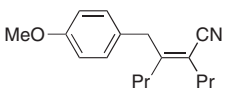
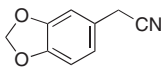
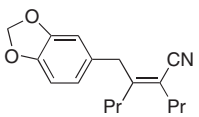
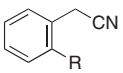
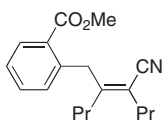
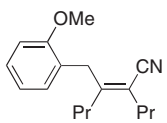
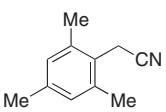
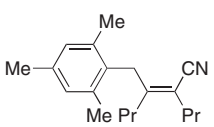
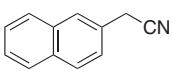
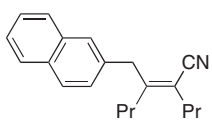
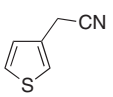
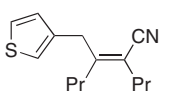
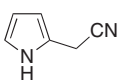
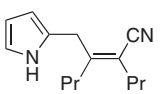
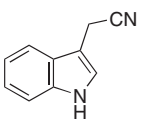
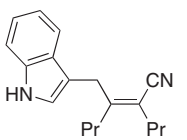
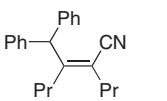



Dienyl cyanide **5** may be derived from **4** and **2a**, because isolated **4** reacted with **2a** under the same reaction conditions to give **5** through alkenylcyanaton of the alkyne.[2d] The observed slow alkylcyanation reaction with **1c** would result from $\beta$-hydride elimination from a propylnickel intermediate to give a propylene–nickel species, the alkene ligand of which would be substituted by alkynes and/or produced **4** and **5** easily, whereas the corresponding ethylene–nickel complex generated by $\beta$-hydride elimination of an ethylnickel intermediate from **1b** would be stable enough to regenerate the ethylnickel species through reinsertion of the coordinating ethylene to result in better yield of the corresponding alkylcyanation product.

**Nickel/$AlMe_2Cl$-Catalyzed Carbocyanation of Alkynes Using Arylacetonitriles.** With the limited success in the carbocyanation of alkynes with alkyl cyanides, we turned our attention to the reaction of substituted acetonitriles, which never suffer from $\beta$-hydride elimination. At the onset, we used arylacetonitriles for carbocyanation, because relatively high reactivity of the substrates was expected for the oxidative addition of their C–CN bonds to nickel(0) as compared with related reactions of allyl cyanides.[2c,2g,8] After a brief survey of reaction conditions with benzyl cyanide (**1d**, 1.0 mmol) and 4-octyne (**2a**, 1.0 mmol), we found that the combination of $Ni(cod)_2$ (2 mol %), **L2** (4 mol %), and $AlMe_2Cl$ (8 mol %) effectively catalyzed the desired benzylcyanation reaction at 35 °C to give **3da** in 90% yield after 8 h (Entry 1 of Table 3).

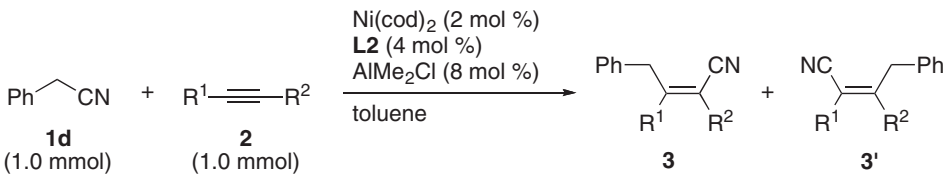
**Table 3.** Carbocyanation of 4-Octyne with Arylacetonitriles

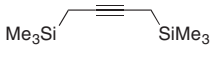
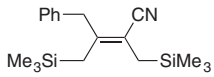
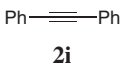
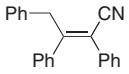
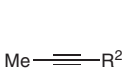
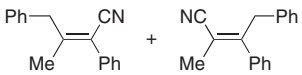
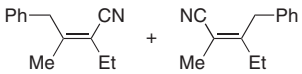
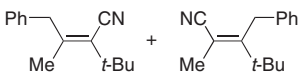
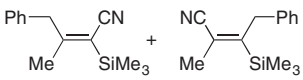
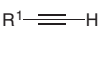
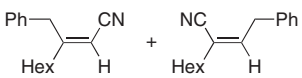
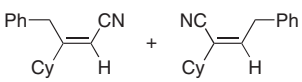
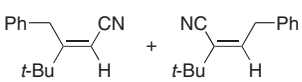



| Entry | Arylacetonitrile | Temp/°C | Time/h | Product, yield/%[a] |
|---|---|---|---|---|
| 1 |  R = H: **1d** | 35 | 8 |  **3da**, 90 |
| 2 | Ph: **1e** | 35 | 8 |  **3ea**, 90 |
| 3 | Cl: **1f** | 80 | 18 |  **3fa**, 74 |
| 4 | MeO: **1g** | 35 | 8 |  **3ga**, 93 |
| 5 |  **1h** | 35 | 24 |  **3ha**, 96 |
| 6 |  R = $CO_2Me$: **1i** | 80 | 5 |  **3ia**, 56 |
| 7 | MeO: **1j** | 35 | 24 |  **3ja**, 83 |
| 8 |  **1k** | 80 | 2 |  **3ka**, 85 |
| 9 |  **1l** | 35 | 96 |  **3la**, 85 |
| 10 |  **1m** | 80 | 2 |  **3ma**, 95 |
| 11[b] |  **1n** | 35 | 10 |  **3na**, 54 |
| 12[b] |  **1o** | 35 | 48 |  **3oa**, 69 |
| 13[b] |  **1p** | 100 | 12 |  **3pa**, 22 |

a) Isolated yields. b) The reaction was carried out using $Ni(cod)_2$ (10 mol %), **L2** (20 mol %), and $AlMe_2Cl$ (40 mol %).

**Table 4.** Carbocyanation of Alkynes with Phenylacetonitrile




| Entry | Alkyne | Temp/°C | Time/h | Product(s), yield/%,[a] ratio[b] |
|---|---|---|---|---|
| 1 |  **2b** | 80 | 70 |  **3db**, 93 |
| 2 |  **2i** | 80 | 73 |  **3di**, 86[c] |
| 3 |  $R^2$ = Ph: **2c** | 35 | 24 |  **3dc**, **3′dc**, 85, 92:8 |
| 4 | Et: **2j** | 35 | 8 |  **3dj**, **3′dj**, 69, 59:41 |
| 5 | *t*-Bu: **2k** | 35 | 21 |  **3dk**, **3′dk**, 94, >99:1 |
| 6[d] | $SiMe_3$: **2l** | 35 | 53 |  **3dl**, **3′dl**, 56, 81:19 |
| 7[e] |  $R^1$ = Hex: **2m** | 35 | 11 |  **3dm**, **3′dm**, 48,[f] 88:12 |
| 8[e] | Cy: **2n** | 35 | 9 |  **3dn**, **3′dn**, 61,[f] 92:8 |
| 9[e] | *t*-Bu: **2o** | 35 | 9 |  **3do**, **3′do**, 54, >99:1 |

a) Isolated yields. b) Estimated by $^1$H NMR of a crude product. c) $E/Z$ = 79:21 (82:18 at 1.5 h). d) The reaction was carried out using $Ni(cod)_2$ (10 mol %), **L2** (20 mol %), and $AlMe_2Cl$ (40 mol %). e) The reaction was carried out using 3.0 equiv of alkyne, $Ni(cod)_2$ (10 mol %), $PMePh_2$ (20 mol %), and $AlMe_2Cl$ (40 mol %). f) 10–20% of an isomeric mixture of 1:2 adducts were also detected.

We further studied the scope of benzyl cyanide having a substituent on the phenyl ring and found that a range of functional groups, such as chloro, acetal, and ester were compatible with both the electron-rich nickel(0) and LA catalysis, C–CN bonds being activated exclusively to give various (*Z*)-3-arylmethyl-2,3-dipropylacrylonitriles (Entries 2–9). Heteroarylacetonitriles also participated in the reaction (Entries 10–12). Notably, no *N*-protecting group was necessary for pyrrolyl- and indolylacetonitriles (Entries 11 and 12). The sterically hindered C–CN bond in diphenylacetonitrile (**1p**) was also activated to give the corresponding adduct **3pa** having a tertiary carbon albeit in a low yield (Entry 13).

The scope of alkynes toward benzyl cyanide (**1d**) is summarized in Table 4. A symmetric alkyne, 1,4-bis(trimethylsilyl)-2-butyne (**2b**), participated in the benzylcyanation reaction to afford **3db** in 93% yield in an exclusive *cis*-fashion (Entry 1), whereas the addition reaction across diphenylacetylene (**2i**) gave a mixture of stereoisomers (Entry 2). The

stereochemistry of (*Z*)-**3di** was unambiguously confirmed by X-ray crystallography (Figure 1). Internal unsymmetrical alkynes with sterically different substituents reacted with modest to excellent regio- and stereoselectivities (Entries 3–6). Whereas the regioselection across 2-pentyne (**2j**) was modest because of small steric difference in the substituents (Entry 4), 1-phenyl-1-propyne (**2c**), 4,4-dimethyl-2-pentyne (**2k**), and trimethyl(1-propynyl)silane (**2l**) all reacted regioselectively to give preferentially isomers having a cyano group at the carbon substituted by a larger group (Entries 3, 5, and 6). Use of $PMePh_2$ as a ligand allowed terminal alkynes to undergo the benzylcyanation to give adducts in good to excellent regioselectivity (Entries 7–9). In the presence of the nickel/**L2** catalyst, tri- and/or oligomerization of terminal alkynes took place rapidly, and no trace amount of the corresponding benzylcyanation products was detected. In contrast to our expectation, the observed regioselectivity was opposite to that with internal alkynes, giving preferentially isomers with a cyano group at the carbon having a smaller substituent (hydrogen). This reversal of regiochemistry might be ascribed to the difference of the ligand. However any of several alternative explanations may be possible. Also observed was formation of 10–20% of structurally unidentified 1:2 adducts, when **2m** and **2n** were employed as an alkyne substrate. Formation of the 1:2 adducts may be attributed to double migratory insertion of 1-octyne into a C–Ni bond (vide infra) based on the experimental fact that isolated **3dm** did not react with **2a** under the same reaction conditions. In all cases, ratios of regioisomers **3**:**3′** were constant during the reaction course, suggesting that these adducts should be kinetic products (vide infra).

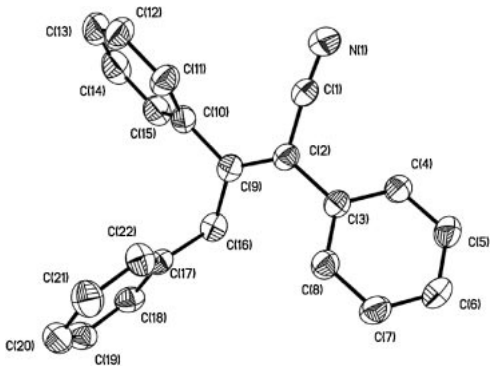
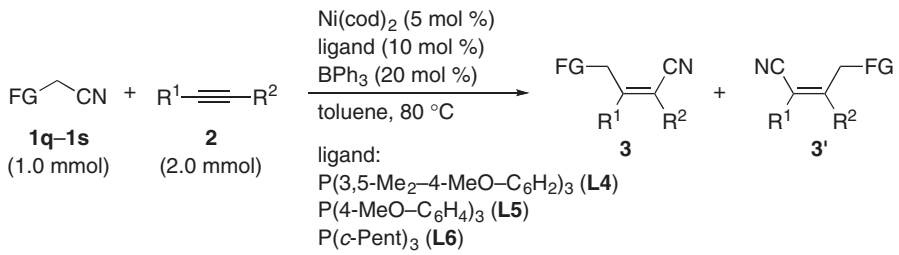
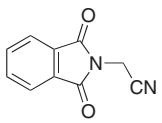
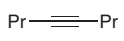
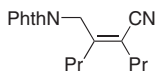
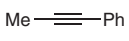
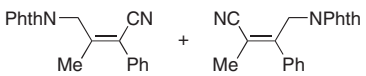
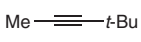
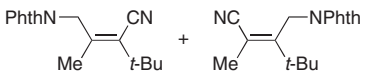
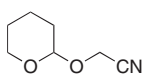
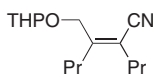
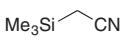
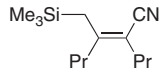



**Figure 1.** ORTEP drawing for (*Z*)-**3di**.

**Table 5.** Carbocyanation of Alkynes with Protected Functionalized Acetonitriles

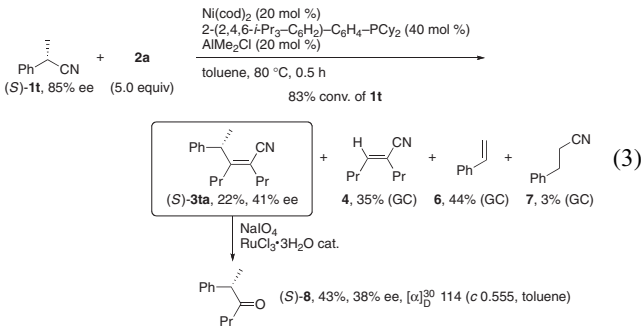



| Entry | Nitrile | Alkyne | Ligand | Time/h | Product(s), yield/%,[a] ratio[b] |
|---|---|---|---|---|---|
| 1 |  **1q** |  **2a** | **L4** | 30 |  **3qa**, 64[c] |
| 2 | **1q** |  **2c** | **L4** | 30 |  **3qc**, **3′qc**, 60,[c] 92[d]:8 |
| 3 | **1q** |  **2k** | **L4** | 30 |  **3qk**, **3′qk**, 79, >99:1 |
| 4[e),f)] |  **1r** | **2a** | **L5** | 3 |  **3ra**, 82[c] |
| 5[f)] |  **1s** | **2a** | **L6** | 13 |  **3sa**, 89 |

a) Isolated yields. b) Estimated by $^1$H NMR of a crude product. c) An isomeric mixture of 1:2 adducts (10–20%) also was detected. d) $E/Z = 13{:}87$ (5:95 at 6 h). e) The reaction was carried out using $Ni(cod)_2$ (10 mol %), **L5** (20 mol %), and $BPh_3$ (40 mol %). f) **2a** (1.5 mmol) was used.

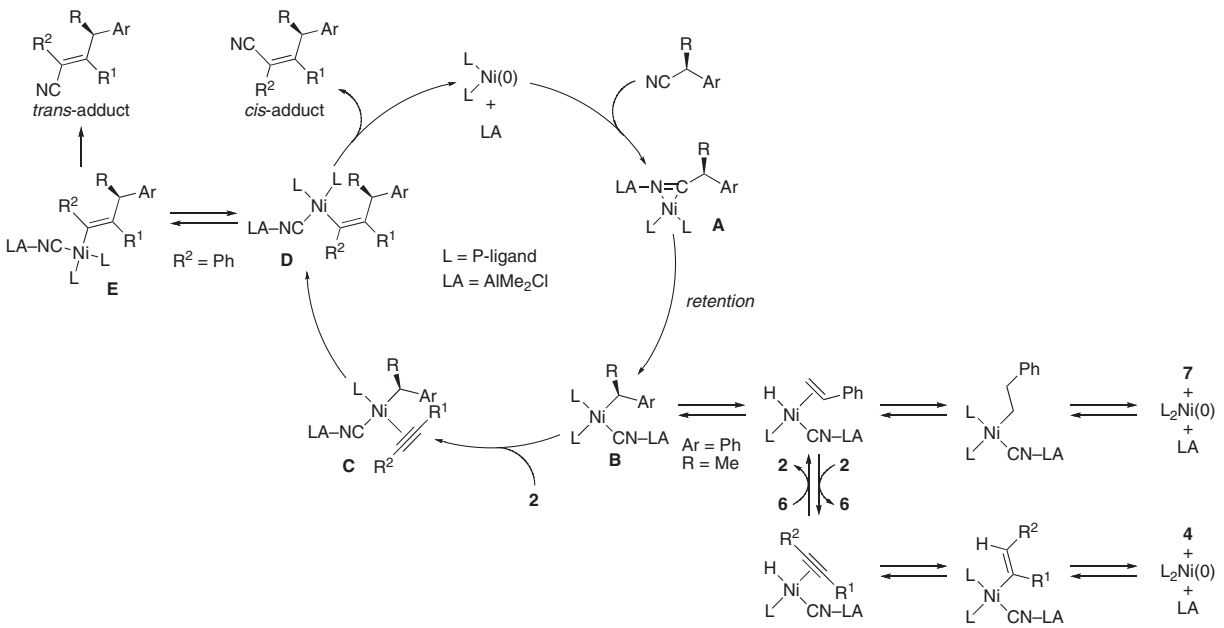
**Nickel/$BPh_3$-Catalyzed Carbocyanation of Alkynes Using Functionalized Acetonitriles.** Having established a broad scope of the carbocyanation of alkynes with arylacetonitriles, we next examined the reaction using other functionalized acetonitriles. We envisioned that the addition of amino- and alkoxyacetonitriles across alkynes would straightforwardly give highly functionalized polysubstituted allylic amines and alcohols with defined stereochemistry. To verify this strategy, we first examined the reaction of *N*-(cyanomethyl)phthalimide (**1q**) with 4-octyne (**2a**). After brief screening of ligands and LA using $Ni(cod)_2$ (5 mol %) in toluene at 80 °C, we found the combination of P(3,5-$Me_2$–4-MeO–$C_6H_2$)$_3$ (10 mol %) and $BPh_3$ (20 mol %) was the best, and obtained protected trisubstituted (*Z*)-allylic amine **3qa** in 64% yield (Entry 1 of Table 5). Unsymmetrical alkynes, **2c** and **2k**, also underwent the addition of **1q** with the same regioselectivity observed for the benzylcyanation reaction (Entries 2 and 3). In the case of 1-phenyl-1-propyne (**2c**), a small amount of stereoisomer (*E*)-**3qc** was obtained, which should be derived from isomerization of initially formed (*Z*)-**3qc**. Indeed, exposure of the isolated sample of (*Z*)-**3qc** to the present reaction conditions caused the isomerization. THP-protected hydroxyacetonitrile (**1r**) also served as a substrate of the alkyne-carbocyanation reaction under slightly modified conditions to give the corresponding THP-protected allylic alcohol **3ra** in a stereoselective manner (Entry 4). For silylmethylcyanation of **2a** with (trimethylsilyl)-acetonitrile (**1s**), a $BPh_3$ cocatalyst was more effective than $AlMe_2Cl$,[2d] possibly because the milder Lewis-acidity of $BPh_3$ is favorable for the reactions of particular nitriles **1q**–**1s** that give products with acid-sensitive functional groups.

**Reaction Mechanism.** To gain stereochemical and mechanistic insight, (*S*)-$\alpha$-phenylpropionitrile [(*S*)-**1t**] of 85% enantiomeric excess (ee) was reacted with **2a** under slightly modified conditions using $Ni(cod)_2$ (20 mol %), 2-(2,4,6-*i*-$Pr_3$–$C_6H_2$)–$C_6H_4$–$PCy_2$ (**L7**, 40 mol %),[7d] and $AlMe_2Cl$ (20 mol %) (eq 3).




(3)

The corresponding adduct (*S*)-**3ta** of 41% ee was obtained in 22% yield, the absolute configuration being determined based on the reported optical rotation of (*R*)-2-phenyl-3-hexanone [(*R*)-**8**][9] after oxidative cleavage of the double bond. Also obtained were hydrocyanation product **4**, styrene (**6**), and hydrocinnamonitrile (**7**) in 35%, 44%, and 3% yields, respectively, as estimated by GC. Recovered **1t** showed 80% ee, suggesting that background racemization of **1t** under these conditions appears to be slower than the carbocyanation event. We also confirmed that no further racemization of **3ta** took place under the present conditions. Accordingly, these results clearly suggest a mechanism shown in Scheme 1, which should start with oxidative addition of a C–CN bond with retention of configuration through LA adduct of $\eta^2$-nitrile–nickel species **A**[4e] to give **B**.[5d] Oxidative addition of acetonitrile to nickel(0) with retention of configuration has also been suggested by theoretical calculations,[5j] in contrast to the nonstereospecific oxidative addition of benzyl halides to nickel(0).[10] The details of the mechanism may be understood in terms of the following steps. Coordination and then migratory insertion of alkynes into the ArC(R)H–Ni bond in **B** give **D** via **C**. Reductive elimination from **D** gives rise to a carbocyanation product and regenerates nickel(0) species. The absolute configuration is retained during these elemental steps.[11] The partial loss of % ee during the addition reaction may be ascribed to $\beta$-hydride




**Scheme 1.** Plausible mechanism.

elimination followed by reinsertion. Particularly, the formation of **4** as well as **6** and **7** is in accord with these possible side reactions. A small degree of racemization observed in recovered **1t** suggests that reductive elimination from *sec*-alkyl(cyano)nickel intermediate **B** to regenerate **1t** would be slower than that from alkenyl- or alkyl(cyano)nickel intermediates giving adducts and alkyl cyanide **7** due presumably to steric repulsion by the phenyl substituent. On the other hand, migratory insertion of the *sec*-alkyl group would be much faster than that of the 2-phenylethyl group, because no detectable amount of (2-phenylethyl)cyanation was observed. In the case of phenyl-substituted alkynes, **D** may isomerize to **E** possibly through conjugate addition of phosphorus ligands[12] followed by reductive elimination to give *trans*-adduct. A LA catalyst would primarily accelerate the oxidative addition step,[2d,4e,4f,8a] although other elemental steps may also be facilitated by its coordination to a cyano group.[13]

## Conclusion

In summary, we have demonstrated the nickel/Lewis acid-catalyzed methylcyanation of alkynes proceeds with high *cis*-selectivity and high regioselectivity. Extension of this catalysis to propionitrile as an alkyl cyanide substrate also meets success by employing bulky phosphorous ligand **L3** having a hemilabile methoxy group, whereas propylcyanation reaction of 4-octyne using butyronitrile proceeded only sluggishly even with the improved catalyst system due to competitive $\beta$-hydride elimination. Instead, a general substrate scope of the carbocyanation reaction with arylacetonitriles has been established under mild reaction conditions with nickel/$AlMe_2Cl$ catalysts. Moreover, functionalized acetonitriles such as protected amino- and hydroxyacetonitriles as well as silylacetonitrile have been demonstrated to add across alkynes in stereo- and regioselective manners under nickel/$BPh_3$ catalysis, producing a wide variety of polysubstituted acrylonitriles having allylic functional groups. Using (*S*)-$\alpha$-phenylpropionitrile, the mechanism of the carbocyanation including the oxidative addition of C–CN bonds with retention of configuration has been elucidated.

## Experimental

**General.** All manipulations of oxygen- and moisture-sensitive materials were conducted with standard Schlenk technique or in a dry box under an argon or nitrogen 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. Proton and carbon nuclear magnetic resonance spectra ($^1$H NMR and $^{13}$C NMR) were recorded on a Varian Mercury 400 spectrometer with solvent resonance as the internal standard ($^1$H NMR, $CHCl_3$ at 7.26 ppm; $^{13}$C NMR, $CDCl_3$ at 77.0 ppm). $^1$H NMR data are reported as follows: chemical shift, spin multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, br = broad, m = multiplet), coupling constants (Hz), and integration. 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*)-**3di**]. 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 × 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.[14] 2-Mes–$C_6H_4$–$PCy_2$ (**L2**),[7b] 2-(2,4,6-*i*-$Pr_3$–$C_6H_2$)–$C_6H_4$–$PCy_2$ (**L7**),[7d] 1,4-bis(trimethylsilyl)-2-butyne (**2b**),[15] 2-pyrrolylacetonitrile (**1n**),[16] (*S*)-$\alpha$-phenylpropionitrile [(*S*)-**1t**] (using (*R*,*S*)-Josiphos as a ligand),[17] *N*-(cyanomethyl)phthalimide (**1q**),[18] and tetrahydro-2*H*-pyran-2-yloxyacetonitrile (**1r**)[19] were prepared according to the respective literature procedure.

**Methyl 6-Trimethylsilyl-5-hexynoate (2f).** A 1.6 M solution of *n*-BuLi (34 mmol, 22 mL) in hexane was added dropwise to a solution of methyl 5-hexynoate (3.6 g, 29 mmol) in THF (29 mL) at −78 °C, and the resulting mixture was stirred for 30 min before dropwise addition of chlorotrimethylsilane (3.4 g, 32 mmol). The reaction mixture was stirred at rt for 19 h before quenching with a saturated $NH_4Cl$ aqueous solution. The resulting mixture was extracted three times with diethyl ether, and the combined organic layers were dried over anhydrous $MgSO_4$, filtered through a Celite pad, and then concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane–ethyl acetate = 30:1) and further by distillation under vacuum to give the title compound (1.12 g, 5.7 mmol, 20%).[20]

**5-*tert*-Butyldimethylsilyloxy-1-trimethylsilyl-1-pentyne (2g).** To a suspension of NaH (0.86 g, 36 mmol) in THF (150 mL) was added dropwise 4-pentyn-1-ol (2.8 g, 33 mmol) at 0 °C. The resulting mixture was stirred at rt for 30 min, cooled at 0 °C, and treated with *tert*-butylchlorodimethylsilane (5.4 g, 30 mmol). The whole mixture was stirred at rt for 15 h, and then quenched with water. The resulting mixture was extracted three times with hexane, and the combined organic layers were washed three times with water, dried over anhydrous $MgSO_4$, filtered through a Celite pad, and then concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane–ethyl acetate = 50:1) to give 1-*tert*-butyldimethylsilyloxy-4-pentyne (3.6 g, 18.3 mmol, 61%).[21] To a solution of the silyl ether (3.6 g, 18.3 mmol) in THF (37 mL) was added dropwise a 1.6 M solution of *n*-BuLi (20 mmol, 13 mL) in hexane at −78 °C. The resulting mixture was stirred for 30 min before dropwise addition of chlorotrimethylsilane (2.4 g, 22.0 mmol). After stirring at rt for 13 h, the reaction was quenched with a saturated $NH_4Cl$ aqueous solution. The

resulting mixture was extracted three times with hexane, and the combined organic layers were washed three times with water, dried over anhydrous $MgSO_4$, filtered through a Celite pad, and then concentrated in vacuo. The residue was purified by distillation under vacuum to give the title compound (4.5 g, 16.6 mmol, 90%).[22]

**(*E*)-6,10-Dimethyl-1-trimethylsilyl-5,9-undecadien-1-yne (2h).** A 1.6 M solution of *n*-BuLi (24 mmol, 15 mL) in hexane was added dropwise to a solution of (*E*)-6,10-dimethyl-5,9-undecadien-1-yne (3.5 g, 20 mmol, prepared[23] from (*E*)-1-chloro-3,7-dimethyl-2,6-octadiene) in THF (40 mL) at −78 °C, and the resulting mixture was stirred for 15 min before dropwise addition of chlorotrimethylsilane (3.3 g, 30 mmol). After stirring at rt for 3 h, the reaction was quenched with water. The resulting mixture was extracted three times with hexane, and the combined organic layers were washed three times with water, dried over anhydrous $MgSO_4$, filtered through a Celite pad, and then concentrated in vacuo. The residue was purified by distillation under vacuum to give the title compound (4.6 g, 18.5 mmol, 92%).[24]

**Methylcyanation of 4-Octyne (2a).** In a dry box, acetonitrile (**1a**, 0.41 g, 10.0 mmol), a 1.0 M solution of $AlMe_3$ in hexane (2.0 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 $PPh_2$(*t*-Bu) (0.24 g, 1.00 mmol) in toluene (10 mL) placed in a vial. The resulting mixture was stirred at 80 °C for 4 h, filtered through a silica gel pad, and concentrated in vacuo. The residue was distilled to give (*E*)-3-methyl-2-propylhex-2-enenitrile (**3aa**, 1.08 g, 71%) as a pale yellow oil, bp 80 °C (20 mmHg), $R_f = 0.18$ (hexane–ethyl acetate = 40:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.93 (t, $J = 7.3$ Hz, 3H), 0.94 (t, $J = 7.3$ Hz, 3H), 1.46 (sext, $J = 7.5$ Hz, 2H), 1.56 (sext, $J = 7.5$ Hz, 2H), 2.05 (s, 3H), 2.12–2.21 (m, 4H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.6, 14.1, 21.0, 21.9, 22.6, 31.5, 35.6, 109.7, 119.3, 155.3. IR (neat): 2964, 2934, 2874, 2208, 1630, 1466, 1381, 1138, 1094, 741 cm$^{-1}$. Anal. Calcd for $C_{10}H_{17}N$; C, 79.41; H, 11.33%. Found: C, 79.47; H, 11.47%.

**Carbocyanation of Alkynes with Acetonitrile. General procedure A**: In a dry box, acetonitrile (41 mg, 1.00 mmol), a 1.0 M solution of $AlMe_3$ in hexane (0.20 mL, 0.20 mmol), an alkyne (1.00 mmol), and dodecane (internal standard, 85 mg, 0.50 mmol) were added sequentially to a solution of $Ni(cod)_2$ (14 mg, 50 μmol) and $PPh_2$(*t*-Bu) (24 mg, 0.10 mmol) in toluene (1.0 mL) placed in a vial. The vial was taken out from the dry box and heated at 80 °C for the time specified in 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 alkylcyanation products in yields listed in Table 1.

**General procedure B**: In a dry box, a 1.0 M solution of $AlMe_3$ in hexane (0.20 mL, 0.20 mmol), an alkyne (1.00 mmol), and dodecane (internal standard, 85 mg, 0.50 mmol) were added sequentially to a solution of $Ni(cod)_2$ (14 mg, 50 μmol) and $PMe_3$ (7.6 mg, 0.10 mmol) in acetonitrile (1.0 mL) placed in a vial. The vial was taken out from the dry box and heated at 80 °C for the time specified in 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 alkylcyanation products in yields listed in Table 1.

**General procedure C**: In a dry box, acetonitrile (82 mg, 2.0 mmol), a 1.0 M solution of $AlMe_2Cl$ in hexane (0.40 mL, 0.40 mmol), an alkyne (1.00 mmol), and dodecane (internal standard, 85 mg, 0.50 mmol) were added sequentially to a solution of $Ni(cod)_2$ (28 mg, 0.10 mmol) and $PPhCy_2$ (55 mg, 0.20 mmol) in toluene (1.0 mL) placed in a vial. The vial was taken out from the dry box and heated at 80 °C for the time specified in 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 alkylcyanation products in yields listed in Table 1.

Regio- and/or stereoisomers were separated by preparative GPC or HPLC and characterized by spectrometry. The spectra of **3ac** and **3ad** agreed well with those reported previously.[25]

**(*E*)-3-($^2$H$_3$)Methyl-2-propylhex-2-enenitrile (3aa-*d*$_3$):** A colorless oil, $R_f = 0.20$ (hexane–ethyl acetate = 40:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.92 (t, $J = 7.3$ Hz, 3H), 0.94 (t, $J = 7.3$ Hz, 3H), 1.45 (sext, $J = 7.5$ Hz, 2H), 1.55 (sext, $J = 7.5$ Hz, 2H), 2.11–2.21 (m, 4H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.6, 14.1, 21.0, 21.9, 31.5, 35.5, 109.7, 119.3, 155.2. IR (neat): 2963, 2934, 2874, 2208, 1624, 1466, 1381, 1090, 1042, 739 cm$^{-1}$. HRMS (EI) Calcd for $C_{10}H_{14}D_3N$: $M^+$, 154.1549. Found: *m*/*z* 154.1557.

**(*Z*)-3-Methyl-4-(trimethylsilyl)-2-[(trimethylsilyl)methyl]-but-2-enenitrile [(*Z*)-3ab]:** A colorless oil, $R_f = 0.20$ (hexane–ethyl acetate = 30:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.09 (s, 9H), 0.11 (s, 9H), 1.56 (s, 2H), 1.70 (s, 2H), 2.04 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ −1.1, −0.4, 21.0, 24.8, 27.4, 102.1, 120.8, 151.2. IR (neat): 2955, 2899, 2205, 1614, 1418, 1250, 1196, 1175, 1144, 1086, 1011, 928, 845, 762, 696, 627, 606, 594, 565, 478, 442 cm$^{-1}$. Anal. Calcd for $C_{12}H_{25}NSi_2$: C, 60.18; H, 10.52%. Found: C, 60.09; H, 10.62%.

**(*E*)-3-Methyl-4-(trimethylsilyl)-2-[(trimethylsilyl)methyl]-but-2-enenitrile [(*E*)-3ab]:** A pale yellow oil, $R_f = 0.20$ (hexane–ethyl acetate = 30:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.11 (s, 9H), 0.12 (s, 9H), 1.64 (s, 2H), 1.75 (s, 3H), 2.02 (s, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ −1.1, −0.4, 21.0, 21.2, 31.1, 102.2, 121.1, 151.1. IR (neat): 2955, 2899, 2207, 1614, 1416, 1377, 1248, 1179, 1152, 1096, 1015, 920, 841, 762, 694 cm$^{-1}$. HRMS (EI) Calcd for $C_{12}H_{25}NSi_2$: $M^+$, 239.1526. Found: *m*/*z* 239.1521.

**(*Z*)-3-Methyl-2-trimethylsilylnon-2-enenitrile [(*Z*)-3ae]:** A colorless oil, $R_f = 0.15$ (hexane–ethyl acetate = 30:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.28 (s, 9H), 0.90 (t, $J = 6.9$ Hz, 3H), 1.24–1.37 (m, 6H), 1.40–1.50 (m, 2H), 2.15 (s, 3H), 2.25 (t, $J = 8.0$ Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 0.1, 14.1, 22.6, 24.4, 28.4, 29.5, 31.7, 38.7, 108.7, 120.3, 174.2. IR (neat): 2957, 2930, 2858, 2197, 1583, 1466, 1377, 1254, 843, 762 cm$^{-1}$. Anal. Calcd for $C_{13}H_{25}NSi$: C, 69.88; H, 11.28%. Found: C, 69.81; H, 11.42%.

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

11.28%. Found: C, 69.98; H, 11.08%.

**(*Z*)-Methyl 6-Cyano-5-methyl-6-trimethylsilylhex-5-enoate [(*Z*)-3af]:** A colorless oil, $R_f = 0.25$ (hexane–ethyl acetate = 5:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.28 (s, 9H), 1.79 (quint, $J = 7.7$ Hz, 2H), 2.17 (s, 3H), 2.30 (t, $J = 8.1$ Hz, 2H), 2.34 (t, $J = 7.3$ Hz, 2H), 3.68 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 0.0, 23.4, 24.2, 33.6, 37.6, 51.7, 110.1, 120.0, 172.3, 172.8. IR (neat): 2955, 2901, 2195, 1740, 1584, 1437, 1375, 1254, 1200, 1157, 1088, 1045, 1007, 905, 843, 762, 698, 631 cm$^{-1}$. Anal. Calcd for $C_{12}H_{21}NO_2Si$: C, 60.21; H, 8.84%. Found: C, 59.99; H, 8.69%.

**(*E*)-Methyl 6-Cyano-5-methyl-6-trimethylsilylhex-5-enoate [(*E*)-3af]:** A colorless oil, $R_f = 0.25$ (hexane–ethyl acetate = 5:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.29 (s, 9H), 1.86 (quint, $J = 7.7$ Hz, 2H), 1.99 (s, 3H), 2.37 (t, $J = 7.5$ Hz, 2H), 2.54 (t, $J = 7.8$ Hz, 2H), 3.69 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ −0.3, 22.4, 23.2, 33.4, 40.0, 51.7, 109.7, 119.7, 172.4, 173.2. IR (neat): 2955, 2195, 1740, 1586, 1437, 1375, 1254, 1200, 1175, 1157, 1088, 1045, 1003, 845, 762, 698, 640 cm$^{-1}$. HRMS (EI) Calcd for $C_{12}H_{21}NO_2Si$: $M^+$, 239.1342. Found: $m/z$ 239.1343.

**(*Z*)-6-(*tert*-Butyldimethylsilyloxy)-3-methyl-2-trimethylsilylhex-2-enenitrile [(*Z*)-3ag]:** A colorless oil, $R_f = 0.10$ (hexane–ethyl acetate = 30:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.06 (s, 6H), 0.29 (s, 9H), 0.90 (s, 9H), 1.60–1.70 (m, 2H), 2.17 (s, 3H), 2.35 (t, $J = 8.1$ Hz, 2H), 3.65 (t, $J = 5.9$ Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ −5.2, 0.0, 18.4, 24.5, 26.0, 31.5, 35.4, 62.7, 109.1, 120.3, 173.8. IR (neat): 2955, 2930, 2897, 2858, 2197, 1583, 1472, 1462, 1437, 1408, 1387, 1362, 1256, 1099, 1022, 1005, 947, 908, 839, 777, 762, 696, 662, 629 cm$^{-1}$. Anal. Calcd for $C_{16}H_{33}NOSi_2$: C, 61.67; H, 10.67%. Found: C, 61.51; H, 10.66%.

**(*E*)-6-(*tert*-Butyldimethylsilyloxy)-3-methyl-2-trimethylsilylhex-2-enenitrile [(*E*)-3ag]:** A colorless oil, $R_f = 0.13$ (hexane–ethyl acetate = 30:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.07 (s, 6H), 0.29 (s, 9H), 0.91 (s, 9H), 1.69–1.77 (m, 2H), 2.00 (s, 3H), 2.55 (t, $J = 8.0$ Hz, 2H), 3.65 (t, $J = 6.4$ Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ −5.1, −0.3, 18.4, 22.7, 26.0, 31.3, 37.5, 62.5, 108.7, 119.8, 173.8. IR (neat): 2955, 2930, 2897, 2858, 2195, 1585, 1472, 1462, 1408, 1389, 1362, 1254, 1103, 1007, 839, 775, 760 cm$^{-1}$. Anal. Calcd for $C_{16}H_{33}NOSi_2$: C, 61.67; H, 10.67%. Found: C, 61.95; H, 10.75%.

**(2*Z*,6*E*)-3,7,11-Trimethyl-2-trimethylsilyldodeca-2,6,10-trienenitrile [(*Z*)-3ah]:** A colorless oil, $R_f = 0.18$ (hexane–ethyl acetate = 30:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.29 (s, 9H), 1.61 (s, 3H), 1.62 (s, 3H), 1.69 (s, 3H), 1.97–2.11 (m, 4H), 2.14–2.22 (m, 2H), 2.18 (s, 3H), 2.30 (t, $J = 8.0$ Hz, 2H), 5.02–5.11 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 0.1, 16.2, 17.8, 24.3, 25.9, 26.6, 26.8, 38.5, 39.7, 109.3, 120.2, 122.1, 123.9, 131.4, 136.5, 173.5. IR (neat): 2965, 2916, 2857, 2195, 1667, 1582, 1445, 1377, 1327, 1254, 1109, 1042, 984, 893, 843, 760, 696, 629 cm$^{-1}$. Anal. Calcd for $C_{18}H_{31}NSi$: C, 74.67; H, 10.79%. Found: C, 74.76; H, 11.01%.

**(2*E*,6*E*)-3,7,11-Trimethyl-2-trimethylsilyldodeca-2,6,10-trienenitrile [(*E*)-3ah]:** A colorless oil, $R_f = 0.23$ (hexane–ethyl acetate = 30:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.29 (s, 9H), 1.61 (s, 3H), 1.62 (s, 3H), 1.69 (s, 3H), 1.96–2.02 (m, 2H), 1.98 (s, 3H), 2.04–2.12 (m, 2H), 2.23 (q, $J = 7.4$ Hz, 2H), 2.53 (t, $J = 7.6$ Hz, 2H), 5.06–5.17 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ −0.3, 16.2, 17.8, 22.9, 25.8, 26.7, 26.8, 39.8, 40.8, 108.8, 119.9, 122.2, 124.1, 131.3, 136.6, 173.5. IR (neat): 2963, 2918, 2857, 2193, 1584, 1451, 1375, 1254, 1109, 1042, 843, 760, 696, 644, 629 cm$^{-1}$. HRMS (EI) Calcd for $C_{18}H_{31}NSi$: $M^+$, 289.2226. Found: $m/z$ 289.2225.

**Ethylcyanation of Alkynes Using Propionitrile (Entry 8 of Table 2 and eq 1). General procedure**: In a dry box, propionitrile (60 mg, 1.00 mmol), a 1.0 M solution of $AlMe_3$ in hexane (0.40 mL, 0.40 mmol), an alkyne (2.00 mmol), and dodecane (internal standard, 85 mg, 0.50 mmol) were added sequentially to a solution of $Ni(cod)_2$ (28 mg, 0.10 mmol) and 2-[2,6-$(MeO)_2$–$C_6H_3$]–$C_6H_4$–$PCy_2$ (82 mg, 0.20 mmol) in toluene (1.0 mL) placed in a vial. The vial was taken out from the dry box and heated at 50 °C for 8 h (for **2a**) or 24 h (for **2b**). The resulting mixture was filtered through a silica gel pad, concentrated in vacuo, and purified by flash column chromatography on silica gel to give the corresponding carbocyanation products in yields listed in Entry 8 of Table 2 and eq 1. Stereoisomers were separated by preparative HPLC and characterized by spectrometry.

**(*Z*)-3-Ethyl-2-propylhex-2-enenitrile (3ba):** A colorless oil, $R_f = 0.18$ (hexane–ethyl acetate = 40:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.940 (t, $J = 7.3$ Hz, 3H), 0.944 (t, $J = 7.3$ Hz, 3H), 1.09 (t, $J = 7.6$ Hz, 3H), 1.43 (sext, $J = 7.6$ Hz, 2H), 1.57 (sext, $J = 7.4$ Hz, 2H), 2.15 (t, $J = 7.9$ Hz, 2H), 2.17 (t, $J = 7.3$ Hz, 2H), 2.40 (q, $J = 7.5$ Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.2, 13.6, 14.3, 21.4, 21.9, 29.3, 31.5, 33.0, 109.2, 119.1, 161.1. IR (neat): 2964, 2936, 2874, 2208, 1624, 1464, 1379, 1138, 1057, 797, 741 cm$^{-1}$. Anal. Calcd for $C_{11}H_{19}N$: C, 79.94; H, 11.59%. Found: C, 79.91; H, 11.71%.

**(*Z*)-2,3-Bis(trimethylsilylmethyl)pent-2-enenitrile [(*Z*)-3bb]:** A colorless oil, $R_f = 0.16$ (hexane–ethyl acetate = 30:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.09 (s, 9H), 0.11 (s, 9H), 1.10 (t, $J = 7.5$ Hz, 3H), 1.55 (s, 2H), 1.70 (s, 2H), 2.34 (q, $J = 7.5$ Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ −1.1, −0.4, 13.7, 21.0, 24.5, 31.2, 101.3, 120.6, 157.5. IR (neat): 2955, 2899, 2203, 1607, 1464, 1418, 1400, 1375, 1250, 1184, 1173, 1142, 1063, 1044, 978, 912, 843, 791, 772, 696, 673, 606, 525 cm$^{-1}$. Anal. Calcd for $C_{13}H_{27}NSi_2$: C, 61.59; H, 10.73%. Found: C, 61.76; H, 10.99%.

**(*E*)-2,3-Bis(trimethylsilylmethyl)pent-2-enenitrile [(*E*)-3bb]:** A colorless oil, $R_f = 0.16$ (hexane–ethyl acetate = 30:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.12 (s, 18H), 1.01 (t, $J = 7.5$ Hz, 3H), 1.64 (s, 2H), 2.00 (s, 2H), 2.06 (q, $J = 7.5$ Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ −1.1, −0.5, 12.0, 20.4, 26.7, 27.6, 101.5, 121.3, 156.7. IR (neat): 2955, 2895, 2205, 1605, 1452, 1418, 1244, 1171, 1150, 1069, 1038, 976, 905, 839, 791, 766, 704, 694, 648 cm$^{-1}$. HRMS (EI) Calcd for $C_{13}H_{27}NSi_2$: $M^+$, 253.1682. Found: $m/z$ 253.1694.

**Propylcyanation of 2a Using Butyronitrile (eq 2).** In a dry box, butyronitrile (69 mg, 1.00 mmol), a 1.0 M solution of $AlMe_3$ in hexane (0.40 mL, 0.40 mmol), 4-octyne (220 mg, 2.00 mmol), and dodecane (internal standard, 85 mg, 0.50 mmol) were added sequentially to a solution of $Ni(cod)_2$ (28 mg, 0.10 mmol) and 2-[2,6-$(MeO)_2$–$C_6H_3$]–$C_6H_4$–$PCy_2$ (82 mg, 0.20 mmol) in toluene (1.0 mL) placed in a vial. The vial was taken out from the dry box and heated at 50 °C for 30 h. GC analysis of the reaction mixture showed the formation of hydrocyanation product **4** in 19% yield. 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 2,3-dipropylhex-2-enenitrile (**3ca**, 18 mg, 10%) and the isomeric mixture of 1:2 adducts (38 mg, 15%).

**2,3-Dipropylhex-2-enenitrile (3ca):** A colorless oil, $R_f = 0.10$ (hexane–ethyl acetate = 30:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.94 (t, $J = 7.3$ Hz, 3H), 0.95 (t, $J = 7.4$ Hz, 3H), 0.96 (t, $J = 7.3$ Hz, 3H), 1.43 (sext, $J = 7.5$ Hz, 2H), 1.52 (sext, $J = 7.5$ Hz, 2H), 1.58 (sext, $J = 7.5$ Hz, 2H), 2.14 (t, $J = 7.9$ Hz, 2H), 2.19 (t, $J = 7.6$ Hz, 2H), 2.38 (t, $J = 7.6$ Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.6, 14.0, 14.3, 21.5, 21.8, 21.9, 31.6, 33.4, 38.0, 110.0, 119.3, 159.4. IR (neat): 2963, 2934, 2874, 2207, 1624, 1458, 1381, 1341, 1258, 1136, 1094, 1076, 895, 743 cm$^{-1}$. Anal. Calcd for $C_{12}H_{21}N$: C, 80.38; H, 11.81%. Found: C, 80.41; H, 11.61%.

**(*E*)-2-Propylhex-2-enenitrile (4):** A colorless oil, $R_f = 0.18$ (hexane–ethyl acetate = 40:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.94 (t, $J = 7.4$ Hz, 3H), 0.95 (t, $J = 7.4$ Hz, 3H), 1.46 (sext, $J = 7.4$ Hz, 2H), 1.58 (sext, $J = 7.4$ Hz, 2H), 2.17 (quint, $J = 7.5$ Hz, 4H), 6.35 (t, $J = 7.6$ Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.5, 13.8, 21.4, 21.9, 30.4, 30.5, 114.8, 120.1, 147.9. IR (neat): 2963, 2934, 2874, 2216, 1634, 1460, 1381, 1067, 908 cm$^{-1}$. HRMS (EI) Calcd for $C_9H_{15}N$: $M^+$, 137.1204. Found: $m/z$ 137.1209.

**Carbocyanation of Alkynes with Arylacetonitriles. General procedure**: In a dry box, to a stirred mixture of an arylacetonitrile (1.00 mmol), an alkyne (1.00 mmol), and tetradecane (internal standard, 99 mg, 0.50 mmol) placed in a vial were 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) placed in a vial. The vial was taken out from the dry box and stirred at 35 °C for the time specified in Tables 3 and 4. 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 Tables 3 and 4. Regio- and/or stereoisomers were separated by preparative GPC or HPLC and characterized by spectrometry.

**(*Z*)-3-Benzyl-2-propylhex-2-enenitrile (3da):** A colorless oil, $R_f = 0.41$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.88 (t, $J = 7.3$ Hz, 3H), 0.97 (t, $J = 7.3$ Hz, 3H), 1.38 (sext, $J = 7.6$ Hz, 2H), 1.63 (sext, $J = 7.5$ Hz, 2H), 2.04 (t, $J = 8.0$ Hz, 2H), 2.24 (t, $J = 7.6$ Hz, 2H), 3.74 (s, 2H), 7.19–7.27 (m, 3H), 7.30 (tt, $J = 7.1$, 1.5 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.5, 14.1, 21.3, 21.8, 31.6, 32.7, 42.0, 111.2, 119.6, 126.7, 128.6, 128.7, 137.8, 157.9. 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%.

**(*Z*)-3-(Biphenyl-4-ylmethyl)-2-propylhex-2-enenitrile (3ea):** A colorless oil, $R_f = 0.41$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.91 (t, $J = 7.3$ Hz, 3H), 0.98 (t, $J = 7.3$ Hz, 3H), 1.42 (sext, $J = 7.6$ Hz, 2H), 1.65 (sext, $J = 7.5$ Hz, 2H), 2.09 (t, $J = 8.0$ Hz, 2H), 2.26 (t, $J = 7.6$ Hz, 2H), 3.78 (s, 2H), 7.29 (d, $J = 8.4$ Hz, 2H), 7.34 (tt, $J = 7.4$, 1.5 Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.53 (dt, $J = 8.4$, 2.0 Hz, 2H), 7.56–7.60 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.5, 14.1, 21.3, 21.7, 31.6, 32.7, 41.6, 111.3, 119.6, 126.9, 127.2, 127.3, 128.7, 129.1, 136.9, 139.6, 140.7, 157.7. 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%.

**(*Z*)-3-[(4-Chlorophenyl)methyl]-2-propylhex-2-enenitrile (3fa):** A colorless oil, $R_f = 0.34$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.89 (t, $J = 7.3$ Hz, 3H), 0.96 (t, $J = 7.3$ Hz, 3H), 1.37 (sext, $J = 7.6$ Hz, 2H), 1.62 (sext, $J = 7.5$ Hz, 2H), 2.03 (t, $J = 7.9$ Hz, 2H), 2.24 (t, $J = 7.6$ Hz, 2H), 3.70 (s, 2H), 7.14 (dt, $J = 8.4$, 2.1 Hz, 2H), 7.27 (dt, $J = 8.6$, 2.3 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.4, 14.1, 21.3, 21.7, 31.6, 32.7, 41.2, 111.7, 119.4, 128.7, 130.0, 132.6, 136.3, 157.2. 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%.

**(*Z*)-3-[(4-Methoxyphenyl)methyl]-2-propylhex-2-enenitrile (3ga):** A colorless oil, $R_f = 0.13$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.88 (t, $J = 7.3$ Hz, 3H), 0.96 (t, $J = 7.4$ Hz, 3H), 1.37 (sext, $J = 7.6$ Hz, 2H), 1.62 (sext, $J = 7.5$ Hz, 2H), 2.03 (t, $J = 8.0$ Hz, 2H), 2.23 (t, $J = 7.6$ Hz, 2H), 3.67 (s, 2H), 3.79 (s, 3H), 6.83 (dt, $J = 8.8$, 2.6 Hz, 2H), 7.13 (dt, $J = 8.8$, 2.6 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.4, 14.0, 21.2, 21.6, 31.5, 32.5, 41.0, 55.1, 110.7, 113.9, 119.6, 129.6, 129.7, 158.2, 158.3. 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%.

**(*Z*)-3-[(3,4-Methylenedioxyphenyl)methyl]-2-propylhex-2-enenitrile (3ha):** A colorless oil, $R_f = 0.39$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.89 (t, $J = 7.4$ Hz, 3H), 0.97 (t, $J = 7.3$ Hz, 3H), 1.37 (sext, $J = 7.6$ Hz, 2H), 1.62 (sext, $J = 7.5$ Hz, 2H), 2.04 (t, $J = 7.9$ Hz, 2H), 2.23 (t, $J = 7.7$ Hz, 2H), 3.65 (s, 2H), 5.94 (s, 2H), 6.66 (dd, $J = 7.9$, 1.6 Hz, 1H), 6.69 (d, $J = 1.8$ Hz, 1H), 6.74 (d, $J = 7.9$ Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.4, 14.1, 21.3, 21.7, 31.5, 32.5, 41.5, 100.9, 108.2, 108.9, 111.1, 119.5, 121.7, 131.4, 146.3, 147.8, 157.9. 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%.

**(*Z*)-3-[(2-Methoxycarbonylphenyl)methyl]-2-propylhex-2-enenitrile (3ia):** A yellow oil, $R_f = 0.31$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.84 (t, $J = 7.6$ Hz, 3H), 0.98 (t, $J = 7.3$ Hz, 3H), 1.33 (sext, $J = 7.6$ Hz, 2H), 1.64 (sext, $J = 7.5$ Hz, 2H), 1.99 (t, $J = 8.0$ Hz, 2H), 2.26 (t, $J = 7.6$ Hz, 2H), 3.91 (s, 3H), 4.22 (s, 2H), 7.22–7.33 (m, 2H), 7.44 (td, $J = 7.6$, 1.5 Hz, 1H), 7.88 (dd, $J = 7.8$, 1.4 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.5, 14.1, 21.5, 21.8, 31.7, 33.0, 38.8, 52.2, 112.0, 119.5, 126.7, 130.1, 130.2, 130.8, 132.1, 139.0, 157.8, 168.1. 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%.

**(*Z*)-3-[(2-Methoxyphenyl)methyl]-2-propylhex-2-enenitrile (3ja):** A colorless oil, $R_f = 0.30$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.87 (t, $J = 7.4$ Hz, 3H), 0.96 (t, $J = 7.3$ Hz, 3H), 1.37 (sext, $J = 7.6$ Hz, 2H), 1.61 (sext, $J = 7.5$ Hz, 2H), 2.02 (t, $J = 8.0$ Hz, 2H), 2.23 (t, $J = 7.5$ Hz, 2H), 3.76 (s, 2H), 3.83 (s, 3H), 6.85 (d, $J = 8.2$ Hz, 1H), 6.89

(td, $J = 7.5$, 1.1 Hz, 1H), 7.13 (dd, $J = 7.3$, 1.6 Hz, 1H), 7.22 (td, $J = 8.1$, 1.8 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.3, 14.1, 21.4, 21.7, 31.6, 32.6, 35.8, 55.1, 110.2, 110.9, 119.6, 120.4, 126.2, 127.9, 129.9, 157.5, 157.8. 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%.

**(*Z*)-2-Propyl-3-[(2,4,6-trimethylphenyl)methyl]hex-2-enenitrile (3ka):** A colorless oil, $R_f = 0.37$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.81 (t, $J =$ 7.3 Hz, 3H), 0.97 (t, $J = 7.3$ Hz, 3H), 1.22 (sext, $J = 7.8$ Hz, 2H), 1.62 (sext, $J = 7.5$ Hz, 2H), 1.86 (t, $J = 8.2$ Hz, 2H), 2.22 (t, $J = 7.7$ Hz, 2H), 2.26 (s, 3H), 2.27 (s, 6H), 3.82 (s, 2H), 6.84 (s, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.6, 14.3, 20.4, 20.8, 21.6, 22.1, 31.7, 32.4, 36.4, 110.0, 119.2, 129.2, 131.3, 136.1, 137.3, 157.5. 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%.

**(*Z*)-3-(2-Naphthylmethyl)-2-propylhex-2-enenitrile (3la):** A colorless oil, $R_f = 0.42$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.88 (t, $J = 7.4$ Hz, 3H), 0.99 (t, $J = 7.3$ Hz, 3H), 1.41 (sext, $J = 7.6$ Hz, 2H), 1.66 (sext, $J = 7.5$ Hz, 2H), 2.07 (t, $J = 8.0$ Hz, 2H), 2.28 (t, $J = 7.5$ Hz, 2H), 3.91 (s, 2H), 7.35 (dd, $J = 8.4$, 1.8 Hz, 1H), 7.42–7.51 (m, 2H), 7.64 (s, 1H), 7.71–7.86 (m, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.4, 14.0, 21.3, 21.7, 31.6, 32.6, 42.1, 111.4, 119.6, 125.6, 126.1, 126.8, 127.2, 127.5, 127.6, 128.3, 132.3, 133.4, 135.3, 157.7. 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%.

**(*Z*)-2-Propyl-3-(3-thienylmethyl)hex-2-enenitrile (3ma):** A colorless oil, $R_f = 0.46$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J = 7.4$ Hz, 3H), 0.96 (t, $J = 7.3$ Hz, 3H), 1.38 (sext, $J = 7.5$ Hz, 2H), 1.61 (sext, $J = 7.4$ Hz, 2H), 2.08 (t, $J = 8.0$ Hz, 2H), 2.23 (t, $J = 7.7$ Hz, 2H), 3.73 (s, 2H), 6.96 (d, $J = 4.9$ Hz, 1H), 7.02 (dd, $J = 1.8$, 0.9 Hz, 1H), 7.24–7.30 (m, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.3, 14.0, 21.2, 21.6, 31.4, 32.8, 36.6, 110.9, 119.2, 121.7, 125.8, 127.9, 137.7, 157.4. 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%.

**(*Z*)-2-Propyl-3-(pyrrol-2-ylmethyl)hex-2-enenitrile (3na):** A slightly brown oil, $R_f = 0.23$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.91 (t, $J = 7.3$ Hz, 3H), 0.95 (t, $J = 7.4$ Hz, 3H), 1.40 (sext, $J = 7.6$ Hz, 2H), 1.60 (sext, $J = 7.5$ Hz, 2H), 2.13 (t, $J = 7.9$ Hz, 2H), 2.20 (t, $J = 7.7$ Hz, 2H), 3.69 (s, 2H), 5.96–6.02 (m, 1H), 6.12 (dd, $J = 5.9$, 2.7 Hz, 1H), 6.70 (ddd, $J = 2.7$, 1.5, 1.3 Hz, 1H), 8.14 (br s, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.5, 14.1, 21.2, 21.7, 31.5, 33.2, 34.4, 107.1, 108.4, 110.6, 117.5, 119.8, 127.5, 157.7. 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%.

**(*Z*)-3-(Indol-3-ylmethyl)-2-propylhex-2-enenitrile (3oa):** A slightly brown oil, $R_f = 0.24$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J = 7.3$ Hz, 3H), 0.98 (t, $J = 7.3$ Hz, 3H), 1.43 (sext, $J = 7.6$ Hz, 2H), 1.65 (sext, $J = 7.4$ Hz, 2H), 2.12 (t, $J = 7.9$ Hz, 2H), 2.26 (t, $J = 7.6$ Hz, 2H), 3.89 (s, 2H), 7.05 (s, 1H), 7.14 (t, $J = 7.5$ Hz, 1H), 7.21 (t, $J = 7.7$ Hz, 1H), 7.37 (d, $J = 8.1$ Hz, 1H), 7.65 (d, $J = 7.9$ Hz, 1H), 8.07 (br s, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.7, 14.3, 21.6, 21.9, 31.8, 32.1, 32.9, 110.1, 111.0, 112.3, 118.8, 119.5, 119.6, 122.0, 122.4, 127.2, 136.0, 158.4. 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%.

**(*Z*)-3-(Diphenylmethyl)-2-propylhex-2-enenitrile (3pa):** A colorless oil, $R_f = 0.37$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.59–0.73 (m, 5H), 1.01 (t, $J = 7.3$ Hz, 3H), 1.68 (sext, $J = 7.5$ Hz, 2H), 2.20 (t, $J =$ 8.0 Hz, 2H), 2.28 (t, $J = 7.7$ Hz, 2H), 5.70 (s, 1H), 7.16 (d, $J = 5.1$ Hz, 4H), 7.23–7.35 (m, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.6, 14.6, 21.6, 22.7, 32.1, 33.5, 57.4, 113.1, 118.9, 126.9, 128.4, 129.1, 140.7, 159.5. 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%.

**(*Z*)-3-Benzyl-4-trimethylsilyl-2-[(trimethylsilyl)methyl]-but-2-enenitrile (3db):** A colorless oil, $R_f = 0.25$ (hexane–ethyl acetate = 20:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.11 (s, 9H), 0.12 (s, 9H), 1.61 (s, 2H), 1.64 (s, 2H), 3.69 (s, 2H), 7.19–7.26 (m, 3H), 7.31 (tt, $J = 7.1$, 1.3 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ −0.9, −0.2, 21.4, 24.2, 43.7, 103.4, 121.0, 126.5, 128.4, 128.6, 138.4, 153.9. 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*)-2,3,4-Triphenylbut-2-enenitrile [(*E*)-3di]:** A colorless solid, mp: 105.0–106.0 °C, $R_f = 0.23$ (hexane–ethyl acetate = 20:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 4.27 (s, 2H), 6.89–6.95 (m, 2H), 7.11–7.26 (m, 13H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 44.9, 112.8, 119.2, 126.7, 128.09, 128.14, 128.3, 128.4, 128.5, 128.7, 129.4, 133.4, 136.6, 137.5, 157.4. 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*)-2,3,4-Triphenylbut-2-enenitrile [(*Z*)-3di]:** A yellow solid, mp: 103.5–104.3 °C, $R_f = 0.15$ (hexane–ethyl acetate = 20:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.96 (s, 2H), 6.95 (d, $J = 6.6$ Hz, 2H), 7.11–7.22 (m, 3H), 7.32–7.51 (m, 10H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 40.0, 113.8, 119.0, 126.4, 128.0, 128.2, 128.4, 128.5, 128.80, 128.83, 129.0, 129.1, 134.0, 136.9, 138.7, 157.8. 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%. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-727199 for compound (*Z*)-**3di**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

**(*Z*)-3-Methyl-2,4-diphenylbut-2-enenitrile (3dc):** A colorless oil, $R_f = 0.33$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.81 (s, 3H), 3.91 (s, 2H), 7.26–7.43 (m, 10H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 19.2, 44.5, 111.6, 119.0, 126.9, 128.3, 128.5, 128.70, 128.73, 129.1, 133.8, 137.3, 156.5. 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.

**(*E*)-2-Methyl-3,4-diphenylbut-2-enenitrile (3′dc):** A colorless oil, $R_f = 0.33$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.85 (s, 3H), 4.04 (s, 2H), 6.90–6.96 (m, 2H), 7.02–7.07 (m, 2H), 7.14–7.23 (m, 3H), 7.26–7.33 (m, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 17.9, 44.5, 106.5, 119.9, 126.5, 127.6, 128.1, 128.2, 128.3, 128.7, 136.8, 137.4, 157.1. 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.

**(*Z*)-2-Ethyl-3-methyl-4-phenylbut-2-enenitrile (3dj):** A colorless oil, $R_f = 0.31$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.17 (t, $J = 7.6$ Hz, 3H), 1.73 (s, 3H), 2.28 (q, $J = 7.6$ Hz, 2H), 3.71 (s, 2H), 7.20–7.34 (m, 5H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 12.8, 17.6, 23.4, 44.4, 112.0, 119.3, 126.8, 128.6, 128.7, 137.7, 153.3. 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.

**(*Z*)-3-Benzyl-2-methylpent-2-enenitrile (3′dj):** A colorless oil, $R_f = 0.31$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.95 (t, $J = 7.7$ Hz, 3H), 1.96 (s, 3H), 2.10 (q, $J = 7.6$ Hz, 2H), 3.74 (s, 2H), 7.20–7.34 (m, 5H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 12.0, 16.1, 24.1, 41.7, 104.5, 120.2, 126.7, 128.5, 128.7, 137.5, 159.5. 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.

**(*Z*)-2-*tert*-Butyl-3-methyl-4-phenylbut-2-enenitrile (3dk):** A colorless oil, $R_f = 0.43$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.33 (s, 9H), 1.91 (s, 3H), 3.76 (s, 2H), 7.19–7.27 (m, 3H), 7.31 (tt, $J = 7.1$, 1.6 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 19.8, 30.6, 33.6, 46.5, 119.3, 120.4, 126.7, 128.5, 128.6, 137.8, 154.4. 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%.

**(*E*)-3-Methyl-4-phenyl-2-trimethylsilylbut-2-enenitrile (3dl):** A colorless oil, $R_f = 0.42$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.31 (s, 9H), 1.88 (s, 3H), 3.82 (s, 2H), 7.20–7.28 (m, 3H), 7.32 (tt, $J = 7.2$, 1.6 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ −0.4, 22.1, 46.7, 110.0, 120.4, 126.8, 128.7, 128.8, 137.5, 171.5. 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%.

**(*E*)-2-Methyl-4-phenyl-3-trimethylsilylbut-2-enenitrile (3′dl):** A colorless oil, $R_f = 0.47$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.08 (s, 9H), 2.17 (s, 3H), 3.87 (s, 2H), 7.11 (d, $J = 7.0$ Hz, 2H), 7.17–7.35 (m, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ −0.4, 20.5, 43.0, 118.8, 119.3, 126.5, 128.4, 128.8, 137.9, 159.3. 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%.

**(*Z*)-3-Benzylnon-2-enenitrile (3dm):** A pale yellow oil, $R_f = 0.33$ (hexane–ethyl acetate = 15:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.87 (t, $J = 7.0$ Hz, 3H), 1.20–1.48 (m, 8H), 2.08 (td, $J = 7.7$, 1.3 Hz, 2H), 3.74 (s, 2H), 5.21 (s, 1H), 7.20–7.25 (m, 5H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 14.1, 22.6, 27.1, 28.8, 31.5, 35.5, 41.1, 95.4, 117.4, 126.8, 128.59, 128.64, 136.9, 167.3. IR (neat): 3086, 3063, 3028, 2955, 2930, 2857, 2216, 1624, 1601, 1495, 1454, 1379, 1076, 1030, 827, 737, 700 cm$^{-1}$. Anal. Calcd for $C_{16}H_{21}N$: C, 84.53; H, 9.31%. Found: C, 84.79; H, 9.27%.

**(*Z*)-2-(2-Phenylethynylidene)octanenitrile (3′dm):** A colorless oil, $R_f = 0.38$ (hexane–ethyl acetate = 15:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.89 (t, $J = 6.9$ Hz, 3H), 1.23–1.37 (m, 6H), 1.51–1.62 (m, 2H), 2.24 (t, $J = 7.5$ Hz, 2H), 3.69 (d, $J = 7.7$ Hz, 2H), 6.26 (t, $J = 7.7$ Hz, 1H), 7.17–7.27 (m, 3H), 7.32 (t, $J = 7.4$ Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 14.1, 22.6, 28.1, 28.4, 31.5, 34.3, 37.8, 115.3, 117.6, 126.7, 128.3, 128.7, 137.7, 145.2. IR (neat): 3030, 2955, 2928, 2859, 2214, 1603, 1495, 1454, 1435, 1379, 1261, 1105, 1076, 1030, 797, 739, 698, 569 cm$^{-1}$. HRMS (EI) Calcd for $C_{16}H_{21}N$: $M^+$, 227.1674. Found: $m/z$ 227.1676.

**(*Z*)-3-Cyclohexyl-4-phenylbut-2-enenitrile (3dn):** A colorless oil, $R_f = 0.16$ (hexane–ethyl acetate = 20:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.00–1.30 (m, 5H), 1.62–1.80 (m, 5H), 1.98 (t, $J = 11.2$ Hz, 1H), 3.78 (s, 2H), 5.24 (s, 1H), 7.19–7.25 (m, 3H), 7.31 (tt, $J = 7.1$, 1.5 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 26.0, 26.3, 32.1, 40.4, 43.3, 94.6, 117.7, 126.7, 128.6, 136.9, 171.8. IR (neat): 3061, 3028, 2930, 2853, 2216, 1618, 1601, 1584, 1495, 1451, 1300, 1269, 1182, 1144, 1076, 1030, 980, 893, 827, 816, 775, 737, 700 cm$^{-1}$. Anal. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50%. Found: C, 85.38; H, 8.61%.

**(*Z*)-2-Cyclohexyl-4-phenylbut-2-enenitrile (3′dn):** A colorless oil, $R_f = 0.23$ (hexane–ethyl acetate = 20:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.10–1.42 (m, 5H), 1.69 (d, $J = 5.3$ Hz, 1H), 1.82 (t, $J = 11.8$ Hz, 4H), 2.15 (td, $J = 11.2$, 3.0 Hz, 1H), 3.69 (d, $J = 7.7$ Hz, 2H), 6.26 (td, $J = 7.7$, 0.9 Hz, 1H), 7.19 (d, $J = 7.3$ Hz, 2H), 7.24 (tt, $J = 7.5$, 2.2 Hz, 1H), 7.32 (t, $J = 7.1$ Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 25.6, 26.0, 31.8, 37.7, 42.6, 117.2, 121.3, 126.6, 128.3, 128.6, 137.8, 143.1. IR (neat): 3063, 3028, 2928, 2853, 2214, 1603, 1495, 1451, 1350, 1076, 1030, 990, 936, 891, 741, 689, 646, 573, 513 cm$^{-1}$. HRMS (EI) Calcd for $C_{16}H_{19}N$: $M^+$, 225.1517. Found: $m/z$ 225.1524.

**(*E*)-3-Benzyl-4,4-dimethylpent-2-enenitrile (3do):** A colorless oil, $R_f = 0.31$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.07 (s, 9H), 3.87 (s, 2H), 5.52 (s, 1H), 7.19–7.25 (m, 3H), 7.27–7.33 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 29.5, 38.2, 38.3, 96.7, 117.8, 126.4, 128.0, 128.4, 137.3, 173.8. IR (neat): 3063, 3028, 2969, 2870, 2216, 1609, 1495, 1479, 1468, 1454, 1397, 1366, 1260, 1215, 1196, 1096, 1076, 1030, 978, 926, 824, 764, 719, 696, 671 cm$^{-1}$. Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60%. Found: C, 84.38; H, 8.56%.

**Carbocyanation of Alkynes with Functionzalized Acetonitriles. General procedure**: In a dry box, to a solution of

$Ni(cod)_2$ (14 mg, 50 μmol) and a ligand (0.10 mmol) in toluene (1.0 mL) placed in a vial were sequentially added a substituted acetonitrile (1.00 mmol), $BPh_3$ (48 mg, 0.20 mmol), an alkyne (2.0 mmol), and dodecane (internal standard, 85 mg, 0.50 mmol). The vial was taken out from the dry box and heated at 80 °C for the time specified Table 5. The resulting mixture was filtered through a silica gel pad, concentrated in vacuo, and purified by flash column chromatography on silica gel to give the corresponding carbocyanation products in yields listed in Table 5. Regio- and/or stereoisomers were separated by preparative GPC or HPLC and characterized by spectrometry.

**(*Z*)-3-(Phthalimidomethyl)-2-propylhex-2-enenitrile (3qa):** A colorless solid, mp: 38.1–38.7 °C, $R_f = 0.12$ (hexane–ethyl acetate = 7:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.91 (t, $J = 7.3$ Hz, 3H), 0.97 (t, $J = 7.3$ Hz, 3H), 1.47 (sext, $J = 7.6$ Hz, 2H), 1.63 (sext, $J = 7.5$ Hz, 2H), 2.08 (t, $J = 8.0$ Hz, 2H), 2.25 (t, $J = 7.6$ Hz, 2H), 4.62 (s, 2H), 7.74 (dd, $J = 5.5$, 3.1 Hz, 2H), 7.87 (dd, $J = 5.5$, 3.1 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.6, 14.2, 21.51, 21.55, 31.6, 32.1, 41.7, 113.8, 117.8, 123.4, 131.7, 134.1, 151.2, 167.6. IR (KBr): 2964, 2934, 2874, 2212, 1773, 1717, 1466, 1425, 1396, 1350, 953, 926, 712, 530 cm$^{-1}$. Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80%. Found: C, 72.78; H, 6.83%.

**(*Z*)-3-Methyl-2-phenyl-4-phthalimidobut-2-enenitrile [(*Z*)-3qc]:** A colorless solid, mp: 104.1–104.8 °C, $R_f = 0.13$ (hexane–ethyl acetate = 4:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.84 (s, 3H), 4.81 (s, 2H), 7.31–7.43 (m, 5H), 7.77 (dd, $J = 5.5$, 2.9 Hz, 2H), 7.91 (dd, $J = 5.4$, 3.0 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 17.6, 43.2, 113.4, 117.3, 123.5, 128.6, 128.7, 128.9, 131.7, 133.2, 134.2, 150.3, 167.6. IR (KBr): 2214, 1773, 1713, 1418, 1396, 1348, 930, 766, 729, 714, 700 cm$^{-1}$. Anal. Calcd for $C_{19}H_{14}N_2O_2$: C, 75.48; H, 4.67%. Found: C, 75.45; H, 4.78%.

**(*E*)-3-Methyl-2-phenyl-4-phthalimidobut-2-enenitrile [(*E*)-3qc]:** A colorless solid, mp: 111.0–111.8 °C, $R_f = 0.16$ (hexane–ethyl acetate = 4:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.15 (s, 3H), 4.45 (s, 2H), 7.32–7.38 (m, 1H), 7.39–7.49 (m, 4H), 7.74 (dd, $J = 5.5$, 3.1 Hz, 2H), 7.84 (dd, $J = 5.5$, 2.9 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 20.0, 40.1, 114.0, 117.8, 123.4, 128.77, 128.81, 129.0, 131.5, 132.7, 134.2, 150.5, 167.5. IR (KBr): 2208, 1776, 1713, 1427, 1396, 1340, 1317, 930, 764, 731, 712, 700, 530 cm$^{-1}$. HRMS (EI) Calcd for $C_{19}H_{14}N_2O_2$: $M^+$, 302.1055. Found: $m/z$ 302.1054.

**(*Z*)-2-Methyl-3-phenyl-4-phthalimidobut-2-enenitrile (3′qc):** A colorless solid, mp: 131.7–132.6 °C, $R_f = 0.17$ (hexane–ethyl acetate = 4:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.88 (t, $J = 1.4$ Hz, 3H), 4.93 (q, $J = 1.3$ Hz, 2H), 7.11 (dt, $J = 6.4$, 1.5 Hz, 2H), 7.21–7.31 (m, 3H), 7.65 (dd, $J = 5.7$, 2.9 Hz, 2H), 7.73 (dd, $J = 5.6$, 3.0 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 18.3, 42.8, 108.8, 118.3, 123.2, 127.6, 128.4, 128.7, 131.4, 133.9, 134.5, 151.6, 167.2. IR (KBr): 2926, 2214, 1773, 1717, 1466, 1421, 1394, 1342, 1325, 1119, 1013, 945, 727, 714, 696, 530 cm$^{-1}$. HRMS (EI) Calcd for $C_{19}H_{14}N_2O_2$: $M^+$, 302.1055. Found: $m/z$ 302.1058.

**(*Z*)-2-*tert*-Butyl-3-methyl-4-phthalimidobut-2-enenitrile (3qk):** A colorless solid, mp: 125.4–126.1 °C, $R_f = 0.18$ (hexane–ethyl acetate = 4:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.33 (s, 9H), 1.92 (s, 3H), 4.67 (s, 2H), 7.75 (dd, $J = 5.5$, 3.1 Hz, 2H), 7.88 (dd, $J = 5.6$, 3.0 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 17.5, 30.5, 34.1, 45.2, 117.5, 122.3, 123.4, 131.6, 134.1, 148.2, 167.6. IR (KBr): 2976, 2206, 1774, 1717, 1423, 1398, 1348, 1119, 924, 729, 712 cm$^{-1}$. Anal. Calcd for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43%. Found: C, 72.59; H, 6.51%.

**(*Z*)-2-Propyl-3-(tetrahydro-2*H*-pyran-2-yloxymethyl)hex-2-enenitrile (3ra):** A colorless oil, $R_f = 0.15$ (hexane–ethyl acetate = 15:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.96 (t, $J = 7.1$ Hz, 3H), 0.97 (t, $J = 7.0$ Hz, 3H), 1.41–1.67 (m, 8H), 1.69–1.89 (m, 2H), 2.21–2.32 (m, 4H), 3.51–3.61 (m, 1H), 3.82–3.92 (m, 1H), 4.26 (d, $J = 12.3$ Hz, 1H), 4.46 (d, $J = 12.3$ Hz, 1H), 4.64 (t, $J = 3.4$ Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.6, 14.3, 19.4, 21.4, 21.6, 25.4, 30.5, 31.7, 31.8, 62.3, 68.4, 98.5, 112.3, 118.1, 154.9. IR (neat): 2961, 2872, 2210, 1630, 1464, 1456, 1383, 1350, 1261, 1202, 1182, 1157, 1119, 1078, 1057, 1034, 972, 907, 870, 816 cm$^{-1}$. Anal. Calcd for $C_{15}H_{25}NO_2$: C, 71.67; H, 10.02%. Found: C, 71.62; H, 10.23%.

**(*Z*)-2-Propyl-3-[(trimethylsilyl)methyl]hex-2-enenitrile (3sa):** A pale yellow oil, $R_f = 0.18$ (hexane–ethyl acetate = 50:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.11 (s, 9H), 0.94 (t, $J = 7.3$ Hz, 3H), 0.95 (t, $J = 7.3$ Hz, 3H), 1.44 (sext, $J = 7.6$ Hz, 2H), 1.56 (sext, $J = 7.5$ Hz, 2H), 2.02 (s, 2H), 2.08 (t, $J = 7.8$ Hz, 2H), 2.16 (t, $J = 7.5$ Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ −0.6, 13.6, 14.2, 21.6, 22.3, 28.8, 31.4, 35.7, 105.7, 120.4, 159.1. IR (neat): 2961, 2874, 2203, 1611, 1464, 1421, 1379, 1250, 1148, 1078, 853, 766, 694 cm$^{-1}$. Anal. Calcd for $C_{13}H_{25}NSi$: C, 69.88; H, 11.28%. Found: C, 70.18; H, 11.17%.

**Carbocyanation of 2a with (*S*)-1t (eq 3).** In a dry box, 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, 0.4 mmol) in toluene (1.0 mL) placed in a vial were added (*S*)-**1t** (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. The vial was taken out from 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 **6**, and hydrocinnamonitrile **7** in 35%, 44%, and 3% yield, respectively. The mixture was filtered through a silica gel pad and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel followed by preparative HPLC to give (*S*)-(*Z*)-3-(1-phenylethyl)-2-propylhex-2-enenitrile [(*S*)-**3ta**] (54 mg, 22%) and (*S*)-**1t** (17 mg, 13%). (*S*)-**3ta**: A colorless oil, $R_f = 0.27$ (hexane–ethyl acetate = 10:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.73–0.91 (m, 4H), 0.96 (t, $J = 7.4$ Hz, 3H), 1.09–1.27 (m, 1H), 1.47 (d, $J = 7.1$ Hz, 3H), 1.64 (sext, $J = 7.5$ Hz, 2H), 1.91 (t, $J = 8.2$ Hz, 2H), 2.18 (t, $J = 7.6$ Hz, 2H), 4.46 (q, $J = 7.1$ Hz, 1H), 7.20–7.35 (m, 5H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.5, 14.6, 17.1, 21.5, 23.1, 30.9, 31.7, 45.6, 110.2, 119.3, 126.8, 127.4, 128.3, 141.6, 162.7. 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%. Ee was determined by HPLC analysis on a Daicel Chiralcel OB-H column with hexane, flow rate: 0.5 mL min$^{-1}$, detection by UV of 254 nm. Retention times: 14.5 min [(*S*)-enantiomer], 17.2 min [(*R*)-enantiomer]. 41% ee. $[\alpha]_D^{30}$ −145.97 (*c* 1.055, toluene). (*S*)-**1t**: The ee was determined by HPLC analysis on a Daicel Chiralcel OD-H column with hexane, flow rate: 0.5 mL min$^{-1}$, detection by UV of 258 nm. Retention times: 37.4 min [(*S*)-enantiomer], 43.8 min [(*R*)-enantiomer]. 80% ee.

**Ruthenium-Catalyzed Oxidation of (*S*)-3ta.** To a solution of (*S*)-**3ta** (42 mg, 0.18 mmol) in $CCl_4$–$CH_3CN$–$H_2O$ (1.0:1.0:1.5, 1.4 mL) were added $NaIO_4$ (0.38 g, 1.6 mmol) and $RuCl_3 \cdot 3H_2O$ (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 $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give (*S*)-2-phenyl-3-hexanone [(*S*)-**8**, 14 mg, 43%] as a pale yellow oil, $R_f = 0.20$ (hexane–ethyl acetate = 30:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.80 (t, $J = 7.4$ Hz, 3H), 1.40 (d, $J = 7.0$ Hz, 3H), 1.47–1.58 (m, 2H), 2.33 (t, $J = 7.5$ Hz, 2H), 3.75 (q, $J = 7.0$ Hz, 1H), 7.19–7.28 (m, 3H), 7.30–7.35 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 13.7, 17.4, 17.6, 43.0, 53.0, 126.9, 127.7, 128.7, 140.6, 210.6. 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. Ee of the ketone was determined by HPLC analysis on a Daicel Chiralcel OD-H column with hexane, flow rate: 0.5 mL min$^{-1}$, detection by UV of 254 nm. Retention times: 17.2 min [(*S*)-enantiomer], 18.8 min [(*R*)-enantiomer]. 38% ee. $[\alpha]_D^{30}$ +113.51 (*c* 0.555, toluene) [lit.[9] $[\alpha]_D^{20}$ −234 (*c* 0.281, toluene) for 91% ee of (*R*)-enantiomer].

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## Supporting Information

Copies of $^1$H and $^{13}$C NMR spectra of compounds **3aa**-$d_3$, (*E*)-**3ab**, (*E*)-**3af**, (*E*)-**3ah**, (*E*)-**3bb**, **4**, **3dc**, **3′dc**, **3dj**, **3′dj**, **3′dm**, **3′dn**, (*E*)-**3qc**, **3′qc**, and (*S*)-**8**. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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