

Nickel/Lewis Acid-Catalyzed Aryl- and Alkenylcyanation of Unsaturated Bonds

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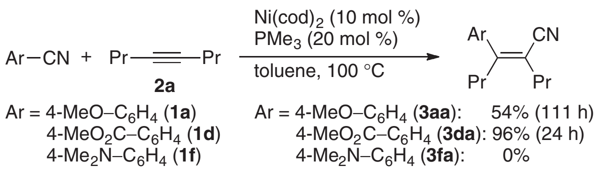
Lewis acid cocatalysts such as organoaluminum and -boron compounds dramatically improve the efficiency of the nickel-catalyzed arylcyanation of alkynes. Electron-rich aryl cyanides, which exhibit poor reactivity in the absence of Lewis acids, smoothly undergo the arylcyanation reaction under the nickel/Lewis acid dual catalysis. Excellent chemoselectivity is observed for aryl cyanides having a chloro or bromo group, which allows a single-step access to a synthetic intermediate of P-3622, a squalene synthetase inhibitor. The scope of the arylcyanation is also expanded to norbornadiene. Alkenylcyanation of alkynes is achieved under the nickel/Lewis acid dual catalysis to give cyano-substituted 1,3-dienes stereoselectively.

Cleavage of the carbon–cyano bond in nitriles followed by addition reaction of the resulting two organic fragments across unsaturated bonds by transition-metal catalysis should provide us with a revolutionary synthetic method, because such transformation allows simultaneous construction of carbon–carbon and carbon–cyano bonds without forming by-products. The reaction, called carbocyanation, was recently achieved using nickel[1] and palladium[2,3] catalysts. Compared to palladium-catalyzed reactions, nickel catalysis allows a wide variety of nitriles including aryl,[1a,1d,1e] alkoxycarbonyl,[1c,1g] allyl,[1b,1i] and alkynyl[1h] cyanides to participate in the carbocyanation reaction. Nevertheless, the reactions still require generally high catalyst loadings and harsh reaction conditions. For example, arylcyanation of alkynes using electron-rich aryl cyanides is feasible but generally sluggish: addition of 4-methoxybenzonitrile (**1a**) across 4-octyne (**2a**) in the presence of 10 mol % of a Ni/PMe_3 catalyst at 100 °C took 111 h for completion to give the corresponding adduct **3aa** in 54% yield, whereas that of methyl 4-cyanobenzoate (**1d**), an electron-deficient one, gave the adduct **3da** in 96% yield after 24 h (eq 1).[1a,1d] Moreover, highly electron-rich 4-dimethylaminobenzonitrile (**1f**) totally failed to give product **3fa** (eq 1).



(1)

Based on the mechanism of the nickel-catalyzed arylcyanation reaction suggested by theoretical calculations,[4] oxidative addition of the C–CN bond to nickel(0) is likely rate-determining: an elemental step that proceeds through η^2-nitrile- and η^2-arenenickel complexes.[5] As Lewis acids (LAs) have been known to accelerate elemental steps such as oxidative addition[6] and reductive elimination[7] of C–CN bonds, the effect of LA catalysts on the arylcyanation reaction of alkynes is investigated in this paper to disclose that the scope of aryl cyanides for the reaction with alkynes and norbornadiene is expanded significantly under the nickel/LA cooperative catalysis. The cooperative bimetal catalysis allows the addition reaction of alkenyl cyanides across alkynes, giving 1-cyano-1,3-dienes with high regio- and stereoselectivities.[8,9]

Results and Discussion

Effect of Lewis Acid Cocatalyst on Nickel-Catalyzed Arylcyanation of Alkynes. We first assessed the effect of various LA catalysts together with $Ni(cod)_2$ (5 mol %) and PMe_3 (10 mol %) as a ligand on the reaction of aryl cyanide (**1a**, 1.0 mmol) with 4-octyne (**2a**, 1.0 mmol) in toluene at 50–80 °C. The results are summarized in Table 1. Of LAs examined, aluminum, boron, and zinc were found to significantly promote the reaction, giving (*Z*)-**3aa** in good to excellent yields at 80 °C (Entries 3, 5, 10, 12, 17, 19, and 26), whereas the absence of the LA catalysts gave (*Z*)-**3aa** in lower yields even at 80 °C (Entries 1 and 2). $AlMeCl_2$ was also found effective for the reaction, but a significant amount of (*E*)-**3aa** was observed at 80 °C probably through isomerization of initially formed (*Z*)-**3aa** (Entry 7). Strong Lewis acidity appears to be responsible for such isomerization (vide infra). Some LAs including $AlMe_3$, $AlMe_2Cl$, $AlMeCl_2$, and BEt_3 are still effective even at 50 °C (Entries 4, 6, 8, and 18). In the case of $ZnCl_2$, formation of insoluble materials was observed after the reaction at 50 °C (Entry 27). $Ti(O^iPr)_4$, $MgBr_2$, $LaCl_3$, and Me_3SiOTf were less effective (Entries 29–32). Other LAs including indium, copper, iron, cobalt, gold, and zirconium LAs inhibited the reaction. Finally, we tested various combinations of LAs and ligands in the presence of 1 mol % of $Ni(cod)_2$ to find that ligands such as $PPhMe_2$, PPh_2Me, and PPh_2Cy give generally better results than PMe_3. For example, the combination of PPh_2Me/$AlMe_3$ or BPh_3 gave (*Z*)-**3aa** in over 90% yield with only a trace amount of (*E*)-**3aa** (Table 2).

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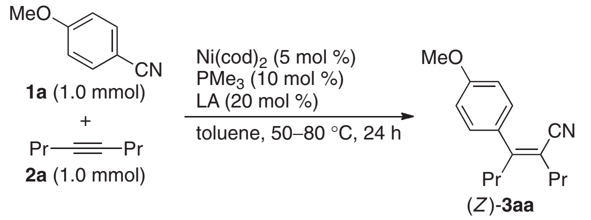
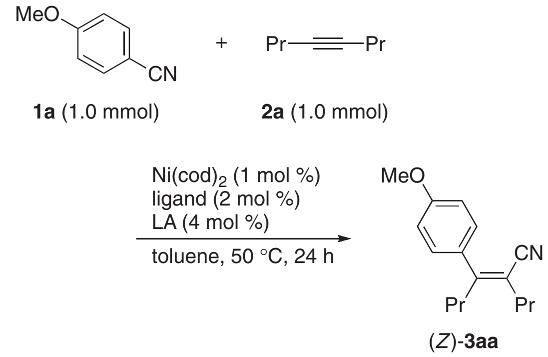
Table 1. Effect of LA Cocatalyst on Nickel-Catalyzed Arylcyanation of **2a** with **1a**[a)]



Entry	Lewis acid	Temp/°C	Yield/%[b)]	
			(*Z*)-**3aa**	(*E*)-**3aa**
1	none	80	36	1
2	none	50	7	0
3	$AlMe_3$	80	91	6
4	$AlMe_3$	50	61	0
5	$AlMe_2Cl$	80	79	21
6	$AlMe_2Cl$	50	94	1
7	$AlMeCl_2$	80	41	50
8	$AlMeCl_2$	50	82	4
9	$AlCl_3$	80	6	0
10	$AlPh_3{\cdot}OEt_2$	80	90	3
11	$AlPh_3{\cdot}OEt_2$	50	47	0
12	MAD[c)]	80	82	10
13	MAD[c)]	50	7	1
14	$Al(O^iPr)_3$	80	48	6
15	$Al(OPh)_3$	80	0	0
16	$Al(OTf)_3$	80	0	0
17	BEt_3	80	88	0
18	BEt_3	50	82	0
19	BPh_3	80	68	0
20	BPh_3	50	37	0
21	$B(C_6F_5)_3$	80	17	0
22	$BF_3{\cdot}OEt_2$	80	1	0
23	$ZnEt_2$	80	0	0
24	$ZnPh_2$	80	8	0
25	$Zn(C_6F_5)_2$	80	2	0
26	$ZnCl_2$	80	86	1
27	$ZnCl_2$	50	68	0
28	$Zn(OTf)_2$	80	61	0
29	$Ti(O^iPr)_4$	80	42	1
30	$MgBr_2{\cdot}OEt_2$	80	54	4
31	$LaCl_3$	80	39	3
32	Me_3SiOTf	80	21	4

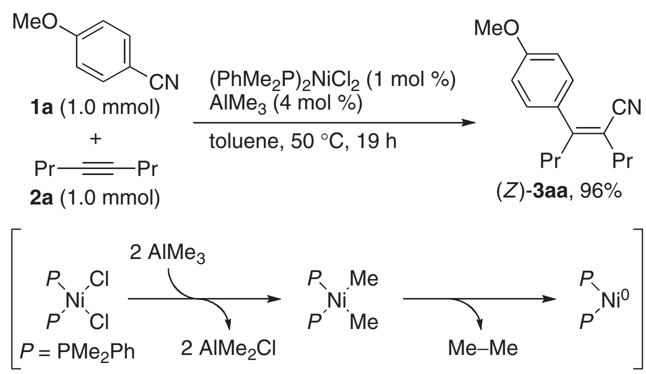
a) All the reactions were carried out using **1a** (1.0 mmol), **2a** (1.0 mmol), $Ni(cod)_2$ (50 µmol), PMe_3 (100 µmol), and Lewis acid (200 µmol) in toluene (1.0 mL) for 24 h. b) Estimated by GC using dodecane as an internal standard. c) Methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate).

Table 2. Optimization of a Combination of a LA and a Ligand for the Reaction of **1a** across **2a**[a)]



Ligand	LA/yield of (*Z*)-**3aa**/%[b)]				
	$AlMe_3$	$AlMe_2Cl$	$AlMeCl_2$	BPh_3	BEt_3
PMe_3	60	88	7	31	9
$P(n\text{-}Bu)_3$	63	41	5	39	<1
$PPhMe_2$	95	>99	8	78	6
PPh_2Me	92	98	<1	92	<1
PPh_2Cy	95	50	<1	79	1
$P(4\text{-}MeO\text{–}C_6H_4)_3$	29	6	<1	53	1
$Ph_2P(CH_2)_6PPh_2$	72	66	<1	60	<1

a) All the reactions were carried out using **1a** (1.0 mmol), **2a** (1.0 mmol), $Ni(cod)_2$ (10 µmol), ligand (20 µmol), and LA (40 µmol) in toluene (1.0 mL) at 50 °C for 24 h. b) Estimated by GC using dodecane as an internal standard.

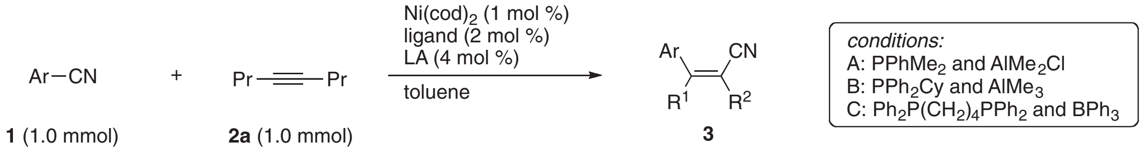


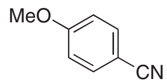
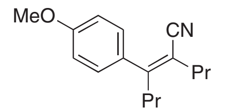
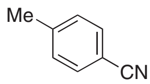
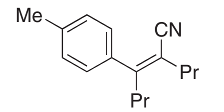
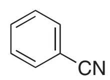
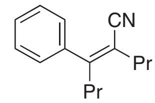
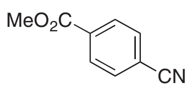
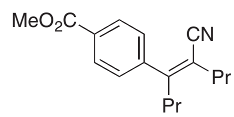
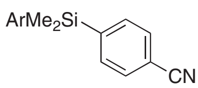
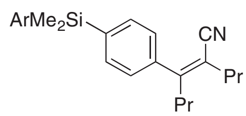
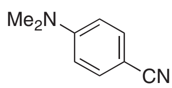
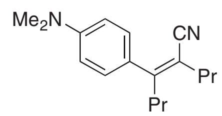
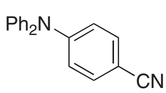
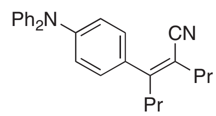
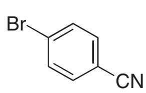
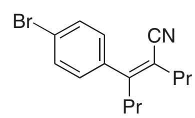
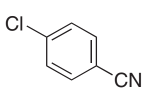
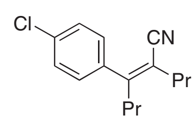
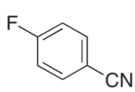
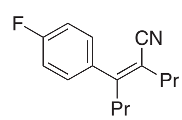
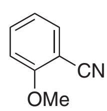
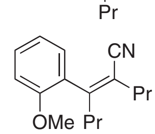
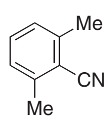
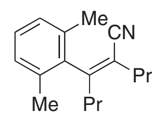
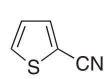
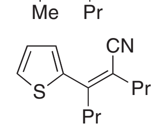
Scheme 1. The reaction of **1a** with **2a** using dichlorobis(dimethylphenylphosphine)nickel(II) as a precatalyst.

From a practical view point, it is worth noting that a similar catalyst prepared in situ from air- and moisture-stable $(PhMe_2P)_2NiCl_2$ (1 mol %) and $AlMe_3$ (4 mol %) effected the reaction to give (*Z*)-**3aa** in 96% yield after 19 h. In the reaction course, the Ni(II) catalyst is reduced to a catalytically active Ni(0) species and simultaneously coproduced $AlMe_2Cl$ as the LA cocatalyst (Scheme 1).

Nickel/Lewis Acid-Catalyzed Arylcyanation of Alkynes. The new catalyst systems thus tuned were then applied to the arylcyanation of **2a** using various aryl cyanides especially those unreactive under the LA-free conditions (Table 3). Under the optimized conditions, *p*-tolunitrile (**1b**) and benzonitrile (**1c**) also smoothly added across **2a** in good to excellent yields in one day (Entries 2 and 3). Functional groups such as an ester and THP-protected [2-(hydroxymethyl)phenyl]dimethylsilyl group[10] tolerated the reaction conditions (Entries 4 and 5). More electron rich nitriles, 4-dimethylamino- (**1f**) and 4-diphenylaminobenzonitrile (**1g**), underwent the arylcyanation to give the corresponding adducts in good yields in one or two days (Entries 6 and 7). It is noteworthy that the Ar–CN bonds of 4-bromo- (**1h**), 4-chloro- (**1i**), and 4-fluorobenzonitrile (**1j**) were selectively activated over the Ar–halogen bonds, giving arylcyanation products in good to excellent yields (Entries 8–10). Even the sterically highly demanding aryl cyanides like 2-methoxybenzonitrile (**1k**) and 2,6-dimethylbenzonitrile (**1l**)

Table 3. Nickel/Lewis Acid-Catalyzed Arylcyanation of 4-Octyne (**2a**)[a)]



Entry	Aryl cyanide		Cond.	Temp/°C	Time/h	Product, yield/%[b)]	
1		**1a**	A	50	16		**3aa**, 96
2		**1b**	A	60	20		**3ba**, 72
3		**1c**	B	50	16		**3ca**, 97
4		**1d**	A	80	25		**3da**, 93
5		**1e**[c)]	B	50	42		**3ea**, 90
6		**1f**	A	80	21		**3fa**, 87
7		**1g**	B	50	47		**3ga**, 91
8[d)]		**1h**	A	50	27		**3ha**, 72
9		**1i**	B	50	18		**3ia**, 94
10		**1j**	B	50	18		**3ja**, 95
11		**1k**	B	80	28		**3ka**, 92
12[d)]		**1l**	A	100	134		**3la**, 78
13		**1m**	B	50	140		**3ma**, 81

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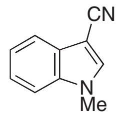
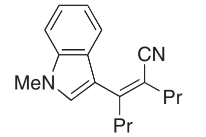
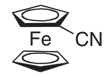
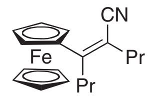
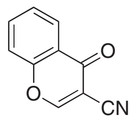
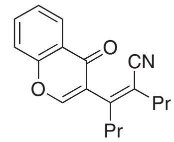
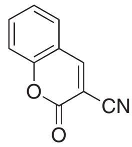
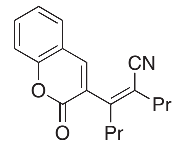
Entry	Aryl cyanide		Cond.	Temp/°C	Time/h	Product, yield/%[b)]	
14		**1n**	A	50	116		**3na**, 58
15[e)]		**1o**	B	80	5		**3oa**, 83[f)]
16[g)]		**1p**	C	80	20		**3pa**, 91
17[g)]		**1q**	C	80	20		**3qa**, 92

a) Condition A, $PPhMe_2$ and $AlMe_2Cl$; condition B, PPh_2Cy and $AlMe_3$; condition C, $Ph_2P(CH_2)_4PPh_2$ and BPh_3. b) Isolated yields. c) Ar = 2-($THPOCH_2$)C_6H_4. d) The reaction was carried out using $Ni(cod)_2$ (50 µmol), $PPhMe_2$ (100 µmol), and $AlMe_2Cl$ (200 µmol). e) The reaction was carried out using $Ni(cod)_2$ (50 µmol), PPh_2Cy (100 µmol), and $AlMe_3$ (200 µmol). f) (*Z*)/(*E*) = 92:8. g) The reaction was carried out using $Ni(cod)_2$ (40 µmol), $Ph_2P(CH_2)_4PPh_2$ (40 µmol), and BPh_3 (160 µmol).

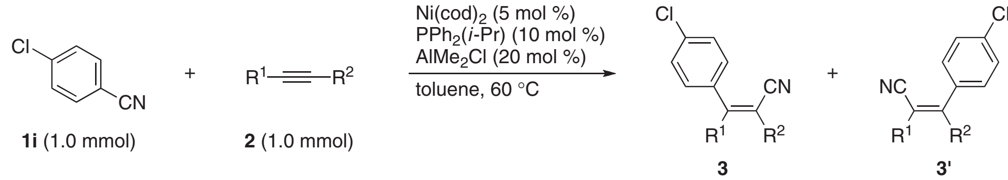
participated in the reaction, although higher reaction temperatures (80–100 °C), higher loadings of catalysts, and/or prolonged reaction time were required (Entries 11 and 12). Heteroaryl cyanides also successfully added across **2a** (Entries 13–17). The selective activation of an Ar–CN bond over the C(2)–H bond in 1-methyl-3-cyanoindole (**1n**) exhibits another chemoselective feature of the present Ni–LA catalysis (Entry 14), whereas the Ar–H bond was activated in the absence of LA.[11] Cyanoferrocene (**1o**) also participated in the reaction efficiently, although a mixture of stereoisomers resulted due possibly to isomerization of the initially formed *cis*-adduct to *trans*-adduct (Entry 15). Indeed, exposure of the isolated sample of (*Z*)-**3oa** to the present reaction conditions caused the isomerization. Heteroaryl cyanides such as 3-cyanochromone (**1p**) and 3-cyanocoumarin (**1q**) were futile under the Ni/Al catalyst system, whereas Ni/BPh_3 effected the reactions to give adducts in good yields (Entries 16 and 17).

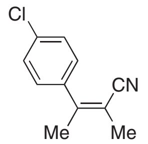
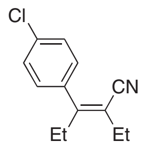
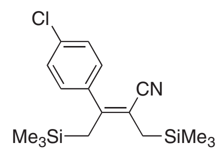
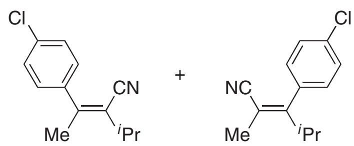
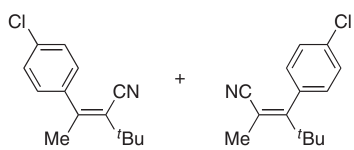
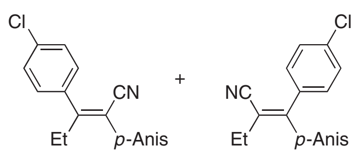
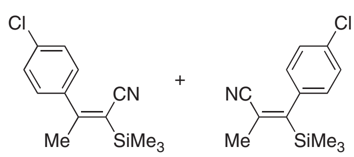
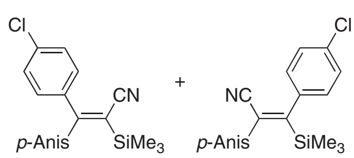
The scope of internal alkynes was next examined with 4-chlorobenzonitrile (**1i**) (Table 4). Symmetric alkynes such as 2-butyne (**2b**), 3-hexyne (**2c**), and 1,4-bis(trimethylsilyl)-2-butyne (**2d**) all participated in the reaction to give products in good yields (Entries 1–3). An unsymmetrical alkyne, 4,4-dimethyl-2-pentyne (**2f**), gave the corresponding adduct **3if** with good regioselectivity (Entry 5), whereas 4-methyl-2-pentyne (**2e**) gave modest selectivity (Entry 4). All the reaction gave the corresponding adducts having a larger substituent at the cyano-substituted carbon as major products. Internal alkynes with aryl- and silyl-substituents reacted with **1i** successfully with similar regioselectivity, although significant amounts of *trans*-adducts were also obtained probably through isomerization of the initial *cis*-adducts as evidenced by time-dependent *E*/*Z* ratios (Entries 6–8). The excellent chemoselectivity of the present Ni–LA catalysis provided a single step preparation of **3ii**, which is a synthetic intermediate of P-3622, a squalene synthetase inhibitor (Entry 8).[12] Under the same catalyst system, terminal alkynes failed to give the corresponding product due to rapid trimerization and/or oligomerization.

Nickel/$AlMe_2Cl$-Catalyzed Arylcyanation of Norbornadiene. We next turned our attention to application of the Ni/LA system to arylcyanation of norbornadiene (**4**), which under the original LA-free conditions reacted only with electron-deficient aryl cyanides.[13] The reaction of **1a** with **4** in the presence of the Ni/$AlMe_2Cl$ catalyst with $Me_2P(CH_2)_2PMe_2$ (DMPE) as a ligand in toluene at 80 °C for 4.5 h proceeded successfully to afford *exo*-*cis*-arylcyanation product **5a** in 69% yield (Entry 1 of Table 5). Monodentate phosphine and bidentate DPPE ligand were totally ineffective. The same catalyst system was further applied to the reactions of a wide variety of aryl cyanides, especially impotent cyanides in the absence of LA, to give the corresponding adducts in good yields (Entries 2–7). No double addition products were detected in any case, whereas norbornene was demonstrated previously to undergo the addition of aryl cyanides in the absence of LA catalysts.[1e] The resulting norbornene derivatives **5** would find further applications as precursors for functionalized cyclopentanes[1e] or as monomers for ring-opening metathesis polymerization.[14]

Nickel/BPh_3-Catalyzed Alkenylcyanation of Alkynes. We then turned our attention to the reaction of alkenyl cyanides with alkynes. After a brief optimization of conditions for the reaction of (*E*)-cinnamonitrile (**6a**) with 4-octyne (**2a**), we found that the combination of $Ni(cod)_2$ (2 mol %), PMe_3 (4 mol %), and BPh_3 (8 mol %) was effective to give the alkenylcyanation product, dienenitrile **7aa**, in 94% yield (Entry 1 of Table 6). LAs such as $AlMe_3$ and $AlMe_2Cl$ were

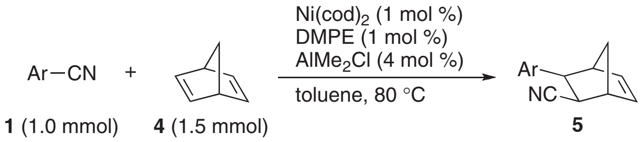
Table 4. Nickel/$AlMe_2Cl$-Catalyzed Arylcyanation of Internal Alkynes with **1i**

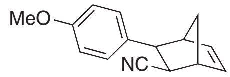
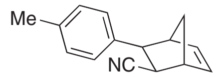
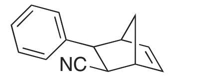
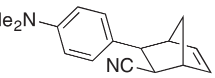
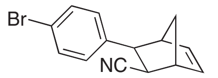
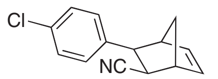
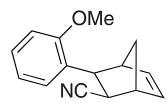


Entry	Alkyne	Time/h	Product(s), yield(s)/%[a] (3/3′)[b]	
1	$Me-C\equiv C-Me$ **2b**	12	 **3ib**	88
2	$Et-C\equiv C-Et$ **2c**	6	 **3ic**	92
3	$Me_3SiCH_2C\equiv CCH_2SiMe_3$ **2d**	6	 **3id**	84
4	$Me-C\equiv C-i\text{-}Pr$ **2e**	5	 **3ie + 3′ie**	87 (64:36)
5	$Me-C\equiv C-t\text{-}Bu$ **2f**	19	 **3if + 3′if**	89 (91:9)
6[c]	$Et-C\equiv C-p\text{-}Anis$ **2g**	32	 **3ig**, **3′ig**	**3ig**, 53[d], **3′ig**, 27
7[e]	$Me-C\equiv C-SiMe_3$ **2h**	13	 **3ih**, **3′ih**	**3ih**, 70[f], **3′ih**, 9
8[g]	$p\text{-}Anis-C\equiv C-SiMe_3$ **2i**	37	 **3ii**, **3′ii**	**3ii**, 73[h], **3′ii**, <5

a) Isolated yields. b) Determined by ^{1}H NMR analysis. c) PPh_2Me was used as a ligand. d) (*E*)-**3ig** was also obtained in 5% yield. e) Reaction run at 80 °C. f) $E/Z = 59{:}41$ (78:22 at 5 h). g) Reaction run with 1 mol % of catalyst. h) $E/Z = 47{:}53$ (57:43 at 12 h).

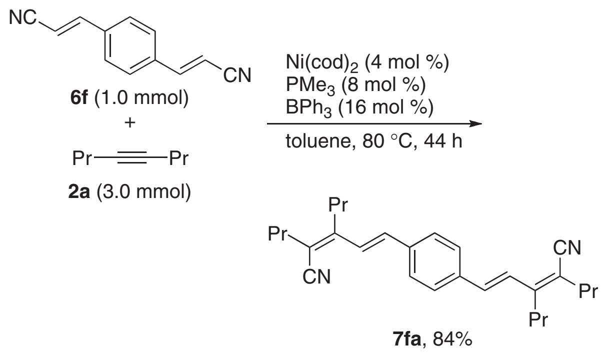
Table 5. Nickel/$AlMe_2Cl$-Catalyzed Arylcyanation of Norbornadiene (**4**)[a)]



Entry	Aryl cyanide	Time /h	Product		Yield /%[b)]
1	**1a**	4.5		**5a**	69
2	**1b**	2		**5b**	70
3	**1c**	2		**5c**	68
4[c)]	**1f**	2		**5f**	57
5	**1h**	10		**5h**	59
6	**1i**	2		**5i**	69
7	**1k**	5.5		**5k**	58

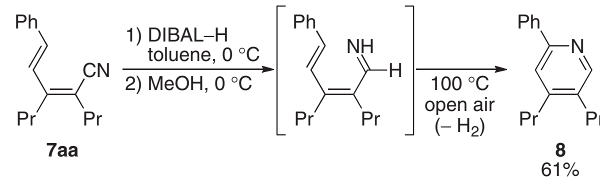
a) All the reactions were carried out using **1** (1.0 mmol), **4** (1.5 mmol), $Ni(cod)_2$ (10 µmol), DMPE (10 µmol), and $AlMe_2Cl$ (40 µmol) in toluene (670 µL). b) Isolated yields. c) Reaction run at 100 °C.

also effective for the reaction, but were accompanied by a significant amount of 2*E*-isomer. It is noteworthy that the catalyst differentiates precisely the alkenyl–CN bonds of starting alkenyl cyanides from those of products probably due to steric and/or electronic factors. Under the same reaction conditions, acrylonitrile failed to participate in the reaction, giving a complex mixture. The reaction of (*Z*)-2-pentenenitrile (**6b**) resulted in contamination of its 4*E*-isomer, possibly because partial isomerization of **6b** to (*E*)-2-pentenenitrile took place before the addition reaction (Entry 2). Disubstituted acrylonitriles gave tetrasubstituted 2,4-pentadienenitriles in good yields (Entries 3–5). Especially worth noting is selective activation of the cyano group trans to the phenyl group in benzylidenemalononitrile (**6e**) to give dicyanosubstituted 1,3-diene **7ea**. Alkenylcyanation of unsymmetrical alkynes were also examined. Whereas the regioselection across 4-methyl-2-pentyne (**2e**) was modest (Entry 6), trimethyl(1-propynyl)silane (**2h**) and 1-phenyl-1-propyne (**2j**) reacted highly regioselectively to give adducts (Entries 7 and 8). In contrast to our expectation, the observed regioselectivity of the reaction with **2h** or **2j** was opposite to the addition reaction of aryl cyanide with unsymmetrical alkynes (Table 4). This reversal of regioselectivity might be ascribed to the difference of the ligand. However any of several alternative explanations may be possible. The reaction of **6f** with two alkenyl cyanide moieties with 3 equivalents of **2a** gave double alkenylcyanation product **7fa** in 84% yield (eq 2).



(2)

Obtained substituted 2,4-pentadienenitriles **7** were readily converted to substituted pyridines via reduction with DIBAL-H and 6π electrocyclization followed by aerobic oxidation as exemplified by the reaction of **7aa** (eq 3).



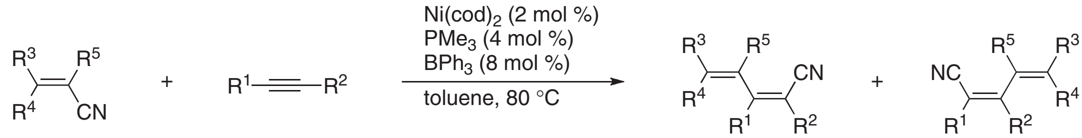
(3)

Reaction Mechanism of Aryl- and Alkenylcyanation Reactions. A six-step catalytic cycle shown in Scheme 2 seems most probable, which starts with (1) formation of LA-bonded η^2-nitrile nickel intermediate **A**;[9c] (2) oxidative addition of C–CN bonds of aryl or alkenyl cyanides to nickel(0) giving aryl- or alkenylnickel intermediate **B**; (3) formation of five-coordinate nickel intermediate **C**; (4) subsequent ligand exchange (path A); (5) migratory insertion of alkynes into the R–Ni bond of **D** to give **E**; (6) reductive elimination to finally give rise to carbocyanation products and regenerate nickel(0) species and LA.[4] In the case of norbornadiene, its migratory insertion would take place directly from five-coordinate nickel **C** to give **E** (path B) because of the use of a chelating bisphosphine. The observed dramatic effects of LA catalysis is attributed primarily to acceleration of oxidative addition of C–CN bonds by coordination of a cyano group to the LA catalyst as expected.[6] LA may also facilitate reductive elimination of C–CN bonds[7] and/or other elemental steps. Coordination of an alkyne to a nickel center in the direction to minimize steric repulsion between bulkier R^2- and aryl or alkenyl groups (**D**) should be responsible for the observed regioselectivity as was the case for the LA-free reaction.[1d] Trans adducts may be derived from phosphine- and/or heat-mediated isomerization of the initial cis adducts, as the stereoisomeric ratios depended on the reaction time and conditions. Stronger Lewis acid appears to more induce such isomerization. A silyl group tends to further facilitate such isomerization.[1d] In the case of aryl-substituted alkynes, alkenylnickel species **E** may isomerize to its isomer **F** possibly through conjugated addition of phosphine ligand[15] followed by reductive elimination to give trans adducts.

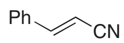
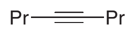
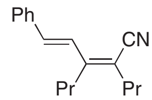
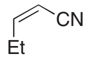
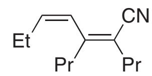
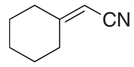
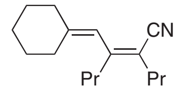
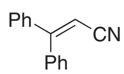
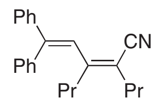
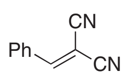
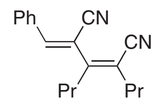
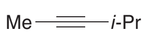
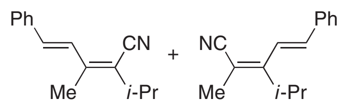
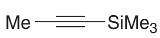
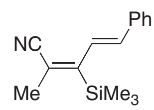
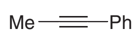
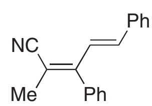
Conclusion

In summary, we have demonstrated a dramatic effect of LA catalysts on nickel-catalyzed arylcyanation of alkynes and

Table 6. Nickel/BPh_3-Catalyzed Alkenylcyanation of Alkynes[a)]



6 (1.0 mmol) 2 7 7'

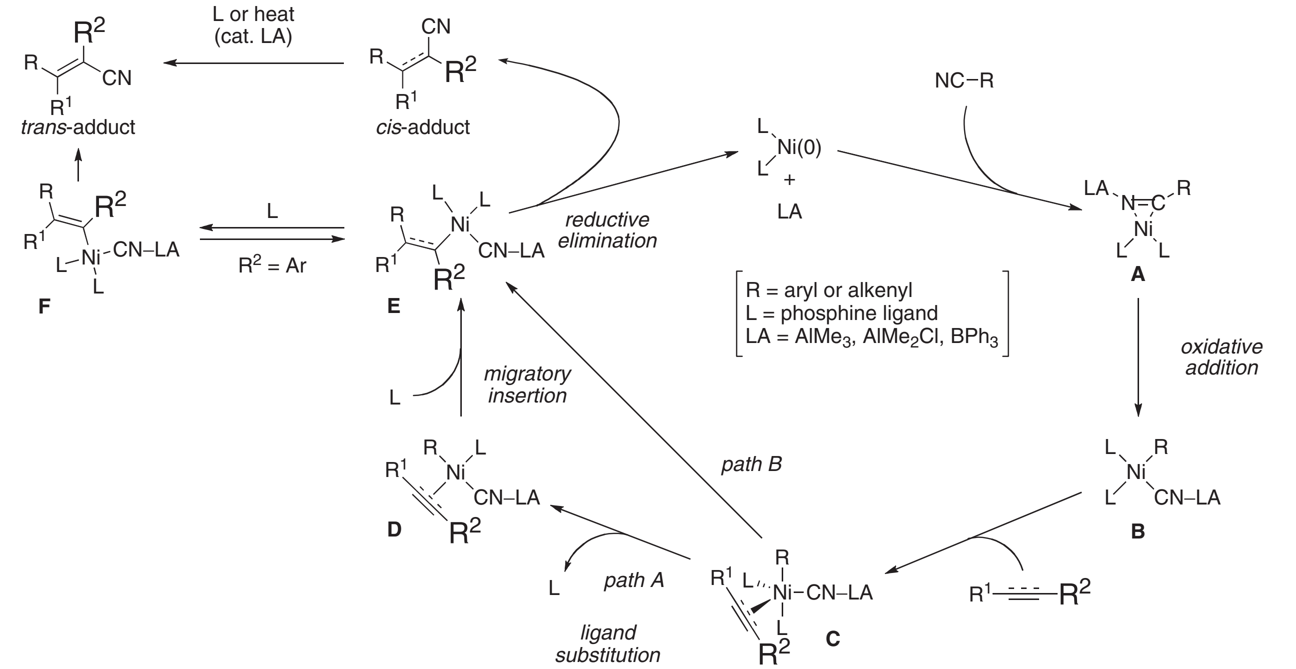
Entry	Alkenyl cyanide	Alkyne (mmol)	Time/h	Product(s), yield/%[b)]	
1	 **6a**	 **2a** (1.2)	20	 **7aa**	94
2	 **6b**	**2a** (1.2)	15	 **7ba**	78[c)]
3	 **6c**	**2a** (1.2)	21	 **7ca**	91
4	 **6d**	**2a** (1.2)	46	 **7da**	94
5[d)]	 **6e**	**2a** (1.2)	13	 **7ea**	81[e)]
6[f)]	**6a**	 **2e** (2.0)	3	 **7ae** + **7′ae**	**7ae**, 44, **7′ae**, 37
7[f)]	**6a**	 **2h** (2.0)	15	 **7′ah**	66[g)]
8[f)]	**6a**	 **2j** (2.0)	6	 **7′aj**	35

a) All the reactions were carried out using **6** (1.0 mmol), **2** (1.2–2.0 mmol), $Ni(cod)_2$ (20–50 µmol), PMe_3 (40–100 µmol), and BPh_3 (80–200 µmol) in toluene (1.0 mL) at 80 °C. b) Isolated yields isomerically pure products. c) $4Z/4E = 84{:}16$. d) The reaction was carried out using $Ni(cod)_2$ (40 µmol), $Ph_2P(CH_2)_4PPh_2$ (40 µmol), and BPh_3 (160 µmol). e) An isomer was also obtained in ≈2% yield. f) The reaction was carried out using $Ni(cod)_2$ (50 µmol), $PCyPh_2$ (100 µmol), and BPh_3 (200 µmol). g) A mixture of isomers was also obtained in ≈7% yield.

norbornadiene. Lewis acids such as organoaluminum and -boron compounds significantly accelerate the whole catalytic cycle of the arylcyanation reaction to allow expansion of the scope of aryl cyanides. Also demonstrated is the first example of the addition reaction of alkenyl cyanides across alkynes by the Ni/BPh_3 cooperative catalysis to give variously substituted 2,4-dienenitriles stereoselectively.

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 spectrom-



Scheme 2. Plausible reaction mechanism.

eter 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, 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. High-resolution mass spectra were obtained with a JEOL JMS-700 (EI). Preparative recycling gel permeation chromatography (GPC) and recycling silica gel chromatography were performed with a JAI LC-908 chromatograph equipped with JAIGEL-1H and -2H (chloroform as an eluent) or COSMOSIL 5SL-II (hexane–ethyl acetate as an eluent), respectively. 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.[16] Aryl cyanides **1g**,[17] **1n**,[11] and **1o**,[18] alkynes **2d**[19] and **2g**,[20] alkenyl cyanides **6c**[21] and **6e**,[22] and dichlorobis(dimethylphenylphosphine)nickel(II)[23] were prepared according to the respective literature procedure.

4-Cyanophenyl-[2-(tetrahydro-2*H*-pyran-2-oxymethyl)-phenyl]dimethylsilane (1e). To a mixture of 4-cyanophenyl[(2-hydroxymethyl)phenyl]dimethylsilane (525 mg, 2.0 mmol)[24] and 3,4-dihydro-2*H*-pyran (673 mg, 8 mmol) was added a drop of a 12 M HCl aqueous solution, and the whole was stirred for 10 min before addition of additional 4-cyanophenyl[(2-hydroxymethyl)phenyl]dimethylsilane (525 mg, 2.0 mmol) at rt. The reaction mixture was stirred at rt for 12 h and concentrated in vacuo to give a residue, which was purified by recrystallization from hexane–ethyl acetate (9:1) to give **1e** (772 mg, 55%) as a colorless solid, mp 59.8–60.8 °C, R_f = 0.25 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.62 (s, 3H), 0.63 (s, 3H), 1.40–1.65 (m, 5H), 1.70–1.81 (m, 1H), 3.41 (m, 1H), 3.73 (distorted td, J = 9.8, 3.1 Hz, 1H), 4.32 (d, J = 11.9 Hz, 1H), 4.43 (t, J = 3.5 Hz, 1H), 4.62 (d, J = 11.9 Hz, 1H), 7.31 (td, J = 7.3, 1.5 Hz, 1H), 7.44 (td, J = 7.4, 1.3 Hz, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.51 (dd, J = 7.4, 1.0 Hz, 1H), 7.61 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ −1.2, −1.1, 19.4, 25.5, 30.5, 62.1, 68.7, 97.7, 112.4, 118.9, 126.9, 128.7, 130.0, 130.8, 134.30, 134.35, 135.3, 143.9, 146.0. IR (KBr): 3470, 3051, 2942, 2864, 2226, 1937, 1589, 1566, 1543, 1493, 1464, 1451, 1437, 1414, 1400, 1385, 1350, 1321, 1314, 1281, 1254, 1200, 1184, 1163, 1155, 1128, 1117, 1098, 1078, 1055, 1032, 974, 909, 887, 870, 829, 826, 802, 781, 758, 748, 721, 689, 656, 557, 530, 496, 459, 444, 436 cm^{-1}. Anal. Calcd for $C_{21}H_{25}NO_2Si$: C, 71.75; H, 7.17%. Found: C, 71.75; H, 7.17%.

1,4-Bis(β-cyanovinyl)benzene (6f). To a solution of NaH (756 mg, 32 mmol) in THF (60 mL) was added diethyl cyanomethylphosphonate (5.6 g, 32 mmol) dropwise at 0 °C, and the whole was stirred for 30 min. To this was added dropwise a solution of terephthalaldehyde (2.0 g, 15.0 mmol) in THF (10 mL), and the resulting mixture was stirred for 18 h before addition of water (100 mL) at rt. The organic layer was separated; the aqueous layer was extracted three times with diethyl ether. The combined organic layers were washed twice with water and brine, dried over anhydrous $MgSO_4$, filtered through a Celite pad, and concentrated in vacuo. The residue was purified by recrystallization from methanol to give **6f** (565 mg, 21%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.95 (d, $J = 16.7$ Hz, 2H), 7.39 (d, $J = 16.7$ Hz, 2H), 7.50 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 98.2, 117.5, 127.9, 135.7, 148.8.[25]

Nickel/Lewis Acid-Catalyzed Arylcyanation of Alkynes. *General procedure*: In a dry box, to a solution of $Ni(cod)_2$ (2.8–13.7 mg, 10–50 µmol) and a ligand (20–100 µmol) in toluene (1.0 mL) placed in a vial, were sequentially added an aryl cyanide (1.00 mmol), a Lewis acid (40–200 µmol), an alkyne (1.00 mmol), and dodecane (internal standard, 56 mg, 0.33 mmol). The vial was closed, taken out from the dry box, and heated at the temperature for the time specified in Tables 1–4. The resulting mixture was filtered through a silica gel pad and concentrated in vacuo. The residue was purified by flash silica gel column chromatography to give the corresponding arylcyanation products in yields listed in Tables 1–4. Regio- and/or stereoisomers were separated by preparative GPC or HPLC and characterized by spectrometry. The spectra of (*Z*)-**3aa**, -**3ba**, -**3ca**, -**3da**, -**3ja**, and -**3ma** agreed well with those reported previously.[1a,1d]

Nickel/Lewis Acid-Catalyzed Arylcyanation of Alkynes Using Dichlorobis(dimethylphenylphosphine)nickel(II) as a Precatalyst (Scheme 1). In a dry box, to **1a** (133 mg, 1.00 mmol) placed in a vial were added a solution of $(PhMe_2P)_2NiCl_2$ (4.1 mg, 10 µmol) in toluene (1.0 mL), **2a** (110 mg, 1.00 mmol), a 1.0 M solution of $AlMe_3$ in hexane (40 µL, 40 µmol), and dodecane (internal standard, 56 mg, 0.33 mmol). The vial was closed, taken out from the dry box, and heated at 50 °C for 19 h. The resulting mixture was filtered through a silica gel pad and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane–ethyl acetate = 8:1) to give (*Z*)-**3aa** (233 mg, 96%).

(*E*)-3-(4-Methoxyphenyl)-2-propylhex-2-enenitrile [(*E*)-3aa]: A pale yellow oil, $R_f = 0.20$ (hexane–ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (t, $J = 7.3$ Hz, 3H), 0.91 (t, $J = 7.4$ Hz, 3H), 1.35 (sext, $J = 7.4$ Hz, 2H), 1.55 (sext, $J = 7.5$ Hz, 2H), 2.10 (t, $J = 7.6$ Hz, 2H), 2.70 (t, $J = 7.5$ Hz, 2H), 3.84 (s, 3H), 6.91 (dt, $J = 8.8$, 2.4 Hz, 2H), 7.02 (dt, $J = 8.8$, 2.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.5, 13.6, 21.2, 21.9, 32.7, 40.5, 55.3, 111.3, 113.7, 119.2, 128.6, 130.3, 158.2, 159.1. IR (neat): 2961, 2934, 2872, 2837, 2207, 1607, 1574, 1510, 1464, 1443, 1412, 1381, 1304, 1288, 1250, 1177, 1109, 1034, 837, 739 cm^{-1}. HRMS (EI) Calcd for $C_{16}H_{21}NO$: M$^+$, 243.1623. Found: m/z 243.1624.

(*Z*)-3-(4-{[2-(Tetrahydro-2*H*-pyran-2-oxymethyl)phenyl]dimethylsilyl}phenyl)-2-propylhex-2-enenitrile (3ea): A colorless oil, $R_f = 0.35$ (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.60 (s, 3H), 0.61 (s, 3H), 0.87 (t, $J = 7.4$ Hz, 3H), 1.01 (t, $J = 7.4$ Hz, 3H), 1.30 (sext, $J = 7.5$ Hz, 2H), 1.40–1.83 (m, 8H), 2.35 (t, $J = 7.6$ Hz, 2H), 2.49 (t, $J = 7.8$ Hz, 2H), 3.39–3.49 (m, 1H), 3.74–3.84 (m, 1H), 4.39 (d, $J = 12.1$ Hz, 1H), 4.48 (t, $J = 3.5$ Hz, 1H), 4.67 (d, $J = 12.1$ Hz, 1H), 7.23–7.33 (m, 3H), 7.41 (td, $J = 7.5$, 1.5 Hz, 1H), 7.47–7.51 (m, 3H), 7.54 (dd, $J = 7.5$, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ −1.11, −0.96, 13.5, 13.8, 19.3, 21.1, 21.7, 25.4, 30.4, 32.5, 35.6, 62.0, 68.8, 97.8, 111.5, 119.6, 126.8, 127.0, 128.5, 129.7, 134.0, 135.5, 135.7, 139.5, 140.6, 144.2, 158.6. IR (neat): 2959, 2872, 2361, 2210, 1458, 1437, 1389, 1350, 1258, 1202, 1119, 1078, 1028, 833, 814, 775, 756 cm^{-1}. Anal. Calcd for $C_{29}H_{39}NO_2Si$: C, 75.44; H, 8.51%. Found: C, 75.53; H, 8.69%.

(*Z*)-3-(4-*N*,*N*-Dimethylaminophenyl)-2-propylhex-2-enenitrile (3fa): A colorless oil, $R_f = 0.61$ (hexane–ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, $J = 7.4$ Hz, 3H), 1.01 (t, $J = 7.3$ Hz, 3H), 1.32 (sext, $J = 7.5$ Hz, 2H), 1.66 (sext, $J = 7.5$ Hz, 2H), 2.33 (t, $J = 7.7$ Hz, 2H), 2.49 (t, $J = 7.7$ Hz, 2H), 2.98 (s, 6H), 6.70 (d, $J = 9.0$ Hz, 2H), 7.26 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.5, 13.8, 21.4, 21.9, 32.7, 35.3, 40.2, 108.9, 111.6, 120.7, 127.3, 128.9, 150.5, 158.8. IR (neat): 2961, 2932, 2872, 2205, 1611, 1524, 1454, 1445, 1360, 1229, 1202, 1167, 947, 820, 733 cm^{-1}. Anal. Calcd for $C_{17}H_{24}N_2$: C, 79.64; H, 9.44%. Found: C, 79.64; H, 9.50%.

(*Z*)-3-(4-*N*,*N*-Diphenylaminophenyl)-2-propylhex-2-enenitrile (3ga): A colorless oil, $R_f = 0.24$ (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, $J = 7.4$ Hz, 3H), 1.01 (t, $J = 7.3$ Hz, 3H), 1.35 (sext, $J = 7.5$ Hz, 2H), 1.67 (sext, $J = 7.5$ Hz, 2H), 2.34 (t, $J = 7.6$ Hz, 2H), 2.49 (t, $J = 7.7$ Hz, 2H), 7.00–7.32 (m, 14H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.5, 13.9, 21.3, 21.8, 32.7, 35.5, 110.5, 120.1, 122.0, 123.4, 125.0, 128.7, 129.3, 133.1, 147.3, 148.1, 158.3. IR (neat): 2963, 2932, 2872, 2208, 1591, 1506, 1493, 1327, 1277, 839, 754, 696 cm^{-1}. HRMS (EI) Calcd for $C_{27}H_{28}N_2$: M$^+$, 380.2252. Found: m/z 380.2244.

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

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

(*Z*)-3-(2-Methoxyphenyl)-2-propylhex-2-enenitrile (3ka): A colorless oil, $R_f = 0.34$ (hexane–ethyl acetate = 7.5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, $J = 7.4$ Hz, 3H), 1.02 (t, $J = 7.4$ Hz, 3H), 1.30 (sext, $J = 7.5$ Hz, 2H), 1.67 (sext, $J = 7.4$ Hz, 2H), 2.36 (t, $J = 7.5$ Hz, 2H), 2.47 (t, $J = 7.8$ Hz, 2H), 3.81 (s, 3H), 6.92 (d, $J = 8.4$ Hz, 1H), 6.96 (td, $J = 7.4$, 1.0 Hz, 1H), 7.09 (dd, $J = 7.5$, 1.8 Hz, 1H), 7.31 (ddd, $J = 7.8$, 7.5, 1.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.4, 14.0, 20.9, 21.7, 31.8, 35.0, 55.5, 111.1, 112.9, 119.4, 120.5, 129.4, 129.68, 129.72, 156.1, 157.0. IR (neat): 2963, 2934, 2872, 2212, 1597, 1578, 1489, 1464, 1435, 1275, 1246, 1178, 1163, 1124, 1097, 1049, 1026, 799, 752 cm^{-1}. Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70%. Found: C, 78.86; H, 8.67%.

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

(*Z*)-3-(1-Methylindol-3-yl)-2-propylhex-2-enenitrile (3na): A pale yellow solid, mp 74.7–75.3 °C, $R_f = 0.30$ (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, $J =$ 7.4 Hz, 3H), 1.05 (t, $J = 7.4$ Hz, 3H), 1.36 (sext, $J = 7.6$ Hz, 2H), 1.71 (sext, $J = 7.5$ Hz, 2H), 2.41 (t, $J = 7.6$ Hz, 2H), 2.66 (t, $J = 7.8$ Hz, 2H), 3.81 (s, 3H), 7.17 (t, $J = 7.5$ Hz, 1H), 7.23–7.30 (m, 2H), 7.34 (d, $J = 8.1$ Hz, 1H), 7.58 (d, $J = 7.9$ Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.6, 13.9, 21.8, 22.0, 32.4, 33.0, 35.3, 109.4, 109.7, 114.3, 119.9, 120.2, 120.9, 122.0, 126.3, 129.0, 137.0, 152.4. IR (KBr): 2961, 2870, 2201, 1614, 1605, 1537, 1477, 1466, 1385, 1331, 1244, 1134, 1105, 1090, 1015, 845, 741 cm^{-1}. Anal. Calcd for $C_{18}H_{22}N_2$: C, 81.16; H, 8.32%. Found: C, 81.02; H, 8.47%.

(*Z*)-3-Ferrocenyl-2-propylhex-2-enenitrile [(*Z*)-3oa]: A red oil, $R_f = 0.18$ (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (t, $J = 7.3$ Hz, 6H), 1.54 (sext, $J = 7.7$ Hz, 2H), 1.67 (sext, $J = 7.5$ Hz, 2H), 2.26 (t, $J = 7.6$ Hz, 2H), 2.48 (distorted t, $J = 8.2$ Hz, 2H), 4.17 (s, 5H), 4.38 (t, $J = 1.9$ Hz, 2H), 4.85 (t, $J = 1.9$ Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.7, 14.6, 21.9, 23.8, 33.5, 35.5, 68.7, 69.7, 70.0, 82.4, 104.8, 121.4, 155.5. IR (neat): 3096, 2961, 2932, 2872, 2201, 1591, 1462, 1456, 1412, 1381, 1343, 1302, 1290, 1275, 1236, 1211, 1186, 1107, 1086, 1065, 1042, 1001, 934, 883, 822, 758, 741, 498 cm^{-1}. Anal. Calcd for $C_{19}H_{23}FeN$: C, 71.04; H, 7.22%. Found: C, 71.24; H, 7.12%.

(*E*)-3-Ferrocenyl-2-propylhex-2-enenitrile [(*E*)-3oa]: A red oil, $R_f = 0.18$ (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (q, $J = 7.1$ Hz, 6H), 1.67 (sept, $J = 7.8$ Hz, 4H), 2.44 (t, $J = 7.9$ Hz, 2H), 2.73 (distorted t, $J =$ 8.0 Hz, 2H), 4.16 (s, 5H), 4.40 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.9, 14.4, 22.0, 24.4, 33.1, 40.1, 69.6, 70.0, 82.0, 108.4, 120.5, 155.8. IR (neat): 3096, 2961, 2930, 2872, 2199, 1589, 1466, 1458, 1412, 1381, 1343, 1327, 1290, 1273, 1261, 1227, 1209, 1119, 1107, 1088, 1061, 1042, 1001, 930, 882, 822, 746, 525 cm^{-1}. HRMS (EI) Calcd for: $C_{19}H_{23}FeN$: M$^+$, 321.1180. Found: m/z 321.1182.

(*Z*)-3-(4-Oxo-4*H*-chromen-3-yl)-2-propylhex-2-enenitrile (3pa): A yellow oil, $R_f = 0.33$ (hexane–ethyl acetate = 7:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, $J = 7.3$ Hz, 3H), 1.04 (t, $J = 7.3$ Hz, 3H), 1.38 (sext, $J = 7.5$ Hz, 2H), 1.69 (sext, $J =$ 7.4 Hz, 2H), 2.39 (t, $J = 7.6$ Hz, 2H), 2.60 (t, $J = 7.8$ Hz, 2H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.48 (d, $J = 8.4$ Hz, 1H), 7.70 (t, $J =$ 7.9 Hz, 1H), 7.89 (s, 1H), 8.23 (d, $J = 7.9$ Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.6, 14.0, 21.2, 21.7, 32.0, 33.3, 115.3, 118.1, 118.6, 124.1, 124.4, 125.4, 125.9, 133.9, 151.0, 153.5, 156.0, 175.5. IR (neat): 3069, 2963, 2932, 2872, 2212, 1649, 1616, 1572, 1466, 1377, 1350, 1321, 1304, 1296, 1221, 1165, 1148, 1107, 1096, 912, 887, 851, 762, 706, 538 cm^{-1}. HRMS (EI) Calcd for $C_{18}H_{19}NO_2$; M$^+$, 281.1416. Found: m/z 281.1418.

(*Z*)-3-(2-Oxo-2*H*-chromen-3-yl)-2-propylhex-2-enenitrile (3qa): A colorless solid, mp 68.6–69.6 °C, $R_f = 0.23$ (hexane–ethyl acetate = 7:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, $J = 7.3$ Hz, 3H), 1.05 (t, $J = 7.3$ Hz, 3H), 1.40 (sext, $J = 7.5$ Hz, 2H), 1.70 (sext, $J = 7.4$ Hz, 2H), 2.39 (t, $J = 7.6$ Hz, 2H), 2.60 (t, $J = 7.8$ Hz, 2H), 7.31 (d, $J = 7.9$ Hz, 1H), 7.36 (d, $J = 8.2$ Hz, 1H), 7.51–7.59 (m, 2H), 7.69 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.7, 14.0, 21.4, 21.7, 32.0, 33.0, 115.2, 116.5, 118.4, 118.5, 124.6, 127.4, 128.1, 132.1, 142.5, 153.5, 153.7, 159.0. IR (KBr): 3036, 2961, 2932, 2872, 2211, 1713, 1611, 1570, 1489, 1458, 1381, 1368, 1252, 1225, 1186, 1126, 1076, 1065, 1036, 984, 972, 926, 910, 800, 764, 741 cm^{-1}. Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81%. Found: C, 76.74; H, 6.75%.

(*Z*)-3-(4-Chlorophenyl)-2-methylbut-2-enenitrile (3ib): A colorless oil, $R_f = 0.13$ (hexane–ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.16 (q, $J = 1.1$ Hz, 3H), 2.41 (q, $J = 1.1$ Hz, 3H), 7.31 (dt, $J = 8.8$, 2.2 Hz, 2H), 7.37 (dt, $J = 9.0$, 2.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 17.7, 20.7, 105.8, 119.9, 128.55, 128.57, 134.5, 139.1, 152.8. IR (neat): 2997, 2926, 2862, 2211, 1906, 1620, 1593, 1491, 1441, 1398, 1294, 1265, 1186, 1094, 1061, 1013, 968, 947, 833, 725, 638, 613, 602, 579, 521 cm^{-1}. HRMS (EI) Calcd for $C_{11}H_{10}ClN$; M$^+$, 191.0502. Found: m/z 191.0497.

(*Z*)-3-(4-Chlorophenyl)-2-ethylpent-2-enenitrile (3ic): A colorless oil, $R_f = 0.13$ (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, $J = 7.5$ Hz, 3H), 1.24 (t, $J = 7.5$ Hz, 3H), 2.41 (q, $J = 7.5$ Hz, 2H), 2.53 (q, $J = 7.6$ Hz, 2H), 7.25 (dt, $J = 8.4$, 2.2 Hz, 2H), 7.37 (dt, $J = 8.6$, 2.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 12.6, 13.3, 24.0, 27.0, 113.0, 119.2, 128.6, 129.1, 134.5, 138.1, 158.0. IR (neat): 2974, 2936, 2876, 2211, 1906, 1618, 1593, 1491, 1460, 1397, 1379, 1317, 1269, 1180, 1096, 1053, 1013, 932, 856, 827, 731, 716, 577, 515 cm^{-1}. Anal. Calcd for $C_{13}H_{14}ClN$: C, 71.07; H, 6.42%. Found: C, 71.10; H, 6.40%.

(*Z*)-3-(4-Chlorophenyl)-4-trimethylsilyl-2-(trimethylsilylmethyl)but-2-enenitrile (3id): A colorless solid, mp 65.9–66.8 °C, $R_f = 0.45$ (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.10 (s, 9H), 0.17 (s, 9H), 1.77 (s, 2H), 2.03 (s, 2H), 7.27 (d, $J = 8.8$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ −0.9, −0.7, 22.6, 27.6, 104.8, 120.8, 128.5, 129.3, 134.1, 139.8, 153.0. IR (KBr): 3437, 2955, 2899, 2203, 1906, 1599, 1589, 1489, 1466, 1397, 1304, 1296, 1246, 1202, 1165, 1152, 1134, 1090, 1030, 1013, 903, 839, 789, 775, 766, 739, 725, 698, 675, 652, 629, 608, 521, 503 cm^{-1}. Anal. Calcd for $C_{17}H_{26}ClNSi_2$: C, 60.76; H, 7.80%. Found: C, 60.54; H, 7.99%.

(*Z*)-3-(4-Chlorophenyl)-2-isopropylbut-2-enenitrile (3ie): A colorless oil, $R_f = 0.20$ (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (d, $J = 6.8$ Hz, 6H), 2.18 (s, 3H), 2.92 (sext, $J = 6.8$ Hz, 1H), 7.29 (dt, $J = 8.8$, 2.2 Hz, 2H), 7.36 (dt, $J = 8.7$, 2.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 20.5, 21.2, 29.2, 117.4, 118.9, 128.5, 128.7, 134.4, 139.5, 150.5. IR (neat): 2970, 2932, 2872, 2211, 1904, 1613, 1593, 1491, 1464, 1398, 1389, 1366, 1292, 1263, 1094, 1076, 1047, 1007, 831, 797, 723, 700, 673, 631, 579, 532, 492 cm^{-1}.

Anal. Calcd for $C_{13}H_{14}ClN$: C, 71.07; H, 6.42%. Found: C, 71.36; H, 6.44%.

(*Z*)-3-(4-Chlorophenyl)-2,4-dimethylpent-2-enenitrile (3′ie): A colorless solid, mp 97.8–98.8 °C, $R_f = 0.13$ (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (d, $J =$ 7.0 Hz, 6H), 2.07 (s, 3H), 3.08 (sext, $J = 6.9$ Hz, 1H), 7.05 (dt, $J = 8.8$, 2.2 Hz, 2H), 7.36 (dt, $J = 8.8$, 2.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 16.1, 20.5, 30.7, 107.0, 119.4, 128.4, 129.5, 134.1, 136.2, 162.9. IR (KBr): 3447, 2974, 2932, 2872, 2209, 1908, 1624, 1589, 1489, 1466, 1391, 1364, 1329, 1113, 1103, 1090, 1049, 1015, 963, 878, 845, 814, 731, 723, 567, 548, 521, 469 cm^{-1}. Anal. Calcd for $C_{13}H_{14}ClN$: C, 71.07; H, 6.42%. Found: C, 71.07; H, 6.37%.

(*Z*)-2-*tert*-Butyl-3-(4-chlorophenyl)but-2-enenitrile (3if): A colorless oil, $R_f = 0.15$ (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (s, 9H), 2.29 (s, 3H), 7.21 (dt, $J = 8.6$, 2.2 Hz, 2H), 7.35 (dt, $J = 8.4$, 2.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 23.1, 30.6, 34.2, 118.7, 121.9, 128.55, 128.62, 134.1, 141.9, 154.1. IR (neat): 2970, 2911, 2874, 2207, 1902, 1593, 1489, 1433, 1397, 1368, 1290, 1238, 1206, 1092, 1034, 1015, 831, 783, 687, 577, 532 cm^{-1}. Anal. Calcd (as a mixture with **3if** and **3′if**) for $C_{14}H_{16}ClN$: C, 71.94; H, 6.90%. Found: C, 72.11; H, 6.90%.

(*Z*)-3-(4-Chlorophenyl)-2,4,4-trimethylpent-2-enenitrile (3′if): A colorless solid, mp 76.7–77.5 °C, $R_f = 0.15$ (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (s, 9H), 2.21 (s, 3H), 7.00 (dt, $J = 8.6$, 2.3 Hz, 2H), 7.34 (dt, $J =$ 8.6, 2.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 19.1, 30.5, 36.9, 109.6, 120.1, 128.4, 128.6, 133.6, 140.2, 165.7. IR (KBr): 3441, 2969, 2868, 2214, 1591, 1487, 1464, 1397, 1364, 1223, 1198, 1177, 1096, 1047, 1017, 968, 949, 939, 928, 860, 841, 826, 791, 725, 718, 608, 563, 546, 530, 478 cm^{-1}.

(*Z*)-3-(4-Chlorophenyl)-2-(4-methoxyphenyl)pent-2-enenitrile [(*Z*)-3ig]: A colorless solid, mp 109.8–110.5 °C, $R_f = 0.34$ (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, $J = 7.5$ Hz, 3H), 2.58 (q, $J = 7.5$ Hz, 2H), 3.85 (s, 3H), 6.96 (d, $J = 8.8$ Hz, 2H), 7.30–7.46 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 12.8, 27.5, 55.4, 112.1, 114.2, 119.2, 126.4, 128.9, 129.3, 130.1, 135.0, 137.5, 159.8, 159.9. IR (KBr): 2980, 2963, 2934, 2841, 2206, 1605, 1589, 1570, 1510, 1491, 1464, 1445, 1302, 1283, 1254, 1177, 1105, 1084, 1036, 1011, 845, 829, 689, 515 cm^{-1}. Anal. Calcd for $C_{18}H_{16}ClNO$: C, 72.60; H, 5.42%. Found: C, 72.68; H, 5.67%.

(*E*)-3-(4-Chlorophenyl)-2-(4-methoxyphenyl)pent-2-enenitrile [(*E*)-3ig]: A pale yellow oil, $R_f = 0.26$ (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (t, $J =$ 7.5 Hz, 3H), 2.92 (q, $J = 7.5$ Hz, 2H), 3.76 (s, 3H), 6.70 (d, $J = 8.8$ Hz, 2H), 6.97–7.03 (m, 4H), 7.22 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 12.6, 32.0, 55.2, 111.4, 113.8, 118.8, 125.7, 128.8, 129.9, 130.7, 134.3, 136.4, 158.2, 159.3. IR (neat): 2972, 2936, 2212, 1607, 1510, 1489, 1464, 1294, 1254, 1178, 1092, 1034, 1015, 912, 826, 733 cm^{-1}. HRMS (EI) Calcd for $C_{18}H_{16}ClNO$: M$^+$, 297.0920. Found: m/z 297.0932.

(*Z*)-3-(4-Chlorophenyl)-3-(4-methoxyphenyl)-2-ethylacrylonitrile (3′ig): A pale yellow oil, $R_f = 0.26$ (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (t, $J =$ 7.4 Hz, 3H), 2.42 (q, $J = 7.5$ Hz, 2H), 3.83 (s, 3H), 6.90 (d, $J = 8.4$ Hz, 2H), 7.03 (d, $J = 9.0$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.3, 25.8, 55.3, 113.0, 113.8, 119.7, 128.5, 130.6, 130.8, 130.9, 135.2, 138.7, 154.9, 160.1. IR (neat): 2974, 2206, 1607, 1510, 1489, 1460, 1288, 1252, 1175, 1092, 1032, 1015, 908, 833, 824, 731 cm^{-1}; Calcd for $C_{18}H_{16}ClNO$: C, 72.60; H, 5.42%. Found: C, 72.40; H, 5.24%.

(*E*)-3-(4-Chlorophenyl)-2-trimethylsilylbut-2-enenitrile [(*E*)-3ih]: A colorless oil, $R_f = 0.14$ (hexane–ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.39 (s, 9H), 2.31 (s, 3H), 7.33–7.39 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ −0.2, 24.5, 111.2, 120.1, 128.1, 128.6, 134.9, 140.5, 168.1. IR (neat): 2959, 2195, 1595, 1578, 1556, 1489, 1254, 1103, 1013, 845, 760, 673 cm^{-1}. Anal. Calcd [as a mixture with (*Z*)-**3ih** and **3′ih**] for $C_{13}H_{16}ClNSi$: C, 62.50; H, 6.46%. Found: C, 62.75; H, 6.52%.

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

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

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

(*Z*)-3-(4-Chlorophenyl)-3-(4-methoxyphenyl)-2-trimethylsilylacrylonitrile [(*Z*)-3ii]: A colorless solid, mp 98.7–99.6 °C, $R_f = 0.35$ (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.07 (s, 9H), 3.83 (s, 3H), 6.87 (d, $J = 8.8$ Hz, 2H), 7.10 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 8.8$ Hz, 2H), 7.36 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 0.0, 55.4, 110.1, 113.5, 121.1, 128.3, 130.7, 131.0, 132.9, 135.3, 139.8, 160.8, 169.4. IR (KBr): 2961, 2191, 1601, 1572, 1543, 1508, 1489, 1306, 1252, 1182, 1167, 1092, 1028, 860, 837 cm^{-1}. Anal. Calcd for $C_{19}H_{20}ClNOSi$: C, 66.74; H, 5.90%. Found: C, 66.48; H, 5.97%.

Arylcyanation of Norbornadiene. *General procedure*: In a dry box, to an aryl cyanide (1.00 mmol) placed in a vial were sequentially added a solution of $Ni(cod)_2$ (2.8 mg, 10 µmol) and $Me_2P(CH_2)_2PMe_2$ (1.5 mg, 10 µmol) in toluene (0.67 mL), a 1.04 M solution of $AlMe_2Cl$ in hexane (39 µL, 40 µmol), norbornadiene (138 mg, 1.50 mmol), and dodecane (internal standard, 85 mg, 0.50 mmol). The vial was closed, taken out from the dry box, and heated at 80 °C for the time specified in

Table 5. The resulting mixture was filtered through a silica gel pad and concentrated in vacuo. The residue was purified by flash silica gel column chromatography to give the corresponding arylcyanation products in yields listed in Table 5.

(5*R,6*S**)-5-Cyano-6-(4-methoxyphenyl)bicyclo[2.2.1]-hept-2-ene (5a):** A colorless solid, mp 67.3–68.1 °C, $R_f = 0.19$ (hexane–ethyl acetate = 7:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.78 (dt, $J = 9.4$, 1.8 Hz, 1H), 2.11 (d, $J = 9.3$ Hz, 1H), 2.78 (dd, $J = 9.1$, 1.8 Hz, 1H), 3.03 (dd, $J = 9.0$, 1.5 Hz, 1H), 3.16 (d, $J = 1.3$ Hz, 1H), 3.33 (s, 1H), 3.80 (s, 3H), 6.18 (dd, $J = 5.8$, 3.0 Hz, 1H), 6.43 (dd, $J = 5.7$, 3.3 Hz, 1H), 6.90 (dt, $J = 8.8$, 2.6 Hz, 2H), 7.17 (dt, $J = 8.4$, 1.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 36.5, 46.2, 46.47, 46.53, 48.2, 55.2, 114.0, 121.3, 129.0, 131.8, 135.3, 140.8, 158.5. IR (KBr): 2976, 2234, 1611, 1512, 1460, 1250, 1182, 1034, 835, 764, 729, 692 cm^{-1}. Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71%. Found: C, 79.92; H, 6.74%.

(5*R,6*S**)-5-Cyano-6-(4-methylphenyl)bicyclo[2.2.1]hept-2-ene (5b):** A colorless solid, mp 81.4–84.0 °C, $R_f = 0.20$ (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.79 (dt, $J = 9.3$, 1.8 Hz, 1H), 2.11 (d, $J = 9.3$ Hz, 1H), 2.34 (s, 3H), 2.81 (dd, $J = 9.1$, 1.9 Hz, 1H), 3.04 (dd, $J = 9.0$, 1.5 Hz, 1H), 3.19 (d, $J = 1.5$ Hz, 1H), 3.33 (d, $J = 0.6$ Hz, 1H), 6.18 (dd, $J = 5.7$, 2.9 Hz, 1H), 6.43 (dd, $J = 5.7$, 3.1 Hz, 1H), 7.14 (d, $J = 8.2$ Hz, 2H), 7.17 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.1, 36.5, 46.2, 46.3, 46.8, 48.2, 121.3, 127.9, 129.4, 135.3, 136.6, 136.8, 140.7. IR (KBr): 2978, 2922, 2234, 1514, 1456, 1327, 1263, 827, 758, 727, 696, 505 cm^{-1}. Anal. Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22%. Found: C, 86.27; H, 7.35%.

(5*R,6*S**)-5-Cyano-6-phenylbicyclo[2.2.1]hept-2-ene (5c):** A colorless solid, mp 94.3–94.7 °C, $R_f = 0.21$ (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.80 (dt, $J = 9.3$, 1.8 Hz, 1H), 2.12 (d, $J = 9.3$ Hz, 1H), 2.83 (dd, $J = 9.1$, 1.9 Hz, 1H), 3.08 (dd, $J = 9.1$, 1.5 Hz, 1H), 3.22 (d, $J = 1.3$ Hz, 1H), 3.34 (s, 1H), 6.19 (dd, $J = 5.7$, 2.9 Hz, 1H), 6.44 (dd, $J = 5.7$, 3.3 Hz, 1H), 7.24–7.30 (m, 3H), 7.34–7.40 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 36.5, 46.2, 46.3, 47.2, 48.2, 121.1, 127.1, 128.0, 128.7, 135.3, 139.9, 140.7. IR (KBr): 2996, 2951, 2230, 1451, 1327, 1263, 1098, 1076, 799, 723, 712, 700 cm^{-1}. Anal. Calcd for $C_{14}H_{13}N$: C, 86.12; H, 6.71%. Found: C, 86.09; H, 6.65%.

(5*R,6*S**)-5-Cyano-6-(4-*N*,*N*-dimethylaminophenyl)bicyclo[2.2.1]hept-2-ene (5f):** A yellow solid, mp 130.5–131.1 °C, $R_f = 0.28$ (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.77 (dt, $J = 9.4$, 1.9 Hz, 1H), 2.12 (d, $J = 9.3$ Hz, 1H), 2.78 (dd, $J = 9.0$, 1.8 Hz, 1H), 2.94 (s, 6H), 2.99 (dd, $J = 9.0$, 1.5 Hz, 1H), 3.14 (d, $J = 1.5$ Hz, 1H), 3.32 (s, 1H), 6.16 (dd, $J = 5.6$, 3.0 Hz, 1H), 6.42 (dd, $J = 5.7$, 3.1 Hz, 1H), 6.74 (d, $J = 7.9$ Hz, 2H), 7.13 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 36.5, 40.5, 46.4, 46.6, 48.1, 112.7, 121.5, 127.3, 128.6, 135.1, 140.8, 149.4. IR (KBr): 2918, 2236, 1614, 1522, 1447, 1354, 1234, 1200, 1167, 1063, 951, 824, 729, 689 cm^{-1}. Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61%. Found: C, 80.38; H, 7.59%.

(5*R,6*S**)-6-(4-Bromophenyl)-5-cyanobicyclo[2.2.1]hept-2-ene (5h):** A colorless solid, mp 141.8–142.1 °C, $R_f = 0.30$ (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.80 (dt, $J = 9.5$, 1.8 Hz, 1H), 2.06 (d, $J = 9.7$ Hz, 1H), 2.82 (dd, $J = 9.1$, 1.9 Hz, 1H), 3.02 (dd, $J = 9.1$, 1.4 Hz, 1H), 3.17 (d, $J = 1.5$ Hz, 1H), 3.35 (s, 1H), 6.20 (dd, $J = 5.6$, 3.0 Hz, 1H), 6.43 (dd, $J = 5.7$, 3.3 Hz, 1H), 7.13 (dt, $J = 8.2$, 2.1 Hz, 2H), 7.49 (dt, $J = 8.6$, 2.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 36.4, 46.16, 46.20, 46.7, 48.2, 120.9, 121.1, 129.7, 131.8, 135.5, 139.0, 140.5. IR (KBr): 2978, 2924, 2236, 1489, 1404, 1327, 1072, 1009, 835, 768, 716 cm^{-1}. Anal. Calcd for $C_{14}H_{12}BrN$: C, 61.33; H, 4.41%. Found: C, 61.53; H, 4.62%.

(5*R,6*S**)-6-(4-Chlorophenyl)-5-cyanobicyclo[2.2.1]hept-2-ene (5i):** A colorless solid, mp 147.4–148.3 °C, $R_f = 0.34$ (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.82 (dt, $J = 9.3$, 1.8 Hz, 1H), 2.08 (d, $J = 9.5$ Hz, 1H), 2.83 (dd, $J = 9.1$, 1.8 Hz, 1H), 3.04 (dd, $J = 9.1$, 1.4 Hz, 1H), 3.19 (d, $J = 1.5$ Hz, 1H), 3.36 (s, 1H), 6.20 (dd, $J = 5.7$, 2.9 Hz, 1H), 6.44 (dd, $J = 5.6$, 3.2 Hz, 1H), 7.19 (dt, $J = 8.4$, 2.0 Hz, 2H), 7.34 (dt, $J = 8.4$, 2.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 36.4, 46.15, 46.24, 46.6, 48.2, 120.8, 129.4, 132.9, 135.5, 138.5, 140.5. IR (KBr): 2978, 2924, 2238, 1493, 1408, 1327, 1088, 1013, 839, 768, 719, 671 cm^{-1}. Anal. Calcd for $C_{14}H_{12}ClN$: C, 73.20; H, 5.27%. Found: C, 73.11; H, 5.34%.

(5*R,6*S**)-5-Cyano-6-(2-methoxyphenyl)bicyclo[2.2.1]-hept-2-ene (5k):** A colorless solid, mp 98.0–98.5 °C, $R_f = 0.38$ (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74 (dt, $J = 9.2$, 1.9 Hz, 1H), 1.97 (d, $J = 9.2$ Hz, 1H), 2.91 (dd, $J = 8.8$, 2.0 Hz, 1H), 3.15 (dd, $J = 8.7$, 1.7 Hz, 1H), 3.26–3.31 (m, 2H), 3.85 (s, 3H), 6.20 (dd, $J = 5.7$, 2.9 Hz, 1H), 6.39 (dd, $J = 5.7$, 3.1 Hz, 1H), 6.90 (dd, $J = 8.2$, 0.9 Hz, 1H), 6.99 (td, $J = 7.5$, 1.0 Hz, 1H), 7.23 (d, $J = 7.7$ Hz, 1H), 7.28 (td, $J = 7.8$, 1.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 35.7, 41.5, 44.0, 45.8, 48.0, 55.2, 110.0, 120.5, 121.5, 126.0, 128.1, 129.0, 135.7, 139.7, 157.8. IR (KBr): 2976, 2236, 1601, 1587, 1489, 1337, 1246, 1101, 1051, 1032, 750, 719, 706 cm^{-1}. Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71%. Found: C, 80.23; H, 6.66%.

Nickel/BPh_3-Catalyzed Alkenylcyanation of Alkynes. *General procedure*: In a dry box, to a solution of $Ni(cod)_2$ (20–50 µmol) and ligand (40–100 µmol) in toluene (1.0 mL) placed in a vial were added an alkenyl cyanide (1.00 mmol), BPh_3 (80–200 µmol), an alkyne (1.20–2.0 mmol), and dodecane (internal standard, 85 mg, 0.50 mmol). The vial was closed, taken out from the dry box, and heated at 80 °C for the time specified in Table 6. The resulting mixture was filtered through a silica gel pad and concentrated in vacuo. The residue was purified by flash silica gel column chromatography to give the corresponding alkenylcyanation products in yields listed in Table 6.

(2*Z*,4*E*)-5-Phenyl-2,3-dipropylpenta-2,4-dienenitrile (7aa): A pale yellow oil, $R_f = 0.13$ (hexane–ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (t, $J = 7.4$ Hz, 3H), 1.02 (t, $J = 7.5$ Hz, 3H), 1.53 (sext, $J = 7.6$ Hz, 2H), 1.66 (sext, $J = 7.5$ Hz, 2H), 2.33 (t, $J = 7.6$ Hz, 2H), 2.46 (t, $J = 8.0$ Hz, 2H), 6.84 (d, $J = 16.1$ Hz, 1H), 7.26–7.40 (m, 4H), 7.52 (d, $J = 7.1$ Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.6, 14.3, 21.8, 22.6, 29.9, 32.2, 112.4, 119.1, 127.0, 127.1, 128.7, 128.8, 133.5, 136.2, 153.1. IR (neat): 2963, 2934, 2874, 2203, 1692, 1450, 962, 754, 692 cm^{-1}. Anal. Calcd for $C_{17}H_{21}N$: C, 85.30; H, 8.84%. Found: C, 85.54; H, 8.78%.

(2*Z*,4*Z*)-2,3-Dipropylhepta-2,4-dienenitrile [(*Z*)-7ba]: A colorless oil, $R_f = 0.15$ (hexane–ethyl acetate = 30:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, $J = 7.3$ Hz, 3H), 0.98 (t, $J = 7.3$ Hz, 3H), 1.03 (t, $J = 7.5$ Hz, 3H), 1.42 (sext, $J = 7.5$ Hz, 2H), 1.62 (sext, $J = 7.4$ Hz, 2H), 2.13 (qdd, $J = 7.5$, 7.3, 1.8 Hz, 2H), 2.20 (t, $J = 7.7$ Hz, 2H), 2.25 (t, $J = 7.6$ Hz, 2H), 5.66 (dt, $J = 11.7$, 7.3 Hz, 1H), 5.89 (d, $J = 11.7$ Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.7, 13.9, 14.1, 21.3, 21.9, 22.9, 31.8, 34.4, 111.5, 119.5, 126.8, 137.6, 154.7. IR (neat): 2964, 2934, 2874, 2208, 1458, 1379 cm^{-1}. Anal. Calcd for $C_{13}H_{21}N$: C, 81.61; H, 11.06%. Found: C, 81.77; H, 10.82%.

(2*Z*,4*E*)-2,3-Dipropylhepta-2,4-dienenitrile [(*E*)-7ba]: A colorless oil, $R_f = 0.15$ (hexane–ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.966 (t, $J = 7.4$ Hz, 3H), 0.972 (t, $J = 7.3$ Hz, 3H), 1.07 (t, $J = 7.4$ Hz, 3H), 1.44 (sext, $J = 7.6$ Hz, 2H), 1.61 (sext, $J = 7.5$ Hz, 2H), 2.19–2.28 (m, 4H), 2.32 (t, $J = 8.0$ Hz, 2H), 6.07 (dt, $J = 15.6$, 6.7 Hz, 1H), 6.60 (dt, $J = 15.6$, 1.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.5, 13.8, 14.4, 21.9, 22.7, 26.4, 30.1, 32.0, 109.8, 119.2, 128.0, 138.3, 153.4. IR (neat): 2964, 2934, 2874, 2205, 1638, 1570, 1462, 1381, 1088, 966 cm^{-1}. HRMS (EI) Calcd for $C_{13}H_{21}N$: M$^+$, 191.1674. Found: *m*/*z* 191.1675.

(*Z*)-4-Cyclohexylidene-2,3-dipropylbut-2-enenitrile (7ca): A pale yellow oil, $R_f = 0.28$ (hexane–ethyl acetate = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, $J = 7.4$ Hz, 3H), 0.96 (t, $J = 7.4$ Hz, 3H), 1.40 (sext, $J = 7.5$ Hz, 2H), 1.52–1.65 (m, 8H), 2.10–2.27 (m, 8H), 5.62 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.5, 14.0, 21.1, 21.8, 26.4, 27.1, 28.3, 30.6, 31.7, 34.7, 37.1, 111.1, 119.9, 121.0, 146.6, 155.3. IR (neat): 2961, 2932, 2872, 2856, 2208, 1647, 1611, 1448, 1379, 1342, 1234, 1109, 1088, 833, 735 cm^{-1}. Anal. Calcd for $C_{16}H_{25}N$: C, 83.06; H, 10.89%. Found: C, 82.85; H, 10.71%.

(*Z*)-5,5-Diphenyl-2,3-dipropylpenta-2,4-dienenitrile (7da): A colorless solid, mp 58.1–58.7 °C, $R_f = 0.25$ (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.74 (t, $J = 7.4$ Hz, 3H), 0.91 (t, $J = 7.3$ Hz, 3H), 1.32 (sext, $J = 7.5$ Hz, 2H), 1.54 (sext, $J = 7.5$ Hz, 2H), 1.89 (t, $J = 7.8$ Hz, 2H), 2.20 (t, $J = 7.5$ Hz, 2H), 6.83 (s, 1H), 7.16–7.40 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.5, 13.9, 21.7, 22.0, 31.8, 32.8, 113.6, 119.5, 126.6, 128.0, 128.2, 129.9, 139.8, 142.2, 146.8, 155.6. IR (KBr): 2963, 2932, 2870, 2203, 1599, 1493, 1445, 1375, 870, 779, 762, 696 cm^{-1}. Anal. Calcd for $C_{23}H_{25}N$: C, 87.57; H, 7.99%. Found: C, 87.46; H, 8.04%.

(2*Z*,4*Z*)-4-Cyano-5-phenyl-2,3-dipropylpenta-2,4-dienenitrile (7ea): A pale yellow oil, $R_f = 0.10$ (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (t, $J = 7.4$ Hz, 3H), 1.03 (t, $J = 7.3$ Hz, 3H), 1.53 (sext, $J = 7.5$ Hz, 2H), 1.69 (sext, $J = 7.5$ Hz, 2H), 2.36 (t, $J = 7.7$ Hz, 2H), 2.49 (t, $J = 7.8$ Hz, 2H), 7.36 (s, 1H), 7.44–7.49 (m, 3H), 7.81–7.89 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.7, 13.9, 21.4, 21.7, 32.8, 33.0, 109.6, 114.7, 116.3, 118.1, 128.9, 129.4, 131.3, 132.4, 148.2, 152.0. IR (neat): 2964, 2933, 2874, 2212, 1605, 1574, 1448, 1381, 1092, 935, 758, 691 cm^{-1}. Anal. Calcd for $C_{18}H_{20}N_2$: C, 81.78; H, 7.63%. Found: C, 81.83; H, 7.66%.

(2*Z*,4*E*)-2-Isopropyl-3-methyl-5-phenylpenta-2,4-dienenitrile (7ae): A pale yellow oil, $R_f = 0.30$ (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (d, $J = 6.8$ Hz, 6H), 2.09 (s, 3H), 2.94 (sept, $J = 6.8$ Hz, 1H), 6.86 (d, $J = 15.9$ Hz, 1H), 7.30 (t, $J = 7.2$ Hz, 1H), 7.36 (t, $J = 7.3$ Hz, 2H), 7.42 (d, $J = 15.9$ Hz, 1H), 7.51 (d, $J = 7.1$ Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.1, 21.5, 28.7, 117.3, 119.3, 127.0, 128.2, 128.56, 128.61, 133.8, 136.0, 146.6. IR (neat): 3080, 3059, 3040, 2969, 2930, 2872, 2201, 1622, 1599, 1580, 1493, 1464, 1449, 1387, 1366, 1317, 1213, 1180, 1157, 1105, 1074, 1045, 1024, 999, 961, 914, 870, 853, 750, 692, 581, 525 cm^{-1}. Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11%. Found (as a mixture with **7ae** and **7′ae**): C, 84.98; H, 8.18%.

(2*Z*,4*E*)-3-Isopropyl-2-methyl-5-phenylpenta-2,4-dienenitrile (7′ae): A pale yellow oil, $R_f = 0.30$ (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (d, $J = 7.0$ Hz, 6H), 2.06 (s, 3H), 3.05 (sept, $J = 7.0$ Hz, 1H), 6.93 (d, $J = 16.3$ Hz, 1H), 7.02 (d, $J = 16.3$ Hz, 1H), 7.29 (t, $J = 7.2$ Hz, 1H), 7.32–7.38 (m, 2H), 7.48 (d, $J = 7.0$ Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 17.1, 20.7, 29.6, 103.9, 120.5, 124.5, 126.8, 128.4, 128.6, 135.1, 136.2, 159.5. IR (neat): 3080, 3057, 3026, 2967, 2932, 2874, 2203, 1632, 1620, 1599, 1576, 1495, 1462, 1449, 1387, 1366, 1329, 1304, 1273, 1236, 1209, 1180, 1157, 1146, 1103, 1067, 1032, 966, 756, 727, 692, 542, 471 cm^{-1}.

(2*E*,4*E*)-2-Methyl-5-phenyl-3-(trimethylsilyl)penta-2,4-dienenitrile (7′ah): A pale yellow oil, $R_f = 0.25$ (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.33 (s, 9H), 2.15 (s, 3H), 6.70 (d, $J = 16.1$ Hz, 1H), 7.02 (d, $J = 16.3$ Hz, 1H), 7.24–7.30 (m, 1H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.45 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 1.0, 21.2, 110.7, 119.5, 126.9, 128.4, 128.9, 130.3, 134.4, 136.8, 157.7. IR (neat): 3080, 3059, 3026, 2955, 2899, 2203, 1616, 1599, 1576, 1539, 1491, 1449, 1410, 1379, 1323, 1254, 1209, 1180, 1157, 1111, 1072, 1013, 963, 909, 885, 843, 804, 746, 692, 629, 509 cm^{-1}. HRMS (EI) Calcd for $C_{15}H_{19}NSi$: M$^+$, 241.1287. Found: *m*/*z* 241.1291. The regiochemistry was assigned based on HMBC experiments.

(2*Z*,4*E*)-2-Methyl-3,5-diphenylpenta-2,4-dienenitrile (7′aj): A pale yellow oil, $R_f = 0.25$ (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.84 (s, 3H), 6.26 (d, $J = 15.7$ Hz, 1H), 7.14 (d, $J = 8.1$ Hz, 2H), 7.27–7.34 (m, 3H), 7.39–7.49 (m, 5H), 7.58 (d, $J = 15.7$ Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 18.1, 106.6, 119.3, 127.0, 127.7, 128.2, 128.5, 128.7, 135.3, 135.7, 137.9, 154.6. IR (neat): 3080, 3057, 3032, 2918, 2857, 2207, 1613, 1579, 1576, 1491, 1449, 1379, 1329, 1302, 1265, 1204, 1179, 1157, 1101, 1072, 1017, 1001, 964, 910, 773, 756, 723, 692, 552, 536 cm^{-1}. HRMS (EI) Calcd for $C_{18}H_{15}N$: M$^+$, 245.1204. Found: *m*/*z* 245.1203. The regiochemistry was assigned based on HMBC experiments.

Nickel/BPh_3-Catalyzed Addition Reaction of 1,4-Bis(β-cyanovinyl)benzene (6f) across 2a (eq 2). In a dry box, to **6f** (180 mg, 1.00 mmol) placed in a vial were sequentially added a solution of Ni(cod)$_2$ (11.0 mg, 40 µmol) and PMe_3 (6.1 mg, 80 µmol) in toluene (1.0 mL), BPh_3 (38 mg, 160 µmol), **2a** (331 mg, 3.0 mmol). The vial was closed, taken out from the dry box, and heated at 80 °C for 44 h. The resulting mixture was filtered through a silica gel pad and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane–toluene = 2:3 to toluene, then CH_2Cl_2) to give **7fa** (335 mg, 84%) as a yellow solid, mp 147.2–148.2 °C, $R_f = 0.20$ (hexane–toluene = 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (t, $J = 7.4$ Hz, 6H), 1.03 (t, $J = 7.4$ Hz, 6H), 1.54 (sext, $J = 7.6$ Hz, 4H), 1.67 (sext, $J = 7.5$ Hz, 4H), 2.34 (t, $J = 7.6$ Hz, 4H), 2.46 (distorted t, $J = 8.0$ Hz, 4H), 6.82 (d, $J = 15.9$ Hz, 2H), 7.37 (d, $J = 15.9$ Hz, 2H), 7.50 (s, 4H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 13.8, 14.5, 21.9, 22.7, 30.0, 32.3, 112.6, 119.0, 127.3, 127.4, 132.7, 136.5, 152.9. IR (KBr): 3428, 3040, 2959, 2934, 2872, 2199, 1614, 1574, 1516, 1479, 1464, 1454, 1433, 1422, 1379, 1335, 1285, 1209, 1161, 1115, 1086, 1071, 968, 903, 880, 822, 739, 658, 552, 534 cm^{-1}. Anal. Calcd for $C_{28}H_{36}N_2$: C, 83.95; H, 9.06%. Found: C, 83.99; H, 9.06%.

Conversion of 7aa to 1-Phenyl-3,4-dipropylpyridine (8) (eq 3): To a solution of **7aa** (72 mg, 0.30 mmol) in toluene (15 mL) was added a 1.5 M solution of DIBAL-H in toluene (0.40 mL, 0.60 mmol) at 0 °C, and the resulting mixture was stirred at the same temperature for 15 min. The reaction was quenched with MeOH (0.150 mL) at 0 °C and heated at 100 °C for 5 h in the open air. To the resulting mixture was added a slurry of SiO_2 (3.0 g) in water (0.90 mL), and the whole was stirred at rt for 45 min. Anhydrous $MgSO_4$ (0.50 g) and K_2CO_3 (0.50 g) were added, and the resulting mixture was further stirred for 90 min, filtered through a Celite pad, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (hexane–ethyl acetate = 35:1) to give **8** (44 mg, 61%) as a pale yellow oil, $R_f = 0.43$ (hexane–ethyl acetate = 7:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (t, $J =$ 7.2 Hz, 3H), 1.02 (t, $J = 7.3$ Hz, 3H), 1.58–1.74 (m, 4H), 2.59–2.68 (m, 4H), 7.34–7.41 (m, 1H), 7.42–7.48 (m, 2H), 7.50 (s, 1H), 7.93–7.99 (m, 2H), 8.43 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.07, 14.11, 23.5, 24.1, 31.8, 34.1, 120.7, 126.7, 128.4, 128.6, 134.5, 139.6, 149.8, 150.3, 155.0. IR (neat): 2959, 2932, 2870, 1597, 1477, 1377, 777, 694 cm^{-1}. Anal. Calcd for $C_{17}H_{21}N$: C, 85.30; H, 8.84%. Found: C, 85.51; H, 9.12%.

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Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of compounds (*E*)-**3aa**, **3ga**, **3ha**, (*E*)-**3oa**, **3pa**, **3ib**, (*E*)-**3ig**, (*E*)-**7ba**, **7′ah**, and **7′aj**. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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