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Arylcyanation of alkynes catalyzed by nickel

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Dedicated to Professor Günther Wilke for his contribution to the field of organonickel chemistry

Abstract—A nickel catalyst prepared from $Ni(cod)_2$ and PMe_3 is found to effect arylcyanation reaction of alkynes, namely, cleavage of a C–CN bond of an aryl cyanide followed by addition of each fragment across an alkyne. A wide range of functional groups in aryl cyanides tolerated the catalysis, giving variously functionalized β-arylalkenenitriles stereoselectively.
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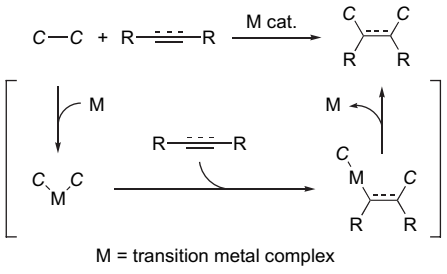
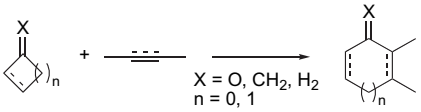
1. Introduction

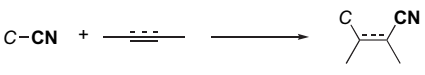
Transition metal-catalyzed cleavage of C–C single bonds followed by addition of the resulting two fragments across unsaturated bonds allows simultaneous formation of two C–C bonds without forming by-products and thus should be of great synthetic potential (Scheme 1). The catalysis may be initiated by oxidative addition of a C–C bond followed by insertion of an unsaturated bond into the resulting C–M bond and reductive elimination to complete the catalytic cycle. However, the initiation is not necessarily feasible due to a directionally and sterically constrained C–C σ-bond having a high bond dissociation energy (~85 kcal/mol).[1] Accordingly, successful catalytic processes reported so far have been limited to those involving activation of strained C–C bonds in such small rings as methylenecyclopropanes,[2] cyclopropenones,[3] cyclobutanes,[4] cyclobutenones,[5] and cyclobutanones (Eq. 1).[6] On the other hand, C–CN bonds that are very common and ubiquitous in many organic molecules have also been found cleavable upon treatment with certain transition metal complexes, in spite of its higher bond dissociation energies (>100 kcal/mol), owing presumably to cyano groups that have affinity to metals and electron-withdrawing nature.[7,8] Indeed, nitriles coordinate to transition metals either in an η^1-fashion or η^2-fashion (Scheme 2).[9] In particular, η^2-coordination is known to further trigger the activation of a C–CN bond via oxidative addition (path A) or via formation of silylisonitrile complexes when a Lewis acidic silyl ligand is located on a metal (path B). A few seminal reports of catalytic reactions utilizing these elemental reactions are available.[10] We envisioned that the oxidative addition of C–CN bonds (path A in Scheme 2) would constitute an initiation step of the catalysis shown in Scheme 1 to achieve addition reaction of nitriles across unsaturated bonds (Eq. 2). Although an addition reaction of benzoyl cyanide across arylacetylenes was recorded some years ago, the suggested mechanism involves acylation of terminal alkynes followed by hydrocyanation of the resulting alkynyl ketones and isomerization, making the reaction scope extensively limited.[11] Very recently, cyanoformate esters are found to add across norbornene and norbornadiene.[12] Herein, we report details of the addition reaction of aryl cyanides across alkynes to give various β-aryl-substituted alkenenitriles.[13]



Scheme 1. Metal-catalyzed cleavage of C–C σ-bonds followed by insertion of unsaturated bonds.



(1)



(2)

Keywords: Nickel; C–C bond activation; Nitrile; Alkyne.
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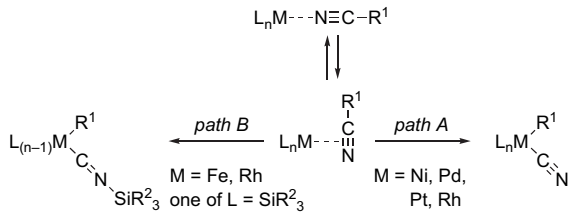
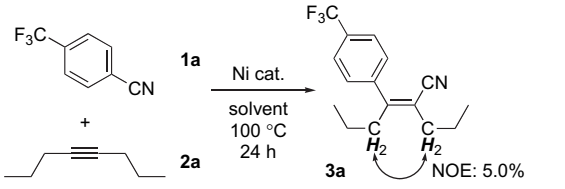


Scheme 2. Activation of C–CN bonds by transition metal complexes.

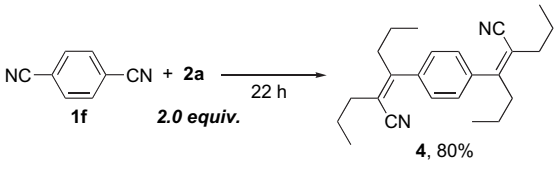
2. Results and discussion

To bring our working hypothesis to reality, we first screened catalysts and solvents effective for an equimolar reaction of 4-(trifluoromethyl)benzonitrile (**1a**) with 4-octyne (**2a**) (Eq. 3 and Table 1). Of the catalysts examined, we found that a combination of $Ni(cod)_2$ with PMe_3 (2.0 equiv to Ni) was the optimum to give expected (*Z*)-3-[4-(trifluoromethyl)phenyl]-2-propyl-2-hexenenitrile (**3a**) in 80% yield after 24 h at 100 °C (entry 1). Stereochemistry of **3a** was determined unambiguously by NOE experiments of ^1H NMR. A similar but more practically useful catalyst was prepared in situ by the reduction of air-stable and commercially available $(Me_3P)_2NiCl_2$[14] with DIBAL-H (2.0 equiv to Ni) and shown to be equally effective (entry 2). Although conversion was high, yield of the desired product was lower with PMe_2Ph or $PMePh_2$ (entries 3 and 4). Other trialkylphosphines such as $P(n\text{-}Bu)_3$, PCy_3, and $P(t\text{-}Bu)_3$ (entries 6–8) as well as PPh_3 (entry 5) gave inferior results.[15] Bidentate ligands, $Me_2P(CH_2)_2PMe_2$, and 2,2′-bipyridyl, and polar solvents like 1,4-dioxane and DMF were less effective (9–12). Other metal complexes such as $Cp(\eta^3\text{-allyl})Pd$, $Pt(cod)_2$, $[RhCl(cod)]_2$, and $[IrCl(cod)]_2$ along with PMe_3 completely retarded the catalysis.

We examined the scope of aryl cyanides under the optimized conditions (Table 2). Benzonitriles having an electron-withdrawing substituent at the *para*-position reacted in good to excellent yields. A wide variety of functional groups including fluoro, keto, ester, and formyl[16] were tolerated to give the corresponding arylcyanation products (entries 1–4). In particular, 1,4-dicyanobenzene (**1f**) reacted at one of the C–CN bonds exclusively with an equimolar amount of 4-octyne (**2a**) (entry 5), whereas double arylcyanation product **4** was obtained with two molar equivalents of **2a** (Eq. 4). The reaction rate and yield were reduced with an electron-neutral or -donating substituent at the *para*-position (entries 6–9). A boryl group that is convertible to various organic groups by the Suzuki–Miyaura coupling survived the present conditions (entry 10). *Meta*- and *ortho*-substituents do not affect the reaction (entries 11–16). Heteroaryl cyanides were also examined as substrates (entries 17–22). Use of PMe_2Ph as a ligand instead of PMe_3 gave superior results with 2-cyanofuran and 2-cyanothiophene (entries 17 and 18); the reaction of 2-cyanothiophene took 90 h for completion, and the yield was modest presumably due to the presence of a sulfur atom. *N*-Boc-3-cyanoindole gave the corresponding 3-functionalized indole albeit in a modest yield (entry 19). Whereas 4- or 3-cyanopyridine participated in the reaction successfully (entries 20 and 21), the addition of 2-cyanopyridine was sluggish and gave an *E*-isomer as a minor product (entry 22). The isomer would be derived from the initially formed *Z*-adduct as the ratio varied depending on the reaction period (*Z*:*E*=78:22 at 22 h). Although the course of the isomerization is yet to be clarified, chelation-assisted formation of a nickelacycle such as **5** or, alternatively, conjugate addition of a nucleophile like PMe_2Ph to the *Z*-isomer might be operative to induce the partial isomerization to the *E*-isomer, which would be thermodynamically more favorable (Scheme 3).



(3)



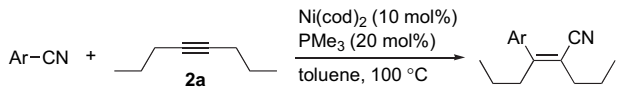
(4)

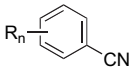
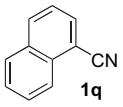
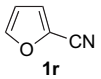
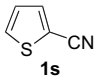
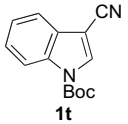
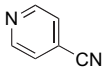
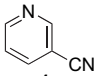
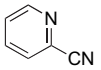
Table 1. Nickel-catalyzed arylcyanation of 4-octyne using 4-(trifluoromethyl)benzonitrile[a]

Entry	Nickel complex	Ligand	Solvent	Conv. of **1a** (%)[b]	Yield of **3a** (%)[b]
1	$Ni(cod)_2$	PMe_3	Toluene	91	84 (80)[c]
2[d]	$(Me_3P)_2NiCl_2$	—	Toluene	93	80
3	$Ni(cod)_2$	PMe_2Ph	Toluene	94	76
4	$Ni(cod)_2$	$PMePh_2$	Toluene	87	44
5	$Ni(cod)_2$	PPh_3	Toluene	54	31
6	$Ni(cod)_2$	$P(n\text{-}Bu)_3$	Toluene	50	30
7	$Ni(cod)_2$	PCy_3	Toluene	69	35
8	$Ni(cod)_2$	$P(t\text{-}Bu)_3$	Toluene	39	13
9	$Ni(cod)_2$	$Me_2P(CH_2)_2PMe_2$	Toluene	24	<5
10	$Ni(cod)_2$	2,2-Bipyridyl	Toluene	14	<5
11	$Ni(cod)_2$	PMe_3	1,4-Dioxane	75	60
12	$Ni(cod)_2$	PMe_3	DMF	58	47

[a] Reactions were carried out using **1a** (171 mg, 1.0 mmol), 4-octyne (110 mg, 1.0 mmol), $Ni(cod)_2$ (28 mg, 0.10 mmol), and a ligand (0.20 mmol) in a solvent (2.5 mL) at 100 °C for 24 h.
[b] Estimated by ^{19}F NMR using 4-F_3C-C_6H_4-I as an internal standard.
[c] Isolated yield.
[d] A catalyst was prepared from $(Me_3P)_2NiCl_2$ (28 mg, 0.10 mmol) and DIBAL-H (1.5 M solution in toluene, 0.20 mmol).

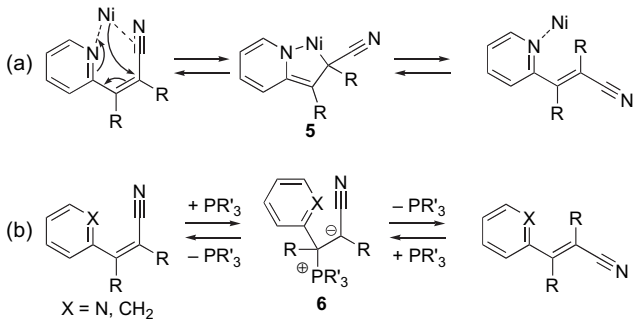
Table 2. Nickel-catalyzed arylcyanation of 4-octyne[a]



Entry	Ar–CN		Time (h)	Yield (%)[b]
1		R= 4-F (**1b**)	30	81 (**3b**)
2		4-C(O)Me (**1c**)	30	73 (**3c**)
3		4-CO_2Me (**1d**)	24	96 (**3d**)
4		4-CHO (**1e**)	25	67 (**3e**)
5		4-CN (**1f**)	19	67 (**3f**)
6		4-Ph (**1g**)	45	78 (**3g**)
7		H (**1h**)	45	64 (**3h**)
8		4-Me (**1i**)	40	70 (**3i**)
9		4-MeO (**1j**)	111	54 (**3j**)
10		4-B(pin) (**1k**)	30	61 (**3k**)
11		3-MeO (**1l**)	38	70 (**3l**)
12		3,5-$(MeO)_2$ (**1m**)	92	76 (**3m**)
13		3,4,5-$(MeO)_3$ (**1n**)	47	67 (**3n**)
14		2-CF_3 (**1o**)	159	76 (**3o**)
15		5-F-2-Me (**1p**)	26	62 (**3p**)
16	 **1q**		48	61 (**3q**)
17[c]	 **1r**		46	75 (**3r**)
18[c]	 **1s**		90	44 (**3s**)
19	 **1t**		45	40 (**3t**)
20	 **1u**		24	85 (**3u**)
21	 **1v**		15	86 (**3v**)
22[c]	 **1w**		44	36 (**3w**)[d]

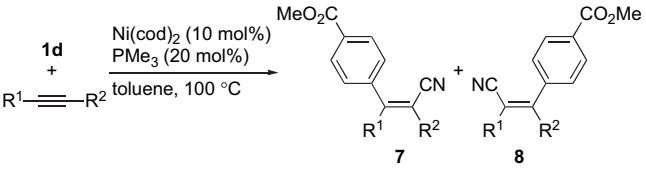
[a] Reactions were carried out using an aryl cyanide (1.0 mmol), 4-octyne (110 mg, 1.0 mmol), $Ni(cod)_2$ (28 mg, 0.10 mmol), and PMe_3 (15.2 mg, 0.20 mmol) in toluene (2.5 mL) at 100 °C for 24 h.
[b] Isolated yield based on an aryl cyanide.
[c] PMe_2Ph (0.20 mmol) was used as a ligand.
[d] *Z*:*E*=68:32.

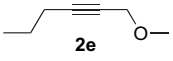
We next examined the scope of alkynes (Table 3). The reaction of methyl 4-cyanobenzoate with 2-butyne (**2b**) proceeded similarly to give the corresponding adduct **7b** in 70% yield (entry 1); an unsymmetrical alkyne, 4-methyl-2-pentyne (**2c**), gave a mixture of regioisomers **7c** and **8c** (entry 2), whereas 4,4-dimethyl-2-pentyne (**2d**) gave **7d** as the sole product (entry 3). The regio- and stereochemistry of **7d** was unambiguously confirmed by X-ray crystallographic analysis (Fig. 1).[17] Thus, an isomer having a cyano group at the carbon bearing a larger substituent was



Scheme 3. Plausible mechanism of *E*–*Z* isomerization of arylcyanation products.

Table 3. Nickel-catalyzed arylcyanation of alkynes using methyl 4-cyanobenzoate (**1d**)[a]



Entry	R^1—≡—R^2	Time (h)	Yield (%)[b]	**7**:**8**[c]
1	Me—≡—Me **2b**	20	70 (**7b**)	—
2	Me—≡—*i*-Pr **2c**	26	84 (**7c**, **8c**)	62:38
3	Me—≡—*t*-Bu **2d**	86	59 (**7d**)	>99:1
4	 **2e**	67	59 (**7e**, **8e**)	37:63
5	Me—≡—$SiMe_3$ **2f**	49	82 (**7f**, **8f**)	85[d]:15

[a] Reactions were carried out using methyl 4-cyanobenzoate (**1d**, 161 mg, 1.0 mmol), an alkyne (1.0 mmol), $Ni(cod)_2$ (28 mg, 0.10 mmol), and PMe_3 (15.2 mg, 0.20 mmol) in toluene (2.5 mL) at 100 °C.
[b] Isolated yield.
[c] Determined by GC.
[d] *Z*:*E*=59:41.

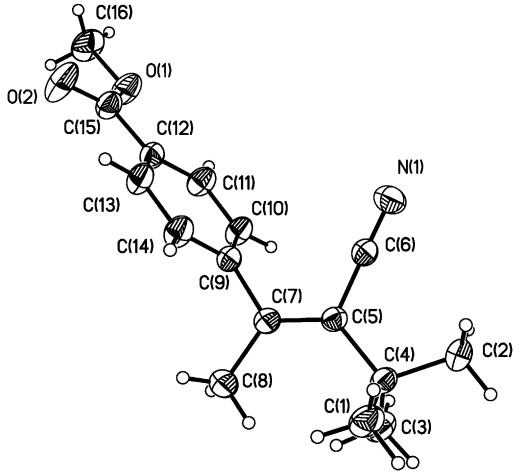
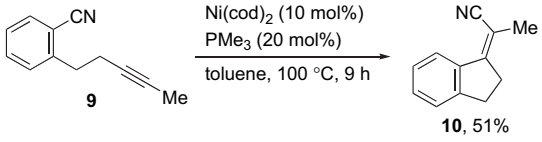


Figure 1. ORTEP drawing for **7d**.

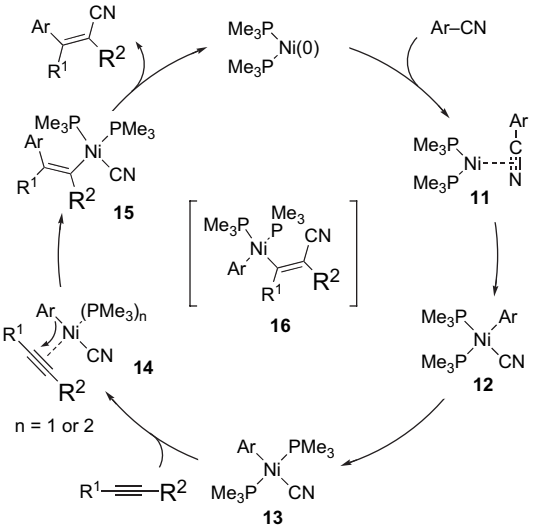
exclusively formed. A 37:63 mixture of two regioisomers, **7e** and **8e**, was obtained with 2-hexynyl methyl ether (**2e**), suggesting that an oxygen atom has no significant influence on the regiochemistry (entry 4). Trimethyl(1-propynyl)silane (**2f**) also participated in the reaction with the same regiochemistry but gave a mixture of stereoisomers of **7f**. Predominant formation of *cis*-adduct (*E*)-**7f** at the beginning of the reaction (*Z*:*E*=15:85 at 1 h) may suggest that an isomerization process is operative that was observed with 2-cyanopyridine (vide supra). Particularly, the silyl group of **7f** can stabilize an anion generated at its β-position in an intermediate like **6** (Scheme 3) during the possible phosphine-mediated isomerization process. Terminal alkynes, such as 1-octyne and phenylacetylene, failed to participate in the reaction due presumably to rapid oligomerization and/or trimerization of alkynes.

Intramolecular arylcyanation was next examined with **9**, which was prepared from *o*-tolunitrile (Eq. 5).[18] As expected, cyclization in a 5-*exo*-*dig* fashion took place to give **10** in 51% yield, whose structure was determined by X-ray crystallographic analysis (Fig. 2).[17]



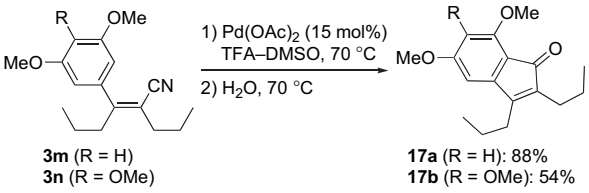
(5)

A plausible mechanism of the arylcyanation is provided in Scheme 4. The catalysis would be initiated by the oxidative addition of a C–CN bond of an aryl cyanide to nickel(0) to give *trans*-nickel(II) complex **13** via π-coordinating intermediate **11** and *cis*-oxidative adduct **12**.[7j] The nickel center of **13** would be coordinated by an alkyne substrate in the direction avoiding the steric repulsion between bulkier R^2 and aryl groups on the nickel to give four- or five-coordinated nickel(II) intermediate **14**. The aryl group would then migrate to the less hindered alkyne-carbon to give alkenylnickel **15** (arylnickelation), which reductively eliminates an arylcyanation product and regenerates the nickel(0). Although insertion of an alkyne into the Ni–CN bond (cyanonickelation) forming **16** cannot be ruled out, this cyanonickelation pathway has no precedents compared to the arylnickelation pathway, which frequently constitutes an elemental step of nickel catalysis.[19]



Scheme 4. Plausible mechanism of the arylcyanation of alkynes.

Arylcyanation products readily undergo intramolecular cyclization reaction to give 2-indenones by utilizing Larock's protocol (Eq. 6).[20] It is worth noting that metal-catalyzed C–C and C–H functionalization processes are demonstrated sequentially to synthesize substituted 2-indenones in a highly atom-economical manner.[21]



(6)

In conclusion, we have demonstrated that a simple catalyst derived from $Ni(cod)_2$ and PMe_3 accomplishes the arylcyanation reaction of alkynes for the first time. The reaction provides us with a ready access to various β-arylalkenenitriles having a diverse range of functional groups, which would be difficult to prepare otherwise. The arylcyanation products are shown to be versatile precursors for functionalized 2-indenones, and would also have broad synthetic applications to functional molecules by virtue of the rich chemistry of a cyano group. The chemistry shown herein is considered to open a door to a new class of transformations of organonitriles to make C–C bonds with perfect atom economy, which are currently under investigation.

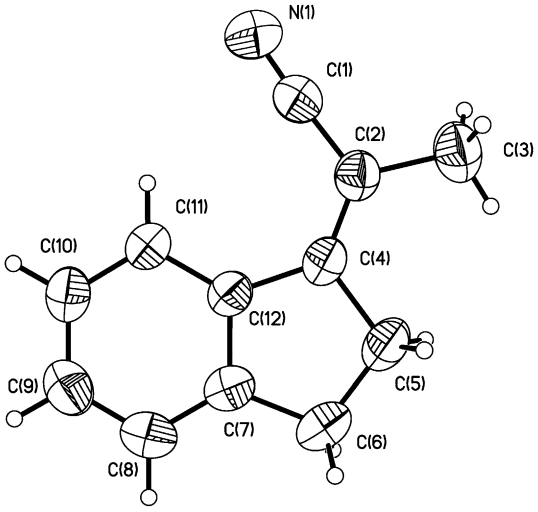


Figure 2. ORTEP drawing for **10**.

3. Experimental

3.1. General

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere or in a dry box under a nitrogen

atmosphere. Flash column chromatography was performed using Merck silica gel 60 (230–400 mesh). 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 UNITY-INOVA 500 (^{1}H NMR, 500 MHz; ^{13}C NMR, 126 MHz) spectrometer, Varian Mercury 400 (^{1}H NMR, 400 MHz; ^{13}C NMR, 101 MHz), JEOL EX-270 (^{13}C, 67.8 MHz), or Varian Mercury 200 (^{1}H, 200 MHz; ^{19}F, 188 MHz; ^{13}C, 50.3 MHz) 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, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, quint=quintet, sext=sextet, m=multiplet, br=broad), coupling constants (hertz), and integration. GC analysis was performed on a Shimadzu GC 14B equipped with an OV-1701 column (25 m×0.25 mm, pressure = 570 kPa, detector = FID, 290 °C) with helium gas as carrier. Preparative recycling gel permeation chromatography (GPC) and preparative recycling silica gel chromatography were performed with a JAI LC-908 chromatograph equipped with JAIGEL-1H and -2H (chloroform as an eluent) and JAIGEL-SIL or Nacalai tesque 5SL-II (hexane–ethyl acetate as an eluent). High-resolution mass spectra were obtained with a JEOL JMS-700 (EI) or JEOL JMS-HX110A (FAB+) spectrometer. Unless otherwise noted, reagents were commercially available and were used without purification. Solvents were distilled from a suitable drying reagent as follows: sodium/benzophenone ketyl for toluene and 1,4-dioxane; calcium hydride for DMF. Anhydrous DMSO was purchased from Aldrich and used without further purification. 2-Hexynyl methyl ether was prepared by the reported procedure[22] using methyl propargyl ether and 1-iodopropane.

3.2. Arylcyanation of alkynes: a general procedure

A solution of $Ni(cod)_2$ (28 mg, 0.10 mmol) and PMe_3 (15.2 mg, 0.20 mmol) in toluene (2.5 mL) was added to a nitrile (1.0 mmol). To this was added an alkyne (1.0 mmol), and the resulting mixture was stirred at 100 °C. The mixture was filtered through a silica gel pad, and the solvent was concentrated in vacuo. The residue was purified by flash chromatography on silica gel. Unreacted nitrile and/or regioisomer(s) were further separated by preparative GPC and/or recycling silica gel chromatography.

3.2.1. (*Z*)-3-[4-(Trifluoromethyl)phenyl]-2-propyl-2-hexenenitrile (3a). A colorless oil, R_f 0.12 (hexane–ethyl acetate = 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, J=8.1, 0.7 Hz, 2H), 7.42 (dd, J=8.1, 0.7 Hz, 2H), 2.52 (t, J=7.8 Hz, 2H), 2.38 (t, J=7.8 Hz, 2H), 1.69 (tq, J=7.8, 7.6 Hz, 2H), 1.31 (tq, J=7.8, 7.6 Hz, 2H), 1.03 (t, J=7.6 Hz, 3H), 0.88 (t, J=7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 143.7, 130.5 (q, J=32.6 Hz), 128.2, 125.5 (q, J=3.8 Hz), 123.9 (q, J=272.1 Hz), 119.0, 113.1, 35.5, 32.4, 21.7, 20.9, 13.7, 13.5; IR (neat): 2964, 2934, 2874, 2212, 1614, 1464, 1435, 1406, 1381, 1325, 1167, 1128, 1069, 1018, 847 cm^{-1}; Anal. Calcd for $C_{16}H_{18}F_3N$: C, 68.31; H, 6.45. Found: C, 68.57; H, 6.52.

3.2.2. (*Z*)-3-(4-Fluorophenyl)-2-propyl-2-hexenenitrile (3b). A colorless oil, R_f 0.43 (hexane–ethyl acetate = 10:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.34–7.24 (m, 2H), 7.14–7.02 (m, 2H), 2.48 (t, J=7.6 Hz, 2H), 2.35 (t, J=7.6 Hz, 2H), 1.67 (tq, J=7.6, 7.3 Hz, 2H), 1.29 (tq, J=7.6, 7.3 Hz, 2H), 1.02 (t, J=7.3 Hz, 3H), 0.87 (t, J=7.3 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 162.5 (d, J=246.6 Hz), 157.5, 135.9 (d, J=3.3 Hz), 129.5 (d, J=8.9 Hz), 119.3, 115.4 (d, J=22.3 Hz), 112.1, 35.7, 32.5, 21.8, 21.1, 13.8, 13.6; IR (neat): 2964, 2934, 2874, 2210, 1603, 1508, 1464, 1232, 1159, 1094, 840 cm^{-1}; Anal. Calcd for $C_{15}H_{18}FN$: C, 77.89; H, 7.84. Found: C, 77.95; H, 7.84.

3.2.3. (*Z*)-3-(4-Acetylphenyl)-2-propyl-2-hexenenitrile (3c). A colorless oil, R_f 0.51 (hexane–ethyl acetate = 2:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.99 (d, J=8.6 Hz, 2H), 7.41 (d, J=8.6 Hz, 2H), 2.62 (s, 3H), 2.54 (t, J=7.6 Hz, 2H), 2.39 (t, J=7.6 Hz, 2H), 1.69 (tq, J=7.6, 7.3 Hz, 2H), 1.31 (tq, J=7.6, 7.3 Hz, 2H), 1.03 (t, J=7.3 Hz, 3H), 0.86 (t, J=7.3 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 197.1, 157.5, 144.7, 136.8, 128.4, 128.0, 119.0, 112.7, 35.5, 32.5, 26.7, 21.8, 21.1, 13.9, 13.6; IR (neat): 2963, 2934, 2874, 2210, 1684, 1605, 1558, 1456, 1402, 1360, 1265, 959, 845 cm^{-1}; Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29. Found: C, 80.23; H, 8.35.

3.2.4. (*Z*)-3-[4-(Methoxycarbonyl)phenyl]-2-propyl-2-hexenenitrile (3d). A colorless oil, R_f 0.62 (hexane–ethyl acetate = 2:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.06 (d, J=8.4 Hz, 2H), 7.37 (d, J=8.4 Hz, 2H), 3.92 (s, 3H), 2.52 (t, J=7.6 Hz, 2H), 2.37 (t, J=7.5 Hz, 2H), 1.68 (tq, J=7.5, 7.3 Hz, 2H), 1.30 (tq, J=7.6, 7.3 Hz, 2H), 1.02 (t, J=7.3 Hz, 3H), 0.87 (t, J=7.3 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 166.4, 157.5, 144.6, 130.1, 129.7, 127.8, 119.0, 112.7, 52.2, 35.6, 32.5, 21.8, 21.1, 13.9, 13.6; IR (neat): 2963, 2934, 2874, 2210, 1726, 1607, 1435, 1404, 1279, 1180, 1115, 1020, 966, 862, 770, 712 cm^{-1}; Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80. Found: C, 75.22; H, 7.88.

3.2.5. (*Z*)-3-(4-Formylphenyl)-2-propyl-2-hexenenitrile (3e). A colorless oil, R_f 0.18 (hexane–ethyl acetate = 9:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 10.0 (s, 1H), 7.92 (d, J=8.1 Hz, 2H), 7.47 (d, J=8.1 Hz, 2H), 2.54 (t, J=7.7 Hz, 2H), 2.39 (t, J=7.7 Hz, 2H), 1.69 (tq, J=7.7, 7.3 Hz, 2H), 1.31 (tq, J=7.7, 7.3 Hz, 2H), 1.03 (t, J=7.3 Hz, 3H), 0.89 (t, J=7.3 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 191.5, 157.3, 146.2, 136.1, 129.8, 128.5, 118.9, 113.0, 35.4, 32.3, 21.6, 20.9, 13.7, 13.4; IR (neat): 2964, 2934, 2874, 2212, 1705, 1605, 1464, 1385, 1306, 1209, 1171, 1103, 914, 841, 735 cm^{-1}; Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.94. Found: C, 79.63; H, 8.05.

3.2.6. (*Z*)-3-(4-Cyanophenyl)-2-propyl-2-hexenenitrile (3f). A colorless oil, R_f 0.15 (hexane–ethyl acetate = 10:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.69 (d, J=8.2 Hz, 2H), 7.41 (d, J=8.2 Hz, 2H), 2.51 (t, J=7.7 Hz, 2H), 2.37 (t, J=7.6 Hz, 2H), 1.67 (tq, J=7.6, 7.4 Hz, 2H), 1.29 (tq, J=7.7, 7.4 Hz, 2H), 1.02 (t, J=7.4 Hz, 3H), 0.88 (t, J=7.4 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 156.5, 144.6, 132.2, 128.5, 118.6, 118.3, 113.5, 112.3, 35.4, 32.4, 21.7, 21.0, 13.8, 13.6; IR (neat): 2963, 2934, 2874, 2230, 2212, 1605, 1502, 1464, 1381, 1273, 1103, 1020, 847, 789, 741,

557 cm^{-1}; Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61. Found: C, 80.76; H, 7.64.

3.2.7. (*Z*)-3-(*p*-Biphenyl)-2-propyl-2-hexenenitrile (3g). A colorless oil, R_f 0.22 (hexane–ethyl acetate = 20:1). ^1H NMR (200 MHz, $CDCl_3$) δ 7.68–7.58 (m, 5H), 7.52–7.32 (m, 4H), 2.56 (t, J=7.6 Hz, 2H), 2.40 (t, J=7.6 Hz, 2H), 1.71 (tq, J=7.6, 7.5 Hz, 2H), 1.37 (tq, J=7.6, 7.4 Hz, 2H), 1.05 (t, J=7.5 Hz, 3H), 0.91 (t, J=7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 141.4, 140.4, 138.9, 128.8, 128.2, 127.5, 127.08, 127.07, 119.7, 111.6, 35.6, 32.5, 21.8, 21.1, 13.8, 13.5; IR (neat): 3030, 2963, 2932, 2872, 2210, 1609, 1580, 1487, 1464, 1431, 1402, 1381, 1105, 1078, 1007, 843, 766, 739, 696 cm^{-1}; Anal. Calcd for $C_{21}H_{23}N$: C, 87.15; H, 8.01. Found: C, 87.32; H, 8.01.

3.2.8. (*Z*)-3-Phenyl-2-propyl-2-hexenenitrile (3h). A colorless oil, R_f 0.43 (hexane–ethyl acetate = 10:1). ^1H NMR (200 MHz, $CDCl_3$) δ 7.45–7.26 (m, 5H), 2.51 (t, J= 7.6 Hz, 2H), 2.36 (t, J=7.6 Hz, 2H), 1.64 (tq, J=7.6, 7.3 Hz, 2H), 1.32 (tq, J=7.6, 7.3 Hz, 2H), 1.02 (t, J=7.3 Hz, 3H), 0.88 (t, J=7.3 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 158.6, 140.0, 128.4, 128.3, 127.6, 119.5, 111.6, 35.8, 32.5, 21.8, 21.1, 13.9, 13.6; IR (neat): 2963, 2932, 2872, 2210, 1443, 758, 700 cm^{-1}; Anal. Calcd for $C_{15}H_{19}N$: C, 84.46; H, 8.98. Found: C, 84.32; H, 8.98.

3.2.9. (*Z*)-3-(4-Methylphenyl)-2-propyl-2-hexenenitrile (3i). A colorless oil, R_f 0.18 (hexane–ethyl acetate = 20:1). ^1H NMR (200 MHz, $CDCl_3$) δ 7.20 (s, 4H), 2.50 (t, J=7.6 Hz, 2H), 2.37 (s, 3H), 2.35 (t, J=7.6 Hz, 2H), 1.67 (tq, J=7.6, 7.4 Hz, 2H), 1.31 (tq, J=7.6, 7.4 Hz, 2H), 1.02 (t, J=7.4 Hz, 3H), 0.87 (t, J=7.4 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 158.6, 138.3, 137.0, 129.0, 127.5, 119.7, 111.1, 35.7, 32.5, 21.8, 21.3, 21.2, 13.9, 13.6; IR (neat): 2963, 2932, 2872, 2208, 1508, 1456, 822, 548 cm^{-1}; Anal. Calcd for $C_{16}H_{21}N$: C, 84.53; H, 9.31. Found: C, 84.59; H, 9.27.

3.2.10. (*Z*)-3-(4-Methoxyphenyl)-2-propyl-2-hexenenitrile (3j). A colorless oil, R_f 0.20 (hexane–ethyl acetate = 10:1). ^1H NMR (200 MHz, $CDCl_3$) δ 7.27 (d, J=9.0 Hz, 2H), 6.91 (d, J=9.0 Hz, 2H), 3.82 (s, 3H), 2.49 (t, J=7.3 Hz, 2H), 2.34 (t, J=7.3 Hz, 2H), 1.66 (qt, J=7.4, 7.3 Hz, 2H), 1.31 (qt, J=7.4, 7.3 Hz, 2H), 1.01 (t, J= 7.4 Hz, 3H), 0.87 (t, J=7.4 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 159.6, 158.2, 132.2, 129.0, 120.0, 113.7, 110.8, 55.2, 35.6, 32.6, 21.9, 21.3, 13.9, 13.6; IR (neat): 2961, 2932, 2872, 2873, 2208, 1697, 1607, 1574, 1510, 1462, 1439, 1379, 1288, 1250, 1178, 1119, 1103, 1034, 835, 787, 727, 696, 544 cm^{-1}; Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70. Found: C, 79.13; H, 8.94.

3.2.11. (*Z*)-3-[4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-2-propyl-2-hexenenitrile (3k). A colorless solid (mp 101.7–102.7 °C), R_f 0.44 (hexane–ethyl acetate = 5:1). ^1H NMR (200 MHz, $CDCl_3$) δ 7.83 (d, J=8.2 Hz, 2H), 7.30 (d, J=8.2 Hz, 2H), 2.51 (t, J=7.9 Hz, 2H), 2.36 (t, J=7.9 Hz, 2H), 1.67 (tq, J=7.9, 7.3 Hz, 2H), 1.34 (tq, J=7.9, 7.3 Hz, 2H), 1.29 (s, 12H), 1.02 (t, J= 7.3 Hz, 3H), 0.86 (t, J=7.3 Hz, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 158.7, 142.9, 134.8, 127.0, 119.4, 111.8, 83.8, 35.5, 32.4, 24.8, 21.7, 21.0, 13.8, 13.5; IR (KBr): 2964, 2934, 2874, 2208, 1609, 1506, 1456, 1398, 1362, 1325, 1271, 1144, 1088, 1020, 962, 858, 658 cm^{-1}; Anal. Calcd for $C_{21}H_{30}BNO_2$: C, 74.34; H, 8.91. Found: C, 74.07; H, 8.83.

3.2.12. (*Z*)-3-(3-Methoxyphenyl)-2-propyl-2-hexenenitrile (3l). A colorless oil, R_f 0.30 (hexane–ethyl acetate = 10:1). ^1H NMR (200 MHz, $CDCl_3$) δ 7.31 (d, J= 8.4 Hz, 1H), 6.93–6.80 (m, 3H), 3.81 (s, 3H), 2.49 (t, J=7.6 Hz, 2H), 2.35 (t, J=7.6 Hz, 2H), 1.67 (qt, J=7.6, 7.5 Hz, 2H), 1.32 (qt, J=7.6, 7.4 Hz, 2H), 1.01 (t, J= 7.5 Hz, 3H), 0.87 (t, J=7.4 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 159.2, 158.3, 141.3, 129.3, 120.0, 119.3, 113.7, 113.4, 111.5, 55.2, 35.7, 32.5, 21.8, 21.1, 13.9, 13.5; IR (neat): 2963, 2934, 2872, 2208, 1578, 1487, 1464, 1429, 1317, 1286, 1246, 1217, 1163, 1045, 874, 781, 705 cm^{-1}; Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70. Found: C, 79.11; H, 8.70.

3.2.13. (*Z*)-3-(3,5-Dimethoxyphenyl)-2-propyl-2-hexenenitrile (3m). A colorless oil, R_f 0.15 (hexane–ethyl acetate = 10:1). ^1H NMR (200 MHz, $CDCl_3$) δ 6.43 (s, 3H), 3.80 (s, 6H), 2.45 (t, J=7.6 Hz, 2H), 2.34 (t, J=7.6 Hz, 2H), 1.66 (qt, J=7.6, 7.3 Hz, 2H), 1.33 (qt, J=7.6, 7.3 Hz, 2H), 1.01 (t, J=7.3 Hz, 3H), 0.88 (t, J=7.3 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 160.4, 158.4, 141.9, 119.3, 111.5, 105.9, 100.2, 55.4, 35.7, 32.5, 21.8, 21.1, 13.9, 13.6; IR (neat): 2963, 2934, 2872, 2839, 2208, 1591, 1456, 1421, 1350, 1265, 1205, 1155, 1063, 927, 847 cm^{-1}; Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48. Found: C, 74.99; H, 8.82.

3.2.14. (*Z*)-3-(3,4,5-Trimethoxyphenyl)-2-propyl-2-hexenenitrile (3n). A colorless oil, R_f 0.23 (hexane–ethyl acetate = 5:1). ^1H NMR (200 MHz, $CDCl_3$) δ 6.50 (s, 2H), 3.84 (s, 9H), 2.46 (t, J=7.6 Hz, 2H), 2.32 (t, J=7.6 Hz, 2H), 1.65 (tq, J=7.6, 7.3 Hz, 2H), 1.32 (tq, J=7.6, 7.3 Hz, 2H), 1.00 (t, J=7.3 Hz, 3H), 0.87 (t, J=7.3 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 158.3, 152.8, 138.1, 135.2, 119.4, 111.2, 105.1, 60.8, 56.2, 35.6, 32.6, 21.8, 21.2, 13.9, 13.6; IR (neat): 2936, 2872, 2839, 2251, 2206, 1582, 1504, 1454, 1433, 1410, 1381, 1348, 1269, 1238, 1184, 1128, 1009, 957, 914, 883, 843, 733, 648, 532 cm^{-1}; Anal. Calcd for $C_{18}H_{25}NO_3$: C, 71.26; H, 8.31. Found: C, 71.07; H, 8.04.

3.2.15. (*Z*)-3-[2-(Trifluoromethyl)phenyl]-2-propyl-2-hexenenitrile (3o). A colorless oil, R_f 0.20 (hexane–ethyl acetate = 10:1). ^1H NMR (200 MHz, $CDCl_3$) δ 7.72 (d, J=7.4 Hz, 1H), 7.62–7.43 (m, 2H), 7.17 (d, J=6.8 Hz, 1H), 2.74–2.56 (m, 1H), 2.52–2.16 (m, 3H), 1.68 (tq, J=7.6, 7.2 Hz, 2H), 1.51–1.16 (m, 2H), 1.03 (t, J=7.2 Hz, 3H), 0.93 (t, J=7.2 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 156.3, 138.8, 131.7, 130.0, 128.3, 127.4 (q, J=31.3 Hz), 126.8 (q, J=5.2 Hz), 123.9 (q, J=272.2 Hz), 118.2, 114.8 (q, J=2.2 Hz), 36.0 (q, J=2.2 Hz), 31.8, 21.5, 20.9, 14.2, 13.5; IR (neat): 2966, 2936, 2876, 2216, 1603, 1576, 1448, 1381, 1315, 1263, 1171, 1126, 1065, 1034, 770, 650 cm^{-1}; Anal. Calcd for $C_{16}H_{18}F_3N$: C, 68.31; H, 6.45. Found: C, 68.51; H, 6.37.

3.2.16. (*Z*)-3-(5-Fluoro-2-methylphenyl)-2-propyl-2-hexenenitrile (3p). A colorless oil, R_f 0.27 (hexane–ethyl

acetate = 20:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.18 (dd, J=8.4, 5.8 Hz, 1H), 6.92 (ddd, J=8.7, 8.4, 2.7 Hz, 1H), 6.75 (dd, J=8.7, 2.7 Hz, 1H), 2.58–2.26 (m, 4H), 2.22 (s, 3H), 1.69 (tq, J=7.4, 7.3 Hz, 2H), 1.52–1.22 (m, 2H), 1.03 (t, J=7.3 Hz, 3H), 0.92 (t, J=7.3 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 160.5 (d, J=244.4 Hz), 157.3, 141.3 (d, J=7.8 Hz), 131.8 (d, J=7.8 Hz), 130.2 (d, J=3.3 Hz), 118.4, 114.8 (d, J=21.2 Hz), 114.6 (d, J=22.3 Hz), 113.7, 35.8, 31.7, 21.7, 20.7, 18.6, 14.2, 13.5; IR (neat): 2964, 2934, 2874, 2212, 1609, 1585, 1493, 1464, 1470, 1381, 1263, 1238, 1211, 1161, 870, 814, 754 cm^{-1}; Anal. Calcd for $C_{16}H_{20}FN$: C, 78.33; H, 8.22. Found: C, 78.19; H, 8.28.

3.2.17. (*Z*)-3-(1-Naphthyl)-2-propyl-2-hexenenitrile (3q). A colorless oil, R_f 0.23 (hexane–ethyl acetate = 20:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.92–7.81 (m, 2H), 7.73–7.63 (m, 1H), 7.56–7.42 (m, 3H), 7.24 (s, 1H), 2.78–2.36 (m, 4H), 1.76 (tq, J=7.4, 7.3 Hz, 2H), 1.48–1.22 (m, 2H), 1.09 (t, J=7.3 Hz, 3H), 0.88 (t, J=7.3 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 157.9, 137.9, 133.6, 130.3, 128.6, 126.3, 125.9, 125.7, 125.1, 124.5, 118.7, 114.5, 36.5, 32.0, 21.9, 21.4, 14.1, 13.7; IR (neat): 2963, 2932, 2872, 2212, 1506, 1456, 804, 779 cm^{-1}; Anal. Calcd for $C_{19}H_{21}N$: C, 86.65; H, 8.04. Found: C, 86.88; H, 8.12.

3.2.18. (*Z*)-3-(2-Furyl)-2-propyl-2-hexenenitrile (3r). A colorless oil, R_f 0.30 (hexane–ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J=1.8 Hz, 1H), 7.00 (d, J=3.7 Hz, 1H), 6.45 (dd J=3.7, 1.8 Hz, 1H), 2.51 (t, J=8.0 Hz, 2H), 2.33 (t, J=7.6 Hz, 2H), 1.47 (tq, J=7.6, 7.5 Hz, 2H), 1.47 (sext, J=7.6 Hz, 2H), 0.98 (t, J=7.5 Hz, 3H), 0.95 (t, J=7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 144.4, 142.9, 120.2, 112.0, 111.7, 105.9, 32.7, 31.8, 22.5, 21.7, 14.0, 13.5; IR (neat): 2964, 2934, 2874, 2205, 1599, 1464, 1381, 1157, 1086, 1026, 934, 903, 887, 818, 745 cm^{-1}; Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43. Found: C, 77.00; H, 8.43.

3.2.19. (*Z*)-3-(2-Thienyl)-2-propyl-2-hexenenitrile (3s). A colorless oil, R_f 0.38 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J=3.7, 1.1 Hz, 1H), 7.38 (dd, J=5.1, 1.1 Hz, 1H), 7.06 (dd, J=5.1, 3.7 Hz, 1H), 2.53 (t, J=7.8 Hz, 2H), 2.36 (t, J=7.8 Hz, 2H), 1.68 (tq, J=7.8, 7.3 Hz, 2H), 1.46 (tq, J=7.8, 7.3 Hz, 2H), 1.01 (t, J=7.3 Hz, 3H), 0.94 (t, J=7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 141.5, 128.2, 127.4, 126.9, 120.1, 109.5, 36.6, 33.1, 22.0, 21.7, 13.9, 13.6; IR (neat): 2963, 2932, 2872, 2205, 1589, 1462, 1425, 1379, 1232, 1111, 1088, 853, 837, 706 cm^{-1}; Anal. Calcd for $C_{13}H_{17}NS$: C, 71.18; H, 7.81. Found: C, 71.45; H, 7.89.

3.2.20. (*Z*)-3-(*N*-*tert*-Butoxycarbonyl-3-indolyl)-2-propyl-2-hexenenitrile (3t). A colorless oil, R_f 0.27 (hexane–ethyl acetate=10:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.17 (br d, J=8.1 Hz, 1H), 7.64 (s, 1H), 7.50–7.22 (m, 3H), 2.58 (t, J=7.6 Hz, 2H), 2.43 (t, J=7.6 Hz, 2H), 1.73 (tq, J=7.6, 7.3 Hz, 2H), 1.69 (s, 9H), 1.38 (tq, J=7.6, 7.3 Hz, 2H), 1.06 (t, J=7.3 Hz, 3H), 0.89 (t, J=7.3 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 150.6, 149.3, 135.1, 128.6, 124.6, 124.4, 122.7, 120.1, 119.7, 119.3, 115.4, 113.3, 84.2, 35.5, 32.4, 28.2, 21.9, 21.5, 14.0, 13.7; IR (neat): 2963, 2934, 2872, 2210, 1738, 1607, 1556, 1454, 1373, 1310, 1286, 1250, 1155, 1111, 1082, 1055, 1020, 854, 837, 748 cm^{-1}; Anal. Calcd for $C_{22}H_{28}N_2O_2$: C, 74.97; H, 8.01. Found: C, 75.21; H, 7.91.

3.2.21. (*Z*)-3-(4-Pyridyl)-2-propyl-2-hexenenitrile (3u). A colorless oil, R_f 0.16 (hexane–ethyl acetate = 2:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.64 (br d, J=3.7 Hz, 2H), 7.20 (br d, J=5.7 Hz, 2H), 2.49 (t, J=7.7 Hz, 2H), 2.36 (t, J=7.6 Hz, 2H), 1.66 (tq, J=7.6, 7.3 Hz, 2H), 1.29 (tq, J=7.7, 7.3 Hz, 2H), 1.00 (t, J=7.3 Hz, 3H), 0.87 (t, J=7.3 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 155.6, 149.9, 147.7, 122.4, 118.4, 113.4, 35.1, 32.4, 21.7, 21.0, 13.8, 13.5; IR (neat): 2963, 2934, 2874, 2212, 1593, 1543, 1456, 1410, 991, 831 cm^{-1}; Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47. Found: C, 78.44; H, 8.56.

3.2.22. (*Z*)-3-(3-Pyridyl)-2-propyl-2-hexenenitrile (3v). A colorless oil, R_f 0.16 (hexane–ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60–8.54 (br m, 2H), 7.65–7.63 (m, 1H), 7.35–7.28 (m, 1H), 2.50 (t, J=7.7 Hz, 2H), 2.36 (t, J=7.7 Hz, 2H), 1.64 (tq, J=7.7, 7.4 Hz, 2H), 1.29 (tq, J=7.7, 7.4 Hz, 2H), 1.00 (t, J=7.4 Hz, 3H), 0.87 (t, J=7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 149.6, 148.3, 135.8, 135.4, 123.2, 118.8, 113.7, 35.4, 32.3, 21.6, 20.8, 13.7, 13.4; IR (neat): 3030, 2963, 2934, 2874, 2210, 1614, 1585, 1566, 1464, 1410, 1381, 1340, 1196, 1105, 1024, 816, 785, 741, 718, 625 cm^{-1}; Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47. Found: C, 78.36; H, 8.42.

3.2.23. (*Z*)-3-(2-Pyridyl)-2-propyl-2-hexenenitrile [(*Z*)-3w]. A colorless oil, R_f 0.40 (hexane–ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66–8.64 (m, 1H), 7.73 (td, J=7.7, 1.8 Hz, 1H), 7.50 (dt, J=7.7, 1.1 Hz, 1H), 7.27 (ddd, J=7.7, 4.8, 1.1 Hz, 1H), 2.69 (t, J=7.8 Hz, 2H), 2.40 (t, J=7.8 Hz, 2H), 1.69 (tq, J=7.8, 7.3 Hz, 2H), 1.31 (tq, J=7.8, 7.3 Hz, 2H), 1.02 (t, J=7.3 Hz, 3H), 0.88 (t, J=7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 157.4, 149.4, 136.5, 123.8, 123.3, 119.2, 113.0, 34.0, 32.7, 21.6, 21.2, 13.9, 13.6; IR (neat): 2963, 2932, 2874, 2210, 1585, 1566, 1464, 1431, 1381, 1151, 1111, 1090, 991, 800, 772, 748 cm^{-1}; Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47. Found [as a mixture with (*E*)-**3w**]: C, 78.42; H, 8.37.

3.2.24. (*E*)-3-(2-Pyridyl)-2-propyl-2-hexenenitrile [(*E*)-3w]. A colorless oil, R_f 0.40 (hexane–ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (br d, J=4.0 Hz, 1H), 7.72 (td, J=7.7, 1.8 Hz, 1H), 7.25 (td, J=7.7, 1.0 Hz, 1H), 7.14 (d, 7.7 Hz, 1H), 2.82 (t, J=7.6 Hz, 2H), 2.11 (t, J=7.6 Hz, 2H), 1.59 (tq, J=7.6, 7.3 Hz, 2H), 1.35 (tq, J=7.6, 7.3 Hz, 2H), 0.92 (t, J=7.3 Hz, 3H), 0.84 (t, J=7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 156.7, 149.8, 136.2, 123.3, 122.8, 118.7, 113.6, 39.0, 32.5, 21.6, 21.1, 13.6, 13.4; IR (neat): 2963, 2932, 2874, 2210, 1583, 1566, 1464, 1429, 1379, 1242, 1047, 991, 750 cm^{-1}.

3.2.25. 3,3′-(*p*-Phenylene)bis[(*Z*)-2-propyl-2-hexenenitrile] (4). A colorless oil, R_f 0.25 (hexane–ethyl acetate = 10:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.34 (s, 4H), 2.52 (t, J=7.6 Hz, 4H), 2.37 (t, J=7.6 Hz, 4H), 1.68 (tq, J=7.6, 7.3 Hz, 4H), 1.33 (tq, J=7.6, 7.3 Hz, 4H), 1.02 (t, J=7.3 Hz, 6H), 0.88 (t, J=7.3 Hz, 6H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 158.0, 140.2, 127.8, 119.4, 111.8, 35.5, 32.5, 21.7, 21.1, 13.8, 13.4; IR (neat): 3017, 2932, 2872, 2208, 1611, 1506, 1464, 1433, 1402, 1379, 1217,

1101, 847, 756, 667 cm^{-1}; Anal. Calcd for $C_{24}H_{32}N_2$: C, 82.71; H, 9.25. Found: C, 82.61; H, 9.20.

3.2.26. (*Z*)-3-[4-(Methoxycarbonyl)phenyl]-2-methyl-2-butenenitrile (7b). A colorless solid (mp 91.8–92.4 °C), R_f 0.31 (hexane–ethyl acetate = 5:1). ^1H NMR (200 MHz, $CDCl_3$) δ 8.05 (d, J=8.2 Hz, 2H), 7.43 (d, J=8.2 Hz, 2H), 3.91 (s, 3H), 2.17 (d, J=1.1 Hz, 3H), 2.07 (d, J=0.9 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 166.3, 153.0, 145.2, 130.1, 129.7, 127.3, 119.7, 106.5, 52.2, 20.5, 17.7; IR (KBr): 3003, 2955, 2208, 1724, 1609, 1429, 1308, 1294, 1279, 1194, 1117, 860, 773, 708 cm^{-1}; Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09. Found: C, 72.49; H, 6.18.

3.2.27. (*Z*)-3-[4-(Methoxycarbonyl)phenyl]-2-isopropyl-2-butenenitrile (7c). A colorless oil, R_f 0.45 (hexane–ethyl acetate = 5:1). ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J=8.7 Hz, 2H), 7.41 (d, J=8.7 Hz, 2H), 3.92 (s, 3H), 2.97–2.89 (m, 1H), 2.20 (s, 3H), 1.22 (d, J=6.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 150.9, 145.8, 130.1, 129.7, 127.5, 119.5, 117.3, 52.2, 29.1, 21.1, 20.2; IR (neat): 2970, 2934, 2874, 2212, 1724, 1609, 1464, 1435, 1404, 1387, 1367, 1312, 1285, 1182, 1113, 1078, 1047, 1018, 1007, 964, 860, 833, 773, 710 cm^{-1}; Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04. Found (as a mixture with **8c**): C, 74.28; H, 7.12.

3.2.28. (*Z*)-3-[4-(Methoxycarbonyl)phenyl]-2,4-dimethyl-2-pentenenitrile (8c). A colorless oil, ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (br d, J=8.2 Hz, 2H), 7.19 (d, J=8.2 Hz, 2H), 3.91 (s, 3H), 3.13–3.05 (m, 1H), 2.06 (s, 3H), 0.98 (d, J=7.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 163.3, 142.7, 129.8, 129.5, 127.5, 119.3, 106.9, 52.1, 30.5, 20.4, 15.9.

3.2.29. (*Z*)-3-[4-(Methoxycarbonyl)phenyl]-2-*tert*-butyl-2-butenenitrile (7d). A colorless solid (mp 127.5–128.3 °C), R_f 0.64 (hexane–ethyl acetate = 2:1). ^1H NMR (200 MHz, $CDCl_3$) δ 8.03 (d, J=8.7 Hz, 2H), 7.32 (d, J=8.7 Hz, 2H), 3.88 (s, 3H), 2.27 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 166.2, 154.2, 148.0, 129.6, 127.1, 122.0, 118.3, 52.0, 34.1, 30.4, 22.7; IR (KBr): 2974, 2955, 2206, 1717, 1601, 1431, 1400, 1373, 1306, 1277, 1242, 1209, 1192, 1177, 1111, 1031, 1016, 961, 856, 827, 772, 708 cm^{-1}; Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44. Found: C, 74.67; H, 7.57.

3.2.30. (*E*)-3-[4-(Methoxycarbonyl)phenyl]-2-methoxymethyl-2-hexenenitrile (7e). A colorless oil, R_f 0.14 (hexane–ethyl acetate=5:1). ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J=8.5 Hz, 2H), 7.40 (d, J=8.5 Hz, 2H), 4.20 (s, 2H), 3.92 (s, 3H), 3.45 (s, 3H), 2.59 (t, J=7.7 Hz, 2H), 1.31 (tq, J=7.7, 7.4 Hz, 2H), 0.87 (t, J=7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 162.1, 143.6, 130.6, 129.8, 127.6, 118.3, 110.0, 68.8, 58.5, 52.2, 35.7, 21.1, 13.7; IR (neat): 2963, 2934, 2874, 2826, 2214, 1724, 1607, 1437, 1404, 1379, 1279, 1190, 1105, 1018, 959, 916, 862, 770, 714 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{19}NO_3$: M^+, 273.1365. Found: *m*/*z* 273.1352.

3.2.31. (*E*)-3-[4-(Methoxycarbonyl)phenyl]-4-methoxy-2-propyl-2-butenenitrile (8e). A colorless oil, R_f 0.14 (hexane–ethyl acetate = 5:1). ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J=8.7 Hz, 2H), 7.47 (d, J=8.7 Hz, 2H), 4.30 (s, 2H), 3.92 (s, 3H), 3.30 (s, 3H), 2.44 (t, J=7.6 Hz, 2H), 1.70 (tq, J=7.6, 7.3 Hz, 2H), 1.02 (t, J=7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 152.2, 142.9, 130.4, 129.7, 128.0, 118.4, 116.6, 70.7, 58.7, 52.2, 32.6, 21.7, 13.4; IR (neat): 2961, 2932, 2874, 2822, 2214, 1724, 1609, 1566, 1435, 1406, 1379, 1281, 1190, 1113, 1018, 962, 914, 862, 775, 729, 710 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{20}NO_3$: $[M+H]^+$, 274.1443. Found: *m*/*z* 274.1447.

3.2.32. (*E*)-3-[4-(Methoxycarbonyl)phenyl]-2-trimethylsilyl-2-butenenitrile [(*E*)-7f]. A colorless solid (mp 101.8–102.5 °C), R_f 0.14 (hexane–ethyl acetate = 10:1). ^1H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J=8.5 Hz, 2H), 7.45 (d, J=8.5 Hz, 2H), 3.91 (s, 3H), 2.31 (s, 3H), 0.38 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 166.2, 146.5, 130.3, 129.7, 126.7, 119.8, 112.0, 52.2, 24.4, −0.3; IR (KBr): 3009, 2953, 2903, 2197, 1720, 1611, 1583, 1492, 1400, 1371, 1310, 1277, 1254, 1188, 1177, 1115, 1016, 956, 853, 773, 762, 706, 660 cm^{-1}; Anal. Calcd for $C_{15}H_{19}NO_2Si$: C, 65.90; H, 7.00. Found: C, 66.06; H, 7.07.

3.2.33. (*Z*)-3-[4-(Methoxycarbonyl)phenyl]-2-trimethylsilyl-2-butenenitrile [(*Z*)-7f]. A colorless solid (mp 69.4–70.1 °C), R_f 0.20 (hexane–ethyl acetate = 10:1). ^1H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J=8.6 Hz, 2H), 7.52 (d, J=8.6 Hz, 2H), 3.94 (s, 3H), 2.48 (s, 3H), 0.04 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 166.2, 146.4, 130.3, 129.6, 126.8, 119.6, 113.4, 52.3, 28.1, −0.3; IR (KBr): 3015, 2961, 2901, 2197, 1715, 1611, 1576, 1562, 1435, 1402, 1371, 1279, 1248, 1182, 1119, 1103, 1018, 984, 966, 847, 777, 760, 710, 635 cm^{-1}; Anal. Calcd for $C_{15}H_{19}NO_2Si$: C, 65.90; H, 7.00. Found: C, 66.06; H, 7.09.

3.2.34. (*E*)-3-[4-(Methoxycarbonyl)phenyl]-3-trimethylsilyl-2-methylpropenenitrile (8f). A colorless solid (mp 137.5–137.9 °C), R_f 0.20 (hexane–ethyl acetate = 10:1). ^1H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J=8.5 Hz, 2H), 7.05 (d, J=8.5 Hz, 2H), 3.91 (s, 3H), 2.19 (s, 3H), 0.15 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 162.5, 147.6, 129.9, 128.9, 126.5, 119.8, 118.2, 52.1, 20.4, −0.5; IR (KBr): 2955, 2214, 1722, 1607, 1435, 1404, 1308, 1273, 1254, 1194, 1175, 1113, 1101, 1018, 914, 841, 822, 760, 710, 691 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{19}NO_2Si$: M^+, 273.1185. Found: *m*/*z* 273.1180.

3.3. Arylcyanation of 4-octyne with 1a using a catalyst prepared from $(Me_3P)_2NiCl_2$ and DIBAL-H

To a solution of $(Me_3P)_2NiCl_2$ (28 mg, 0.10 mmol) in toluene (2.4 mL) was added a 1.5 M solution of DIBAL-H in toluene (0.13 mL, 0.20 mmol) at 0 °C. After a few minutes, **1a** (171 mg, 1.0 mmol) and 4-octyne (110 mg, 1.0 mmol) were added at rt, and the resulting mixture was stirred at 100 °C for 24 h. The mixture was analyzed by ^{19}F NMR using 4-(trifluoromethyl)iodobenzene as an internal standard to estimate the yield of **3a** (80%).

3.4. Intramolecular arylcyanation

A solution of $Ni(cod)_2$ (28 mg, 0.10 mmol) and PMe_3 (15.2 mg, 0.20 mmol) in toluene (2.5 mL) was added to **9**

(167 mg, 1.0 mmol), and the resulting mixture was stirred at 100 °C for 9 h. The mixture was filtered through a silica gel pad and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give (*Z*)-2-indene-1-ylidenepropionitrile (**10**) (86 mg, 51%) as a colorless solid (mp 116.9–117.3 °C), R_f 0.28 (hexane–ethyl acetate = 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J=7.5 Hz, 1H), 7.30–7.20 (m, 3H), 2.97 (t, J=6.0 Hz, 2H), 2.79–2.73 (m, 2H), 2.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 149.3, 137.6, 130.4, 127.0, 125.4, 124.1, 120.4, 95.4, 31.1, 29.3, 18.5; IR (KBr): 2920, 2197, 1622, 1464, 1447, 1261, 1159, 762 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{11}N$: M^+, 169.0891. Found: *m/z* 169.0898.

3.5. Palladium-catalyzed intramolecular cyclization of 3m[20]

A solution of **3m** (27 mg, 0.10 mmol) and $Pd(OAc)_2$ (3.4 mg, 15 μmol) in trifluoroacetic acid (0.1 mL) and DMSO (2.5 mL) was stirred at 70 °C for 4 h before addition of H_2O (15 mL). Stirring was continued at the same temperature for 24 h, and then the mixture was extracted with Et_2O for three times. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give 5,7-dimethoxy-2,3-dipropyl-1-indenone (**17a**, 24 mg, 88%) as a yellow solid (mp 78.4–78.9 °C), R_f 0.25 (hexane–ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.29 (d, J=1.7 Hz, 1H), 6.14 (d, J=1.7 Hz, 1H), 3.91 (s, 3H), 3.85 (s, 3H), 2.44 (t, J=7.5 Hz, 2H), 2.20 (t, J=7.5 Hz, 2H), 1.60 (sext, J=7.5 Hz, 2H), 1.48 (sext, J=7.5 Hz, 2H), 1.00 (t, J=7.5 Hz, 3H), 0.91 (t, J=7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.2, 166.6, 157.7, 153.1, 150.2, 136.7, 108.9, 102.2, 95.5, 55.8, 55.7, 27.9, 24.9, 22.5, 21.9, 14.3, 14.1; IR (KBr): 2959, 1693, 1605, 1466, 1379, 1204, 1157 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{22}O_3$: M^+, 274.1569. Found: *m/z* 274.1579.

3.6. Palladium-catalyzed intramolecular cyclization of 3n[20]

A solution of **3n** (30 mg, 0.10 mmol) and $Pd(OAc)_2$ (3.4 mg, 15 μmol) in trifluoroacetic acid (0.1 mL) and DMSO (2.5 mL) was stirred at 70 °C for 20 h before addition of H_2O (15 mL). Stirring was continued at the same temperature for 2 h, and then the mixture was extracted with Et_2O for three times. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel followed by preparative recycling silica gel chromatography to give 5,6,7-trimethoxy-2,3-dipropyl-1-indenone (**17b**, 16 mg, 54%) as a yellow oil, R_f 0.28 (hexane–ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (s, 1H), 4.10 (s, 3H), 3.92 (s, 3H), 3.80 (s, 3H), 2.45 (t, J=7.5 Hz, 2H), 2.19 (t, J=7.5 Hz, 2H), 1.62 (sext, J=7.5 Hz, 2H), 1.47 (sext, J=7.5 Hz, 2H), 1.03 (t, J=7.5 Hz, 3H), 0.93 (t, J=7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.3, 157.4, 154.1, 152.2, 143.7, 141.1, 135.7, 113.4, 100.9, 62.4, 61.5, 56.7, 28.0, 25.4, 22.8, 22.1, 14.6, 14.4; IR (neat): 2961, 1697, 1597, 1470, 1404, 1369, 1244, 1132 cm^{-1}; Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 70.90; H, 7.86.

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