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Alkynylcyanation of alkynes and dienes catalyzed by nickel

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ABSTRACT

Alkynyl cyanides are found to add across alkynes and 1,2-dienes in the presence of a catalyst prepared in situ from Ni(cod)$_2$, xantphos, and BPh$_3$. A range of functionalized conjugated *cis*-enynes are obtained with high regioselectivity. The addition reaction across norbornadiene proceeds in the absence of BPh$_3$ to give *exo-cis* adduct exclusively. A stoichiometric reaction of an alkynyl cyanide, Ni(cod)$_2$, xantphos, and BPh$_3$ gives *trans*-(xantphos)Ni(CNBPh$_3$)(C≡CSiMe$_2$*t*-Bu), which is suggested to be a plausible reaction intermediate of the alkynylcyanation reaction.

1. Introduction

Transition metal-catalyzed direct insertion of unsaturated bonds into C–C σ-bonds has gained much attention as a method for efficient construction of carbon frameworks with high regio- and stereoselectivity as well as atom efficiency. Whereas ring expansion reactions of strained three-[1] and four-membered[2] compounds have served as this new synthetic strategy, we and others have demonstrated that nickel or palladium-catalyzed addition of nitriles across unsaturated bonds provides a new entry to this class of transformation, namely carbocyanation reactions,[3] that proceed through oxidative addition of C–CN bonds to nickel(0) or palladium(0).[4–6] Scope of nitriles for the carbocyanation covers aryl, allyl, alkenyl, and alkyl cyanides by virtue of Lewis acid cocatalysis,[3j,4q] that has been developed originally by DuPont in the adiponitrile process.[6] Alkynyl cyanides, readily available from terminal alkynes and cyano phenolate,[7] have also been demonstrated to undergo the oxidative addition to platinum(0) through the activation of C(sp)–CN bonds.[8] We therefore have anticipated that the carbocyanation reaction using alkynyl cyanides would be achieved by transition metal catalysts to allow direct installation of alkynyl and cyano groups in a single operation. Herein we report nickel/BPh$_3$-catalyzed regio- and stereoselective alkynylcyanation of alkynes and 1,2-dienes to afford highly functionalized conjugated enynes.[9] Also demonstrated is that alkynyl cyanides add across norbornadiene stereoselectively. A mechanism for the alkynylcyanation reaction is discussed based on both stoichiometric and catalytic reactions using structurally characterized *trans*-(xantphos)Ni(CNBPh$_3$)(C≡CSiMe$_2$*t*-Bu), which is obtained by the oxidative addition of an alkynyl cyanide to nickel/xantphos in the presence of BPh$_3$.

2. Results and discussion

2.1. Nickel/BPh$_3$-catalyzed alkynylcyanation of alkynes

We first examined the reaction of 3-*tert*-butyldimethylsilylpropynenitrile (**1a**) with 4-octyne (**2a**) in the presence of a catalytic amount of Ni(cod)$_2$ with various ligands and Lewis acid (LA) catalysts (Table 1). All the phosphorous ligands examined including monodentate or bidentate gave at most only a detectable amount of expected alkynylcyanation product **3aa**, whereas use of xantphos was significantly effective to obtain **3aa** in a moderate yield (entry 14). The cis-addition was unambiguously confirmed by NOE experiments of ^{1}H NMR after reduction of the cyano group to formyl.[10] We then examined the effect of Lewis acid cocatalysts and found that triarylboranes such as BPh$_3$ and B(C$_6$F$_5$)$_3$ were highly effective (entries 15 and 16), while aluminum-based Lewis acid catalysts, which are effective for arylcyanation reaction,[3j] gave lower yields of **3aa** (entries 17 and 18). A high catalyst turnover was attained even in the presence of 1 mol % of the nickel catalyst and 3 mol % of BPh$_3$ to give **3aa** in 95% yield after isolation by flash column chromatography on silica gel (entry 19). Use of BPh$_3$ in less

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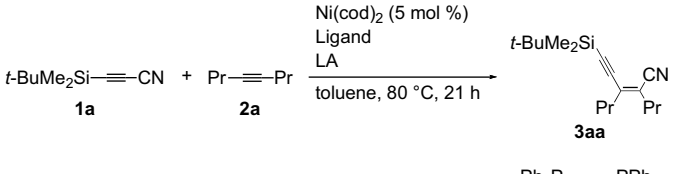
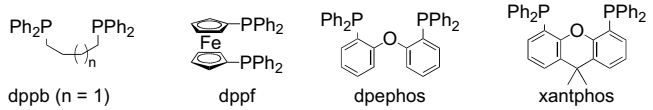
Table 1
Alkynylcyanation of 4-octyne (**2a**) using alkynyl cyanide **1a**[a]





Entry	Ligand (mol %)	Lewis acid (mol %)	Solvent	Yield[b] (%)
1	PMe_3 (10)	None	Toluene	0
2	PCy_3 (10)	None	Toluene	0
3	P*t*-Bu_3 (10)	None	Toluene	6
4	PMe_2Ph (10)	None	Toluene	5
5	$PMePh_2$ (10)	None	Toluene	9
6	PPh_3 (10)	None	Toluene	5
7	P(4-MeO–C_6H_4)$_3$ (10)	None	Toluene	4
8	P(4-CF_3–C_6H_4)$_3$ (10)	None	Toluene	14
9	dppb (5)	None	Toluene	0
10	dpppent (5)	None	Toluene	2
11	dpphex (5)	None	Toluene	6
12	dppf (5)	None	Toluene	0
13	dpephos (5)	None	Toluene	5
14	Xantphos (5)	None	Toluene	62
15	Xantphos (5)	BPh_3 (15)	Toluene	100
16	Xantphos (5)	B(C_6F_5)$_3$ (15)	Toluene	92
17	Xantphos (5)	$AlMe_3$ (15)	Toluene	15
18	Xantphos (5)	$AlMe_2Cl$ (15)	Toluene	39
19[c]	Xantphos (1)	BPh_3 (3)	Toluene	100 (95)[d]
20[c]	Xantphos (1)	BPh_3 (2)	Toluene	59
21[c]	Xantphos (1)	BPh_3 (1)	Toluene	23
22[c]	Xantphos (1)	BPh_3 (3)	DMF	0
23[c]	Xantphos (1)	BPh_3 (3)	Dioxane	21

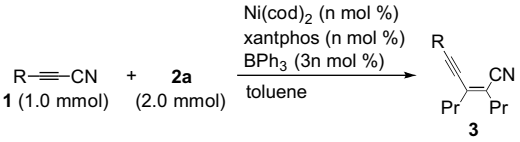
[a] All the reactions were carried out using **1a** (0.20 mmol), **2a** (0.20 mmol), $Ni(cod)_2$ (5.0 mol %), a ligand, and a Lewis acid catalyst in toluene (0.3 mL).
[b] Estimated by GC using tetradecane as an internal standard.
[c] $Ni(cod)_2$ (1.00 mol %) was used.
[d] Isolated yield obtained with a 1 mmol scale.

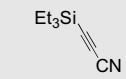
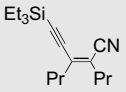
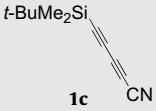
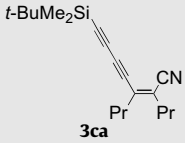
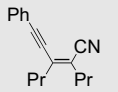
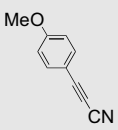
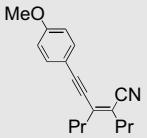
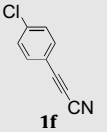
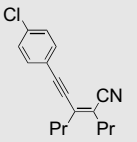
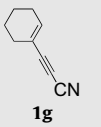
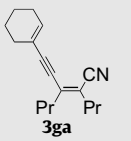
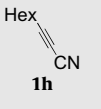
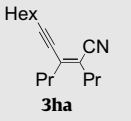
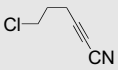
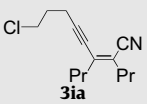
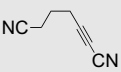
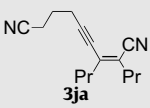
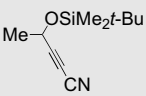
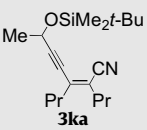
than 3 mol % resulted in low yield of **3aa** (entries 20 and 21). Polar solvents like 1,4-dioxane and DMF were less effective (entries 22 and 23). Attempted reactions set up outside a dry box using nickel(0) catalysts prepared in situ from air-stable $NiCl_2$·DME/Zn or $Ni(acac)_2$/$AlMe_3$ with xantphos did not give **3aa**, presumably because the residue of the reducing agents inhibits this particular carbocyanation reaction.

With the optimized conditions in hand, we next studied scope of alkynyl cyanides with **2a** as an alkyne substrate (Table 2). Triethylsilyl variant **1b** also added across **2a** in an excellent yield (entry 1). Using diynyl cyanide **1c** as a nitrile substrate, conjugated endiyne **3ca** was successfully obtained in 72% yield (entry 2). Reactions of aryl-, alkenyl-, and alkylethynyl cyanides with 2 mol equiv of **2a** also gave the corresponding conjugated enynes in modest to good yields in the presence of 10 mol % of the nickel catalyst and 30 mol % of BPh_3 at higher reaction temperatures (entries 3–10).[11] It is noteworthy that a C(sp)–CN bond is preferentially activated over C–Cl and C(sp^3)–CN bonds, which may also oxidatively add to nickel(0) (entries 5, 8, and 9). A conjugated dienyne structure was obtained with 3-cyclohexenylpropynenitrile (**1g**) (entry 6).

Scope of alkynes was next investigated with **1a** (Table 3). All the reactions proceeded through exclusive cis-addition of the alkynyl cyanide as confirmed by NOE experiments of ^1H NMR, ^1H–^1H

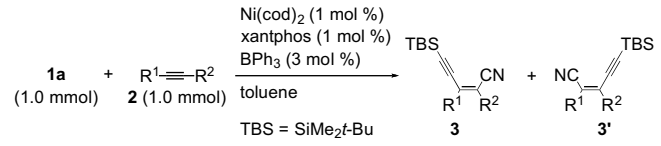
Table 2
Nickel/BPh_3-catalyzed alkynylcyanation of 4-octyne (**2a**)[a]

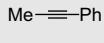
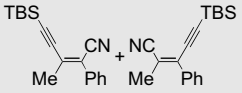
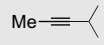
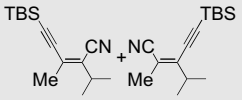
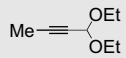
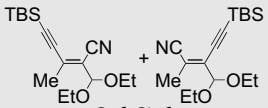
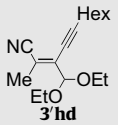
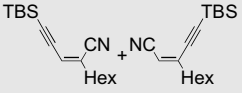
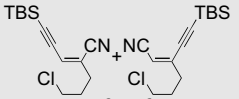
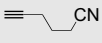
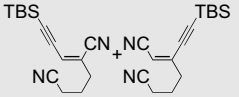
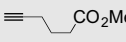
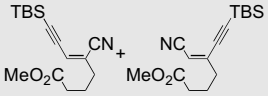
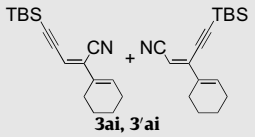


Entry	Alkynyl cyanide	*n*	Temp (°C)	Time (h)	Product	Yield[b] (%)
1[c]	 **1b**	1	80	24	 **3ba**	95
2[c]	 **1c**	3	80	21	 **3ca**	72
3	 **1d**	10	100	3	 **3da**	69
4	 **1e**	10	100	2	 **3ea**	68
5	 **1f**	10	100	3	 **3fa**	45
6	 **1g**	10	80	2	 **3ga**	67
7	 **1h**	10	100	3	 **3ha**	72
8	 **1i**	10	100	3	 **3ia**	54
9	 **1j**	10	100	4	 **3ja**	35
10	 **1k**	10	100	1	 **3ka**	47

[a] All the reactions were carried out using an alkynyl cyanide (1.00 mmol), **2a** (2.0 mmol), $Ni(cod)_2$ (1.00–10.0 mol %), xantphos (1.00–10.0 mol %), and BPh_3 (3.0–30 mol %) in toluene (1.50 mL).
[b] Isolated yield.
[c] Compound **2a** (1.00 mmol) was used.

Table 3
Nickel/BPh_3-catalyzed alkynylcyanation of alkynes using **1a**[a]

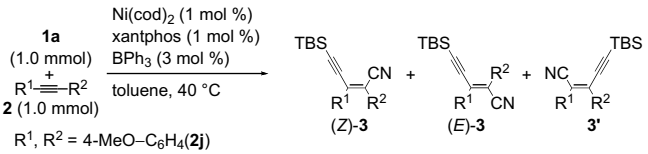


Entry	2	Temp (°C)	Time (h)	Products	Yield[b] (%) (**3**/**3′**)[c]
1	 **2b**	80	56	 **3ab, 3′ab**	94 (60:40)
2	 **2c**	80	49	 **3ac, 3′ac**	82 (22:78)
3	 **2d**	80	39	 **3ad, 3′ad**	84 (13:87)
4[d]	**2d**	100	12	 **3′hd**	47 (5:>95)
5	 **2e**	40	15	 **3ae, 3′ae**	96 (83:13)
6	 **2f**	40	15	 **3af, 3′af**	79 (82:18)[e]
7	 **2g**	40	15	 **3ag, 3′ag**	99 (88:12)
8[f]	 **2h**	40	17	 **3ah, 3′ah**	93 (87:13)
9	 **2i**	40	15	 **3ai, 3′ai**	86 (95:5)

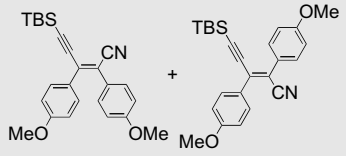
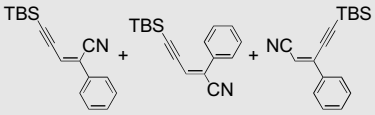
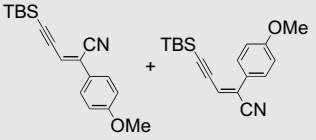
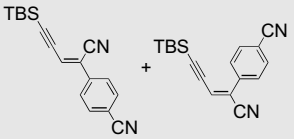
[a] All the reactions were carried out using **1a** (1.00 mmol), an alkyne (1.00 mmol), Ni(cod)$_2$ (1.00 mol %), xantphos (1.00 mol %), and BPh_3 (3.0 mol %) in toluene (1.50 mL).
[b] Isolated yield.
[c] Estimated by ^{1}H NMR analysis of an isolated product.
[d] The reaction was carried out using Ni(cod)$_2$ (10.0 mmol %), xantphos (10.0 mol %), and BPh_3 (30 mol %).
[e] Calculated based on yields of isolated products.
[f] The amount of **2h** used was 1.10 mmol.

couplings, and/or HMBC experiments of the corresponding aldehydes **24** (vide infra).[10] Addition of **1a** across 1-phenyl-1-propyne (**2b**) gave the corresponding adducts (**3ab** and **3′ab**) in good yields but with poor regioselectivitiy (entry 1). Alkynes having sterically

Table 4
Nickel/BPh_3-catalyzed alkynylcyanation of aryl-substituted alkynes using **1a**[a]



R^1, R^2 = 4-MeO–C_6H_4(**2j**)
H, Ph (**2k**)
H, 4-MeO–C_6H_4 (**2l**)
H, 4-NC–C_6H_4 (**2m**)

Entry	2	Time (h)	Products	Yield[b] (%) [(*Z*)-**3**/(*E*)-**3**/**3′**][c]
1[d]	**2j**	48		100 (11:89)
2	**2k**	36		97 (77:11:12)
3	**2l**	48		93 (75:25)
4	**2m**	17		96 (98:2)

[a] All the reactions were carried out using **1a** (1.00 mmol), an alkyne (1.00 mmol), Ni(cod)$_2$ (1.00 mol %), xantphos (1.00 mol %), and BPh_3 (3.0 mol %) in toluene (1.50 mL).
[b] Isolated yield.
[c] Estimated by ^{1}H NMR analysis of an isolated product.
[d] The reaction was carried out using Ni(cod)$_2$ (3.0 mol %), xantphos (3.0 mol %), and BPh_3 (9.0 mol %) in toluene (1.50 mL) at 80 °C.

biased substituents such as 4-methyl-2-pentyne (**2c**) and 2-butyn-1-al diethyl acetal (**2d**) showed regioselectivities opposite to arylcyanation of alkynes,[3c,g,j] giving adducts with a bulkier substituent at the alkynyl substituted carbon (entries 2 and 3). The addition of **1h** across **2d** showed higher regioselectivity, and **3′hd** was isolated as a sole product albeit in a modest yield (entry 4). Terminal alkynes also participated in the reaction with **1a** to give conjugated enynes having a substituent at the cyano-substituted carbon with fair to excellent regioselectivities (entries 5–9). Functional groups like chloro, alkanenitrile, and ester were tolerated (entries 6–8).

The addition reaction across aryl-substituted alkynes gave trans-adducts in varying amounts (Table 4). Diaryl acetylene **2j** gave trans-adduct (*E*)-**3aj** as a major product, the stereochemistry of which was determined by X-ray crystallographic analysis (Fig. 1).[12] Electron-neutral and -poor arylacetylenes **2k** and **2m** showed moderate to good regioselectivities similar to those observed with other terminal alkynes and gave only a small amount of trans-adducts and regioisomers (entries 2 and 4), whereas electron-rich one **2l** reacted regioselectively but gave trans-adducts in a larger amount (entry 3). In all cases, ratios of these isomers were constant throughout the reaction revealed by GC analyses.

To gain a mechanistic insight, we examined a stoichiometric reaction. Upon mixing stoichiometric amounts of **1a**, Ni(cod)$_2$, xantphos, and BPh_3 in benzene, the initially heterogeneous reaction

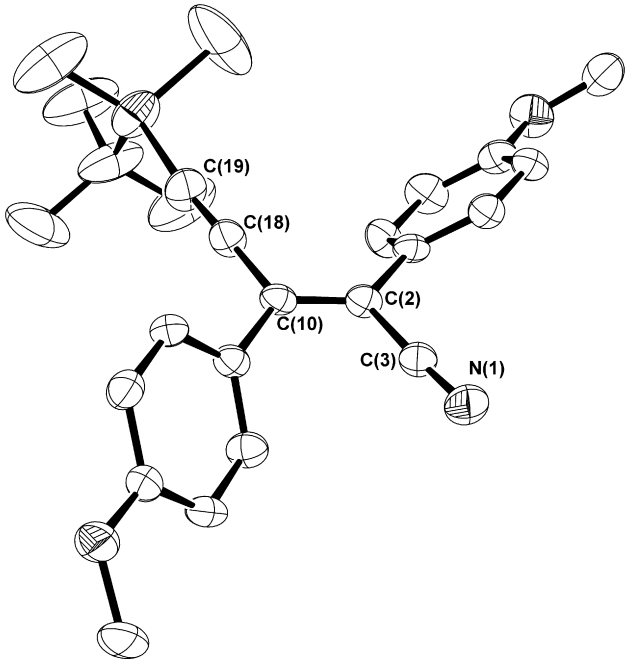
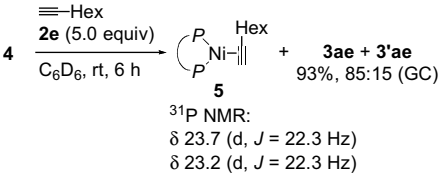


Figure 1. ORTEP drawing of (*E*)-**3aj**.

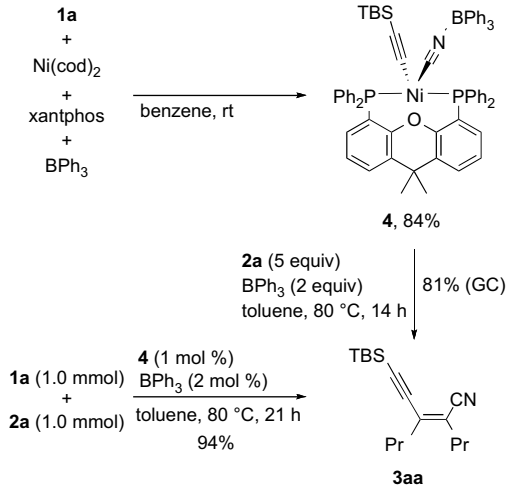
mixture immediately turned to a homogeneous solution at room temperature. After evaporation of benzene in vacuo followed by washing the resulting precipitates with hexane, *trans*-(xantphos)Ni(CNBPh$_3$)(C≡CSiMe$_2$*t*-Bu) (**4**) was obtained as a brown powder in 84% yield (Scheme 1). Dark red single crystals suitable for X-ray crystallographic analysis were obtained by recrystallization from hexane and dichloromethane. The X-ray structure of **4** shown in Figure 2 clearly indicates the trans geometry with a cyano ligand coordinating to BPh$_3$.[12] Treatment of **4** with **2a** (5.0 equiv) and BPh$_3$ (2.0 equiv) in toluene at 80 °C for 14 h gave alkynylcyanation product **3aa** in 81% yield as estimated by GC. Reaction below 50 °C showed no appreciable change in both **4** and **2a**: thus, the coordination of **2a** to the nickel center appears to be a plausible rate-determining step. Moreover, the reaction of **1a** (1.00 mmol) with **2a** (1.00 mmol) in the presence of a catalytic amount of **4** (1 mol %) and BPh$_3$ (2 mol %) in toluene at 80 °C for 21 h also gave **3aa** in 94% yield, clearly indicating that **4** should be a plausible reaction intermediate for the present alkynylcyanation reaction.

On the other hand, the reaction of **4** with 1-octyne (**2e**, 5.0 equiv) in C$_6$D$_6$ proceeded at room temperature, and **4** was completely consumed after 6 h to give a complex, which showed signals for ^{31}P NMR at 23.7 ppm (d, *J*=22.3 Hz) and 23.2 ppm (d, *J*=22.3 Hz), and alkynylcyanation products **3ae** and **3′ae** were also observed in ^{1}H NMR in 79% and 14% yields as estimated by GC, respectively (Eq. 1). The new nickel complex observed was assigned to be *cis*-(xantphos)Ni(1-octyne) (**5**) based on the same set of peaks observed in the reaction of Ni(cod)$_2$, xantphos, and **2e** (5.0 equiv). These data indicate that coordination and migratory insertion followed by reductive elimination are very rapid with terminal alkynes as has also been anticipated by the difference of the reaction temperature (80 °C vs 40 °C, Table 3).



(1)

Thus, the catalytic cycle for the alkynylcyanation reaction should be initiated by oxidative addition of a C(sp)–CN bond to nickel(0) by the aid of BPh$_3$[4q,6] to give **4** (Scheme 2). Coordination of an alkyne to the nickel center of **4** followed by migration of the alkynyl group in **6** or **7** to the alkyne gives *cis*-alkenylnickel intermediate **8** or **9**, which then reductively eliminates cis-alkynylcyanation product **3** or **3′**, respectively. With internal alkynes, the coordination of alkynes seems to be rate-determining to favor alkyne-coordinated nickel **6** to avoid steric repulsion between C≡N–***B*** and bulkier R^3 to give **3′** as a major product through **8**. Improved regioselectivity observed with **1h** over **1a** in the reaction with **2d** (entry 3 vs entry 4, Table 3) may be understood rationally by this scenario. On the other hand, migration of the alkynyl group to the less-hindered alkyne carbon through **7** may be favored with terminal alkynes to give **9** and then finally **3** as a major product, because coordination of terminal alkynes to the nickel center is likely to be feasible. The excellent regioselectivity attained with **2i** (entry 9 of Table 3) may indicate the presence of π-allylnickel-like stabilization in **9**. Such stabilization provided by an additional π-system connecting directly to an alkyne may also be important in the reactions of aryl-substituted alkynes, especially those having electron-donating aryl groups, to direct regioselective migratory insertion. Alternatively, an electron-withdrawing group could also affect the regioselection by making the LUMO of the alkyne-terminus low enough to allow the nucleophilic alkynyl group to migrate selectively at this position. The trend of regioselectivities observed with arylacetylenes (entries 2–4 of Table 4) would be derived from the sum of those effects. Formation of trans-adducts could be ascribed to partial isomerization of *cis*-alkenylnickel intermediates **10** through resonance forms **11** or **12** (Scheme 3).[13] Electron-donating aryl groups may facilitate this isomerization by stabilizing the transient nickel–carbene species having formal positive charge on nickel, thus favoring trans-adducts. Alternatively, isomerization of the double bond of alkenylnickel intermediates catalyzed by phosphorus in an intramolecular manner cannot be ruled out.[14]



Scheme 1. Synthesis and reactions of *trans*-(xantphos)Ni(CNBPh$_3$)(C≡CSiMe$_2$*t*-Bu) (**4**).

2.2. Nickel/BPh$_3$-catalyzed alkynylcyanation of 1,2-dienes

In the presence of the same catalyst, 1,2-dienes also underwent the alkynylcyanation. The reaction took place at an internal double bond of 1,2-dienes, and an alkynyl group was introduced to the cumulative carbon to give conjugated enynes **15** having a substituted cyanomethyl substituent (entries 1–4 of Table 5). On the other hand, silylallene **14e** showed opposite regioselectivity, giving (*Z*)-alkenylsilane **15′e** exclusively (entry 5). The reactions of propadiene and phenylallene gave no desired product due to rapid

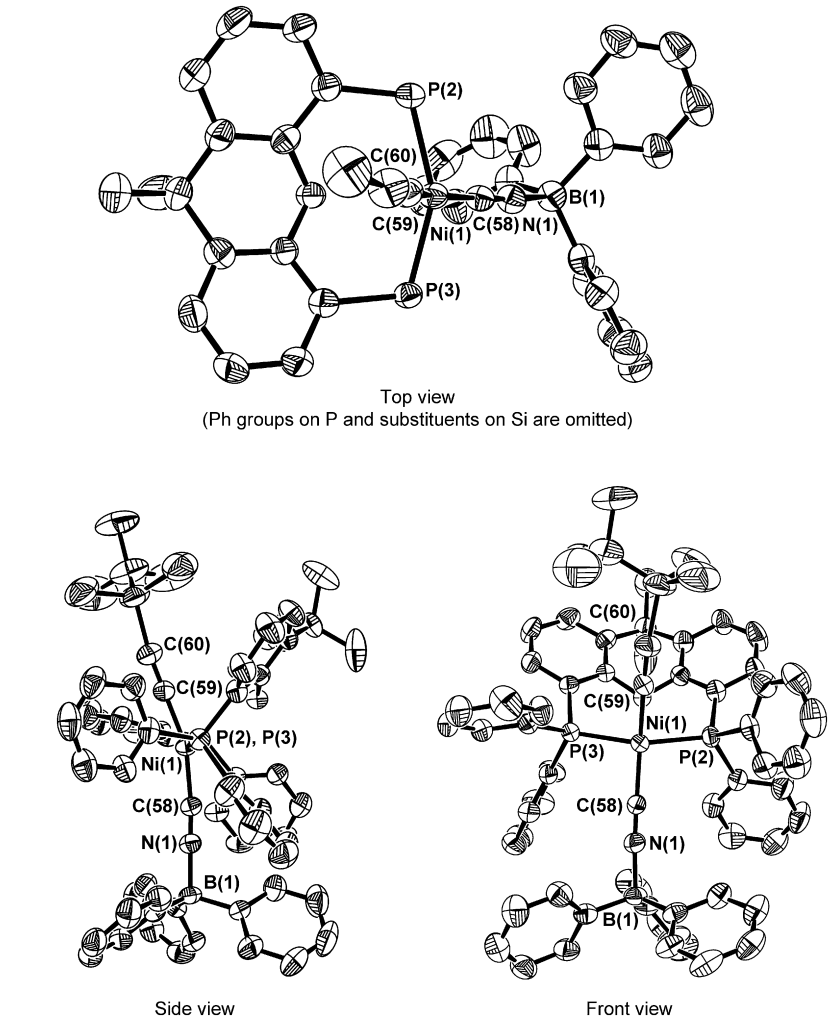
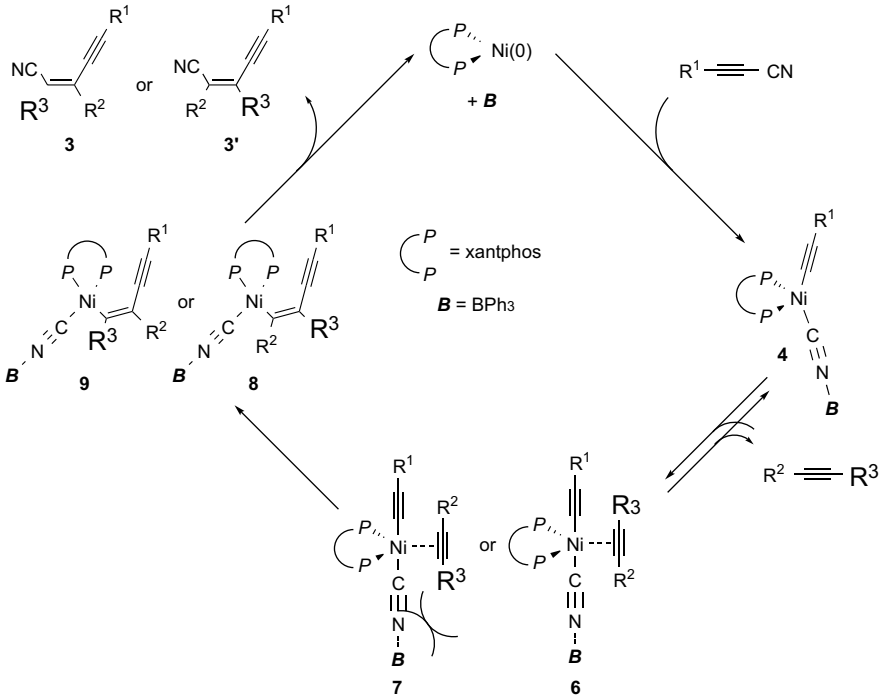
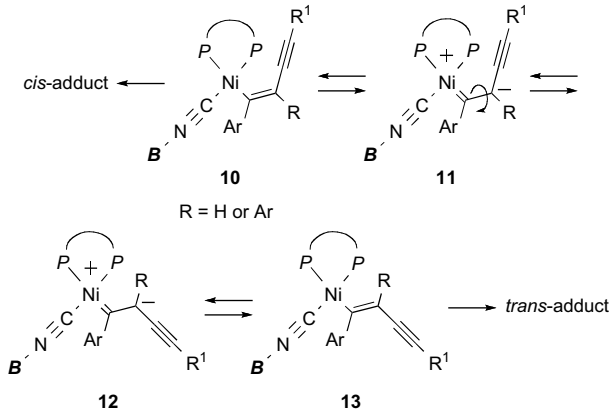


Figure 2. ORTEP drawings of **4**.



Scheme 2. Plausible mechanism for the nickel/BPh_3-catalyzed alkynylcyanation of alkynes.

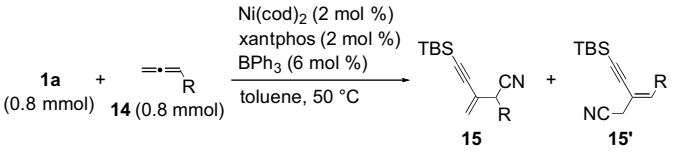


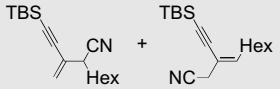
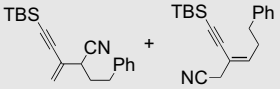
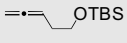
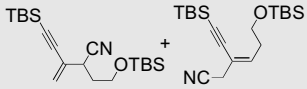
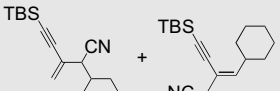
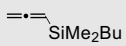
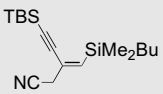
Scheme 3. Plausible mechanism for the formation of trans-alkynylcyanation products (**3aj–3am**).

oligomerization of the allenes. The reactions of 1,1- and 1,3-disubstituted allenes such as 3-methyl-1,2-butadiene and 5,6-dodecadiene did not proceed, and these 1,2-dienes were recovered intact due presumably to steric hindrance to prevent the dienes coordinating to the nickel center of **4**.

The catalytic cycle for the alkynylcyanation of 1,2-dienes shown in Scheme 4 should also be initiated by formation of **4**. The terminal double bond in 1,2-dienes coordinates to the nickel center to give **16**, and migratory insertion of the 1,2-diene takes place into the alkynyl–Ni bond to give a π-allylnickel species **18**, which may be thermodynamically more stable than **19**.[5g] Reductive elimination of the allyl and cyano groups would give conjugated enynes **15**. Regioisomers **15′** may be formed through the coordination of **14** in an opposite direction to give **20**, followed by similar steps through π-allylnickel intermediates. However, **20** should be sterically unfavored. A bulky silyl group for R may inhibit C–C bond-forming reductive elimination from **18**. Instead, reductive elimination from **19** could be operative to afford **15′** with particular 1,2-diene **14e**.

Table 5
Nickel/BPh_3-catalyzed alkynylcyanation of 1,2-dienes using **1a**[a]



Entry	14	Time (h)	Products	Yield[b] (**15**/**15′**)[c]
1	 **14a**	19	 **15a, 15′a**	73 (93:7)[d]
2	 **14b**	24	 **15b, 15′b**	82 (91:9)
3	 **14c**	17	 **15c, 15′c**	75 (92:8)[e]
4	 **14d**	59	 **15d, 15′d**	74 (>95:5)[d]
5	 **14e**	66	 **15′e**	55 (5:>95)

[a] All the reactions were carried out using **1a** (0.80 mmol), a 1,2-diene (0.80 mmol), $Ni(cod)_2$ (2.0 mol %), xantphos (2.0 mol %), and BPh_3 (6.0 mol %) in toluene (ca. 1 mL).
[b] Isolated yield.
[c] Calculated based on yields of isolated products.
[d] Estimated by ^1H NMR analysis of an isolated product.
[e] *E*/*Z* of **15′c** was 11:89.

2.3. Nickel-catalyzed alkynylcyanation of norbornadiene

We next turned our attention to the addition reaction of alkynyl cyanides across alkene substrate. Attempted reactions of alkynyl cyanide **1a** with simple alkenes including 1-octene, styrene, and 1,3-dodecadiene in the presence of a diverse range of nickel, a ligand, and a Lewis acid catalyst disappointedly gave no alkynylcyanation products in any detectable amounts. On the other hand, the reaction of **1a** with norbornadiene (**21**) took place in the presence of $Ni(cod)_2$ (2 mol %) and xantphos (2 mol %) in toluene at 80 °C for 17 h to afford *exo*-*cis*-alkynylcyanation product **22** in 89% yield (Scheme 5). The structure of **22** was assigned based on NOE experiments of ^1H NMR of aldehyde **23**, which was obtained by reduction of **22**. Lewis acid cocatalysts were not effective for the alkynylcyanation of **21** to result in lower yields of **22**. Highly functionalized norbornene derivatives like **22** may find further applications as precursors for functionalized cyclopentanes[3e] or monomers for functionalized cyclic olefin polymers through ring-opening metathesis polymerization.[15]

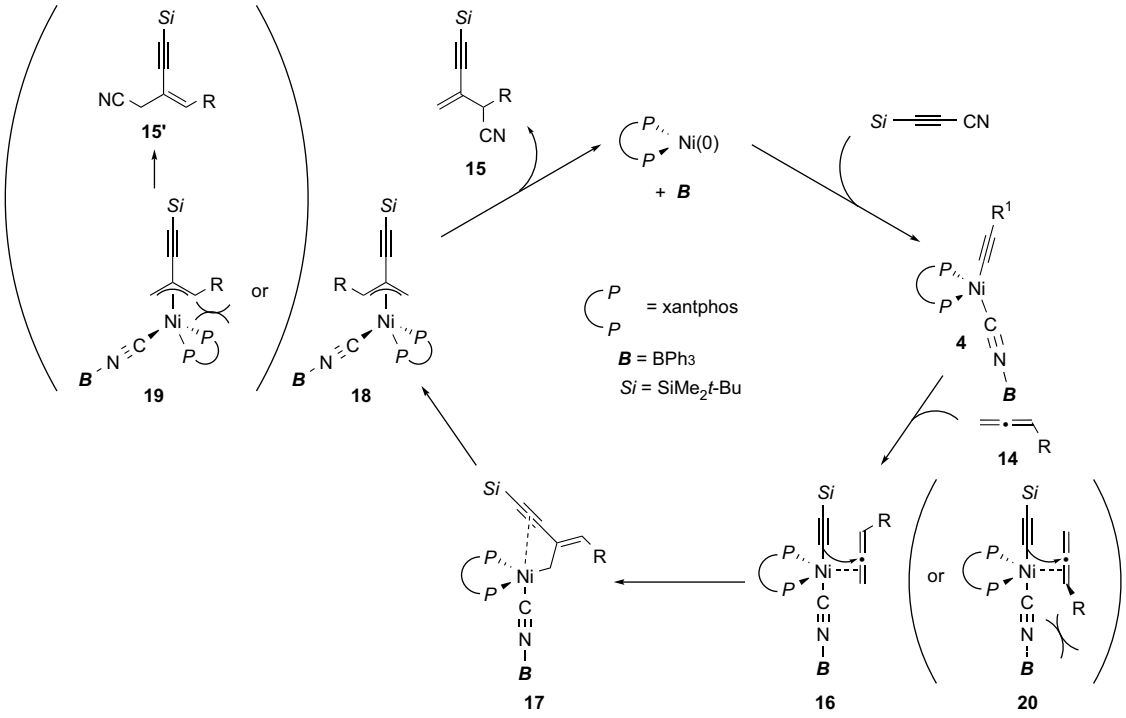
2.4. Transformations of alkynylcyanation products

Reduction of the cyano group in alkynylcyanation product **3da** to formyl was successfully performed with DIBAL-H with complete retention of stereochemistry (Scheme 6).[10] The resulting formyl group in **24da** was further transformed to afford highly substituted allylic alcohol **25** upon treatment with a Grignard reagent. Aldehydes **24** and allylic alcohols **25** have been demonstrated to serve as versatile synthetic intermediates for a variety of highly substituted cyclic compounds.[16]

Desilylation of 1,2-diene-alkynylcyanation product **15b** followed by stannylative cross-cycloaddition reaction of the resulting **26** with ethyl (*Z*)-2-undecene-4-ynoate (**27**) in the presence of a palladium/iminophosphine **28** catalyst gave highly substituted phenylstannane **29** (Scheme 7).[17]

3. Conclusion

In conclusion, we have demonstrated alkynylcyanation reactions of alkynes and 1,2-dienes catalyzed by nickel/xantphos/BPh_3. The transformations proceed with high stereo-, regio-, and chemoselectivities to afford a wide variety of highly functionalized conjugated enynes in an atom-economic manner. These enyne products are shown to serve as potent versatile synthetic precursors for various cyclic and linear compounds. We have also achieved stereoselective alkynylcyanation of norbornadiene to afford a highly functionalized norbornene. The catalytic cycles of the alkynylcyanation reactions initiated by oxidative addition of alkynyl cyanides to nickel(0)/xantphos have been investigated in detail by isolation, structural characterization, and stoichiometric and catalytic reactions of *trans*-(xantphos)Ni($CNBPh_3$)(C≡C$SiMe_2$*t*-Bu) (**4**).

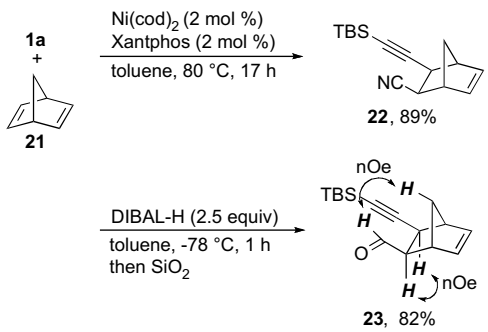


Scheme 4. Plausible mechanism for the nickel/BPh_3-catalyzed alkynylcyanation of 1,2-dienes.

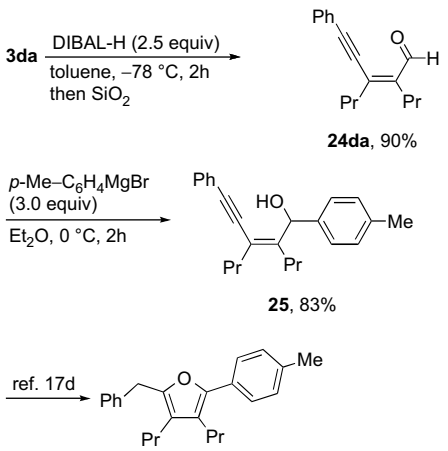
4. Experimental

4.1. General

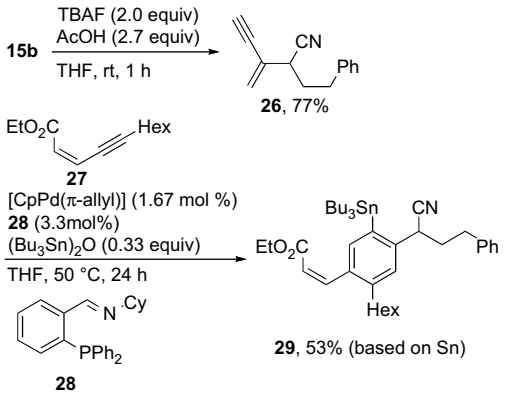
All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique or in a dry box under an argon atmosphere. Flash column chromatography was performed using Kanto Chemical silica gel (spherical, 40–50 μm). Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F_{254} (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating. Proton and carbon nuclear magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded on a Varian Mercury 400 (^1H NMR, 400 MHz; ^{13}C NMR, 101 MHz) or a Varian Gemini 300 (^{31}P NMR, 121 MHz) spectrometer with solvent resonance as an internal standard (^1H NMR, $CHCl_3$ at 7.26 ppm, C_6D_5H at 7.15 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm, C_6D_6 at 128.6 ppm) or resonance of phosphoric acid as an external standard (^{31}P NMR at 0 ppm). Melting points were determined using a YANAKO MP-500D. Elemental analyses were performed by Elemental Analysis Center of Kyoto University.



Scheme 5. Nickel-catalyzed alkynylcyanation of norbornadiene (**21**).



Scheme 6. Possible transformations of alkynylcyanation products.



Scheme 7. Transformations of the 1,2-diene-alkynylcyanation product **15b**.

High-resolution mass spectra were obtained with a JEOL JMS-700 (EI) or JEOL JMS-HX110A (FAB+) spectrometer. X-ray crystal data were collected with a Bruker SMART APEX diffractometer. 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). 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 a helium gas as a carrier. Unless otherwise noted, commercially available reagents were used without purification. Toluene was distilled from sodium/benzophenone ketyl or purchased from Kanto Chemical and degassed by purging vigorously with argon for 20 min and further purified by passing through activated alumina under positive argon pressure as described by Grubbs et al.[18] Anhydrous benzene was purchased from Nacalai Tesque and degassed by bubbling an argon gas vigorously for 20 min before use. Benzene-d_6 was distilled from sodium/benzophenone ketyl. Alkynyl cyanides[7] and 1,2-dienes[19] were prepared according to the respective literature procedure.

4.2. Synthesis of alkynyl cyanides. A general procedure

To a solution of a terminal alkyne (40 mmol) in diethyl ether (10 mL) was added a 1.6 M solution of *n*-BuLi (28 mL, 44 mmol) in hexane at −78 °C. The resulting reaction mixture was stirred at −78 °C for 1 h, and then cyano phenolate (5.2 g, 44 mmol) was added. The reaction mixture was warmed up to room temperature and further stirred for 1 h before quenching with water. The aqueous layer was extracted with diethyl ether for three times. The combined organic layers were washed with water and brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give the corresponding alkynyl cyanides.

*4.2.1. 3-tert-Butyldimethylsilylpropynenitrile (**1a**)*

A colorless oil, R_f 0.28 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 9H), 0.21 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 104.9, 94.3, 76.6, 25.8, 16.6, −5.5; IR (neat) 2955, 2934, 2862, 2259, 2104, 1472, 1366, 1256, 1047, 966, 843, 824, 810, 783, 685, 581, 511, 459 cm^{-1}; HRMS (EI) calcd for $C_9H_{15}NSi$: M^+, 165.0974. Found: *m*/*z* 165.0975.

*4.2.2. 3-(Triethylsilyl)propynenitrile (**1b**)*

A colorless oil, R_f 0.28 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (t, *J*=8.0 Hz, 9H), 0.71 (q, *J*=7.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 104.8, 93.8, 76.9, 7.3, 3.7; IR (neat) 2961, 2914, 2880, 2259, 2102, 1460, 1416, 1236, 1045, 1007, 964, 731 cm^{-1}; HRMS (EI) calcd for $C_9H_{15}NSi$: M^+, 165.0974. Found: *m*/*z* 165.0979.

*4.2.3. 5-tert-Butyldimethylsilylpenta-2,4-diynenitrile (**1c**)*

A yellow oil, R_f 0.38 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 105.2, 93.0, 85.8, 67.4, 49.2, 25.9, 16.8, −5.3; IR (neat) 2955, 2932, 2860, 2239, 2179, 2079, 1472, 1254, 1209, 843, 824, 812, 781 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{15}NSi$: M^+, 189.0974. Found: *m*/*z* 189.0980.

*4.2.4. 2-Heptynedinitrile (**1j**)*

A pale yellow oil, R_f 0.20 (hexane–ethyl acetate=2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 (t, *J*=7.0 Hz, 2H), 2.52 (t, *J*=7.0 Hz, 2H), 1.99 (quint, *J*=7.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 117.9, 104.7, 84.0, 56.9, 23.2, 18.0, 16.4; IR (neat) 2957, 2874, 2315, 2263, 1762, 1686, 1599, 1454, 1425, 1350, 1329, 1312, 1296, 1215, 1074, 1042, 773 cm^{-1}; HRMS (FAB$^+$) calcd for $C_7H_6N_2$: M^+, 118.0531. Found: *m*/*z* 118.0535.

*4.2.5. 4-tert-Butyldimethylsiloxypent-2-ynenitrile (**1k**)*

A colorless oil, R_f 0.43 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.58 (q, *J*=6.6 Hz, 1H), 1.48 (d, *J*=6.6 Hz, 3H), 0.91 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 104.7, 86.8, 58.9, 57.7, 25.7, 24.3, 18.2, −4.7, −4.9; IR (neat) 2957, 2932, 2888, 2861, 2311, 2280, 1748, 1472, 1464, 1445, 1391, 1371, 1362, 1339, 1308, 1260, 1153, 1109, 1028, 1005, 984, 939, 839, 829, 812, 781, 739, 667 cm^{-1}. Anal. Calcd for $C_{11}H_{19}NOSi$: C, 63.11; H, 9.15. Found: C, 63.32; H, 9.11.

4.3. Alkynylcyanation of alkynes. A general procedure

In a dry box, an alkynyl cyanide (1.00 mmol), an alkyne (1.00–2.0 mmol), and tetradecane (internal standard, 99 mg, 0.50 mmol) were added sequentially to a solution of $Ni(cod)_2$ (2.8–28 mg, 10.0–100 μmol), BPh_3 (7.3–73 mg, 30–300 μmol), and xantphos (5.8–58 mg, 10.0–100 μmol) in toluene (1.5 mL) placed in a vial, which was taken outside the dry box and heated at the temperature for the time specified in Tables 1–4. The resulting reaction mixture was filtered through a silica gel pad. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography on silica gel to give the corresponding alkynylcyanation products in yields listed in Tables 1–4. Mixtures of regioisomers were further separated by preparative recycling silica gel chromatography to give isomerically pure products.

*4.3.1. (Z)-3-tert-Butyldimethylsilylethynyl-2-propylhex-2-enenitrile (**3aa**)*

A brownish oil, R_f 0.63 (hexane–ethyl acetate=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (q, *J*=7.2 Hz, 4H), 1.66–1.54 (m, 4H), 0.96 (s, 9H), 0.97 (t, *J*=7.4 Hz, 3H), 0.95 (t, *J*=7.3 Hz, 3H), 0.18 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 119.8, 118.7, 103.2, 102.0, 34.1, 31.9, 26.2, 21.7, 21.4, 16.8, 13.8, 13.7, −4.6; IR (neat) 2961, 2932, 2858, 2210, 2143, 1464, 1252, 1159, 839, 826, 812, 777, 735, 679 cm^{-1}. Anal. Calcd for $C_{17}H_{29}NSi$: C, 74.11; H, 10.61. Found: C, 74.22; H, 10.60. The stereochemistry was assigned based on ^{1}H NMR NOE experiments of **24aa**.[10]

*4.3.2. (Z)-3-Triethylsilylethynyl-2-propylhex-2-enenitrile (**3ba**)*

A pale yellow oil, R_f 0.22 (hexane–ethyl acetate=50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (q, *J*=7.1 Hz, 4H), 1.61 (sept, *J*=7.3 Hz, 4H), 1.04 (t, *J*=7.9 Hz, 9H), 0.96 (q, *J*=7.0 Hz, 6H), 0.67 (q, *J*=7.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 119.7, 118.7, 103.8, 101.2, 34.1, 31.9, 21.7, 21.4, 13.8, 13.7, 7.6, 4.4; IR (neat) 2961, 2876, 2212, 2143, 1458, 1416, 1381, 1236, 1157, 1005, 727 cm^{-1}. Anal. Calcd for $C_{17}H_{29}NSi$: C, 74.11; H, 10.61. Found: C, 74.13; H, 10.61.

*4.3.3. (Z)-7-tert-Butyldimethylsilyl-2,3-dipropylhept-2-en-4,6-diynenitrile (**3ca**)*

A yellow oil, R_f 0.35 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (q, *J*=8.1 Hz, 4H), 1.65–1.54 (m, 4H), 0.97 (s, 9H), 0.99–0.93 (m, 6H), 0.17 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 122.3, 118.4, 93.5, 87.6, 81.6, 73.8, 34.2, 32.2, 26.2, 21.6, 21.5, 16.9, 13.8, 13.6, −4.7; IR (neat) 2959, 2932, 2858, 2214, 2095, 1464, 1252, 1007, 920, 841, 827, 810, 777, 735, 681 cm^{-1}. Anal. Calcd for $C_{19}H_{29}NSi$: C, 76.19; H, 9.76. Found: C, 76.35; H, 9.85.

*4.3.4. (Z)-3-Phenylethynyl-2-propylhex-2-enenitrile (**3da**)*

A pale yellow oil, R_f 0.48 (hexane–ethyl acetate=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.48 (m, 2H), 7.39–7.29 (m, 3H), 2.32 (q, *J*=7.7 Hz, 4H), 1.74–1.58 (m, 4H), 0.99 (t, *J*=7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 132.0, 129.1, 128.4, 122.2, 119.1, 119.0, 97.2, 88.0, 34.0, 31.8, 21.6, 21.4, 13.7, 13.5; IR (neat) 2963, 2932, 2874, 2208, 1491, 756, 691 cm^{-1}. Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07. Found: C, 85.73; H, 8.16. The stereochemistry was assigned based on ^{1}H NMR NOE experiments of **24da**.[10]

*4.3.5. (Z)-3-(4-Methoxyphenyl)ethynyl-2-propylhex-2-enenitrile (**3ea**)*

A pale yellow oil, R_f 0.13 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J=9.0 Hz, 2H), 6.85 (d, J=9.0 Hz, 2H), 3.81 (s, 3H), 2.30 (q, J=7.5 Hz, 4H), 1.74–1.56 (m, 4H), 0.98 (t, J=7.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 139.4, 133.3, 119.1, 117.7, 114.0, 113.8, 97.4, 87.0, 55.2, 34.0, 31.7, 21.7, 21.5, 13.7, 13.5; IR (neat) 2963, 2872, 2185, 1607, 1508, 1458, 1290, 1252, 1173, 1032, 833 cm^{-1}. Anal. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92. Found: C, 80.98; H, 8.01.

*4.3.6. (Z)-3-(4-Chlorophenyl)ethynyl-2-propylhex-2-enenitrile (**3fa**)*

A pale yellow oil, R_f 0.23 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J=8.4 Hz, 2H), 7.31 (d, J=8.4 Hz, 2H), 2.36–2.28 (m, 4H), 1.72–1.57 (m, 4H), 1.00 (t, J=7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 135.1, 133.0, 128.6, 120.1, 119.4, 118.9, 95.8, 88.8, 34.0, 31.9, 21.8, 21.6, 13.8, 13.6; IR (neat) 2963, 2932, 2212, 1489, 1458, 1398, 1381, 1090, 1015, 829 cm^{-1}. Anal. Calcd for $C_{17}H_{18}NCl$:C, 75.13; H, 6.68. Found: C, 75.39; H, 6.83.

*4.3.7. (Z)-5-(1-Cyclohexenyl)-2,3-dipropylpent-2-en-4-ynenitrile (**3ga**)*

A pale yellow oil, R_f 0.13 (hexane–ethyl acetate=30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30–6.25 (m, 1H), 2.30–2.11 (m, 8H), 1.72–1.52 (m, 8H), 1.00–0.92 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 137.4, 120.2, 119.2, 117.6, 99.3, 85.7, 34.2, 31.7, 28.9, 25.9, 22.2, 21.8, 21.51, 21.45, 13.8, 13.6; IR (neat) 2963, 2932, 2872, 2210, 2187, 1576, 1456, 1435, 1348, 918, 843, 799, 737 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{23}N$: M^+, 241.1830. Found: m/z 241.1833.

*4.3.8. (Z)-2,3-Dipropylundec-2-en-4-ynenitrile (**3ha**)*

A brown oil, R_f 0.15 (hexane–ethyl acetate=30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (t, J=7.0 Hz, 2H), 2.27–2.18 (m, 4H), 1.65–1.24 (m, 12H), 0.95 (q, J=7.7 Hz, 6H), 0.90 (t, J=6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 119.3, 117.4, 99.3, 79.4, 34.5, 31.7, 31.4, 28.6, 28.5, 22.6, 21.7, 21.5, 19.7, 14.2, 13.8, 13.6; IR (neat) 2961, 2932, 2872, 2206, 1589, 1458, 1379, 1329, 1111 cm^{-1}. Anal. Calcd for $C_{17}H_{27}N$: C, 83.20; H, 11.09. Found: C, 83.45; H, 11.00. The stereochemistry was assigned based on ^{1}H NMR NOE experiments of **24ha**.[10]

*4.3.9. (Z)-8-Chloro-2,3-dipropyloct-2-en-4-ynenitrile (**3ia**)*

A brown oil, R_f 0.22 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (t, J=6.2 Hz, 2H), 2.63 (t, J=6.7 Hz, 2H), 2.28–2.18 (m, 4H), 2.05 (quint, J=6.5 Hz, 2H), 1.65–1.53 (m, 4H), 0.96 (q, J=5.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 119.1, 118.2, 96.6, 80.3, 43.5, 34.2, 31.5, 31.1, 21.6, 21.4, 17.0, 13.7, 13.5; IR (neat) 2963, 2874, 2206, 1589, 1458, 1290, 1231, 1113, 854, 656 cm^{-1}. Anal. Calcd for $C_{14}H_{20}ClN$: C, 70.72; H, 8.48. Found: C, 70.97; H, 8.41.

*4.3.10. (Z)-8-Cyano-2,3-dipropyloct-2-en-4-ynenitrile (**3ja**)*

A pale yellow oil, R_f 0.30 (hexane–ethyl acetate=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62 (t, J=6.6 Hz, 2H), 2.61 (t, J=7.0 Hz, 2H), 2.25 (t, J=7.6 Hz, 2H), 2.21 (t, J=7.6 Hz, 2H), 1.95 (quint, J=6.9 Hz, 2H), 1.65–1.51 (m, 4H), 0.96 (q, J=7.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 119.2, 119.0, 118.9, 95.4, 81.2, 34.2, 31.6, 24.4, 21.7, 21.5, 18.7, 16.2, 13.8, 13.6; IR (neat) 2965, 2934, 2874, 2247, 2207, 1589, 1462, 1456, 1431, 1381, 1346, 1316, 1173, 1113, 1090, 889, 791, 741 cm^{-1}. Anal. Calcd for $C_{15}H_{20}N_2$: C, 78.90; H, 8.83. Found: C, 79.19; H, 8.95.

*4.3.11. (Z)-6-tert-Butyldimethylsiloxy-2,3-dipropylhept-2-en-4-ynenitrile (**3ka**)*

A pale yellow oil, R_f 0.20 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73 (q, J=6.5 Hz, 1H), 2.24 (q, J=7.6 Hz, 4H), 1.67–1.53 (m, 4H), 1.49 (d, J=6.6 Hz, 3H), 0.96 (t, J=7.4 Hz, 3H), 0.94 (t, J=7.5 Hz, 3H), 0.92 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 118.8, 99.7, 81.6, 59.4, 34.2, 31.8, 25.9, 25.8, 25.3, 21.7, 21.4, 18.4, 13.8, 13.6, −4.5, −4.8; IR (neat) 2961, 2932, 2874, 2859, 2211, 1591, 1464, 1341, 1252, 1119, 1101, 1057, 988, 949, 835, 812, 779 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{24}NOSi$: [M−(*t*-Bu)]$^+$, 262.1627. Found: m/z 262.1617.

*4.3.12. (Z)-5-tert-Butyldimethylsilyl-3-methyl-2-phenylpent-2-en-4-ynenitrile (**3ab**)*

A colorless oil, R_f 0.30 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.32 (m, 5H), 2.09 (s, 3H), 1.03 (s, 9H), 0.23 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1, 132.6, 128.9, 128.8, 128.6, 119.6, 118.3, 104.4, 104.2, 26.2, 20.9, 16.8, −4.7; IR (neat) 2955, 2930, 2885, 2858, 2214, 2127, 1580, 1493, 1472, 1445, 1373, 1364, 1252, 1227, 1005, 926, 839, 826, 812, 777, 766, 700, 677, 625, 588 cm^{-1}. Anal. Calcd for $C_{18}H_{23}NSi$: C, 76.81; H, 8.24. Found (as a mixture with **3′ab**): C, 76.97; H, 8.40. The stereochemistry was assigned based on ^{1}H NMR NOE experiments, and the regiochemistry was determined based on HMBC experiments of **24ab**.[10]

*4.3.13. (Z)-5-tert-Butyldimethylsilyl-2-methyl-3-phenylpent-2-en-4-ynenitrile (**3′ab**)*

A colorless solid, mp 65.2–65.6 °C, R_f 0.25 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.34 (m, 5H), 2.07 (s, 3H), 1.00 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 134.9, 129.1, 128.5, 128.3, 119.5, 115.0, 103.2, 103.0, 26.2, 18.3, 16.8, −4.7; IR (KBr) 2951, 2926, 2883, 2856, 2212, 2143, 1566, 1491, 1470, 1448, 1439, 1389, 1362, 1296, 1275, 1250, 1103, 1072, 1007, 826, 812, 773, 721, 702, 677, 538, 455 cm^{-1}. The stereochemistry was assigned based on ^{1}H NMR NOE experiments.

*4.3.14. (Z)-5-tert-Butyldimethylsilyl-2-isopropyl-3-methylpent-2-en-4-ynenitrile (**3ac**)*

A colorless oil, R_f 0.23 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78 (sept, J=6.8 Hz, 1H), 1.99 (s, 3H), 1.14 (d, J=6.8 Hz, 6H), 0.99 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.0, 126.7, 116.9, 104.4, 100.7, 28.7, 26.2, 21.1, 19.1, 16.8, −4.6; IR (neat) 2957, 2930, 2858, 2212, 2143, 1464, 1364, 1277, 1252, 1026, 926, 876, 839, 824, 810, 777, 689 cm^{-1}. Anal. Calcd for $C_{15}H_{25}NSi$: C, 72.81; H, 10.18. Found (as a mixture with **3′ac**): C, 73.02; H, 10.30. The stereochemistry was assigned based on ^{1}H NMR NOE experiments.

*4.3.15. (Z)-5-tert-Butyldimethylsilyl-3-isopropyl-2-methylpent-2-en-4-ynenitrile (**3′ac**)*

A colorless oil, R_f 0.23 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.77 (sept, J=6.7 Hz, 1H), 1.97 (s, 3H), 1.10 (d, J=6.8 Hz, 6H), 0.99 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 119.4, 112.4, 103.6, 100.7, 29.8, 26.2, 20.9, 16.7, 16.1, −4.6; IR (neat) 2930, 2858, 2216, 2145, 1466, 1364, 1252, 1153, 1043, 1007, 914, 826, 777, 731, 675 cm^{-1}. The stereochemistry was assigned based on ^{1}H NMR NOE experiments, and the regiochemistry was determined by HMBC experiments of **24′ac**.[10]

*4.3.16. (Z)-5-tert-Butyldimethylsilyl-2-diethoxymethyl-3-methylpent-2-en-4-ynenitrile (**3ad**)*

A pale yellow oil, R_f 0.13 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 (s, 1H), 3.71–3.54 (m, 4H), 2.09 (s, 3H), 1.25 (t, J=7.0 Hz, 6H), 0.99 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 119.3, 116.3, 104.6, 103.5, 96.3, 61.7, 26.2, 19.9, 16.7, 15.1, −4.7; IR (neat) 2980, 2955, 2930, 2885, 2856, 2218, 2147, 1591, 1539, 1472, 1462, 1445, 1391, 1364, 1335, 1286, 1252, 1173, 1105, 1061, 1007, 934, 841, 826, 812, 777, 683, 665 cm^{-1}. Anal. Calcd for $C_{17}H_{29}NO_2Si$: C, 66.40; H, 9.51. Found (as a mixture with **3′ad**): C, 66.67; H, 9.35. The stereochemistry was assigned based on NOE experiments of ^{1}H NMR.

*4.3.17. (Z)-5-tert-Butyldimethylsilyl-2-methyl-3-diethoxymethylpent-2-en-4-ynenitrile (**3′ad**)*

A pale yellow oil, R_f 0.10 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 (s, 1H), 3.72–3.63 (m, 2H), 3.60–3.51 (m, 2H), 2.09 (s, 3H), 1.24 (t, J=7.0 Hz, 6H), 0.98 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 118.8, 118.5, 105.1, 100.7, 98.0, 62.1, 26.1, 16.9, 16.8, 15.2, −4.7; IR (neat) 2976, 2955, 2930, 2885, 2858, 2218, 2145, 1578, 1541, 1472, 1462, 1445, 1391, 1373, 1364, 1337, 1286, 1252, 1167, 1113, 1063, 1007, 920, 841, 826, 812, 777 cm^{-1}. The stereochemistry was assigned based on ^{1}H NMR NOE experiments, and the regiochemistry was determined by HMBC experiments of **24′ad**.[10]

*4.3.18. (Z)-3-Diethoxymethyl-2-methylundec-2-en-4-ynenitrile (**3′hd**)*

An orange oil, R_f 0.33 (hexane–ethyl acetate=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.06 (s, 1H), 3.73–3.62 (m, 2H), 3.60–3.50 (m, 2H), 2.44 (t, J=7.0 Hz, 2H), 2.07 (s, 3H), 1.60 (quint, J=7.3 Hz, 2H), 1.52–1.16 (m, 6H), 1.24 (t, J=7.0 Hz, 6H), 0.89 (t, J=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 119.2, 116.1, 102.2, 98.1, 77.1, 62.3, 31.4, 28.6, 28.3, 22.6, 20.2, 16.6, 15.2, 14.2; IR (neat) 2976, 2957, 2932, 2870, 2861, 2209, 1686, 1454, 1373, 1333, 1123, 1063, 764, 725, 696 cm^{-1}. Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.61; H, 9.81. Found: C, 73.73; H, 9.51. The stereochemistry was assigned based on ^{1}H NMR NOE experiments, and the regiochemistry was determined by HMBC experiments of **24′hd**.[10]

*4.3.19. (Z)-5-tert-Butyldimethylsilyl-2-hexylpent-2-en-4-ynenitrile (**3ae**)*

A colorless oil, R_f 0.20 (hexane–ethyl acetate=30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (s, 1H), 2.29 (t, J=7.6 Hz, 2H), 1.62–1.50 (m, 2H), 1.39–1.23 (m, 6H), 0.99 (s, 9H), 0.90 (t, J=6.6 Hz, 3H), 0.18 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 126.0, 123.3, 117.1, 103.9, 100.1, 34.5, 31.5, 28.5, 27.9, 26.1, 22.6, 16.7, 14.1, −4.7; IR (neat) 2930, 2858, 2218, 1464, 1252, 1111, 1074, 841, 826, 812, 777 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{29}NSi$: M^+, 275.2069. Found: m/z 275.2061. The stereochemistry was assigned based on ^{1}H NMR NOE experiments, and the regiochemistry was determined by ^{1}H NMR spectra of **24ae**.[10]

*4.3.20. (Z)-5-tert-Butyldimethylsilyl-3-hexylpent-2-en-4-ynenitrile (**3′ae**)*

A colorless oil, R_f 0.13 (hexane–ethyl acetate=30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 (s, 1H), 2.28 (t, J=7.5 Hz, 2H), 1.60–1.50 (m, 2H), 1.39–1.20 (m, 6H), 1.00 (s, 9H), 0.90 (t, J=6.4 Hz, 3H), 0.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 116.5, 106.2, 103.2, 101.2, 37.4, 31.5, 28.5, 27.7, 26.1, 22.6, 16.7, 14.2, −4.7; IR (neat) 2930, 2858, 2220, 1585, 1466, 1364, 1252, 880, 839, 824, 808, 777 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{29}NSi$: M^+, 275.2069. Found: m/z 275.2069. The stereochemistry was assigned based on NOE experiments of ^{1}H NMR.

*4.3.21. (Z)-5-tert-Butyldimethylsilyl-2-(3-chloroprop-1-yl)pent-2-en-4-ynenitrile (**3af**)*

A pale yellow oil, R_f 0.20 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (t, J=1.3 Hz, 1H), 3.56 (t, J=6.1 Hz, 2H), 2.49 (td, J=7.2, 1.0 Hz, 2H), 2.03 (quint, J=6.7 Hz, 2H), 0.97 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 124.8, 123.6, 116.6, 105.0, 99.7, 43.2, 31.2, 30.2, 26.1, 16.6, −4.8; IR (neat) 2955, 2930, 2858, 2218, 1593, 1472, 1462, 1445, 1364, 1252, 1092, 1007, 841, 826, 777, 694, 681 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{22}ClNSi$: M^+, 267.1210. Found: m/z 267.1213. The stereochemistry was assigned based on NOE experiments of ^{1}H NMR.

*4.3.22. (Z)-3-tert-Butyldimethylsilylethynyl-6-chloropent-2-enenitrile (**3′af**)*

A pale yellow oil, R_f 0.15 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 (t, J=1.4 Hz, 1H), 3.56 (t, J=6.2 Hz, 2H), 2.48 (td, J=7.2, 1.2 Hz, 2H), 2.06 (quint, J=7.0 Hz, 2H), 0.99 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 116.1, 107.1, 104.5, 100.5, 43.4, 34.2, 30.3, 26.1, 16.7, −4.8; IR (neat) 2955, 2930, 2858, 2220, 1587, 1472, 1445, 1364, 1252, 885, 866, 841, 824, 808, 779, 681 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{22}ClNSi$: M^+, 267.1210. Found: m/z 267.1209.

*4.3.23. (Z)-8-tert-Butyldimethylsilyl-5-cyanopent-5-en-6-ynenitrile (**3ag**)*

A pale brown oil, R_f 0.15 (hexane–ethyl acetate=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (s, 1H), 2.47 (t, J=7.5 Hz, 2H), 2.41 (t, J=7.0 Hz, 2H), 1.93 (quint, J=7.2, 2H), 0.96 (s, 9H), 0.16 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 125.3, 122.7, 118.3, 116.2, 105.7, 99.5, 32.6, 26.0, 23.4, 16.6, 16.2, −4.9; IR (neat) 2955, 2930, 2858, 2247, 2218, 1595, 1462, 1364, 1252, 1094, 841, 826, 812, 777, 681 cm^{-1}. Anal. Calcd for $C_{15}H_{22}N_2Si$: C, 69.71; H, 8.58. Found: C, 69.84; H, 8.68. The stereochemistry was assigned based on NOE experiments of ^{1}H NMR.

*4.3.24. (Z)-3-tert-Butyldimethylsilylethynylhept-2-enedinitrile (**3′ag**)*

A pale brown oil, R_f 0.10 (hexane–ethyl acetate=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (t, J=1.3 Hz, 1H), 2.47 (td, J=5.3, 1.3 Hz, 2H), 2.41 (t, J=7.0 Hz, 2H), 1.97 (quint, J=7.2, 2H), 0.99 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 118.4, 115.8, 107.9, 105.1, 100.0, 35.5, 26.1, 23.5, 16.7, 16.4, −4.8; IR (neat) 3055, 2953, 2930, 2858, 2247, 2220, 2147, 1589, 1464, 1364, 1252, 1157, 1007, 874, 841, 824, 808, 779, 681, 478 cm^{-1}; HRMS (FAB$^+$) calcd for $C_{15}H_{23}N_2Si$: $[M+H]^+$, 259.1631. Found: m/z 259.1635.

*4.3.25. Methyl (Z)-8-tert-butyldimethylsilyl-5-cyano-oct-5-en-7-ynoate (**3ah**)*

A colorless oil, R_f 0.13 (hexane–ethyl acetate=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (t, J=1.4 Hz, 1H), 3.64 (s, 3H), 2.32 (t, J=7.2 Hz, 4H), 1.87 (quint, J=7.4, 2H), 0.94 (s, 9H), 0.13 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 124.5, 124.1, 116.6, 104.5, 99.8, 51.6, 33.3, 32.4, 26.0, 23.0, 16.5, −4.9; IR (neat) 2953, 2930, 2858, 2218, 1740, 1437, 1364, 1252, 1202, 1173, 1094, 1007, 841, 826, 812, 777, 683 cm^{-1}. Anal. Calcd for $C_{16}H_{25}NO_2Si$: C, 65.93; H, 8.65. Found (as a mixture with **3′ah**): C, 66.18; H, 8.66. The stereochemistry was assigned based on NOE experiments of ^{1}H NMR.

*4.3.26. Methyl (Z)-7-tert-butyldimethylsilyl-5-cyanomethylenehept-6-ynoate (**3′ah**)*

A colorless oil, R_f 0.10 (hexane–ethyl acetate=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 (s, 1H), 3.69 (s, 3H), 2.40–2.31 (m, 4H), 1.92 (quint, J=7.5 Hz, 2H), 0.99 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 145.4, 116.2, 106.9, 104.1, 100.7, 51.7, 36.3, 32.7, 26.1, 23.0, 16.7, −4.8; IR (neat) 2953, 2930, 2858, 2220, 1740, 1587, 1462, 1437, 1364, 1252, 1175, 1150, 1007, 872, 841, 824, 808, 779, 681 cm^{-1}.

*4.3.27. (Z)-5-tert-Butyldimethylsilyl-2-(cyclohexen-1-yl)pent-2-en-4-ynenitrile (**3ai**)*

A colorless solid, mp 71.3–72.7 °C, R_f 0.35 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46 (td, J=4.4, 0.6 Hz, 1H), 6.03 (d, J=0.7 Hz, 1H), 2.30–2.21 (m, 2H), 2.14–2.05 (m, 2H), 1.76–1.56 (m, 4H), 0.99 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.1, 131.4, 127.2, 116.3, 115.4, 106.2, 101.5, 26.1, 24.5, 22.1, 21.7, 16.7, −4.7; IR (KBr) 3032, 2930, 2856, 2226, 2129, 1620, 1470, 1462, 1448, 1433, 1362, 1254, 1096, 1080, 824, 681 cm^{-1}. Anal. Calcd for $C_{17}H_{25}NSi$: C, 75.21; H, 9.28. Found: C, 75.06; H, 9.20. The stereochemistry was assigned based on ^{1}H NMR NOE experiments. The regiochemistry was assigned based on ^{1}H NMR experiments of **24ai**.[10]

*4.3.28. (Z)-5-tert-Butyldimethylsilyl-3-(cyclohexen-1-yl)pent-2-en-4-ynenitrile (**3′ai**)*

A pale yellow oil, R_f 0.38 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54–6.48 (m, 1H), 6.11 (s, 1H), 2.62–2.52 (m,

2H), 2.29–2.19 (m, 2H), 1.73–1.55 (m, 4H), 0.95 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.6, 132.3, 126.0, 118.6, 117.9, 109.7, 101.6, 27.3, 26.1, 26.0, 22.3, 21.4, 16.9, −4.8; IR (neat) 2930, 2858, 2224, 1616, 1556, 1470, 1462, 1433, 1250, 1194, 1092, 1072, 839, 824, 810, 777, 685, 633 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{25}NSi$: M^+, 271.1756. Found: *m*/*z* 271.1764.

4.3.29. (*Z*)-5-tert-Butyldimethylsilyl-2,3-di(4-methoxyphenyl)-pent-2-en-4-ynenitrile [(*Z*)-**3aj**]

A yellow oil, R_f 0.33 (hexane–ethyl acetate=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J*=8.6 Hz, 2H), 7.17 (d, *J*=8.4 Hz, 2H), 6.76 (d, *J*=8.6 Hz, 2H), 6.75 (d, *J*=8.4 Hz, 2H), 3.80 (s, 6H), 1.03 (s, 9H), 0.23 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 159.7, 134.7, 131.0, 130.7, 127.4, 125.3, 119.3, 117.2, 114.0, 113.6, 104.5, 55.3, 31.7, 26.3, 16.9, −4.6; IR (neat) 2953, 2930, 2899, 2857, 2209, 2141, 1605, 1574, 1512, 1505, 1470, 1462, 1443, 1416, 1362, 1323, 1298, 1287, 1254, 1177, 1128, 1105, 1032, 1013, 984, 939, 878, 833, 812, 799, 777, 694, 683, 654, 633, 602, 571 cm^{-1}. Anal. Calcd for $C_{25}H_{29}NO_2Si$: C, 74.40; H, 7.24. Found: C, 74.22; H, 7.24.

4.3.30. (*E*)-5-tert-Butyldimethylsilyl-2,3-di(4-methoxyphenyl)-pent-2-en-4-ynenitrile [(*E*)-**3aj**]

A colorless crystal, mp 96.2–96.4 °C, R_f 0.40 (hexane–ethyl acetate=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J*=9.0 Hz, 2H), 7.73 (d, *J*=9.0 Hz, 2H), 6.96 (d, *J*=9.0 Hz, 2H), 6.92 (d, *J*=9.1 Hz, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 0.92 (s, 9H), 0.14 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 160.1, 134.3, 130.23, 130.17, 129.4, 126.5, 119.3, 116.4, 113.7, 113.5, 108.8, 103.9, 55.44, 55.40, 26.2, 16.9, −4.8; IR (KBr) 2951, 2930, 2857, 2205, 1605, 1578, 1541, 1512, 1466, 1441, 1418, 1360, 1323, 1306, 1277, 1256, 1179, 1113, 1078, 1047, 1022, 937, 837, 777, 768, 704, 681, 586, 540, 527 cm^{-1}. Anal. Calcd for $C_{25}H_{29}NO_2Si$: C, 74.40; H, 7.24. Found: C, 74.56; H, 7.27. The stereochemistry was assigned based on X-ray crystallography. Colorless single crystals were obtained by recrystallization from methanol suitable for X-ray crystallographic analysis.

4.3.31. (*Z*)-5-tert-Butyldimethylsilyl-2-phenylpent-2-en-4-ynenitrile [(*Z*)-**3ak**]

A colorless solid, mp 75.1–75.9 °C, R_f 0.22 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.54 (m, 2H), 7.46–7.38 (m, 3H), 6.64 (s, 1H), 1.04 (s, 9H), 0.24 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.0, 130.1, 129.0, 125.5, 124.8, 120.8, 116.0, 108.3, 101.1, 26.2, 16.8, −4.7; IR (KBr) 3065, 3051, 3038, 3013, 2947, 2928, 2885, 2856, 2222, 2139, 1936, 1871, 1740, 1582, 1497, 1472, 1464, 1448, 1410, 1391, 1364, 1327, 1257, 1248, 1101, 1005, 978, 939, 908, 872, 829, 810, 772, 754, 679, 596, 502, 476, 434, 422 cm^{-1}. Anal. Calcd for $C_{17}H_{21}NSi$: C, 76.35; H, 7.91. Found [as a mixture with (*E*)-**3ak** and **3′ak**]: C, 76.45; H, 7.87. The stereochemistry was assigned based on ^{1}H NMR NOE experiments. The regiochemistry was determined by ^{1}H NMR experiments of (*Z*)-**24ak**.[10]

4.3.32. (*E*)-5-tert-Butyldimethylsilyl-2-phenylpent-2-en-4-ynenitrile [(*E*)-**3ak**]

A pale yellow oil, R_f 0.30 (hexane–ethyl acetate=30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–7.98 (m, 2H), 7.44–7.39 (m, 3H), 6.46 (s, 1H), 0.97 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.7, 130.2, 128.3, 127.9, 123.5, 121.1, 118.8, 111.5, 101.0, 26.1, 16.9, −4.8; IR (neat) 2953, 2928, 2897, 2856, 2218, 1583, 1560, 1541, 1497, 1470, 1445, 1412, 1364, 1252, 1202, 1086, 1070, 1007, 839, 824, 812, 770, 689, 667 cm^{-1}; The stereo- and regiochemistry was assigned based on ^{1}H NMR NOE experiments of (*E*)-**24ak**.[10]

4.3.33. (*Z*)-5-tert-Butyldimethylsilyl-3-phenylpent-2-en-4-ynenitrile (**3′ak**)

A colorless solid, mp 58.7–59.2 °C, R_f 0.15 (hexane–ethyl acetate=30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.64 (m, 2H), 7.49–7.41 (m, 3H), 6.00 (s, 1H), 1.05 (s, 9H), 0.27 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 134.1, 130.8, 128.7, 126.6, 117.1, 107.8, 101.2, 100.1, 26.2, 16.8, −4.7; IR (KBr) 3055, 2949, 2926, 2883, 2855, 2214, 2152, 1618, 1582, 1556, 1493, 1470, 1450, 1408, 1389, 1360, 1344, 1333, 1313, 1252, 1184, 1067, 1026, 1005, 970, 947, 835, 804, 768, 692, 679, 664, 642, 592, 517, 444, 413 cm^{-1}. The stereochemistry was assigned based on ^{1}H NMR NOE experiments.

4.3.34. (*Z*)-5-tert-Butyldimethylsilyl-2-(4-methoxyphenyl)pent-2-en-4-ynenitrile [(*Z*)-**3al**]

A yellow solid, mp 55.7–56.3 °C, R_f 0.12 (hexane–ethyl acetate=30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J*=9.0 Hz, 2H), 6.92 (d, *J*=9.0 Hz, 2H), 6.51 (s, 1H), 3.84 (s, 3H), 1.02 (s, 9H), 0.22 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 127.0, 124.6, 124.4, 118.2, 116.2, 114.4, 107.0, 101.4, 55.5, 26.2, 16.8, −4.7; IR (KBr) 3059, 3032, 3007, 2926, 2855, 2224, 2133, 1879, 1744, 1609, 1576, 1512, 1464, 1443, 1421, 1410, 1391, 1362, 1333, 1319, 1285, 1254, 1186, 1119, 1101, 1034, 1011, 974, 937, 876, 824, 810, 773, 754, 681, 637, 625, 588, 519 cm^{-1}. Anal. Calcd for $C_{18}H_{23}NOSi$: C, 72.68; H, 7.79. Found [as a mixture with (*E*)-**3al**]: C, 72.62; H, 7.79. The stereochemistry was determined by ^{1}H NMR NOE experiments, and the regiochemistry was assigned based on ^{1}H NMR experiments of (*Z*)-**24al**.[10]

4.3.35. (*E*)-5-tert-Butyldimethylsilyl-2-(4-methoxyphenyl)pent-2-en-4-ynenitrile [(*E*)-**3al**]

A pale yellow oil, R_f 0.13 (hexane–ethyl acetate=30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J*=8.8 Hz, 2H), 6.91 (d, *J*=9.0 Hz, 2H), 6.32 (s, 1H), 3.86 (s, 3H), 0.98 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 129.5, 124.5, 122.9, 119.0, 118.3, 113.7, 110.6, 101.5, 55.5, 26.2, 16.9, −4.8; IR (neat) 2953, 2930, 2897, 2856, 2218, 1605, 1580, 1555, 1514, 1464, 1443, 1420, 1364, 1304, 1259, 1205, 1182, 1078, 1049, 1028, 1007, 939, 835, 831, 810, 777, 685, 631, 519 cm^{-1}; The stereo- and regiochemistry was assigned based on ^{1}H NMR NOE experiments of (*E*)-**24al**.[10]

4.3.36. (*Z*)-5-tert-Butyldimethylsilyl-2-(4-cyanophenyl)pent-2-en-4-ynenitrile [(*Z*)-**3am**]

A colorless solid, mp 113.7–114.2 °C, R_f 0.20 (hexane–ethyl acetate=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J*=8.8 Hz, 2H), 7.67 (d, *J*=8.8 Hz, 2H), 6.76 (s, 1H), 1.01 (s, 9H), 0.22 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 132.7, 126.0, 124.0, 123.0, 117.8, 115.2, 113.6, 111.9, 100.5, 26.1, 16.8, −4.8; IR (KBr) 3098, 3065, 3026, 2953, 2926, 2885, 2856, 2230, 2135, 1935, 1605, 1572, 1558, 1506, 1470, 1462, 1441, 1416, 1391, 1362, 1333, 1319, 1252, 1186, 1097, 1005, 976, 937, 889, 841, 812, 779, 683, 602, 550, 479, 453, 426 cm^{-1}. Anal. Calcd for $C_{18}H_{20}N_2Si$: C, 73.92; H, 6.89. Found: C, 73.73; H, 6.89. The stereochemistry was assigned based on ^{1}H NMR NOE experiments, and the regiochemistry was assigned based on ^{1}H NMR experiments of (*Z*)-**24am**.[10]

4.3.37. (*E*)-5-tert-Butyldimethylsilyl-2-(4-cyanophenyl)pent-2-en-4-ynenitrile [(*E*)-**3am**]

A colorless oil, R_f 0.25 (hexane–ethyl acetate=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J*=8.6 Hz, 2H), 7.71 (d, *J*=8.4 Hz, 2H), 6.61 (s, 1H), 0.97 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.8, 132.1, 128.4, 124.1, 121.6, 117.9, 117.8, 114.7, 113.6, 100.3, 26.1, 16.9, −4.9; IR (neat) 3021, 2953, 2930, 2886, 2859, 2232, 1609, 1578, 1547, 1508, 1470, 1464, 1408, 1364, 1252, 1207, 1078, 1007, 912, 843, 824, 812, 779, 735, 685, 631, 540 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{20}N_2Si$: M^+, 293.1474. Found: *m*/*z* 293.1463. The stereo- and regiochemistry was assigned based on ^{1}H NMR NOE experiments of (*E*)-**24am**.[10]

4.4. Sythesis of *trans*-(xantphos)Ni(CNBPh$_3$)(C≡CSiMe$_2$*t*-Bu) (4)

To a benzene solution (3.5 mL) of $Ni(cod)_2$ (138 mg, 0.50 mmol) and xantphos (145 mg, 0.50 mmol) placed in a vial were added **1a**

(83 mg, 0.50 mmol) and BPh_3 (121 mg, 0.50 mmol) in a dry box at room temperature. The vial was shaken vigorously to give a homogeneous solution within 10 min. The resulting dark red solution was concentrated in vacuo, and the resulting precipitates were washed with hexane to give the title compound (439 mg, 84%) as a brown powder. ^{1}H NMR (400 MHz, C_6D_6) δ 8.10–7.96 (br m, 4H), 7.55 (q, J=6.2 Hz, 4H), 7.30–6.94 (m, 25H), 6.86 (t, J=7.5 Hz, 2H), 6.76 (t, J=7.6 Hz, 2H), 6.70 (t, J=7.7 Hz, 4H), 1.49 (s, 3H), 1.26 (s, 3H), 0.36 (s, 9H), −0.46 (s, 6H); ^{13}C NMR (101 MHz, C_6D_6) δ 155.9 (t, J_{C-P}=5.9 Hz), 155.3 (br, s), 136.3 (t, J_{C-P}=6.1 Hz), 136.1, 135.1, 133.8 (t, J_{C-P}=23.0 Hz), 133.6 (t, J_{C-P}=5.8 Hz), 131.9, 131.5, 131.3, 129.9 (t, J_{C-P}=5.0 Hz), 129.2 (t, J_{C-P}=5.4 Hz), 128.5, 128.2, 127.4, 125.1, 125.0, 124.8 (t, J_{C-P}=26.8 Hz), 122.8 (t, J_{C-P}=44.1 Hz), 37.1, 33.9, 27.1, 24.5, 17.1, −3.1; ^{31}P NMR (121 MHz, C_6D_6) δ 15.7 (s); IR (KBr) 3414, 3061, 2953, 2924, 2851, 2180, 2035, 1586, 1481, 1435, 1404, 1242, 1213, 1096, 826, 745, 702, 617, 530, 519, 471 cm^{-1}. Dark red single crystals suitable for X-ray crystallographic assay were obtained by recrystallization from hexane and dichloromethane.

4.5. Alkynylcyanation of 1,2-dienes. A general procedure

In a dry box, a 1.00 M solution of **1a** (132 mg, 0.80 mmol) and a 1,2-diene (0.80 mmol) in toluene (0.80 mL) and a solution of BPh_3 (11.6 mg, 48 μmol) in toluene (0.40 mL) were added successively to a solution of Ni(cod)$_2$ (4.4 mg, 16 μmol) and xantphos (9.3 mg, 16 μmol) in toluene (0.40 mL) placed in a vial. The vial was taken outside the dry box and heated at 50 °C for the time specified in Table 5. The resulting mixture was filtered through a silica gel pad, concentrated in vacuo, and purified by flash column chromatography on silica gel to give the corresponding alkynylcyanation products in yields listed in Table 5.

4.5.1. 2-(4-tert-Butyldimethylsilyl-1-buten-3-yl)octanenitrile (**15a**)

A pale yellow oil, R_f 0.23 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (s, 1H), 5.61 (s, 1H), 3.31 (t, J=7.0 Hz, 1H), 1.94–1.78 (m, 2H), 1.56–1.22 (m, 8H), 0.96 (s, 9H), 0.90 (t, J=6.9 Hz, 3H), 0.153 (s, 3H), 0.150 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 126.2, 124.2, 119.0, 102.0, 96.0, 38.3, 31.9, 31.5, 28.7, 26.5, 26.2, 22.6, 16.8, 14.2, −4.6; IR (neat) 2955, 2930, 2858, 2247, 2152, 1612, 1466, 1364, 1252, 1007, 914, 839, 826, 810, 777, 737, 681 cm^{-1}. Anal. Calcd for $C_{18}H_{31}NSi$: C, 74.67; H, 10.79. Found (as a mixture with **15′a**): C, 74.96; H, 10.76.

4.5.2. (Z)-3-(tert-Butyldimethylsilylethynyl)dec-3-enenitrile (**15′a**)

A pale yellow oil, R_f 0.10 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (tt, J=7.5, 1.4 Hz, 1H), 3.20 (d, J=1.1 Hz, 2H), 2.32 (q, J=7.4 Hz, 2H), 1.48–1.24 (m, 8H), 0.97 (s, 9H), 0.90 (t, J=6.8 Hz, 3H), 0.10 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 116.6, 112.2, 101.1, 99.1, 31.7, 30.8, 29.0, 28.6, 26.2, 25.0, 22.7, 16.7, 14.2, −4.5; IR (neat) 2955, 2930, 2856, 2147, 1464, 1252, 1007, 839, 810, 777, 683 cm^{-1}.

4.5.3. 5-tert-Butyldimethylsilyl-3-methylene-2-(2-phenylethyl)-pent-4-ynenitrile (**15b**)

A colorless oil, R_f 0.57 (hexane–ethyl acetate=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.28 (m, 2H), 7.26–7.18 (m, 3H), 5.66 (d, J=0.73 Hz, 1H), 5.64 (s, 1H), 3.32–3.25 (m, 1H), 2.90–2.72 (m, 2H), 2.30–2.10 (m, 2H), 0.96 (s, 9H), 0.160 (s, 3H), 0.155 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 128.5, 128.3, 126.3, 125.8, 124.6, 118.7, 101.8, 96.3, 37.5, 33.6, 32.6, 26.2, 16.7, −4.6; IR (neat) 3028, 2953, 2930, 2856, 2149, 1605, 1497, 1472, 1456, 1362, 1250, 914, 839, 826, 777, 748, 700 cm^{-1}. Anal. Calcd for $C_{20}H_{27}NSi$: C, 77.61; H, 8.79. Found: C, 77.79; H, 8.56.

4.5.4. (Z)-3-(tert-Butyldimethylsilylethynyl)-6-phenylhex-3-enenitrile (**15′b**)

A colorless oil, R_f 0.50 (hexane–ethyl acetate=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.26 (m, 2H), 7.23–7.16 (m, 3H), 6.10 (tt, J=7.3, 1.5 Hz, 1H), 3.19 (d, J=1.5 Hz, 2H), 2.78–2.71 (m, 2H), 2.70–2.61 (m, 2H), 0.97 (s, 9H), 0.16 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.84, 140.80, 128.3, 128.2, 125.9, 116.4, 113.1, 100.8, 99.7, 34.8, 32.5, 26.2, 25.0, 16.7, −4.5; IR (neat) 2953, 2930, 2856, 2253, 2149, 1497, 1458, 1364, 1252, 1007, 839, 777, 700 cm^{-1}. Anal. Calcd for $C_{20}H_{27}NSi$: C, 77.61; H, 8.79. Found: C, 77.83; H, 8.86. The stereochemistry was assigned based on ^{1}H NMR NOE experiments.

4.5.5. 5-tert-Butyldimethylsilyl-2-(2-tert-butyldimethylsiloxyethy-1-yl)-3-methylenepent-4-ynenitrile (**15c**)

A pale yellow oil, R_f 0.20 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 (t, J=0.82 Hz, 1H), 5.61 (s, 1H), 3.82–3.71 (m, 2H), 3.59 (dd, J=9.0, 5.9 Hz, 1H), 2.18–2.08 (m, 1H), 2.00–1.90 (m, 1H), 0.96 (s, 9H), 0.91 (s, 9H), 0.151 (s, 3H), 0.148 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 126.0, 124.5, 118.9, 101.8, 96.1, 59.2, 35.1, 34.9, 26.2, 25.9, 18.3, 16.7, −4.6, −5.26, −5.30; IR (neat) 2955, 2930, 2858, 2154, 1610, 1472, 1389, 1362, 1254, 1109, 1007, 939, 914, 837, 812, 777, 681 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{34}ONSi_2$: [M−Me]$^+$, 348.2179. Found: m/z 348.2191.

4.5.6. 3-(tert-Butyldimethylsilylethynyl)-6-(tert-butyldimethylsiloxy)hex-3-enenitrile (**15′c**, E/Z=11:89)

A pale yellow oil, R_f 0.08 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (tt, J=7.3, 1.5 Hz, 0.89H), 5.75 (tt, J=4.8, 2.4 Hz, 0.11H), 3.69 (t, J=6.6 Hz, 1.78H), 3.68 (t, J=6.6 Hz, 0.22H), 3.21 (d, J=1.5 Hz, 1.78H), 3.05 (d, J=2.2 Hz, 0.22H), 2.55 (dt, J=7.3, 6.6 Hz, 1.78H), 2.37 (dt, J=7.3, 6.2 Hz, 0.22H), 1.04 (s, 0.99H), 0.99 (s, 0.99H), 0.97 (s, 8.01H), 0.90 (s, 8.01H), 0.39 (s, 0.66H), 0.36 (s, 0.66H), 0.15 (s, 5.34H), 0.07 (s, 5.34H); ^{13}C NMR (for *Z*-isomer, 101 MHz, $CDCl_3$) δ 138.7, 116.4, 113.7, 100.9, 99.6, 61.7, 34.5, 26.2, 26.0, 25.2, 18.4, 16.7, −4.5, −5.1; IR (neat) 2955, 2930, 2858, 2149, 1472, 1416, 1389, 1362, 1256, 1103, 939, 837, 810, 777, 685 cm^{-1}. Anal. Calcd for $C_{20}H_{37}NOSi_2$: C, 66.05; H, 10.25. Found: C, 66.15; H, 10.26.

4.5.7. 5-tert-Butyldimethylsilyl-2-cyclohexyl-3-methylpent-4-ynenitrile (**15d**)

A yellow oil, R_f 0.25 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 (t, J=0.6 Hz, 1H), 5.63 (dd, J=1.2, 0.6 Hz, 1H), 3.18 (d, J=5.0 Hz, 1H), 2.00–1.62 (m, 6H), 1.36–1.04 (m, 5H), 0.96 (s, 9H), 0.153 (s, 3H), 0.149 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 125.2, 125.0, 118.1, 102.3, 95.9, 45.1, 38.9, 31.4, 28.9, 26.19, 26.15, 25.9, 16.8, −4.6; IR (neat) 2930, 2856, 2249, 2149, 1470, 1450, 1362, 1252, 1007, 939, 839, 777, 683 cm^{-1}; HRMS (FAB$^+$) calcd for $C_{18}H_{30}NSi$: [M+H]$^+$, 288.2148. Found: m/z 288.2158.

4.5.8. (Z)-5-tert-Butyldimethylsilyl-3-butyldimethylsilyl-methylenepent-4-ynentirile (**15′e**)

A colorless oil, R_f 0.25 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (t, J=1.6 Hz, 1H), 3.30 (d, J=1.6 Hz, 2H), 1.40–1.24 (m, 4H), 0.96 (s, 9H), 0.90 (t, J=7.0 Hz, 3H), 0.75–0.40 (m, 2H), 0.19 (s, 6H), 0.15 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 126.2, 116.3, 103.8, 98.5, 29.0, 26.6, 26.2, 26.1, 16.8, 15.0, 14.0, −2.9, −4.7; IR (neat) 2955, 2930, 2858, 2143, 1578, 1472, 1464, 1414, 1250, 1111, 839, 826, 810, 777, 677 cm^{-1}. Anal. Calcd for $C_{18}H_{33}NSi_2$: C, 67.64; H, 10.41. Found: C, 67.44; H, 10.63. The stereochemistry was assigned based on ^{1}H NMR NOE experiments.

4.6. Alkynylcyanation of norbornadiene (21)

Alkynyl cyanide **1a** (165 mg, 1.00 mmol), **21** (92 mg, 1.00 mmol), and $C_{14}H_{29}$ (internal standard, 99 mg, 0.50 mmol) were added sequentially to a solution of Ni(cod)$_2$ (5.5 mg, 20 μmol) and xantphos (11.6 mg, 20 μmol) in toluene (1.00 mL) in a dry box. The vial was taken outside the dry box and heated at 80 °C for 17 h. The resulting mixture was filtered through a silica gel pad, concentrated in vacuo,

and purified by flash column chromatography on silica gel to give (5*R**,6*S**)-6-(*tert*-butyldimethylsilylethynyl)-5-cyanobicyclo[2.2.1]-hept-2-ene (**22**, 0.23 g, 89%) as an colorless solid, R_f 0.20 (hexane–ethyl acetate=20:1), mp 58.9–59.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 (dd, *J*=5.6, 3.0 Hz, 1H), 6.11 (dd, *J*=5.7, 3.1 Hz, 1H), 3.28 (s, 1H), 3.10 (s, 1H), 2.60 (dd, *J*=8.6, 2.1 Hz, 1H), 2.56 (dd, *J*=8.5, 1.8 Hz, 1H), 1.95 (d, *J*=9.5 Hz, 1H), 1.65 (dt, *J*=9.5, 1.9 Hz, 1H), 0.97 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 135.6, 120.2, 105.5, 87.7, 50.0, 48.1, 46.0, 35.5, 35.2, 26.2, 16.7, −4.4; IR (KBr) 2994, 2953, 2928, 2884, 2857, 2234, 2174, 1472, 1460, 1410, 1387, 1360, 1331, 1317, 1250, 1072, 1007, 939, 922, 912, 901, 837, 827, 775, 745, 714, 679, 631, 583, 529, 476 cm^{-1}. Anal. Calcd for $C_{16}H_{23}NSi$: C, 74.65; H, 9.00. Found: C, 74.74; H, 8.93. The stereochemistry was assigned based on ^{1}H NMR NOE experiments of **23**.

4.7. Reduction of 22 with DIBAL-H

To a solution of **22** (26 mg, 0.100 mmol) in toluene (1.00 mL) was added a 1.5 M solution of DIBAL-H (170 μL, 0.25 mmol) in toluene at −78 °C, and the resulting mixture was stirred at the same temperature for 1 h. The reaction was quenched with MeOH at −78 °C, and the resulting mixture was warmed to room temperature. The mixture was diluted with CH_2Cl_2 and filtered through a glass filter. The filtrate was concentrated in vacuo. The residue was purified by flash chromatography on silica gel (hexane–ethyl acetate=50:1 as an eluent) to give (5*R**,6*S**)-6-(*tert*-butyldimethylsilylethynyl)-5-formylbicyclo[2.2.1]hept-2-ene (**23**, 21 mg, 82%) as a colorless oil, R_f 0.28 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (d, *J*=2.9 Hz, 1H), 6.17 (m, 2H), 3.17 (s, 1H), 3.06 (s, 1H), 2.67 (dd, *J*=9.1, 1.8 Hz, 1H), 2.27 (dt, *J*=9.3, 2.3 Hz, 1H), 1.81 (d, *J*=9.1 Hz, 1H), 1.54 (dt, *J*=9.1, 1.8 Hz, 1H), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.7, 137.1, 136.9, 106.5, 87.0, 52.6, 50.2, 45.3, 43.7, 33.5, 26.1, 16.6, −4.4; IR (neat) 2953, 2928, 2884, 2857, 2729, 2172, 1724, 1472, 1462, 1391, 1362, 1329, 1250, 1076, 1007, 907, 839, 826, 812, 775, 733, 710, 681, 617 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{15}OSi$: [M−*t*-Bu]$^+$, 203.0892. Found: *m*/*z* 203.0885.

4.8. Reduction of 3da with DIBAL-H

To a solution of **3da** (48 mg, 0.20 mmol) in toluene (2.0 mL) was added a 1.5 M solution of DIBAL-H (0.33 mL, 0.5 mmol) in toluene at −78 °C, and the resulting mixture was stirred at the same temperature for 2 h before quenching with MeOH at −78 °C. The mixture was warmed to room temperature, diluted with CH_2Cl_2, and filtered through a glass filter. The filtrate was concentrated in vacuo to give a residue, which was purified by flash chromatography on silica gel (hexane–ethyl acetate 50:1) to give (*Z*)-3-phenylethynyl-2-propylhex-2-en-4-ynal (**24da**, 44 mg, 90%) as a yellow oil, R_f 0.53 (hexane–ethyl acetate=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.4 (s, 1H), 7.55–7.44 (m, 2H), 7.40–7.32 (m, 3H), 2.48 (t, *J*=7.7 Hz, 2H), 2.33 (t, *J*=7.8 Hz, 2H), 1.76 (sext, *J*=7.5 Hz, 2H), 1.39 (sext, *J*=7.6 Hz, 2H), 1.03 (t, *J*=7.4 Hz, 3H), 0.94 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 145.5, 142.9, 131.6, 129.1, 128.5, 122.4, 99.7, 86.3, 35.9, 27.0, 22.4, 21.5, 14.2, 13.9; IR (neat) 2963, 2932, 2872, 2195, 1672, 1599, 1578, 1489, 1458, 1443, 1256, 1225, 1138, 756, 691 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{20}O$: M$^+$, 240.1514. Found: *m*/*z* 240.1517.

4.9. Reaction of 24da with a *p*-tolyl Grignard reagent

A solution of *p*-tolylmagnesium bromide in diethyl ether (ca. 1.20 mmol) was added to a solution of **24da** (96 mg, 0.40 mmol) in diethyl ether (2.0 mL) at 0 °C, and the resulting mixture was stirred at 0 °C for 2 h before quenching with a saturated NH_4Cl aqueous solution. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with a saturated NH_4Cl aqueous solution and brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (hexane–ethyl acetate=10:1 as an eluent) to give (*Z*)-3-phenylethynyl-2-propyl-1-*p*-tolylpent-2-en-1-ol[16d] (**25**, 110 mg, 83%) as a yellow oil, R_f 0.13 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.41 (m, 2H), 7.41 (d, *J*=8.1 Hz, 2H), 7.36–7.27 (m, 3H), 7.16 (d, *J*=8.1 Hz, 2H), 6.29 (s, 1H), 2.36 (s, 3H), 2.27 (t, *J*=7.6 Hz, 2H), 2.20–1.97 (m, 3H), 1.72 (sext, *J*=7.5 Hz, 2H), 1.48–1.32 (m, 1H), 1.20–1.05 (m, 1H), 1.00 (t, *J*=7.4 Hz, 3H), 0.86 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 139.6, 136.5, 131.3, 128.8, 128.3, 127.9, 125.3, 123.6, 120.8, 93.4, 89.3, 75.2, 34.0, 29.8, 23.8, 21.8, 21.1, 14.8, 13.9; IR (neat) 2959, 2930, 2870, 1504, 1495, 1454, 1111, 1034, 818, 754, 691 cm^{-1}.

4.10. Desilylation of 15b

To a solution of **15b** (0.43 g, 1.40 mmol) in THF (28 mL) were added AcOH (0.23 g, 3.8 mmol) and a 1.0 M solution of TBAF (2.8 mL, 2.8 mmol) in THF successively at 0 °C. The resulting reaction mixture was warmed to room temperature and further stirred for 1 h before quenching with water. The aqueous layer was extracted three times with diethyl ether. The combined organic layers were washed with water and brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (hexane–ethyl acetate=40:1 as an eluent) to give 3-methylene-2-(2-phenylethyl)-pent-4-ynenitrile (**26**, 0.21 g, 77%) as a pale yellow oil, R_f 0.44 (hexane–ethyl acetate=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.28 (m, 2H), 7.27–7.19 (m, 3H), 5.72 (d, *J*=0.73 Hz, 1H), 5.71 (s, 1H), 3.31 (t, *J*=7.1 Hz, 1H), 3.06 (s, 1H), 2.90–2.73 (m, 2H), 2.28–2.13 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 128.5, 128.3, 126.4, 125.9, 125.0, 118.6, 80.2, 80.1, 37.4, 33.3, 32.6; IR (neat) 3285, 3028, 2930, 2864, 2243, 1616, 1603, 1497, 1454, 1030, 922, 750, 700 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{13}N$: M$^+$, 195.1048. Found: *m*/*z* 195.1046.

4.11. Stannylative cross-cyclodimerization of 26 with ethyl (*Z*)-2-undecen-4-ynoate (27)

To a solution of Cp(π-allyl)Pd (1.06 mg, 5.0 μmol) in THF (0.60 mL) were added *N*-(2-diphenylphosphinobenzylidene)cyclohexylamine (**28**) (3.7 mg, 10.0 μmol), $(Bu_3Sn)_2O$ (60 mg, 0.100 mmol), **26** (59 mg, 0.30 mmol), and ethyl (*Z*)-2-undecen-4-ynoate (**27**) (63 mg, 0.30 mmol) sequentially. The resulting mixture was stirred at 50 °C for 24 h, filtered through a Florisil pad, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (hexane–ethyl acetate=30:1 with 0.2% Et_3N as an eluent) followed by preparative GPC gave ethyl (*Z*)-3-[2-hexyl-4-(1-cyano-3-phenylprop-1-yl)-5-(tributylstannyl)phenyl]-2-propenoate (**29**, 74 mg, 53%) as a pale yellow oil, R_f 0.30 (hexane–ethyl acetate=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.20 (m, 7H), 7.15 (d, *J*=11.7 Hz, 1H), 6.03 (d, *J*=12.1 Hz, 1H), 4.04 (q, *J*=7.1 Hz, 2H), 3.53 (dd, *J*=11.0, 4.9 Hz, 1H), 3.08–2.96 (m, 1H), 2.92–2.80 (m, 1H), 2.59 (t, *J*=7.9 Hz, 2H), 2.32–2.18 (m, 1H), 2.10–1.96 (m, 1H), 1.62–1.24 (m, 20H), 1.09 (t, *J*=7.1 Hz, 3H), 0.98–0.86 (m, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 143.0, 142.3, 141.5, 139.6, 137.6, 137.3, 134.1, 128.6, 128.4, 127.2, 126.4, 121.6, 120.9, 60.0, 39.5, 38.4, 33.9, 33.8, 31.7, 30.6, 29.3, 29.1, 27.4, 22.7, 14.2, 14.1, 13.7, 10.5; IR (neat): 2957, 2928, 2870, 2855, 2239, 1726, 1634, 1589, 1464, 1456, 1416, 1377, 1173, 1032, 908 cm^{-1}; HRMS (EI) calcd for $C_{35}H_{50}NO_2Sn$: [M−Bu]$^+$, 636.2864. Found: *m*/*z* 636.2859.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.03.079.

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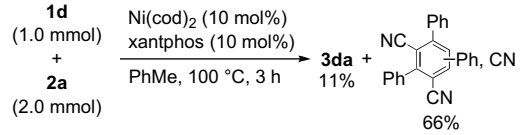
11. The reaction of **1d** (1.00 mmol) with **2a** (2.0 mmol) in the absence of BPh_3 gave a mixture of substituted benzenes as major products in 66% yield through cyclotrimerization of **1d**. The yield of **3da** was only 11%.



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12. Crystallographic data (excluding structure factors) for structures of (*E*)-**3aj** and **4** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 718299 and CCDC 717696. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).
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