C–C Activation

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Highly Chemoselective Carbon–Carbon σ-Bond Activation: Nickel/Lewis Acid Catalyzed Polyfluoroarylcyanation of Alkynes**

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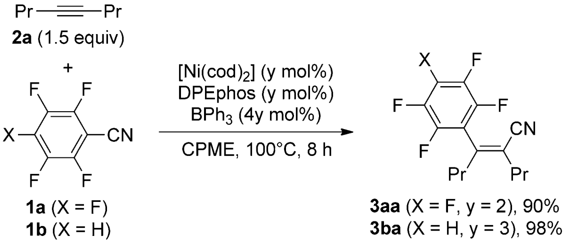
Metal-catalyzed activation of saturated C–C bonds has a great potential in economical and ecofriendly transformations.[1] For example, the reaction involving cleavage of the C–C σ bond and subsequent addition to unsaturated bonds is ideal for the simultaneous formation of two C–C σ bonds without the generation of by-products (100% atom economy). On the other hand, C–F and C–H activation of polyfluoroarenes by various metal complexes has been well investigated for synthetic organic chemistry.[2,3] However, the catalytic functionalization of polyfluoroarenes through C–C activation remains to be explored. In this respect, the work by Gunay and Jones is seminal: the C(sp^1)–C_6F_5 bond in bis(pentafluorophenyl)acetylene is shown to add oxidatively to a platinum(0) complex under UV irradiation.[4] Our group demonstrated that the nickel(0)/Lewis acid catalyst system is highly effective for the carbocyanation of alkynes and alkenes using various organic nitriles.[1b,5] On the basis of these studies, we expected that C–CN activation by nickel(0)/Lewis acid catalyst is preferred rather than C–H and C–F activation. Herein, we report the selective cleavage of the C–CN bond in polyfluorobenzonitriles by the nickel(0)/DPEphos complex (DPEphos = bis(2-diphenylphosphinophenyl)ether) and BPh_3; all other reactive C–H and C–F bonds are unaffected, thus resulting in the smooth addition of the polyfluorophenyl and cyano moieties to C≡C and C=C bonds.

First, we tested the typical conditions ([Ni(cod)$_2$], $PPhCy_2$, and $AlMe_3$ as catalysts; cod = 1,5-cyclooctadiene) for the arylcyanation of 4-octyne (**2a**, 1.5 mmol)[5d] with pentafluorobenzonitrile (**1a**, 1.0 mmol) and were disappointed to find that no trace of the desired adduct (*Z*)-4-pentafluorophenyl-5-cyano-4-octene (**3aa**) was formed. However, the use of DPEphos as a ligand and BPh_3 as a Lewis acid in cyclopentylmethylether (CPME) at 100 °C was highly effective, and arylcyanation proceeded to afford **3aa** in 90% yield after purification by preparative TLC [Eq. (1)]. The *Z* configuration was unambiguously confirmed by NOESY NMR analysis. Of note, all the C–F bonds remained intact during the reaction. The use of BPh_3 was found to be crucial to enhance the reactivity of the C–CN bond. Other Lewis acids, such as BF_3, $B(C_6F_5)_3$, $ZnCl_2$, and $AlMe_3$, were less effective. When the optimum catalyst system was applied to 2,3,5,6-tetrafluorobenzonitrile **1b**, which has an acidic C–H bond, only the C–CN bond participated in the reaction to give **3ba** in 98% yield. On the other hand, C–H activation of **1b** by [Ni(cod)$_2$]/$PCyp_3$ catalyst[3a,c] was not observed. These results clearly show that the C–CN bond in **1b** is exclusively activated in the presence of the C–H and C–F bonds in **1b** and **3ba**.



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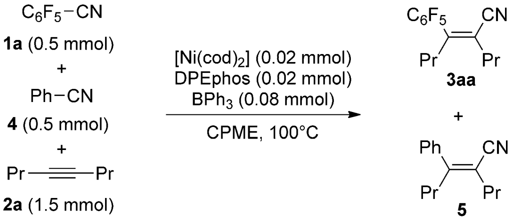
Competition experiments between **1a** and benzonitrile **4** were carried out to get a deeper insight into the reactivity of **1**. Substrates **1a**, **4**, and **2a** were added to a solution of [Ni(cod)$_2$], DPEphos, and BPh_3 in CPME [Eq. (2)]. The reaction mixture was stirred at 100 °C for 1 h and assayed by GC, which showed that **3aa** was selectively formed in 91% yield without a trace of **5**. Thereafter, **4** gradually participated in the reaction, and the yield of **5** reached 91% within 3 h (Figure 1).[6] The original arylcyanation conditions ([Ni(cod)$_2$], $PPhMe_2$, and $AlMe_2Cl$ as catalysts)[5d] gave minute amounts of **3aa** and **5** in a nonselective manner. Possibly, **1a**



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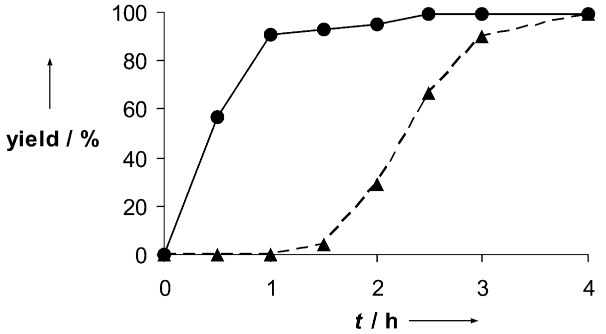
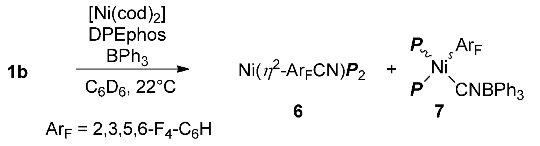


Figure 1. Time course of the competition reaction between **1a** and **4** catalyzed by [Ni(cod)$_2$], DPEphos, and BPh$_3$. ●: yield of **3aa**. ▲: yield of **5**.

and AlMe$_2$Cl interacted to render the Ni species inactive for the desired catalysis.[7]

Next, we carried out stoichiometric reactions in order to shed light on the polyfluoroarylcyanation mechanism. The reaction of **1b** with [Ni(cod)$_2$] and DPEphos (1:1:1 ratio) was monitored by ^{1}H, ^{19}F, and ^{31}P NMR spectroscopy using hexafluorobenzene as the internal standard [Eq. (3)].[8]



(3)

ligand (*P*, *P*) = DPEphos	5 h	**6a**, 25%	*cis*-**7a**, 64%
ligand (*P*, *P*) = DPEphos (without BPh$_3$)	17 h	**6a**, >99%	**7a'**, 0%
ligand (*P*) = PCyp$_3$	1 h	**6b**, 0%	*trans*-**7b**, >99%

When the reaction was carried out at 22 °C in the presence of BPh$_3$, an oxidative addition under cleavage of the C–CN bond occurred to give *cis*-**7a** ([*cis*-Ni(2,3,5,6-F$_4$-C$_6$H)(CNBPh$_3$)(DPEphos)], ^{31}P NMR: $\delta = 18.3$ ppm (s)) in 64 % yield along with an η^2-nickel(0) complex **6a** ([Ni(η^2-2,3,5,6-F$_4$-C$_6$HCN)(DPEphos)], ^{31}P NMR: $\delta = 19.8$ (d, $J = 41$ Hz), 28.4 ppm (d, $J = 41$ Hz)) in 25 % yield, as determined by ^{1}H, ^{19}F, and ^{31}P NMR spectroscopy and X-ray crystallographic analysis (Figure 2).[9] Of note, no hydrido or fluoro complex was produced, in sharp contrast to the oxidative addition of polyfluoroarenes to a metal complex,[2,3] thus indicating that fluorine atoms bound to the aryl group promote the oxidative addition of the C–CN bond through their high electronegativity. In contrast to our previous observations,[8a] no BPh$_3$-bound η^2-nitrile nickel(0) complex was observed. In the absence of BPh$_3$, **6a** was quantitatively formed, but **7a'** was not formed at all, showing that BPh$_3$ dramatically facilitated the oxidative addition of the C–CN bond from **6a**.[10] Moreover, when PCyp$_3$ was used as a ligand, oxidative addition immediately proceeded to give the C–CN bond adduct *trans*-**7b** (^{31}P NMR: $\delta = 24.2$ ppm (s)) quantitatively; no hydrido nickel complex was formed according to ^{1}H, ^{19}F, and ^{31}P NMR spectroscopy, thus indicating that the C–CN bond is much more reactive than the C–H bond.

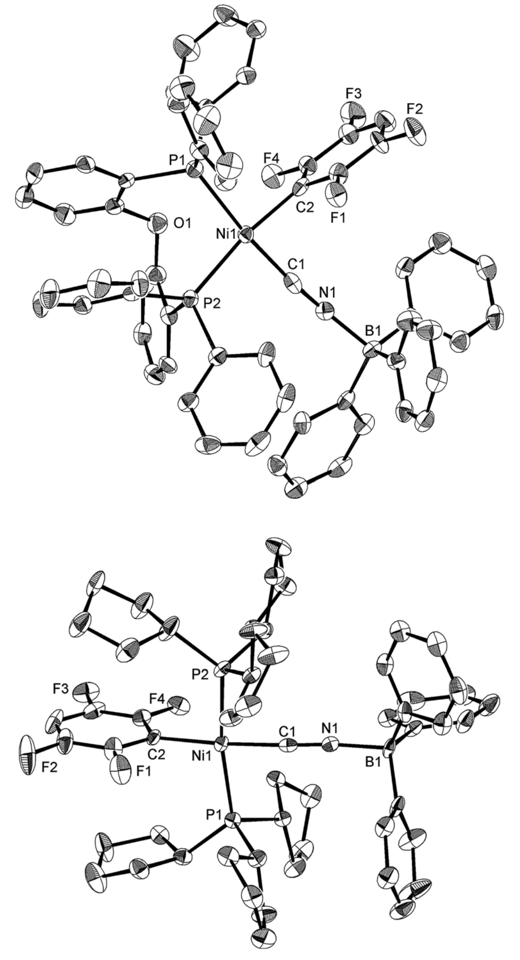
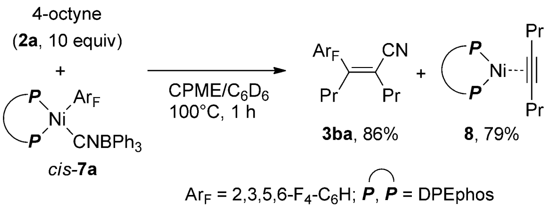


Figure 2. ORTEP diagram of *cis*-**7a** (top) and *trans*-**7b** (bottom).

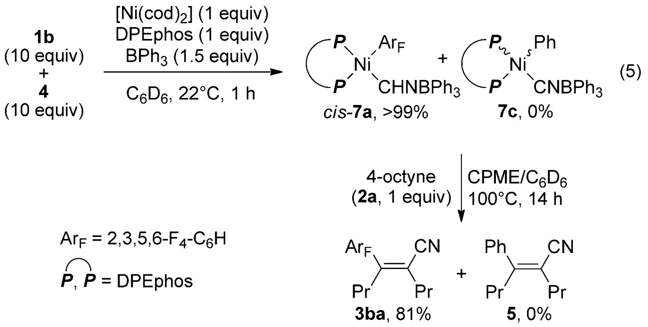
When *cis*-**7a** was allowed to react with **2a** (10 equiv) in CPME/C$_6$D$_6$ (1:1) at 100 °C for 1 h [Eq. (4)], the adduct **3ba**



(4)

was produced in 86 % yield (determined by NMR spectrosopy), together with the η^2-alkyne nickel(0) complex **8** (79 % by ^{31}P NMR spectrospopy: $\delta = 27.2$ ppm (s)).[9,11] On the other hand, *trans*-**7b** did not react with **2a**. Thus, DPEphos was clearly shown to be effective for the alkyne insertion.

We carried out competition experiments between **1b** and **4** for the oxidative addition and the following insertion of 4-octyne [Eq. (5)]. Oxidative addition at 22 °C for 1 h resulted in the sole formation of *cis*-**7a**. This result showed that the formation of *cis*-**7a** was thermodynamically favored over that of [Ni(Ph)(CNBPh$_3$)(DPEphos)] **7c**, possibly because of the



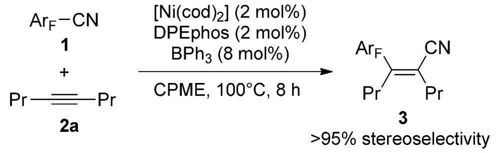
(5)

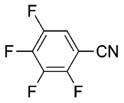
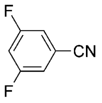
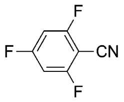
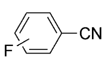
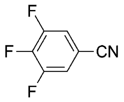
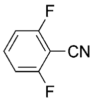
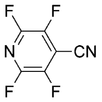
electron deficiency of the tetrafluoroaryl group. When **2a** (1 equiv) in CPME was added to the solution, and the resultant mixture was heated to 100 °C for 14 h, only **3ba** was produced in 81 % yield.[12] These results demonstrated that the thermodynamics of the oxidative addition of **1** and **4** is the key to the difference in the reactivity of nitriles.

With the information obtained by the mechanistic analysis, we examined the scope of the polyfluorobenzonitriles under the optimum conditions (Table 1). The reaction of 2,3,4,5-tetrafluorobenzonitrile **1c** with **2a** proceeded smoothly to give **3ca** in 98 % yield (Table 1, entry 1). Mono-, di-, and trifluorobenzonitriles **1d**–**1j** gave the corresponding adducts **3da**–**3ja** in over 90 % yield (Table 1, entries 2–8).

Similarly, 2,3,5,6-tetrafluoro-4-pyridinecarbonitrile **1k** reacted smoothly with **2a** to give **3ka** in 93 % yield, although a stoichiometric amount of BPh_3 was required for this conversion. A catalytic amount of BPh_3 failed to promote the reaction, possibly because the nitrogen atom in the polyfluoropyridyl group lowered the Lewis acidity of BPh_3 throught coordination (Table 1, entry 9).

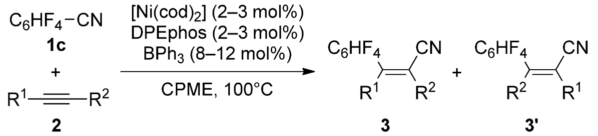
Table 1: Reaction of polyfluorobenzonitriles with 4-octyne **2a**.[a]

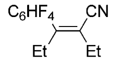
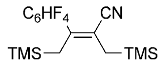
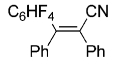
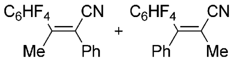
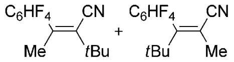
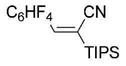


Ent.	1	Yield [%][b]	Ent.	1	Yield [%][b]
1	**1c** 	**3ca**, 98	5	**1g** 	**3ga**,90
2[c]	**1d** 	**3da**, 98			
			6	**1h** o-F	**3ha**, 97
3	**1e** 	**3ea**, 98	7	**1i** m-F	**3ia**, 98
			8	**1j** p-F	**3ja**, 98
4	**1f** 	**3fa**, 97	9[d]	**1k** 	**3ka**, 93

[a] Unless otherwise noted, a mixture of **1** (1.0 mmol), **2a** (1.5 mmol), $[Ni(cod)_2]$ (0.02 mmol), DPEphos (0.02 mmol), BPh_3 (0.08 mmol), and CPME (1.0 mL) was heated to 100 °C for 8 h. [b] Yield of isolated product. [c] $[Ni(cod)_2]$ (0.03 mmol), DPEphos (0.03 mmol), and BPh_3 (0.12 mmol) were used. [d] $[Ni(cod)_2]$ (0.03 mmol), DPEphos (0.03 mmol), and BPh_3 (1.00 mmol) were used.

Table 2: Reaction of **1c** with various alkynes.[a]

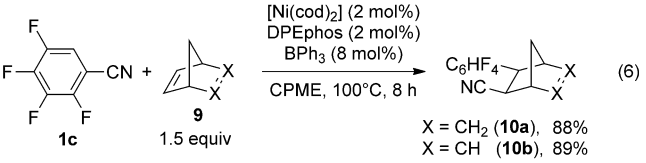


Entry	R¹, R² (2)	t [h]	Product	Yield [%][b]	3:3′[c]
1	Et, Et (**2b**)	8	 **3cb**	87	
2	CH_2TMS, CH_2TMS (**2c**)	26	 **3cc**	72	
3[d]	Ph (**2d**)	23	 **3cd**	71	
4[e]	Me, Ph (**2e**)	8	 **3ce** (E/Z=4:96), **3ce′**	87	54:46
5[f]	Me, tBu (**2f**)	52	 **3cf**, **3cf′**	83	86:14
6	H, TIPS (**2g**)	24	 **3cg**	55	>99:1

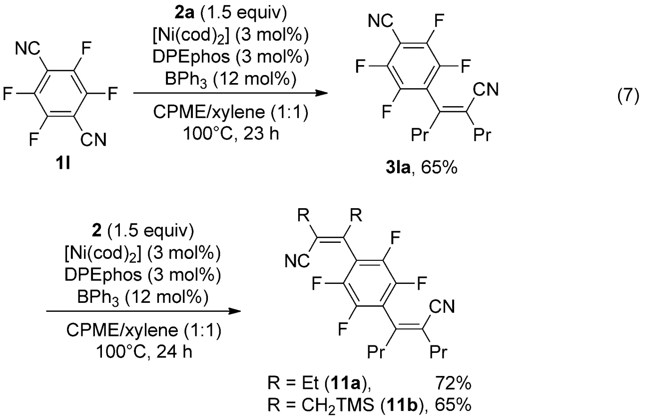
[a] Unless otherwise noted, a mixture of **1c** (1.0 mmol), **2** (1.5 mmol), $[Ni(cod)_2]$ (0.02 mmol for entries 1, 2, and 5; 0.03 mmol for entries 3 and 4; and 0.05 mmol for entry 6), DPEphos (0.02 mmol for entries 1, 2, and 5; 0.03 mmol for entries 3 and 4; and 0.05 mmol for entry 6), BPh_3 (0.08 mmol for entries 1, 2, and 5; 0.12 mmol for entries 3 and 4; and 0.20 mmol for entry 6), and CPME (1.0 mL) was heated to 100 °C for 8–52 h. [b] Yields of isolated products. [c] Determined by ^1H NMR spectroscopy. [d] **2d** (3.0 mmol). [e] 80 °C. [f] 120 °C. TIPS = triisopropylsilyl.

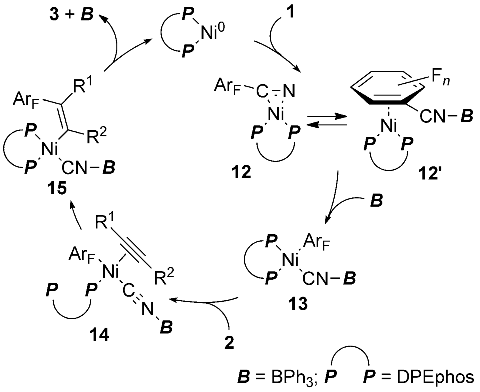
Using **1c** as the substrate, we examined the scope of the alkynes (Table 2). Symmetrical alkynes, such as 3-hexyne **2b**, bis(trimethylsilylmethyl)acetylene **2c**, and diphenylacetylene **2d**, gave the corresponding adducts **3cb**, **3cc**, and **3cd** in good yields (Table 2, entries 1–3). 1-Phenyl-1-propyne **2e** gave the corresponding adducts **3ce** and **3ce′** in 87 % combined yield with poor selectivity (54:46); this result stands in sharp contrast to that observed for the arylcyanation of 1-(4-methoxyphenyl)-1-butyne with 4-chlorobenzonitrile (Table 2, entry 4).[5d,13] The structures of **3cd** and **3ce′** were unambiguously established by X-ray crystallographic analysis.[9] 4,4-Dimethyl-2-pentyne **2f** gave **3cf** and **3cf′** in 86:14 ratio, demonstrating that the CN group prefers a more-hindered alkyne carbon center, similar to the arylcyanation reaction (Table 2, entry 5).[5d] Of note, the addition of **1c** to triisopropylsilylacetylene **2g** gave **3cg** with excellent regioselectivity, albeit in modest yield (Table 2, entry 6). Presumably, the use of DPEphos, which is a weak donor ligand, and/or an electron-withdrawing polyfluoroaryl group allows the polyfluoroarylcyanation of terminal alkynes. Facile trimerization and oligomerization of terminal alkynes are prone to take place in the presence of nickel catalysts with electron-donating phosphine ligands, as described in the previous carbocyanation results.[5d]

The nickel/BPh_3 catalyst could also be used for the polyfluoroarylcyanation of norbornene **9a** and norbornadiene **9b**.[5d,14] Both alkenes reacted with **1c** to afford $(2R^*,3S^*)$-3-aryl-2-cyanobicyclo[2.2.1]heptane (**10a**) and $(2R^*,3S^*)$-3-aryl-2-cyano-bicyclo[2.2.1]hept-5-ene (**10b**), respectively, in high yields [Eq. (6)].



Site-selective polyfluoroarylcyanation of tetrafluoroterephthalonitrile **1l** was easily achieved by using **2a** (1.5 equiv): only the monoalkenylation adduct **3la** was obtained in 65% yield (73% conversion of **1l**), without cleavage of the other C–CN bond. These results indicate that it is possible to use two different alkynes to react with **1l**. Thus, **11a** and **11b** were isolated in 72% and 65% yields, respectively, from the reaction of **3la** with **2b** and **2c** [Eq. (7)].

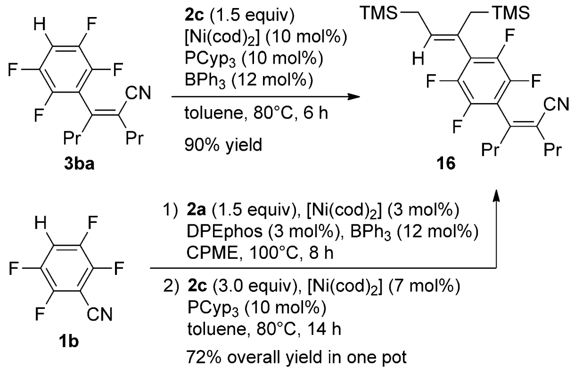




Scheme 1. A plausible mechanism for the reaction of polyfluorobenzonitrile with alkyne.

A plausible mechanism for the reaction of polyfluorobenzonitrile with an alkyne is shown in Scheme 1. The catalytic reaction should be initiated by the formation of the η^2-complex **12** or **12′**. Subsequent oxidative addition of the C–CN bond to nickel(0) affords **13** after the cyano group nitrogen atom is bound to BPh_3. Insertion of alkyne **2** into the Ar_F–Ni bond in **13** gives **15** via the alkyne-coordinated complex **14**. Steric repulsion between the bulkier group R^2 and the polyfluorophenyl group on the Ni center in **14** is assumed to be minimal.[15] Finally, C–C bond-forming reductive elimination of **3** from **15** generates a nickel(0) complex to complete the catalytic cycle. The low regioselectivity in the reaction with 1-phenyl-1-propyne **2e** may be ascribed to a plausible π-stacking interaction between the electron-deficient Ar_F and the phenyl ring (R^1) in **14**, followed by arylnickelation toward the alkyne.[16] This interaction apparently competes with the regioselectivity caused by the steric repulsion.

Encouraged by the selective C–CN activation of polyfluorobenzonitriles, we examined the orthogonal C–H activation of the adducts for the reaction of **3ba** with **2c** (Scheme 2).[3a,c] A catalyst system consisting of nickel(0), $PCyp_3$, and BPh_3 was effective for the production of the desired hydropolyfluoroarylation product **16** in 90% yield. The effect of BPh_3 remains to be carefully examined, but it is assumed that ligation of the cyano group to the boron atom enhances the reactivity of the C–H bond by lowering the electron density of the polyfluoroaryl moiety. In the absence of BPh_3, the yield of the double adduct **16** significantly decreased. The feasibility of one-pot sequential C–CN and C–H activation was also confirmed: **16** was obtained in 72% yield without isolation of the intermediate **3ba**.



Scheme 2. Aryl cyanation/hydroarylation of alkynes.

In conclusion, the present study has substantiated the role of a nickel/BPh_3 catalyst system in the addition of polyfluorobenzonitriles to alkynes through selective C–CN activation without C−H and C−F bond cleavages. This method allows access to a variety of fluorinated organic compounds as functional materials for liquid crystals and organic light-emitting diodes.[17,18] The fluorine atoms bound to the aryl groups significantly enhance the reactivity of the C−CN bond toward the oxidative addition to the nickel(0) complex. Site-selective alkenylation between the C−CN and C−H bond also proceeds successfully. Efforts to extend the present polyfluoroarylcyanation reaction to various other substrates are underway.

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Keywords: alkynes · fluorides · insertion · nickel · nitriles

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[13] The catalytic addition of 4-chlorobenzonitrile to 1-(4-methoxyphenyl)-1-butyne gives *Z*-(4-chlorophenyl)(Me)C=C(CN)(4-methoxyphenyl) and *Z*-(4-chlorophenyl)(4-methoxyphenyl)C=C(CN)(Me) in 66:34 ratio.

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