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Nickel-Catalyzed Amination of Aryl Nitriles for Accessing Diarylamines through C–CN Bond Activation

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Abstract: A nickel-catalyzed amination to access diarylamines has been developed through C–CN bond activation of aryl nitriles with anilines. In this developed catalytic protocol, various aromatic and heteroaromatic nitriles could be utilized as the electrophiles to couple with substituted anilines. A diversity of diarylamines were obtained in 15–95% yields.

Keywords: Amination; C–CN bond activation; Nickel; Diarylamines; Aryl nitriles

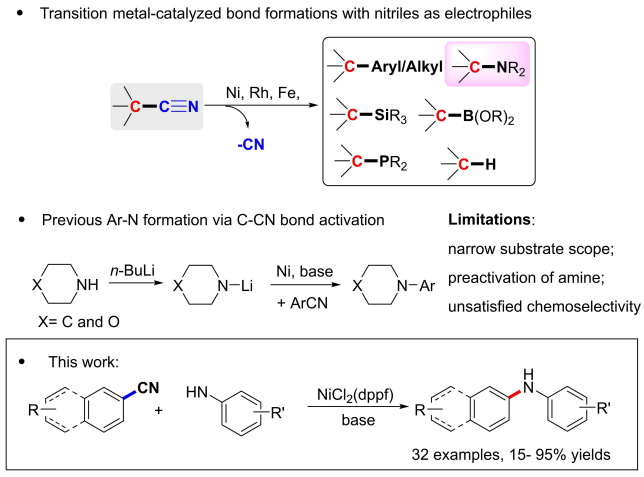
Functional group transformation is a central issue in organic synthetic chemistry.[1] Nitrile moieties, as a prevalent functional group in organic molecules, are versatile intermediates in synthetic community that undergo a wide variety of transformations.[2] Traditionally, the transformation of a cyano group allows the installation of various functional groups, such as, amide, ester, aldehyde, ketone, amine, and thioamide, etc.[3] Recently, the development of transition metal-catalyzed inert C–C bond activation has significantly diversified the transformations of C–CN bond,[4] including cross-coupling using nitriles as electrophiles, cyanation of aryl halides and arenes using organic nitriles as cyanating agents, and carbocyanation of unsaturated bonds.[5]

In the past decades, transition metal-catalyzed coupling reactions with nitriles as alternative electrophiles to replace aryl halides and pseudohalides have received considerable achievements. Among them, nickel-catalyzed C–C bond formations of aryl nitriles with various organometallic reagents have been declared, such as, Grignard reagents,[6] boronic esters[7] and manganese reagents.[8] Chatani and Tobisu demonstrated that aryl nitriles could be converted to aryl silanes,[9] arenes[10] and aryl boronic esters[11] under Rh catalysis via a silicon or boron-assisted cleavage of C–CN bond. Moreover, nickel-catalyzed C–P bond formations of aryl nitriles and alkyl nitriles were disclosed by Yang[12] and Han,[13] respectively. Other than the application of nitriles as the coupling partner in the cross-coupling reactions, hydrodecyanation of nitriles via C–CN bond activation, catalyzed by Fe,[14] Ni[15] and Rh,[16] were developed with suitable hydride sources.

Although a manifold of methods for Ar–N bond formations have been demonstrated with aryl halides or triflates as the coupling partners,[17] a simple and efficient transformation of Ar–CN to Ar–N is interesting and valuable to be developed. Miller and co-workers firstly reported a Ni-catalyzed amination of aryl nitriles with secondary amines.[6b] However, the protocol was only suitable for accessing tertiary amines. In addition, the amine substrate must be employed as its 'preformed' lithium amide, whose strong basicity led to the issue of low chemoselectivity

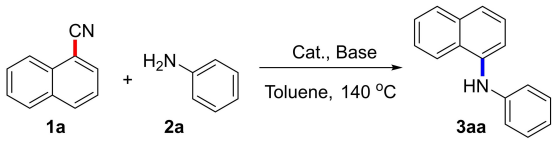
(e. g., metallation of acidic C–H bonds). Recently, we reported a Ni-catalyzed reductive decyanation of aryl nitriles.[15e] Based on the protocol and inspired by these important studies of C–CN activation, we are interested in the exploration of the amination of aryl nitriles through C–CN bond activation. Herein, we reported a simple and efficient nickel-catalyzed C–N coupling of aryl nitriles with various anilines for the synthesis of diarylamines via C–CN cleavage (Scheme 1).

We started to investigate the Ni-catalyzed decyanation coupling between aryl nitrile and aryl amine, with 1-naphthonitrile and aniline as the model substrates. Initially, screening of nickel precatalysts were carried out with KHMDS as the base in toluene. To our delight, moderate to good yields of the desired amination product **3 aa** were obtained (Table 1, Entries 1–4). Then, several bidentate nitrogen ligands were examined using $NiBr_2$(dme) as the precursor, which could not provide enhanced effects for the transformation (Table 1, Entries 5–7). It is noteworthy that nickel complexes with phosphine ligands could improve the reactions to deliver the target amination products **3 aa** in good to excellent yields, while $NiCl_2$(dppf) provided an obviously advantage and gave **3 aa** up to 90% yield (Table 1, Entries 8–10). Different bases were evaluated as well (Table 1, Entries 11–16). The results indicated that potassium as the counter cation was much more effective than their sodium or lithium analogs, and KHMDS was proven to be the best choice in all tested bases. Further exploration (see SI) suggested that 6 h of reaction was suitable, up to 95% isolated yield of **3 aa** obtained (Table 1, Entry 17). Besides, the control experiments showed that both nickel and base were indispensable in this decyanative amination protocol (Table 1, Entries 18 and 19).



Scheme 1. Transition metal-catalyzed C–X bond formations via C–CN bond activation.

Table 1. Optimization of Ni-catalyzed coupling between 1-naphthonitrile and aniline.[a]

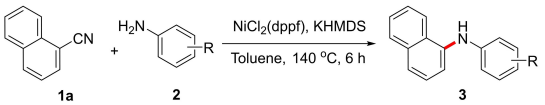


Entry	Ni/L	Base	Yield%
1	$NiCl_2$(dme)	KHMDS	78
2	$NiBr_2$(dme)	KHMDS	83
3	$Ni(OAc)_2$	KHMDS	77
4	$Ni(OTf)_2$	KHMDS	66
5	$NiBr_2$(dme)/bpy	KHMDS	79
6	$NiBr_2$(dme)/6,6'-dimethyl-bpy	KHMDS	84
7	$NiBr_2$(dme)/phen	KHMDS	35
8	$NiCl_2$(dppf)	KHMDS	90
9	$NiCl_2$(dppe)	KHMDS	85
10	$NiCl_2$(dppp)	KHMDS	86
11	$NiCl_2$(dppf)	NaHMDS	10
12	$NiCl_2$(dppf)	LiHMDS	6
13	$NiCl_2$(dppf)	*t*-BuOK	39
14	$NiCl_2$(dppf)	*t*-BuONa	14
15	$NiCl_2$(dppf)	*t*-BuOLi	0
16	$NiCl_2$(dppf)	*t*-AmOK	29
17	$NiCl_2$(dppf)	KHMDS	95[b]
18	-	KHMDS	0
19	$NiCl_2$(dppf)	-	0

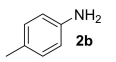
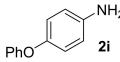
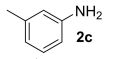
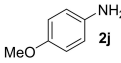
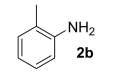
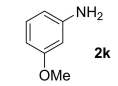
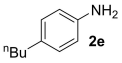
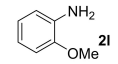
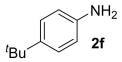
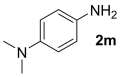
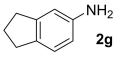
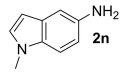
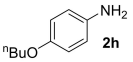
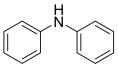
[a] Reaction conditions: **1 a** (0.5 mmol), **2 a** (1 mmol), [Ni] (5 mol%), ligand (6 mol%), base (1 mmol), toluene (2 mL), 140 °C for 8 h. GC yield with biphenyl as the internal standard. potassium bis(trimethylsilyl)amide (KHMDS), dimethoxyethane (dme), bipyridine (bpy), 1,10-phenanthroline (phen), bis(diphenylphosphino)ferrocene (dppf), 1,2-bis (diphenylphosphino)ethane (dppe), 1,3-bis (diphenylphosphino)propane (dppp).
[b] 6h, Isolated yield.

With the optimal reaction conditions in hand, we then examined the generality of this C–N coupling. First, various substituted anilines were explored. As shown in Table 2, alkyl substituted anilines could smoothly react with 1-naphthonitrile to provide the target products in moderate to excellent yields (Table 2, Entries 1–6). 2-Methylaniline dramatically diminished the transformation for its steric hindrance (Table 2, Entry 1). Of note is the tolerance of C–O bond in this protocol, since C–O bond activation could be enabled by nickel catalysis in many other reports (Table 2, Entries 7–11).[18] Gratifyingly, 4-butoxyaniline and 4-phenoxyaniline provided the amination products in 87% and 83% yields, respectively (Table 2, Entries 7 and 8). The results suggested that alkoxyl and aryloxyl groups binding to anilines were intact in

Table 2. Ni-catalyzed amination of 1-naphthonitrile with various anilines.[a]



1a 2 3

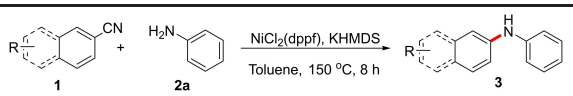
Entry	2	3 Yield (%)	Entry	2	3 Yield (%)
1	 2b	**3ab** 75	8	 2i	**3ai** 83
2	 2c	**3ac** 65	9	 2j	**3aj** 44
3	 2b	**3ad** 45	10	 2k	**3ak** 65
4	 2e	**3ae** 94	11	 2l	**3al** 25
5	 2f	**3af** 94	12	 2m	**3am** 67
6	 2g	**3ag** 88	13	 2n	**3an** 25
7	 2h	**3ah** 87	14	 2o	**3ao** 15[b]

[a] Reaction conditions: **1a** (1 mmol), **2** (2 mmol), $NiCl_2$(dppf) (5 mol%), KHMDS (2 mmol, 0.5 mol/L in toluene, 4.0 mL), 140 °C, 6 h.
[b] $NiCl_2$(dppf) (20 mol%), 150 °C, 10 h. ^{1}H NMR yield was obtained.

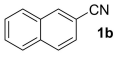
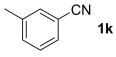
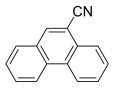
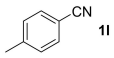
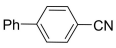
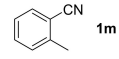
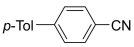
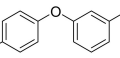
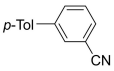
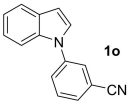
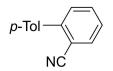
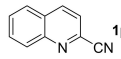
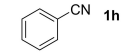
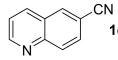
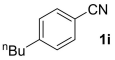
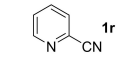
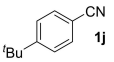
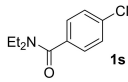
this decyanative amination protocol. Whereas, 4- and 3-anisidines were slightly less efficient (Table 2, Entries 9 and 10). For the reaction applying 2-anisidine, again, the steric hindrance effect of -OMe led to the target product with only 25% isolated yield (Table 2, Entry 11). 4-Dimethylamino group was also compatible (Table 2, Entry 12). In addition, heteroaromatic amines, such as 2-, 3-, 4-amino pyridine and 5-aminoquinoline, were tested as well, however, complicated reactions were observed and no target products were detected. Only *N*-methyl protected indolyl amine delivered 25% yield of the desired product (Table 2, Entry 13). Besides, aliphatic primary amines, such as *n*-$BuNH_2$ and $CyNH_2$ were examined, while no or trace target products were detected. Naphthalene and 1,1′-binaphthyl were confirmed as the major outcomes by GC–Ms analysis. We propose that decyanation and reductive coupling of **1a** occurred under the strong basic conditions (see SI, Figure S1). Secondary anilines, such as $PhNHCH_3$ and Ph_2NH were explored as well. We found that $PhNHCH_3$ was not a suitable substrate in this protocol. Ph_2NH can react with **1a** under a modified procedure (procedure B in the experimental section), while only 15% yield of the target product was given (Table 2, Entry 14).

Having investigated the coupling partner of aryl amines, we set out exploring the scope of aryl nitriles. With slightly modified reaction conditions, the results were listed in Table 3. The coupling of 2-cyanonaphthalene with aniline underwent smoothly to deliver the target product in moderate yield (Table 3, Entry 1). The fused ring substrate, such as 9-cyanophenanthrene, was suitable to release the target product in good yield (Table 3, Entry 2). Several substituted biphenyl nitriles reacted with aniline under this protocol to provide the amination products in moderate to good yields, irrespective of whether the cyano group was located in *ortho*-, *meta*-, or *para*- position on the phenyl ring (Table 3, Entries 3–6). Moreover, aniline could smoothly react with simple benzonitrile and alkyl substituted benzonitriles to give the corresponding

Table 3. Ni-catalyzed amination of various aryl nitriles with aniline.[a]



1 2a 3

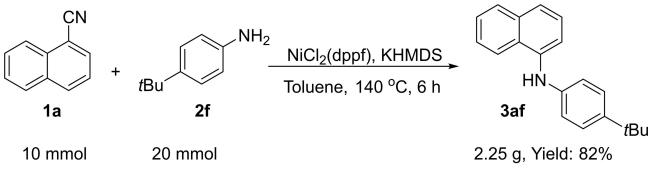
Entry	1	3 Yield (%)	Entry	1	3 Yield (%)
1	 1b	**3ba** 64	10	 1k	**3ka** 77
2	 1c	**3ca** 74[b]	11	 1l	**3la** 84
3	 1d	**3da** 70[c]	12	 1m	**3ma** 0
4	 1e	**3ea** 36[c]	13	 1n	**3na** 50[d]
5	 1f	**3fa** 70[d]	14	 1o	**3oa** 52[d]
6	 1g	**3ga** 51[e]	15	 1p	**3pa** 47[d]
7	 1h	**3ha** 85	16	 1q	**3qa** 63[d]
8	 1i	**3ia** 78	17	 1r	**3ra** 24[d]
9	 1j	**3ja** 73	18	 1s	**3sa** 41[f]

[a] Reaction conditions: **1** (1 mmol), **2a** (2 mmol), $NiCl_2$(dppf) (5 mol%), KHMDS (3 mmol, 0.5 mol/L in toluene, 6.0 mL), 150 °C, 8 h.
[b] 2 mmol KHMDS, 140 °C, 6 h.
[c] $NiCl_2$(dppf) (30 mol%).
[d] $NiCl_2$(dppf) (10 mol%).
[e] $NiCl_2$(dppf) (15 mol%).
[f] $NiCl_2$(dppf) (20 mol%), 150 °C, 10 h.

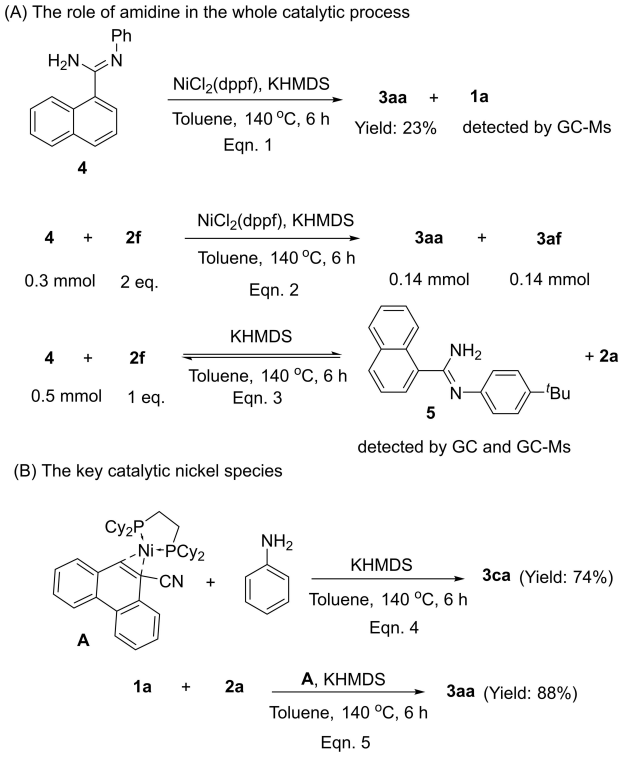
products in good yields (Table 3, Entries 7–11). Unfortunately, 2-methylbenzonitrile was problematic under the current conditions, and intramolecular addition of **1 m** was observed (see SI). This could be ascribed to the activation of C–H bond of methyl group by the neighboring CN group under strong basic condition, (Table 3, Entry 12). Furthermore, nitrile with Ar–O bond was tolerated (Table 3, Entry 13). In addition, the reactions employing heterocyclic nitriles were explored as well, for example 3-(1*H*-indol-1-yl) benzonitrile (**1 o**), 2-cyano quinoline (**1 p**), 6-cyano quinoline (**1 q**) and 2-cyano pyridine (**1 r**) (Table 3, Entries 14–17). With slightly modified procedure (procedure B in the experimental section), the desired products were obtained in moderate yields apart from less efficient **1 r**. Aryl nitriles with electron-withdrawing substituents were also tested in our protocol. Halides, ester and carboxylic acid were not tolerated.[19] To our delight, 4-cyano-*N*,*N*-diethylbenzamide (**1 s**) was a suitable substrate and delivered the target product in 41% yield under a modified condition (Table 3, Entry 18).

To further demonstrate the efficiency of this developed protocol, a scale-up reaction was conducted. As shown in Scheme 2, 10 mmol of **1 a** successfully reacted with **2 f** under the optimal conditions to deliver 2.25 g of **3 af** in 82% isolated yields (Scheme 2).

To get the insights into this Ni-catalyzed decyanative amination, mechanistic studies were performed. With the reaction between **1 a** and **2 a** as the model, the reaction progress was monitored by GC (see SI). The results clearly exhibited that **1 a** was completely consumed within two hours and 71% yield of the desired product was obtained. Simultaneously, a comparable amount of amidine **4** was detected in GC. As prolonging the reaction time, the decline of amidine **4** and the increase of **3 aa** were observed. When **1 a** and **2 a** were mixed at room temperature in the presence of KHMDS, **4** was quickly formed almost in a quantitative yield. With these observations in hands, we thus reckoned that amidine **4** might be an intermediated to be involved in the catalytic cycle. To verify this assumption, with **4** as the substrate under the standard amination conditions, **3 aa** was obtained in 23% yield (Scheme 3, Eqn. 1). Surprisingly, **1 a** was also detected. Therefore, another possibility might exist, that is, amidine **4** could decompose to generate nitrile **1 a** and amine **2 a**. To clarify the assumption, a



Scheme 2. Scale-up reaction.

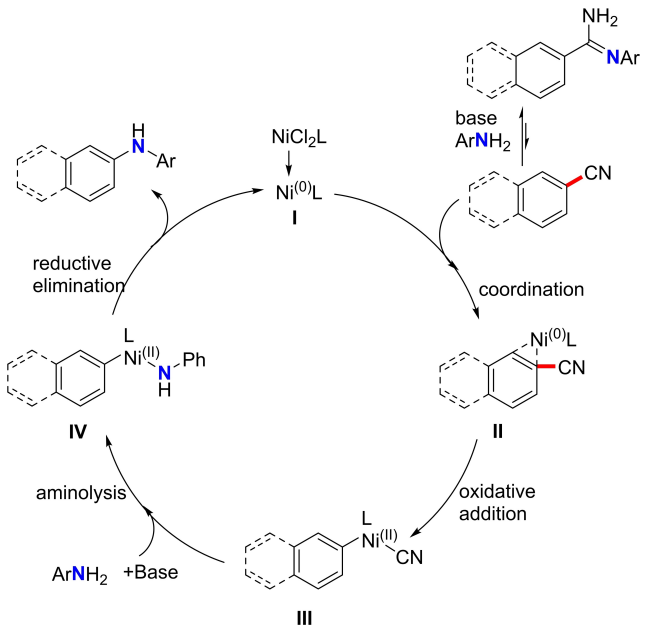


Scheme 3. Mechanistic experiments.

crossover experiment applying **4** and **2 f** under the standard conditions was carried out. Both **3 aa** and **3 af** were produced in a ratio of almost 1:1 (Scheme 3, Eqn. 2, see SI, Figure S69). In addition, when **4** and **2 f** were mixed in the presence of KHMDS at 140 °C, amidine **5** and **2 a** were detected (Scheme 3, Eqn. 3). On the basis of these results, we believed that a balance between amidine and nitrile existed under basic conditions, while the possibility of involving amidine in the catalytic cycle could not be ruled out (Scheme 4).

In our previous work, complex **A** was assigned as the key species in nickel-catalyzed decyanation of aryl nitriles.[15e] To gain more information about the active nickel species, additional stoichiometric experiments were conducted. Mixing complex **A** with aniline in the presence of KHMDS at 140 °C for 6 h provided the amination product **3 ca** in 74% yield (Scheme 3, Eqn. 4). Besides, with complex **A** as the catalyst, the amination of **1 a** with **2 a** under the optimal conditions gave **3 aa** in 88% yield (Scheme 3, Eqn. 5). Thus, complex **A** was believed to be the authentic intermediate in the catalytic cycle and acted as a key intermediate of the following C–CN cleavage.

With all obtained information, a mechanism for this Ni-catalyzed amination of nitrile is proposed and shown in Scheme 4. The Ni(0) species **I** *in situ* generated from nickel precatalyst, firstly coordinated with the C=C double bond of aromatic ring adjacent to



Scheme 4. Proposed mechanism of Ni-catalyzed amination of aryl nitrile.

cyano group, to afford intermediate **II**. The intermediate **II** underwent oxidative addition to break C–CN bond affording intermediate **III**. The aminolysis of **III** in the presence of base produced intermediate **IV**, which could finally undergo reductive elimination to release the aminated product and regenerate Ni(0) species to fulfil the catalytic cycle.

In summary, we have developed a nickel-catalyzed C–N coupling with aryl nitriles as the electrophiles via C–CN bond activation. This catalytic protocol requires no any additive to activate the C–CN bond. Broad functional groups in anilines, including alkyl, alkoxyl, aryloxyl and dimethylamino, were compatible. Aryl and heteroaryl nitriles could be aminated with aniline in 15–95% yields. Further investigation of expanding the substrate scope and potential applications of this methodology is underway in our laboratories.

Experimental Section

Procedure A

Representative procedure for the preparation of diaryl amines **3ab-3an**, **3ba-3na** and **3sa**: To a Schlenk tube was added 1-naphthonitrile (153 mg, 1 mmol), $NiCl_2$(dppf) (34 mg, 5 mol%), KHMDS (2 mmol, 0.5 mol/L in toluene, 4 mL), and aniline (186 μL, 2 mmol). Stirred the mixture at room temperature for 2 min, then the tube was put into a preheated oil bath at 140 °C for 6 h. The reaction mixture was cooled down, quenched with water (50 mL), and extracted with ethyl acetate (30 mL × 2). The organic phase was combined and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, petroleum ether and ethyl acetate as the eluent) to afford 208 mg of **3 aa** (95%).

Procedure B

Representative procedure for the preparation of heteroaromatic amines **3ao** and **3oa-3ra**: To a Schlenk tube was added KHMDS (2 mmol, 0.5 mol/L in toluene, 4 mL), aniline (186 mg, 2 mmol) was added dropwise with stirring. The mixture was stirred at room temperature for 10 min and concentrated in vacuu. Then, heterocyclic nitrile (1 mmol), $NiCl_2$(dppf) (68 mg, 10 mol%), toluene (4 mL) were added. The tube was put into a preheated oil bath at 150 °C for 8 h. The reaction mixture was cooled down, quenched with water (50 mL), and extracted with ethyl acetate (30 mL × 2). The organic phase was combined and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, petroleum ether and ethyl acetate as the eluent).

Acknowledgements

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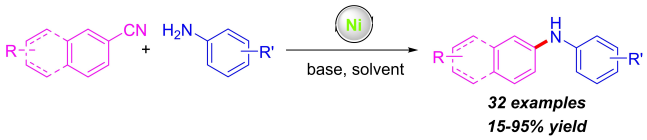
[19] When 4-fluorobenzonitrile was applied, no target product was detected. 4-(phenylamino)benzonitrile was isolated in 30% yield. We proposed that C–F bond was activated by the cyano group. When *tert*-Butyl 4-cyanobenzoate was utilized, the amination of *t*ert-butyl ester occurred to release the corresponding amide and no decyanation C–N coupling product was detected. The reaction of 4-cyanobenzoic acid was complicated and no desired product was detected.

COMMUNICATIONS

Nickel-Catalyzed Amination of Aryl Nitriles for Accessing Diarylamines through C–CN Bond Activation



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