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Letter

# Nickel-Catalyzed N,N-Diarylation of 8-Aminoquinoline with Large Steric Aryl Bromides and Fluorescence of Products

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R. R' = arvl. alkvl



developed. A direct *N*,*N*-diarylatin of 8-aminoquinoline with sterically hindered bromides, making use of inexpensive nickel as a catalyst and simple sodium salt as a base, gives the products in good to excellent yields. Various bromides and substituted 8-aminoquinolines are tolerated. Preliminary fluorescence results indicate that these sterically hindered and conjugated triarylamines may have some potential in material chemistry.

Large sterically hindered triarylamines, especially those with large conjugated systems, such as carbazole and quinolines, have attracted wide attention in material chemistry.<sup>1</sup> They are important skeletons in organic light-emitting diodes (OLEDs), sensitized solar cells, and photochromic materials. For example, as shown in Figure 1, TPD,<sup>2</sup> TCTA,<sup>3</sup> TPA-AC,<sup>4</sup> and 4CzIPN<sup>5</sup> and their structurally related compounds are well known for their use in LED materials and photocatalysis.



Because of their wide applications in material chemistry, the efficient synthesis of triarylamines, which were previously obtained mainly from the Buchwald–Hartwig reaction and Ullmann coupling, has attracted much attention in organic synthesis. The first kind of reliable synthetic route is the *N*-arylation of secondary arylamine with aryl halide under the catalysis of Pd,<sup>6</sup> Ni,<sup>7</sup> or Cu<sup>8</sup> salts (Scheme 1a). Another straightforward route is the use of primary aryl amines to react with two equivalents of aryl halides (Scheme 1b).<sup>9</sup> With noblemetal Pd catalysts, the relatively large sterically hindered triarylamines can be synthesized in good yields.<sup>9e,10</sup> The cheap copper catalyst system with the second route has also been disclosed but is mainly used in the occasion of active aryl iodides as a coupling partner,<sup>11</sup> and only a few examples with more stable, cheaper, and relatively available aryl bromides

# Scheme 1. Synthetic Routes of Triarylamines

Ni catalyzed N,N-Diarylation of 8-Aminoq
 Large steric-hindrance aryl bromides
 Ligand-free and highly efficient
 30 Examples, isolated yields up to 96%



have been disclosed.<sup>12</sup> However, these copper systems usually gave moderate yields when they were applied in the synthesis of large hindered triarylamines from primary amines.<sup>13</sup>

We are interested in the nickel catalysis.<sup>14</sup> With the second route, only one substrate was disclosed as a side product (26%) catalyzed by a nickel/carbene complex.<sup>15</sup> Although the yield is somewhat lower, this pioneering work indicates that proper coordination would be essential for the formation of

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#### Table 1. Screening of Reaction Conditions<sup>a</sup>

		H <sub>2</sub> → H <sub>2</sub> → Cr H <sub>2</sub> → Cr H <sub>2</sub> → Cr Br Cr Br Cr Br Cr Br Cr Br Cr Br Cr Br Cr Br Cr Br Cr Br Cr Br Cr Br Cr Br Cr Br Cr Cr Br Cr Cr Br Cr Cr Br Cr Cr Br Cr Cr Cr Cr Cr Cr Cr Cr Cr C	ttalyst (10 mol%) se (3.0 eq) vivent (2 mL) mp., 16 h			
entry	catalyst (10 mol %)	base (3.0 equiv)	solvent (2.0 mL)	temperature (°C)	yield of <b>3a</b> (%)	yield of $3a'$ (%)
1	NiCl <sub>2</sub> (dppe)	CH <sub>3</sub> ONa	DMF	150	72	24
2	NiCl <sub>2</sub>	CH <sub>3</sub> ONa	DMF	150	93	trace
3	$Ni(OAc)_2$	CH <sub>3</sub> ONa	DMF	150	91	trace
4	$Ni(OTf)_2$	CH <sub>3</sub> ONa	DMF	150	90	trace
5	NiCl <sub>2</sub>	КОН	DMF	150	trace	13
6	NiCl <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	DMF	150	trace	trace
7	NiCl <sub>2</sub>	NaOH	DMF	150	96	0
8	NiCl <sub>2</sub>	NaOH	1,4-dioxane	150	ND	trace
9	NiCl <sub>2</sub>	NaOH	toluene	150	29	35
10	NiCl <sub>2</sub>	NaOH	CH <sub>3</sub> CN	150	ND	trace
11	NiCl <sub>2</sub>	NaOH	DMF	140	72	19
12	NiCl <sub>2</sub>	NaOH	DMF	160	94	trace
13 <sup>b</sup>	NiCl <sub>2</sub>	NaOH	DMF	150	87	10
14 <sup>c</sup>	NiCl <sub>2</sub>	NaOH	DMF	150	85	13

<sup>a</sup>la (0.2 mmol), 2a (0.6 mmol), catalyst (0.02 mmol), and base (0.6 mmol) in solvent (2.0 mL), 150 °C, N<sub>2</sub>, 16 h, sealed tube, isolated yield. <sup>b</sup>NiCl<sub>2</sub> (0.01 mmol). <sup>c</sup>NaOH (0.4 mmol). ND: not detected.

triarylamine by nickel catalysis. Our previous work demonstrated that 8-aminoquinole exhibits excellent coordination ability,  $^{14c-f,16}$  especially to nickel.  $^{14c-f}$  Herein we developed a highly efficient synthesis of large sterically hindered triarylamines by a nickel-catalyzed *N*,*N*-diarylation of 8-aminoquinoline with large sterically hindered bromides in the presence of a simple sodium base (Scheme 1b-2).

Initially, 8-aminoquinoline (1a) and 9-(4-bromophenyl)-9H-carbazole (2a) were selected as substrates for optimizing the reaction conditions (Table 1). The target product 3a was detected by adding 10 mol % nickel catalyst (NiCl<sub>2</sub>(dppe), NiCl<sub>2</sub>, Ni(OAc)<sub>2</sub>, or Ni(OTf)<sub>2</sub>) and 3.0 equiv of CH<sub>3</sub>ONa as the base (entries 1-4), and NiCl<sub>2</sub> was found to be the best (93%, entry 2). Among the bases investigated, NaOH was found to be the best base, with a 96% yield of 3a (entries 5–7). DMF was used prior to other investigated solvents, such as 1,4dioxane, toluene, and acetonitrile (entries 8-10). Among the reaction temperatures investigated, 150 °C was the best (entries 11 and 12). When we tried to reduce the amount of NiCl<sub>2</sub> (entry 13) or NaOH (entry 14), the reaction effect was worse than before. The structure of 3a was unambiguously confirmed by single-crystal X-ray analysis (shown in Scheme 2).17

With the optimized reaction conditions in hand, we investigated the substrate scopes with respect to various aryl bromides (Scheme 2). For the highly hindered 9-(4-bromophenyl)carbazole analogues, the desired products 3a-d could be obtained in high yields (79–96%). For 4-bromo-N,N-diphenylaniline, the target product was obtained in 91% yield (3e). For 4-bromobiphenyl and 4-bromoterphenyl bromides, the corresponding products 3f and 3g were obtained in 90 and 87% yields, respectively. With electron-withdrawing groups of bromobenzene at the para position of the phenyl moiety (4-F, 4-Cl, 4-CF<sub>3</sub>), the corresponding products 3h-j were obtained in good yields (84–93%). When the methyl group was attached to the meta or para position of the phenyl group, the target compound could be obtained in good yield (31(m), 31(m,m), and 31(p): 73, 71, and 72%, respectively,





<sup>a</sup>1a (0.2 mmol), 2 (3.0 equiv), NiCl<sub>2</sub> (10 mol %), NaOH (3.0 equiv), DMF (2.0 mL), N<sub>2</sub>, sealed tube, isolated yield. <sup>bt</sup>BuONa (3.0 equiv) and H<sub>2</sub>O (15.0 uL) was used instead of NaOH, 165 °C.

whereas when the methyl group was attached to the ortho position, a higher temperature was required to obtain the corresponding compound 3l(o) in moderate yield (22%). Through the present method, the tetraphenyl ethylene (TPE) motif that has been demonstrated to be one of the most common structures in the aggregation-induced emission (AIE) molecular library<sup>18</sup> and its analogues can be introduced to 8-aminoquinoline in good yields (3m-o).

As depicted in Scheme 3, we explored these reactions of 2a with various 8-aminoquinoline derivatives. When different substituent groups attached to the C2, C4, C5, C6, or C7

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#### Scheme 3. Substrate Scope for 8-Aminoquinolines<sup>4</sup>



<sup>a</sup>1 (0.2 mmol), 2a (3.0 equiv), NiCl<sub>2</sub> (10 mol %), <sup>t</sup>BuONa (3.0 equiv),  $H_2O$  (15.0 uL), DMF (2.0 mL),  $N_2$ , sealed tube, isolated yield. <sup>b</sup>NaOH (3.0 equiv) was used instead of <sup>t</sup>BuONa and  $H_2O$ ; the isolated yield is listed in parentheses.

position of the 8-aminoquinoline ring, the reactions proceeded well with good yields of the corresponding products (4a-l) by simply changing the base from NaOH to <sup>t</sup>BuONa and water. A possible reason might be that different substituents would have various steric and electronic effects on the coordination of the nickel catalyst and aminoquinolines. Thus the in situ formation of the base by <sup>t</sup>BuONa and H<sub>2</sub>O was required in some case. When the quinoline ring had a methyl substitution at the C2 position, it could react with 9-(4-bromophenyl)-9H-carbazole to form the corresponding product 4a in 68% yield. When a phenyl group was attached to the C4 position, the desired product 4b was obtained in 95% yield. As for the C5 substituents, when electron-withdrawing groups (5-Br, 4fluorophenyl, 4-trifluoromethylphenyl) or electron-donating groups (phenyl, 4-methylphenyl, 1-naphthyl) were attached to the C5 position, the corresponding products were generated in 62-92% yields(4c-h). Furthermore, when a heterocyclic group, such as 3-furanyl or 4-pyridyl, was attached to the C5 position, the corresponding products 4i and 4j were generated in 67 and 89% yields, respectively. Other positions, such as a methoxy group at the C6 position (4k) or a methyl group at the C7 position (41), of the 8-aminoquinoline core were also investigated, and the desired products were obtained in good yields.

To show the potential use of this protocol, a gram-scale synthesis was carried out. When using 2.0 mmol of 1a and 6.0 mmol of 2a under standard conditions, the corresponding triarylamine product 3a could be obtained in 83% yield (1.04 g) (eq 1). Because the nitro-substituted quinolines have the



potential for further transformation,<sup>19</sup> we achieved the nitration of the large sterically hindered **3a** in moderate yield under the condition of  $Ni(NO_3)_2$ .6H<sub>2</sub>O as the nitrating reagent (eq 2). The structure of **5** was confirmed by single-crystal X-ray analysis.<sup>17</sup>



With two series of triarylamine compounds (3a-o; 4a-l) in hand, we proceeded to characterize their fluorescence performance (Figure 2, Table 2). The UV absorption



Figure 2. Fluorescence spectra of (A) 3a-o and (B) 4a-l in toluene compared with  $Al(q)_3$  in  $CH_2Cl_2$  as reference. For the full-size panels A and B, see the SI (Figure S5).

wavelengths of all compounds ranged from 363 to 412 nm. (See the Supporting Information, Figure S3 and S4.) The maximum fluorescence emission wavelengths of these compounds were from 435 to 584 nm, ranging from blue to yellowish orange. Among the compounds 3a-o, compound 3g had the highest fluorescence quantum yield of 23%. The quantum yields of triarylamine products with different substituents on the quinoline ring (4a-1) were higher than those of the products without substitution (3a). Because of the steric effect of the C2 methyl group of the quinoline ring on the inhibition of rotation, 4a gave the best quantum yields (31%), and the heterocyclic groups C5-furan (4i) and C5-pyridine (4j) also increased the quantum yields to 27 and 25%, respectively.

Previously, triarylamine was demonstrated to have good AIE performance.<sup>21</sup> We therefore tested the AIE performance of compound **3a** and found that the fluorescence intensity increased two-fold when the water fraction was increased from 0 to 95% (Figure 3A), indicating some potential in AIE, but its background signal was a problem. This property of **3a** could be modified after the introduction of a less conjugated and rigid TPE motif, which was demonstrated to play an important role in AIE by Tang et al.<sup>22</sup> As shown in Figure 3B, **3m** with two TPE motifs exhibited a 9.5 times better AIE effect when the water fraction was increased from 0 to 95%. Furthermore, compared with the single TPE and **3a** (Figure 3A–D), **3m** had

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#### Table 2. UV Absorption and Fluorescence Properties<sup>4</sup>

compd.	$\lambda_{\max}$ (nm)	$\lambda_{\rm em}~({\rm nm})$	Φ (%)	compd.	$\lambda_{\max}$ (nm)	$\lambda_{ m em}~( m nm)$	Φ (%)
3a	388	508	12	3b	393	519	11
3c	385	515	6	3d	405	524	20
3e	412	584	4	3f	395	501	12
3g	358	501	23	3h	385	491	1
3i	384	477	7	3j	363	435	5
3k	387	493	10	3l( <i>p</i> )	399	511	9
3m	373	509	5	3n	385	512	9
30	385	513	16	4a	379	496	31
4b	397	522	16	4c	385	512	16
4d	399	519	27	4e	405	530	17
4f	399	515	23	4g	402	519	20
4h	397	512	18	4i	398	513	27
4j	408	537	25	4k	379	499	14
41	381	502	17	$Al(q)_3$	381	518	17

<sup>*a*</sup>UV absorption was controlled between 0.025 and 0.050 in toluene for the fluorescence quantum yield. The data of fluorescence emission were excited at the maximum absorption wavelength.  $\Phi_{\rm F}$  of Al(q)<sub>3</sub> is 17% in CH<sub>2</sub>Cl<sub>2</sub><sup>20</sup>



**Figure 3.** Photoluminescence (PL) spectra of (A) **3a**, (B) **3m**, and (C) TPE in THF with varying amounts of water (% fraction of volume) with the same initial concentration of 5  $\mu$ mol/L. (D) Changes in the PL peak intensity with the water fraction. The definition of  $f_w$  is as follows:  $f_w = V_{water}/(V_{THF} + V_{water})$ . For the full-size panels A–D, see the SI (Figure S6).

a higher fluorescence intensity than that of TPE and a weaker background signal than that of **3a** at the same concentration.

To understand the reaction, we performed some control experiments to explore the possible reaction mechanism (Scheme 4). When using 1-naphthylamine (1a') without a bidentate coordination site to react with 2a under standard conditions, neither the N,N-diarylated product 6 nor the Narylated product 6' was obtained (Scheme 4a), indicating that the bidentate coordination of quinoline is critical (Scheme 4a). In addition, when  $Ni(COD)_2$  was used as the catalyst instead of NiCl<sub>2</sub> (Scheme 4b), the target product 3a was also obtained in good yield (86%), indicating that the active species of the reaction might involve a nickel(0)/nickel(II) process. Without a base and with the addition of 15.0  $\mu$ L of H<sub>2</sub>O to the DMF solution, the N-arylated product 3a' could be isolated in 40% yield (Scheme 4c), but no N,N-diarylated product 3a was detected, indicating that the strong base plays an important role in the N,N-diarylation of quinoline. Then, we used 3a' to react with 2a with NaOH, and the target product 3a was obtained in 95% yield under standard conditions (Scheme 4d),

Scheme 4. Control Experiments



which indicates that the N-arylated product 3a' is a probable intermediate.

On the basis of the previously described control experiments and related literature,  ${}^{6c,7b,16a,23}$  we propose here a possible mechanism (Scheme 5). First, the NiCl<sub>2</sub> is reduced to Ni(0) by 8-aminoquinoline (1a); then, catalytic cycle I starts. After the oxidative addition of aryl bromide, intermediate **B** is formed. Then, 1a coordinated with **B** forms intermediate **C**. After successively undergoing deprotonation and reductive elimination, the monosubstituted intermediate **E** is generated, which then participates in the next catalytic cycle II. After reacting with intermediate **B** for the second time, the intermediate **F** is generated, which undergoes deprotonation with the base to form **G**, followed by reductive elimination to generate the *N*,*N*-diarylated product **H**, and the Ni(0) catalyst is regenerated.

In summary, we have developed a simple and efficient methodology for the synthesis of large sterically hindered triarylamines in a one-pot manner. A series of triarylamines can be obtained in good yields by using the inexpensive  $NiCl_2$  and sodium base. Preliminary fluorescence results indicate that these triarylamines with large conjugated systems may have some potential in material chemistry.

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# Scheme 5. Proposed Mechanism



# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00463.

Detailed experimental procedures, characterization data, spectra copies of the <sup>1</sup>H, <sup>19</sup>F, <sup>13</sup>C NMR for obtained products, and X-ray data of 3a and 5 (PDF)

FAIR data, including the primary NMR FID files for compounds 1b-j, 2c, 2o, 3a-o, 4a-l, 5, and 3a' (ZIP)

# **Accession Codes**

CCDC 2056743 and 2060002 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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 $\begin{array}{l} D_{\rm calc} = 1.083 \ {\rm g/cm^3}, \ 14549 \ {\rm reflections} \ {\rm measured} \ (4.002 \le 2\theta \le \\ 49.998), \ 6768 \ {\rm unique} \ (R_{\rm int} = 0.0306, \ R_{\rm sigma} = 0.0541), \ {\rm which} \ {\rm were} \\ {\rm used} \ {\rm in} \ {\rm all} \ {\rm calculations}. \ {\rm The} \ {\rm final} \ [(I > 2\sigma(I)] \ {\rm R1} \ {\rm was} \ 0.0574, \ {\rm and} \ wR2 \\ {\rm was} \ 0.1422. \ {\rm Crystal} \ {\rm data} \ {\rm for} \ {\rm C}_{45} {\rm H}_{29} {\rm N}_5 {\rm O}_2 \ ({\rm 5}) \ (M = 671.73 \ {\rm g/mol}): \\ {\rm monoclinic}, \ {\rm space} \ {\rm group} \ {\rm P21}/n \ ({\rm no}. \ 14), \ a = 18.984(6) \ {\rm \AA}, \ b = \\ {\rm 10.280(2)} \ {\rm \AA}, \ c = 20.565(6) \ {\rm \AA}, \ \beta = 115.39(4), \ V = 3626(2) \ {\rm \AA}^3, \ Z = 4, \\ T = 149.99(10) \ {\rm K}, \ \mu({\rm Mo} \ {\rm K}\alpha) = 0.077 \ {\rm mm}^{-1}, \ D_{\rm calc} = 1.231 \ {\rm g/cm}^3, \\ {\rm 16\ 000\ reflections} \ {\rm measured} \ (4.384 \le 2\theta \le 49.998), \ 6379 \ {\rm unique} \\ (R_{\rm int} = 0.1510, \ R_{\rm sigma} = 0.1720), \ {\rm which} \ {\rm were} \ {\rm used} \ {\rm in} \ {\rm all \ calculations}. \\ {\rm The\ final} \ [(I > 2\sigma(I)] \ {\rm R1} \ {\rm was} \ 0.1114, \ {\rm and} \ wR2 \ {\rm was} \ 0.2701. \end{array}$ 

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