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C–N Bond Formation

Iodine(III)-Mediated *para*-Selective Direct Imidation of Anilides

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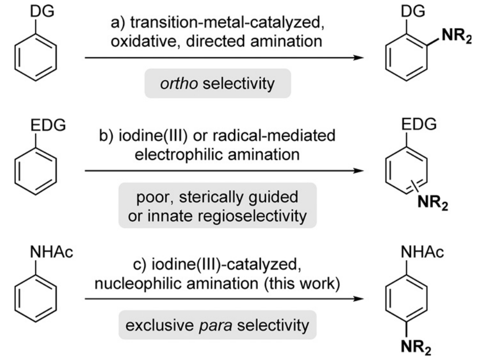
Abstract: The direct, nucleophilic imidation of acetanilide derivatives has been performed under mild, iodine(III)-mediated or -catalyzed conditions, employing lithium triflimide as the nitrogen source. The reaction exhibits exclusive regioselectivity for the *para* position and shows a good tolerance for varied functional groups at both the *ortho* or *meta* positions. Preliminary mechanistic data suggest that the $LiNTf_2$ reagent plays a key role in the reactivity.



Scheme 1. Direct, intermolecular C–N bond-forming reactions of simple arenes.

Direct C–N bond forming reactions have recently gained great interest,[1] as the reaction obviates the need for prefunctionalization,[2] which can significantly increase the number of synthetic steps to access a specific target. Since the initial report on the Pd-catalyzed intramolecular dehydrogenative coupling of biaryl amides,[3] related intermolecular, *ortho*-directed, transition-metal-catalyzed aminations have been the subject of numerous studies (Scheme 1 a).[4,5] Essentially developed with Pd, Cu, and Rh catalysts, and with a wide array of directing groups, these reactions usually employ an external or internal oxidant and require high temperatures. However, they offer excellent regioselectivity for the *ortho* position. This selectivity can be partially diverted towards the *meta* and *para* positions, under electrophilic amination conditions, typically conducted in the presence of a radical initiator or mediated by hypervalent iodine reagents (Scheme 1 b). In the former case, reactions are often performed under relatively harsh conditions and with superstoichiometric quantities of substrate and/or oxidant.[6] To address these issues, milder methods have been developed, for which new reagents or catalyst systems have been specifically designed.[6g,h] More recently, approaches based on visible-light-induced photocatalysis have also emerged as promising alternatives to generate reactive nitrogen-centered radical species.[6i–k] In addition, a few reports on iodine(III)-mediated electrophilic aryl amination have appeared in the past few years.[7–9] As above, excess reagents and high temperatures are routinely applied in order to obtain the desired reactivity. More importantly, the regioselectivity, if not innate,[6h,l] is generally difficult to control, despite the use of additional transition-metal catalysts,[9c,e] resulting in the isolation of complex mixtures of isomers.

Arene functionalization with *exclusive* selectivity for the *para* position has been previously accomplished for C–C, C–O, and C–X bond formation (X = halide),[10] notably under oxidative nucleophilic iodine(III)-mediated conditions.[11] In the context of C–N bond formation, Muñiz and co-workers have reported a single example of *para*-imidation of a benzylanilide substrate with non-commercially available $PhI(NTs)_2$.[12] Furthermore, Zhang and co-workers disclosed a rare example of a *para*-selective imidation reaction, where 2-alkoxyanilide derivatives were coupled with *N*-fluorobenzenesulfonimide (NFSI) in the presence of a palladium catalyst.[13]

Herein we report our findings on the oxidative direct imidation of anilides, exhibiting exclusive regioselectivity for the *para* position (Scheme 1 c). The reaction conditions are mild, employ commercially available reagents in stoichiometric amounts, and are compatible with varied functional groups. In addition, an iodine(III)-catalyzed version of this transformation has been developed and further experiments led us to propose a mechanism.

On the basis of our previous work on the nucleophilic *para*-triflation of anilides with AgOTf, where the latter was found to play an important role for the observed reactivity,[11g] we started our investigation on the related C–N bond forming reaction by employing analogous silver triflimide as the nitrogen source.[14] In the presence of $PhI(OCOCF_3)_2$ (1.2 equiv) in CH_2Cl_2 at room temperature, acetanilide **1 a** was converted into imidation product **2 a** in 30 % NMR yield (Table 1, Entry 1). When the reaction was performed in 1,2-dichloroethane and with $PhI(OAc)_2$ as the oxidant, the yield was further increased to

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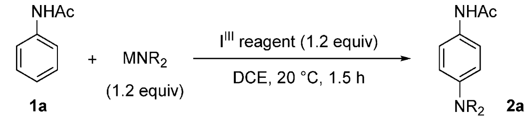
Table 1. Optimization of the reaction conditions for the iodine(III)-mediated *para*-imidation of acetanilide **1 a**.[a]

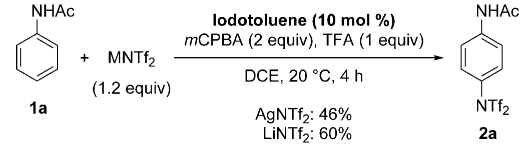


Entry	MNR$_2$	Oxidant	Yield [%][b]
1[c]	AgNTf$_2$	PhI(OCOCF$_3$)$_2$	30
2	AgNTf$_2$	PhI(OCOCF$_3$)$_2$	50
3	AgNTf$_2$	PhI(OPiv)$_2$	44
4	AgNTf$_2$	PhI(OAc)$_2$	50
5[d]	AgNTf$_2$	PhI(OAc)$_2$	60
6[d,e]	LiNTf$_2$	PhI(OAc)$_2$	54
7[d]	LiNTf$_2$	PhI(OAc)$_2$	59(73)[16]
8	AgNPhth	PhI(OAc)$_2$	nd[f]

[a] Reactions performed on 0.25 mmol scale ([**1 a**] = 0.125 M, unless otherwise specified); Tf = SO$_2$CF$_3$, NPhth = Phthalimide. [b] Determined by ^{19}F NMR analysis of the crude reaction mixture, using 4,4′-difluorobenzophenone as an internal standard; isolated yield in parentheses.[16] [c] Reaction performed in CH$_2$Cl$_2$. [d] [**1 a**] = 0.06 M. [e] AgBF$_4$ (10 mol %) was used as an additive. [f] Product not detected by GC-MS or ^{1}H NMR analysis of the crude reaction mixture.

50 %, then to 60 % in a more dilute environment (Entries 4 and 5). Aware of the cost of AgNTf$_2$ as a stoichiometric reagent, we envisaged substituting it for the more practical LiNTf$_2$,[15] together with a catalytic amount of AgBF$_4$, presumably acting as a mild Lewis acid. This modification afforded *para*-phenylenediamine (PPD) derivative **2 a** in 54 % NMR yield (Table 1, Entry 6). Later, in a control experiment, we realized that the metallic counterion Ag$^+$ was in fact unnecessary for the reaction to proceed. Ultimately, treating anilide **1 a** with LiNTf$_2$ (1.2 equiv) and PhI(OAc)$_2$ (1.2 equiv) in 1,2-dichloroethane (DCE) at 20 °C over 1.5 h gave compound **2 a** in 73 % isolated yield (Table 1, Entry 7).[16] Of note, silver-based reagent AgNPhth (NPhth = phthalimide)[17] was completely ineffective for this transformation and only led to the recovery of starting material **1 a** (Table 1, Entry 8).[6a,b,e,i,k, 9a,c,e]

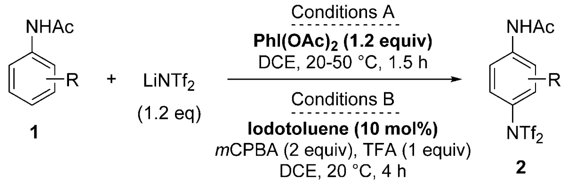
Since first introduced by Fuchigami and Jujita in 1994 and explored ten years later by the groups of Kita and Ochiai,[18] iodine(III)-*catalyzed* coupling reactions have gained considerable attention.[19] Indeed, not only do *stoichiometric* λ^3-iodane reagents generate equimolar amounts of heavy iodoarenes as byproducts, but they are usually unsuitable for large-scale reactions. Hence, we decided to explore the feasibility of a catalytic version of the *para*-imidation of anilides. Based on these initial reports,[18b,c] a rapid survey of various aryl iodides, terminal oxidants, Brønsted and/or Lewis acid additives, and solvents led to the use of iodotoluene (10 mol %), *meta*-chloroperoxybenzoic acid (*m*CPBA, 2 equiv) and trifluoroacetic acid (TFA, 1 equiv) in DCE at room temperature (Scheme 2). In these conditions, PPD derivative **2 a** could be prepared from acetanilide **1 a** and silver or lithium triflimide in 46 or 60 % isolated yield, respectively. Remarkably, no other isomers were detected.

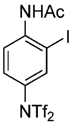
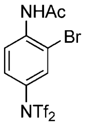
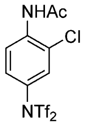
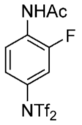
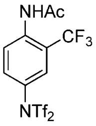
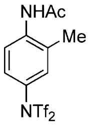
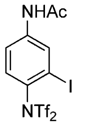
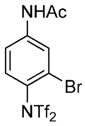
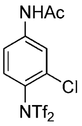
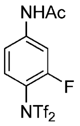
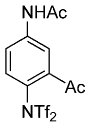
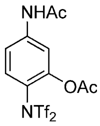
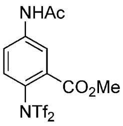
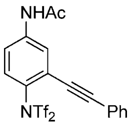
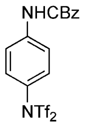
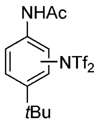


Scheme 2. Iodine(III)-catalyzed *para*-imidation of acetanilide **1 a**.

The scope of this mild oxidative arene imidation was examined with diversely substituted acetanilides **1**, under both stoichiometric and catalytic conditions (Table 2, Conditions A and B, respectively). Anilides bearing an iodide, bromide, chloride, fluoride, methyl, or trifluoromethyl group at the *ortho* position were all found to be compatible substrates, providing the corresponding products **2 b**–**g** in 57 to 81 % yield (Conditions A) or 30 to 66 % yield (Conditions B). *meta*-Substituted halo-acetanilides **1 h**–**k** were also imidated in yields ranging from 40 to 50 %, under Conditions A. These moderate yields may be due to repulsive electronic interactions between the numerous lone pairs present in the two SO$_2$CF$_3$ groups of the nucleophile and the halide substituent of the substrate. This feature seemed even more pronounced under catalytic conditions; whereas 2-fluoro-arylimide **2 k** could be prepared in 56 % yield, the analogous iodo product **2 h** was only generated in trace

Table 2. Scope of the reaction.[a]



2b  A: 70% B: 30%	**2c**  A: 81% B: 60%	**2d**  A: 80% B: 66%	**2e**  A: 61% B: 56%
2f  A: 60% B: 66%	**2g**  A: 57% B: 52%	**2h**  A: 40%[b] B: trace	**2i**  A: 50%[b] B: 24%
2j  A: 40%[b] B: 27%	**2k**  A: 40%[b] B: 56%	**2l**  A: 53% B: 50%	**2m**  A: 30%[b]
2n  A: 47% B: 32%	**2o**  A: 40%[b]	**2p**  A: 42% B: 15%	**2q**  A: 0%

[a] Reactions performed on 0.5 mmol scale, at 20 °C (unless otherwise specified); isolated yields. [b] Reaction performed at 50 °C.

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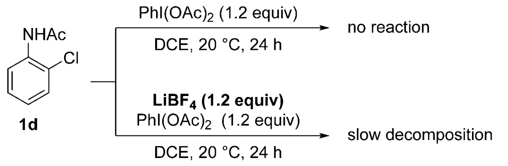
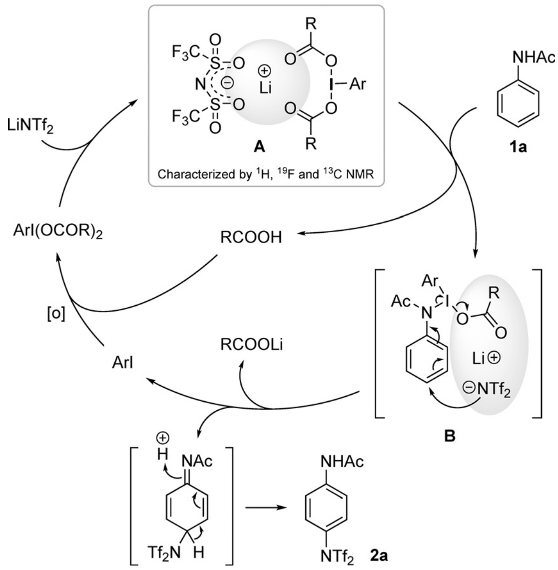
amounts. PPD derivatives **2l**–**n** possessing carbonyl-containing functional groups Ac, OAc, and CO_2Me, and 2-ethynyl-imide **2o**, were obtained in 30–53 and 40% yield, respectively, using $PhI(OAc)_2$ as the oxidant. Cbz-protected anilines (Cbz = carboxybenzyl) are also compatible coupling partners, as illustrated with product **2p**, prepared in 42% yield under Conditions A. This provides the opportunity for complementary deprotection conditions and further functionalization. Interestingly, when acetanilide **1q**, bearing a *tert*-butyl group blocking the *para* position, was submitted to the reaction conditions, neither *ortho* nor *meta* imidation product could be detected. This suggests that a different mode of action than those generally proposed for electrophilic amination processes[6,9] may be operating (see below). Finally, strong electron-donating (OMe) or -withdrawing (NO_2) groups were found to be more problematic, owing to exacerbated or lessened reactivity, leading to over-oxidized products or recovered starting material, respectively. It is, however, worth mentioning that this iodine(III)-mediated/catalyzed arene C–N bond-forming reaction is the first method to provide a direct access to a varied range of substrates[20] under mild conditions, and with exclusive regioselectivity, thus avoiding very difficult separations between two or more isomers.[6e,g,i,k, 9a,c,e]

To gain some insight into this mode of reactivity, several experiments were performed. Acetanilide **1d** was chosen as the starting material, because it allows for a better identification of the different species present during the analyses. Running a typical experiment under Conditions A, in the presence of 1,1-diphenylethylene or 3,5-di-*tert*-butylhydroxytoluene (BHT), had little to no effect on the outcome of the reaction, therefore ruling out a mechanism involving radical species. We then observed that, although prolonged exposure of **1d** to $PhI(OAc)_2$ led to no reaction, the additional presence of $LiBF_4$ induced slow decomposition [Eqs. (1) and (2)]. This is indicative of the probable role of Li^+ as a weak Lewis acid, which may be responsible for the activation of the hypervalent iodine reagent towards the poorly nucleophilic anilide starting material. Additionally, lithium triflimide, initially poorly soluble in chlorinated solvents, could be instantly brought into solution in the presence of an equimolar amount of $PhI(OAc)_2$. The resulting species **A** was characterized by ^1H, ^{19}F, and ^{13}C NMR, showing evidence for weak coordination of the lithium atom to the carbonyl functional groups of the acetate moieties (Scheme 3).[17] Notably, whereas a defined coordination mode around the lithium atom could not be established,[21] displacement of one or two of the acetate "ligands" to form $PhI(OAc)(NTf_2)$ or $PhI(NTf_2)_2$ species,[12] respectively, can reasonably be excluded.[22]



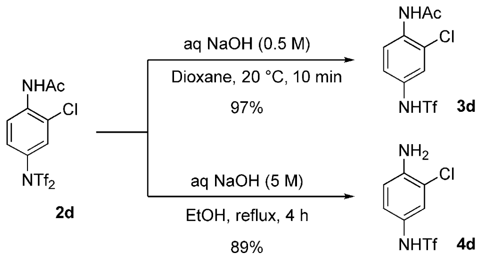
(1)
(2)



Scheme 3. Proposed mechanism of the iodine(III)-catalyzed *para*-selective imidation of anilides (R = CH_3 or CF_3, Ar = phenyl or tolyl).

On the basis of the above observations and previous studies,[7,11,19] a proposed mechanism is depicted in Scheme 3. Formation of species **A** from λ^3-iodane $ArI(OCOR)_2$ and $LiNTf_2$ increases the electrophilicity of the iodine(III) centre towards anilide **1a**, thus leading to intermediate **B**. Next, nucleophilic attack of the proximal triflimide anion occurs in an associative fashion,[11g,23] with concomitant loss of iodoarene and lithium (trifluoro)acetate. Aromaticity is restored to yield triflimide **2a**. Under catalytic Conditions B, the $ArI(OCOR)_2$ species is regenerated in the presence of *m*CPBA. It is difficult at this time to account for the exceptional regioselectivity encountered in these reactions;[11] nevertheless, it is unlikely that it could solely be explained by steric effects and/or enhanced electrophilicity at the *para* position of intermediate **B**.

Finally, the products may be selectively deprotected to yield the corresponding aryl triflamides (ArNHTf),[24] which have been shown to be of interest for both medicinal chemistry and agrochemical industry.[25] For example, aryl triflamide **3d** was readily obtained from compound **2d** in nearly quantitative yield in only 10 min under mild basic conditions [Eq. (3)]. In addition, aniline **4d** was prepared in very good yield, though under stronger conditions [Eq. (4)].



(3)
(4)

In summary, we have developed a practical method for the direct, nucleophilic imidation of acetanilides, with exclusive regioselectivity for the *para* position. The reaction conditions employ either a stoichiometric amount of $PhI(OAc)_2$ or a combi-

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nation of iodotoluene as the catalyst and *m*CPBA as the terminal oxidant. This mild, operationally simple arene C–N bond-forming reaction is realized with $LiNTf_2$ as the nitrogen source, a feature that appears to play a key role in the reactivity, due to both the Li^+ cation acting as a mild Lewis acid and the Tf_2N^- anion as a unique nucleophile. Preliminary studies provide a better understanding of the reaction mechanism, which should facilitate the discovery of milder, more regioselective methods for carbon–heteroatom bond formation from simple arenes.

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Keywords: C–N bond formation · hypervalent iodine · oxidative coupling · *para*-phenylenediamines · umpolung

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