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An Improved Catalyst for Iodine(I/III)-Catalysed Intermolecular C-H Amination

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Abstract: 1,2-Diiodobenzene is presented as an efficient catalyst precursor for the intermolecular amination of arenes under homogeneous conditions. *N*-Troc and *N*-phthalimido-substituted methoxyamines serve as suitable nitrogen sources providing the corresponding aniline derivatives in up to 99% yield and with up to 66:1 regioselectivity. Key for this successful C-N coupling protocol is the strained μ -oxo-bridged conformation of the bisiodine(III) catalyst, which induces unparalleled high reactivity.

Introduction

The development of synthetic methodology for the direct amination of arene hydrocarbons has been a long-standing interest in organic chemistry and life sciences due to the ubiquity of nitrogen-containing molecules in natural products, pharmaceuticals and agrochemicals.^[1,2] It has implication for the defined installment of C-N bonds from ubiquitously available precursors. The particular attractiveness of the synthetic endeavor of C-H amination^[3] lies in the potential to replace the currently most established protocols for arylamine synthesis (Buchwald-Hartwig or Ullmann coupling), which require the use of pre-fabricated aryl halides and related substrates under palladium^[4] and copper catalysis,^[5] respectively. A conceptually alternative approach of direct C-H to C-N transformation should be of sufficiently broad application and has recently been pursued widely using transition metal catalysis.^[3,6] However, in most of the cases the presence of a directing group was needed to pre-coordinate the metal center and engage it in a directed regioselectivity control (Figure 1, eq. 1).^[3,7]

An alternative entry into C-H amination relies on the use of an iodine(III) promoter (eq. 2).^[8] The viability of such a concept was initially demonstrated by Chang,^[9] DeBoef^[10] and Antonchick.^[11] Several complimentary intra-^[12] and intermolecular^[13] protocols followed.^[14] Pioneering was the work of Kita to introduce nitrogenated groups in form of an azido moiety into the aromatic ring.^[15] Finally, the iodine(III) promoter could be conceived as a catalyst by identification of suitable terminal oxidants to re-oxidize the aryl iodide(I) after the organic transformation (eq. 3).^[16] A particularly effective approach from Antonchick was obtained using Kita catalyst **1**.^[17]

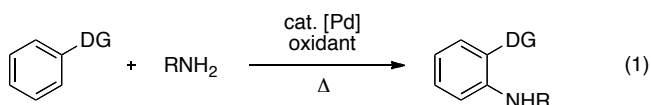
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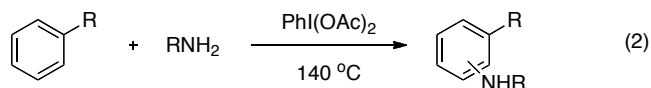
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Intermolecular Directed C-H Amination

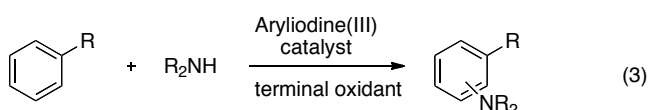


Intermolecular Metal-Free C-H Amination: Stoichiometric



R = electron donating and withdrawing

Intermolecular Metal-Free C-H Amination: Catalytic



R = electron donating and withdrawing

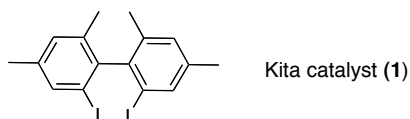


Figure 1. Representative examples for oxidative amination of arenes.

The current *status quo* in the field still leaves room for an improved catalytic system that could improve the turnover number of the intermolecular approach using less harsh conditions, and increasing the scope of the reaction. We here report on an advanced iodine(III) catalyst for the direct intermolecular amination of arenes using Troc-protected amines as nitrogen sources.

Results and Discussion

We initially investigated the possible amination of arenes using preformed diaryliodonium salts with *N*-tosyl *N*-methoxyamine **2a** as the currently most successful nitrogen source (Table 1).^[12b,13e,13j] The aim of this investigation was to arrive at detailed knowledge on the transferability of different aryl groups and thus to identify an optimum aryl monoiodine(I) catalyst. We started testing different iodonium salts, both commercially available and literature-known ones.^[18] The presence of a small counter-ion effect was observed from these studies. For diphenyliodonium, the chloride anion provided arylation product **3a** in 73% yield (entry 1), which could be increased by using hexafluorophosphate, acetate or nitrate (77-82% yield, entries 3-5). Selective phenylation was also observed with a mixed iodonium reagent containing phenyl and 4-anisyl as arenes (entry 8). DCE was identified as the optimum solvent, other solvents such as CH₂Cl₂, CHCl₃ and fluorinated ones were observed to provide lower or no yields (entries 7-10). Exchanging the tosyl for a benzoyl group (reagent **2b**), provided a less efficient process (entry 11). Reactions at higher temperature resulted in decreased conversions (entries 2,12).

These orientation experiments revealed the general feasibility to employ hypervalent iodine reagents of the general bisaryliodonium structure for arylamine synthesis. While this work was under investigation, a related investigation by Olofsson became available.^[19]

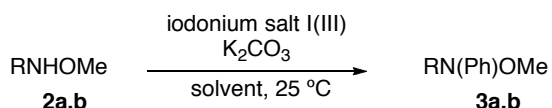


Table 1. Stoichiometric amination using preformed diaryliodonium salts.

Entry	R	Iodine(III)	Solvent	Yield [%] ^[a]
1	Ts (2a)	[Ph ₂]Cl	DCE	73

2 ^[b]	Ts (2a)	[Ph ₂ I]Cl	DCE	-
3	Ts (2a)	[Ph ₂ I]PF ₆	DCE	82
4	Ts (2a)	[Ph ₂ I]OAc	DCE	79
5	Ts (2a)	[Ph ₂ I]NO ₃	DCE	77
6	Ts (2a)	[PhIAn]OTs ^[c]	DCE	63
7	Ts (2a)	[PhIAn]OTs	DCM	73
8	Ts (2a)	[PhIAn]OTs	CHCl ₃	75
9	Ts (2a)	[PhIAn]OTs	TFE	nr ^[d]
10	Ts (2a)	[PhIAn]OTs	HFIP	nr
11	Bz (2b)	[Ph ₂ I]Cl	DCE	38
12 ^[b]	Bz (2b)	[Ph ₂ I]Cl	DCE	20

[a] Isolated yield after purification. [b] Reaction at 40 °C. [c] An = 4-anisyl. [d] nr = no reaction.

In the subsequent investigation, we centered on the possibility to arrive at appropriate catalytic conditions for the corresponding iodine(III)-promoted arylamine formation. We started screening oxidants, additives, solvents and temperature using the *N*-methoxysulfonamide as nitrogen source and iodobenzene as catalyst precursor. The reaction for synthesis of **3a** could be transferred to a catalytic reaction of direct C-H amination of benzene (Table 2) employing peracetic acid as oxidant. With an equimolar amount, the reaction with 10 equivalents of benzene provided 22% yield of **3a** (entry 1). Increasing to 1.5 equivalents improved the yield to 55% (entry 2). Similar values were obtained in the absence of DCE and with 20 equivalents of benzene (entries 3,4). Addition of HFIP improved the yield to 70% (entry 5), while lowering the temperature had little effect (entry 6).

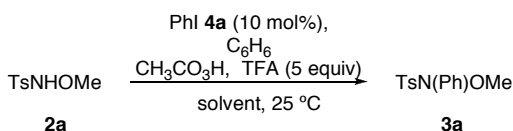


Table 2. Catalytic amination of benzene using iodobenzene as catalyst.

Entry	CH ₃ CO ₃ H (equiv.)	C ₆ H ₆ (equiv)	Solvent	Time [h]	Yield [%] ^[a]
1	1.0	10	DCE	22	22
2	1.5	10	DCE	3	55
3	1.5	10	-	2	52
4	1.5	20	DCE	2	57
5	1.5	20	DCE/HFIP	2	70
6	1.5	20	DCE/HFIP	16	73

[a] Isolated yield after purification. [b] Reaction at 0 °C.

Following the outcome from Table 1, different sterically demanding iodine derivatives were investigated as catalysts in this transformation under these conditions, in view to improve future C-H amination reactions with substituted arenes. Iodoarenes bearing methyl-substitution led to unexpectedly low performances (Figure 2). While iodobenzene as standard gave yields of **3a** of 57% and 70% depending on the solvent, dimethylated derivatives **4b** and **4c** performed less efficient in DCE and did not provide any product in the presence of HFIP. Iodomesitylene **4d** was found to be entirely non-reactive. In contrast, halogenated iodoarenes **4e** and **4f** led to

yields comparable to **4a**, although required significantly prolonged reaction times. Finally, the 1,2-diiodobenzene **4g** proved surprisingly efficient even at a reduced catalyst loading of 3 mol% and provided the highest yield of 89% within 2 h reaction time.

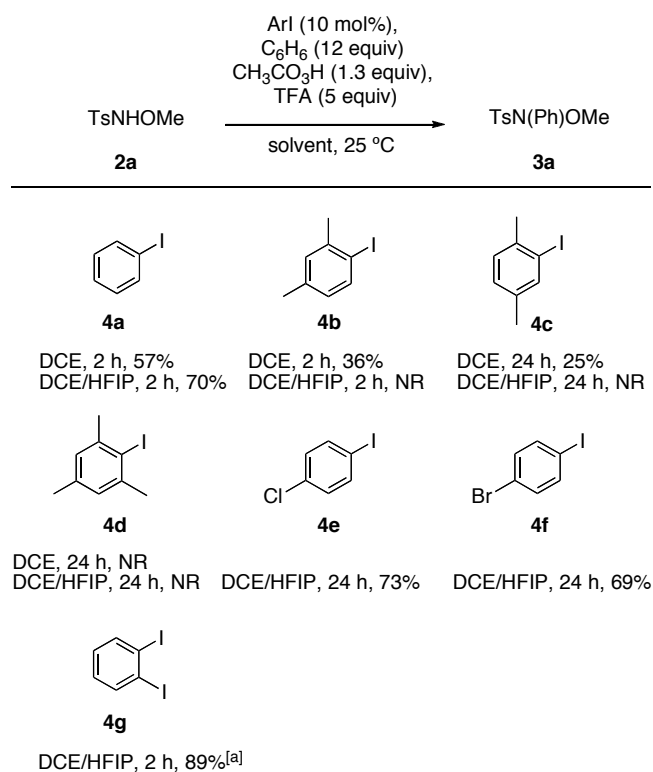


Figure 2. Evaluation of aryl iodides for the catalytic amination of benzene with **2a**. [a] With 3 mol% catalyst loading.

This compound was explored in a rapid screening of several different nitrogen sources (Figure 3). While due to solubility problems the mesyl derivative **2c** gave a low yield of 19%, the corresponding Cbz and Troc derivatives **2d,e** formed the corresponding products **3d,e** in 65% each. Although **3a** formed in comparably high yield, further attempts on substituted arenes failed to give substantial regio- and chemoselectivity for this nitrogen source. Due to the interesting deprotecting properties of the Troc group,^[20,21] this group was subsequently investigated further for several arenes (Figure 4). In the presence of 4 mol% of **4g** as catalyst, **2e** underwent several arylation reactions with different arene components, which include hydrocarbons such as toluene, ethyl benzene, *tert*-butyl benzene and cyclohexyl benzene. The corresponding products **3f-i** are formed in good yields and with acceptable regioselectivities. Halogenated arenes chlorobenzene, bromobenzene and fluorobenzene are also tolerated and yield products with good selectivities. For the chloro and bromo derivatives **3j,k** the regioisomers could be separated, and for **3l** two isomers are formed in large excess. Disubstituted arenes underwent clean amination as well as deduced from dimethyl derivative **3m** and derivative **3n**. In order to demonstrate that other nitrogen sources can be employed equally, Cbz derivative **2d** was arylated with toluene giving regioisomeric derivatives **3o** in an outcome comparable to **3f**.

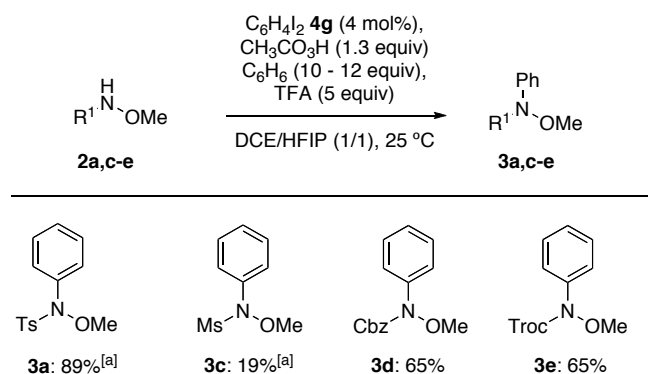


Figure 3. Variation of nitrogen sources in the amination of benzene catalysed by **4g**. [a] With 3 mol% catalyst loading.

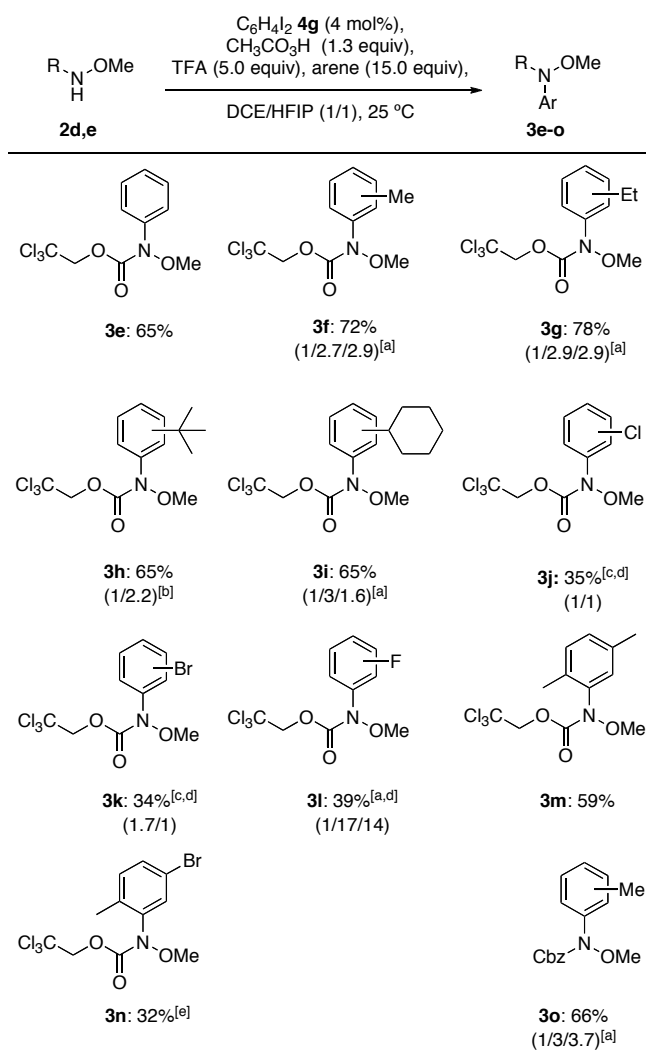


Figure 4. Scope of the amine arylation catalysed by **4g**. [a] ratio of o,m,p-regioisomers (unseparated and undetermined regarding the position); regioisomeric ratios were calculated on the ¹H-NMR spectra. [b] Ratio of m,p-isomers (unseparated); regioisomeric ratios were calculated on the ¹H-NMR spectra. [c] the ortho/para-regioisomers were fully separated by column chromatography. [d] reaction temperature of 40 °C. [e] 2.0 equivalents of arene were used.

In order to compare the efficiency of **4g** against the benchmark in the area,^[13e] *N*-acetyl aminophthalimide **5** was employed as nitrogen source (Figure 5). Excellent chemical yields were obtained for the four C-N coupling products **6a-d** from the arenes benzene, toluene, chlorobenzene and bromobenzene, respectively. In addition, excellent regioselectivities were obtained for the cases of **6c** and **6d**, in which the 1,4-derivatives were by far the predominating constitutions. These values surpass previous results and demonstrate the potential of **4g** as catalyst in the oxidative amination of arenes.

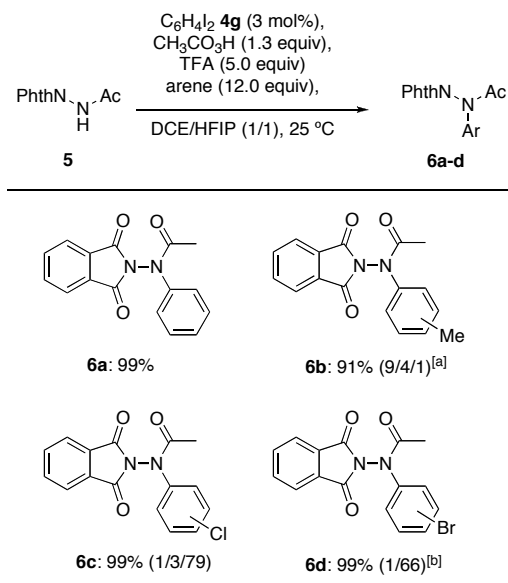
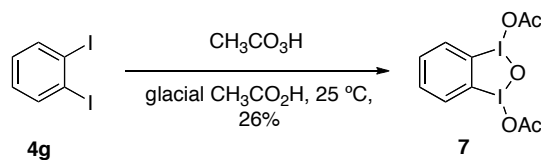


Figure 5. Catalytic arylation of *N*-acetyl aminophthalimide with **4g** as catalyst. [a] values in brackets refer to regioisomers (ortho/meta/para). [b] values in brackets refer to regioisomers (ortho/para).

To gain mechanistic understanding, the reaction of precatalyst **4g** with peracetic acid was investigated (Scheme 1). Upon oxidation,^[22] 1,2-diiodobenzene provides the expected μ -oxo-bridged bisiodine(III) derivative **7**, which due to its high reactivity could only be isolated in pure form in 26% yield. Crystals suitable for X-ray analytical studies were grown from a solution of **7** in $\text{CH}_2\text{Cl}_2/n$ -hexane. The molecular structure of **7** (Figure 6) shows significant deviation from linearity for the central I-O-I group.^[23] We reason that the observed high reactivity in catalysis with **4g** results from the marked fragility of the five-membered μ -oxo-arrangement. Indeed, as demonstrated above, the performance of the **4g/7** catalytic system is essentially better than for comparable diiodine derivatives such as **1**.^[13e,24,25]



Scheme 1. Synthesis of μ -oxo-bridged bisiodine(III) derivative **7**.

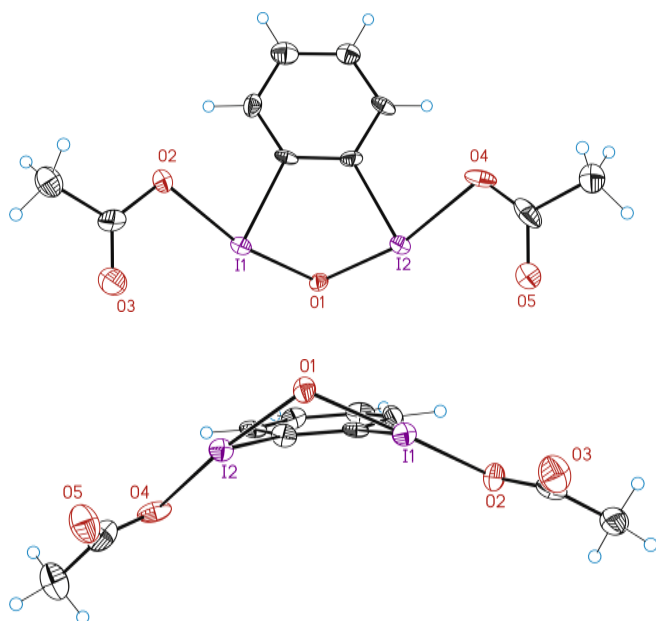
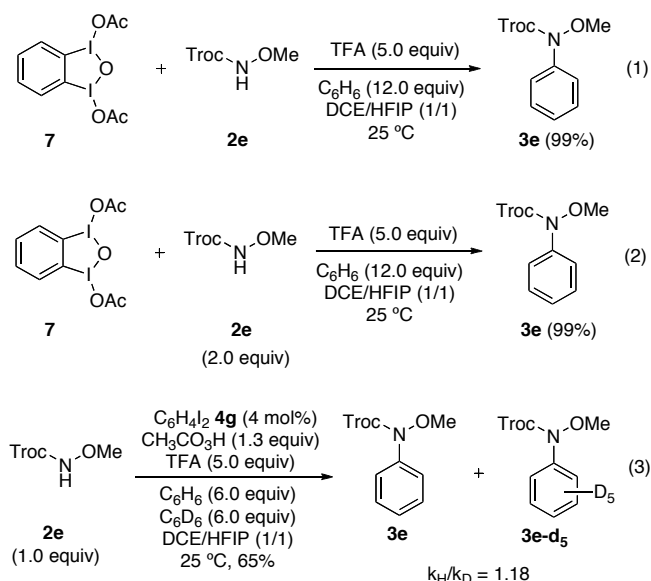


Figure 6. Solid state structure of catalyst **7**.^[23] Five-membered μ -oxo-arrangement (top) and deviation from linearity of the I-O-I arrangement (bottom). Selected bond lengths (Å) and angles ($^\circ$): I1-O1 2.035(7), I2-O1 2.028(7), I1-O2 2.214(7), I2-O4 2.260(8), I2-O1-I1 110.7(3), O1-I1-C1 83.8(3), O1-I2-C2 82.9(4).



Scheme 2. Control experiments regarding the reactivity of **4g/7**.

To further study this context, three control reactions were carried out (Scheme 2). First, a control reaction was carried out employing preformed **7** as reagent in the phenylation of **2e** under conditions comparable to the catalysis (Scheme 1, eq. 1). In this case, formation of **3e** as the only product was encountered. Importantly, raising the ratio between **2e** and **7** to 2:1, an overall yield of 99% (based on **2e**) confirms that, in an apparent contrast to earlier systems, both iodine(III) centers in **7** are capable of promoting arylation (eq. 2). This is a marked contrast to earlier mechanistic suggestions.^[13e]

The opening of the five-membered I-O-I ring in **7** and therefore the arylation at the electrophilic iodine(III) centers is indeed not rate-limiting as a control experiment with C_6H_6 **3e** and C_6D_6 **3e-d₅** suggests (eq. 3). A low kinetic isotope effect of 1.18 was observed suggesting that the arylation is rapid for **7**. This implies other events as the slow step of the overall catalysis, which may rest with the introduction of the nitrogen partner into the coordination sphere of the iodine(III) or with the final C-N bond forming reaction.

Conclusions

In summary, we have developed a new catalyst system for the direct C-H amination of arenes. This compound is derived from oxidation of 1,2-diiodobenzene with peracetic acid as convenient oxidant. The reactions proceed with unprecedented low catalyst loading of 3-4 mol% and provide the amination of substituted arenes with up to 66:1 regioisomeric control. We expect this catalyst to be of successful applicability in related oxidative transformations as well.

Experimental Section

Representative synthesis of protected anilines using preformed diaryliodonium salts: The respective nitrogen source (0.15 mmol, 1.0 equiv.) was dissolved in 1,2-dichloroethane (0.5 mL) and K_2CO_3 (1.0 equiv.) and diphenyliodonium hexafluorophosphate (1.0 equiv.) were added. The mixture was stirred at rt for 24 h and then washed with water, extracted with CH_2Cl_2 (10 mL x 3), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography (*n*-hexane/EtOAc, 95/5, v/v).

Synthesis of 1,3-diacetoxy-1,3-dihydro-1,3,2-benzooiodoxole (7**):** In a Schlenk tube under argon atmosphere, 1,2-diiodobenzene (40 μ L, 0.3 mmol) was dissolved in glacial acetic acid (2.0 mL) and the mixture was warmed to 30 $^\circ$ C. Peracetic acid (0.23 mL, 35 wt% in acetic acid, 1.2 mmol) was added dropwise. After all the peracetic acid had been added, the mixture was stirred for 20 min. Distilled water was added leading to formation of a white precipitate. The white solid was filtered, washed with water and diethyl ether and afforded the desired title compound in pure form (37 mg, 26% yield); m.p.: 172-175 $^\circ$ C. 1H -NMR ($CDCl_3$, 500 MHz): δ = 2.09 (s, 6H), 7.61-7.65 (m, 2H), 8.01-8.05 (m, 2H). ^{13}C -NMR ($CDCl_3$, 125 MHz): δ = 21.6, 120.1, 131.9, 135.3, 178.4. IR (cm^{-1}): 1629, 1364, 1301, 740, 666, 550, 471. HRMS (MALDI⁺): calc. for $[C_8H_7I_2O_3]^+$: 404.8479; found: 404.8443 [M-OAc].

Catalytic synthesis of protected anilines using catalyst 4g: The respective nitrogen source (0.15 mmol, 1.0 equiv.) was dissolved in a mixture of 1,2-dichloroethane and 1,1,1,3,3,3-hexafluoro-2-isopropanol (1/1, v/v) (0.5 mL). 1,2-Diiodobenzene (3 mol%), benzene (12.0 equiv.), peracetic acid 35% wt (1.3 equiv.) and trifluoroacetic acid (5.0 equiv.) were added in the order. The mixture was stirred at rt for the time indicated and then washed with water, extracted with CH₂Cl₂ (10 mL x 3), dried over Na₂SO₄ and concentrated under reduced pressure. The crude was purified by flash chromatography (n-hexane/EtOAc, 95/5, v/v).

Full product characterization and additional experimental details are given in the Supporting Information.

Acknowledgements

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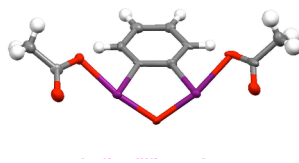
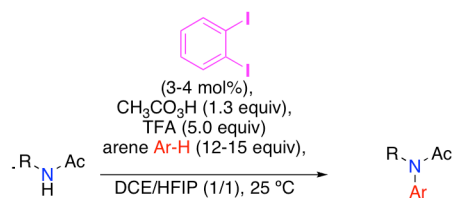
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Entry for the Table of Contents (Please choose one layout)

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Page No. – Page No.

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Catalysed Intermolecular C-H
Amination**

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