DOI: 10.1002/adsc.201600191

Advanced Synthesis & Catalysis

Very Important Publication

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

Nicola Lucchetti,[a] Michelangelo Scalone,[b] Serena Fantasia,[b] and Kilian Muñiz[a,c,*]

[a] Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, 16 Avgda. Països Catalans, 43007 Tarragona, Spain
E-mail: kmuniz@iciq.es
[b] F. Hoffmann-La Roche Ltd., Process Research & Development, Grenzacherstrasse 124, 4070 Basel, Switzerland
[c] Catalan Institution for Research and Advanced Studies (ICREA), Pg. Lluís Companys 23, 08010 Barcelona, Spain

Received: February 15, 2016; Revised: March 2, 2016; Published online: ■■ ■■, 0000

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201600191.

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.

Keywords: amination; arenes; C–H functionalization; catalysis; hypervalent iodine

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 as natural products, pharmaceuticals and agrochemicals.[1,2] It has implications for the defined instalment 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 complementary intra-[12] and intermolecular[13] protocols followed.[14] Pioneering was the work of Kita to

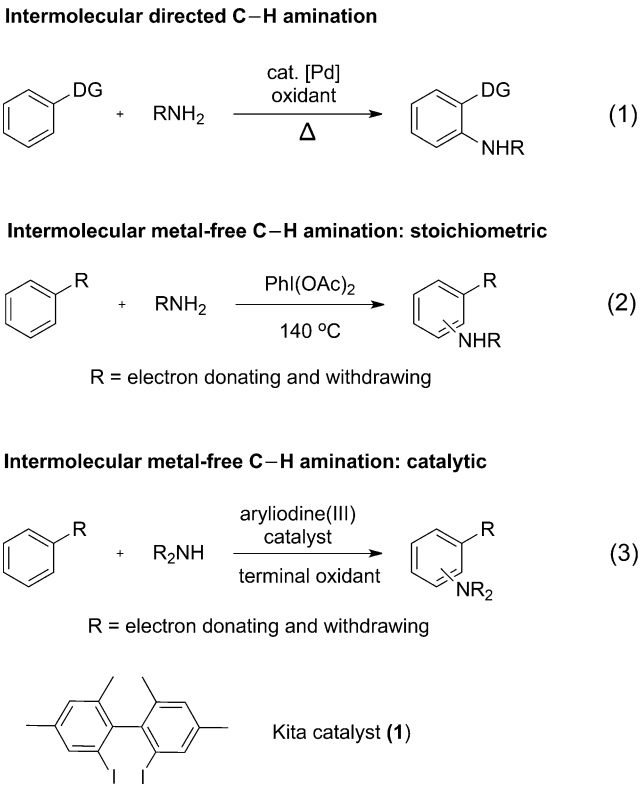


Figure 1. Representative examples for oxidative amination of arenes.

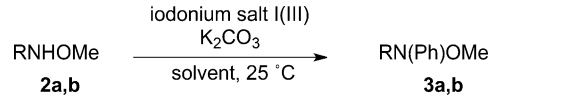
introduce nitrogenated groups in form of an azido moiety into the aromatic ring.[15] Finally, the iodine(III) promoter could be conceived as a catalyst by identification of suitable terminal oxidants to re-oxidize the aryl iodide(I) after the organic transformation [Eq. (3)].[16] A particularly effective approach from Antonchick was obtained using the Kita catalyst **1**.[17]

The current *status quo* in the field still leaves room for an improved catalytic system that could enhance 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,j] The aim of this investigation was to acquire 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 CH_2Cl_2, $CHCl_3$ 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 and 12).

Table 1. Stoichiometric amination using preformed diaryliodonium salts.



Entry	R	Iodine(III)	Solvent	Yield [%][a]
1	Ts (**2a**)	$[Ph_2I]Cl$	DCE	73
2[b]	Ts (**2a**)	$[Ph_2I]Cl$	DCE	–
3	Ts (**2a**)	$[Ph_2I]PF_6$	DCE	82
4	Ts (**2a**)	$[Ph_2I]OAc$	DCE	79
5	Ts (**2a**)	$[Ph_2I]NO_3$	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**)	$[Ph_2I]Cl$	DCE	38
12[b]	Bz (**2b**)	$[Ph_2I]Cl$	DCE	20

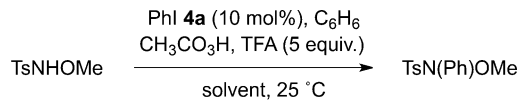
[a] Isolated yield after purification.
[b] Reaction at 40 °C.
[c] An = 4-anisyl, [d] NR = no reaction.

These orientation experiments revealed the applicability of hypervalent iodine reagents of the general bisaryliodonium structure for arylamine synthesis. While the present work was under investigation, a related publication by Olofsson became available.[19]

In the following, we centred 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 the synthesis of **3a** could be transferred to a catalytic reaction for direct C–H amination of benzene (Table 2) employing peracetic acid as oxidant. With an equimolar amount of oxidant, the reaction with 10 equivalents of benzene provided a 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 and 4). Addition of HFIP improved the yield to 70% (entry 5), while lowering the temperature had little effect (entry 6).

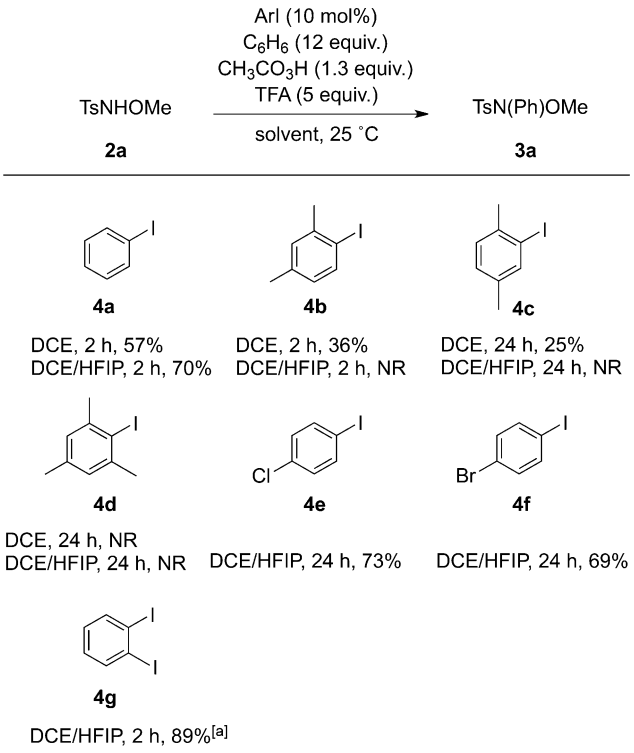
Following the outcome from Table 1, different sterically demanding iodine derivatives were investigated as catalysts in this transformation under these conditions, with a view to improve future C–H amination reactions with substituted arenes. Iodoarenes bearing methyl substitution led to unexpectedly low perform-

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



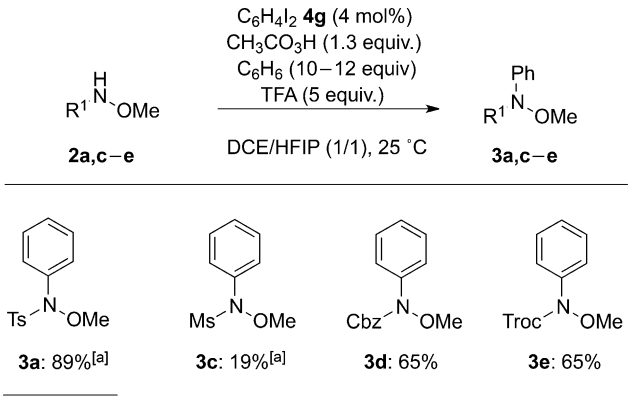
Entry	CH_3CO_3H (equiv.)	C_6H_6 (equiv.)	Solvent	Time [h]	Yield [%][a]
1	1.0	10	DCE	22	22
2	1.5	10	DCE	3	55
3	1.5	10	–	2	52
4	1.5	20	DCE	2	57
5	1.5	20	DCE/HFIP	2	70
6[b]	1.5	20	DCE/HFIP	16	73

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



[a] With 3 mol% catalyst loading.

Figure 2. Evaluation of iodoarenes for the catalytic amination of benzene with **2a**.



[a] With 3 mol% catalyst loading.

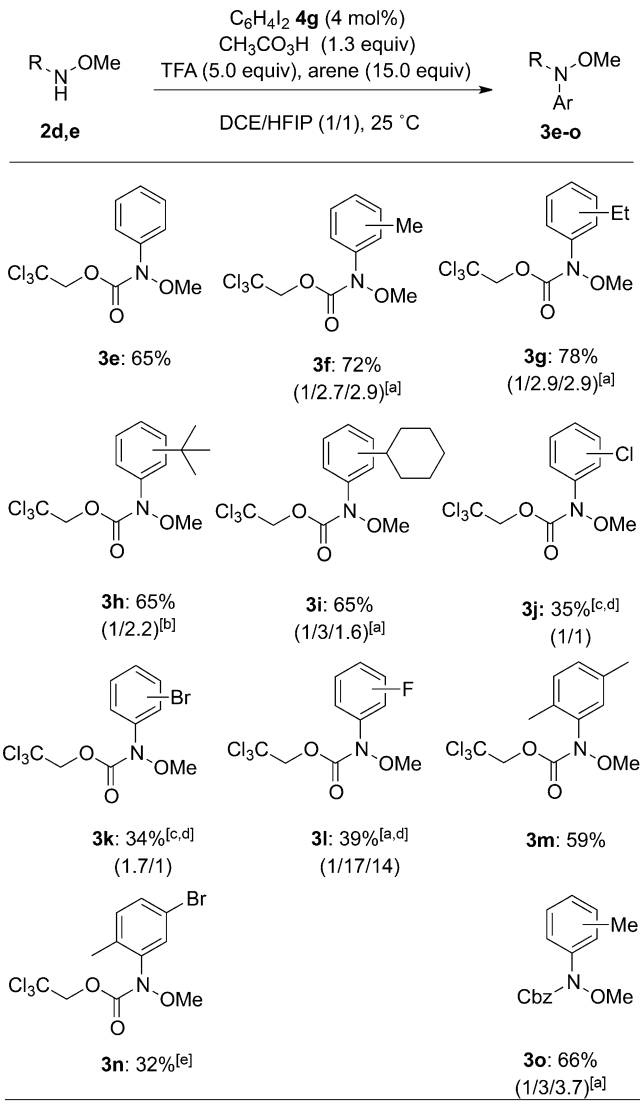
Figure 3. Variation of nitrogen sources in the amination of benzene catalysed by **4g**.

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

This compound was explored in a preliminary 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** and **2e** formed the corresponding products **3d** and **3e** 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] it 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 included hydrocarbons such as toluene, ethylbenzene, *tert*-butylbenzene and cyclohexylbenzene. 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** and **3k** 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 methyl, bromo 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 that of **3f**.

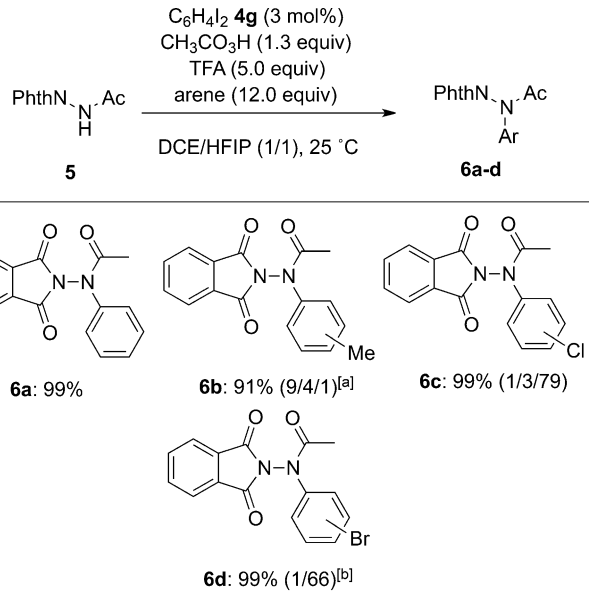
In order to compare the efficiency of **4g** against the benchmark in the area,[13e] *N*-acetylaminophthalimide **5** was employed as nitrogen source (Figure 5). Excellent chemical yields were obtained for the four C–N coupling products **6a–d** from the arenes benzene, toluene, chlorobenzene and bromobenzene, 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.

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 CH_2Cl_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-



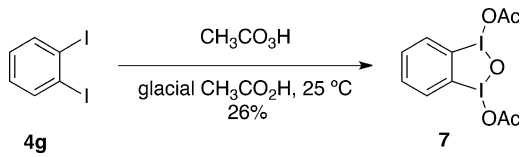
[a] Ratio of *o*,*m*,*p*-regioisomers (unseparated and undetermined regarding the position); regioisomeric ratios were calculated on the ^{1}H NMR spectra.
[b] Ratio of *m*,*p*-isomers (unseparated); regioisomeric ratios were calculated on the ^{1}H NMR spectra.
[c] The *o*/*p*-regioisomers were fully separated by column chromatography.
[d] Reaction temperature of 40 °C.
[e] 2.0 equiv. of arene were used.

Figure 4. Scope of the amine arylation catalysed by **4g**.



[a] Values in brackets refer to regioisomers (*o*/*m*/*p*).
[b] Values in brackets refer to regioisomers (*o*/*p*).

Figure 5. Catalytic arylation of *N*-acetylaminophthalimide with **4g** as catalyst.



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

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]

To further study this context, three control reactions were carried out (Scheme 2). First, a control reaction employed preformed **7** as reagent in the phenylation of **2e** under conditions comparable to the catalysis [Scheme 2, Eq. (4)]. 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. (5)]. This is in 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**-d_5 suggests [Eq. (6)]. 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 for the direct C–H amination of arenes. This compound

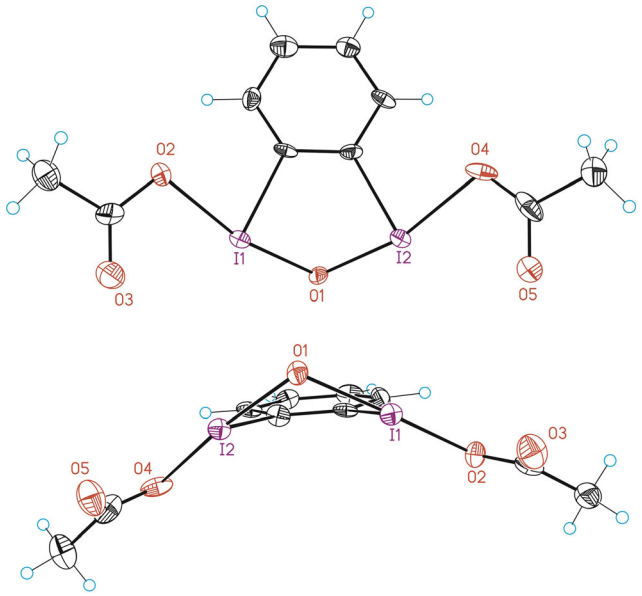
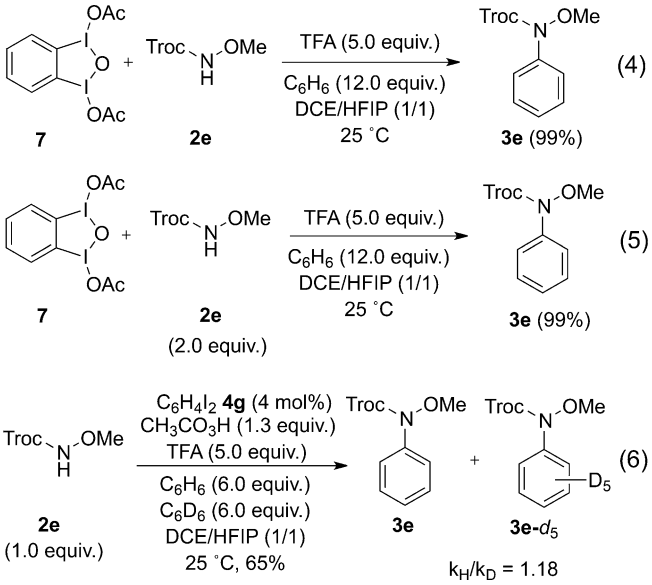


Figure 6. Solid state structure of catalyst **7**.[23] Five-membered μ-oxo-arrangement (*top*) and deviation from linearity of the I–O–I arrangement (*bottom*). Selected bond lengths (Å) and angles (°): I1–O1 2.035(7), I2-O1 2.028(7), I1–O2 2.214(7), I2–O4 2.260(8), I2–O1–I1 110.7(3), O1–I1–C1 83.8(3),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



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

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 room temperature for 24 h and then washed with water, extracted with CH_2Cl_2 (10 mL × 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-benzooiodooxole (7)

In a Schlenk tube under an argon atmosphere, 1,2-diiodobenzene (40 μL, 0.3 mmol) was dissolved in glacial acetic acid (2.0 mL) and the mixture was warmed to 30 °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; yield: 37 mg (26%); mp 172–175 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 2.09$ (s, 6H), 7.61–7.65 (m, 2H), 8.01–8.05 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 21.6$, 120.1, 131.9, 135.3, 178.4. IR: $\nu = 1629$, 1364, 1301, 740, 666, 550, 471 cm^{-1}; HR-MS (MALDI$^+$): $m/z = 404.8443$ $[M-OAc]^+$, calcd. for $[C_8H_7I_2O_3]^+$: 404.8479.

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 that order. The mixture was stirred at room temperature for the time indicated and then washed with water, extracted with CH_2Cl_2 (10 mL × 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).

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

Acknowledgements

We thank F. Hoffmann-La Roche Ltd., the Spanish Ministry for Economy and Competitiveness and FEDER (CTQ2014-56474R grant to K. M., Severo Ochoa Excellence Accreditation 2014-2018 to ICIQ, SEV-2013-0319) for financial support and Dr. E. Escudero-Adán for the X-ray analysis.

References

[1] a) A. Ricci, *Modern Amination Methods*, Wiley-VCH, Weinheim, **2000**; b) A. Ricci, *Amino Group Chemistry: From Synthesis to the Life Sciences*, Wiley-VCH, Weinheim, **2008**; c) R. Hili, A. K. Yudin, *Nat. Chem. Biol.* **2006**, *2*, 284; d) *Chiral Amine Synthesis: Methods, Developments and Applications*, (Ed.: T. C. Nugent), Wiley-VCH, Weinheim, **2010**.

[2] *The Chemistry of Anilines*, (Ed.: Z. Rappoport), Vols. 1 and 2, John Wiley & Sons, New York **2007**.

[3] a) J. Jiao, K. Murakami, K. Itami, *ACS Catal.* **2016**, *6*, 610; b) *Amination and Formation of sp^2 C-N Bonds*, in: *Topics in Organomet. Chemistry*, (Eds.: M. Taillefer, D. Ma), Vol. 46, Springer, Berlin, Heidelberg, **2012**; c) F. Collet, R. H. Dodd, P. Dauban, *Chem. Commun.* **2009**, 5061; d) S. H. Cho, J. Y. Kim, J. Kwak, S. Chang, *Chem. Soc. Rev.* **2011**, *40*, 5068; e) M.-L. Louillat, F. W. Patureau, *Chem. Soc. Rev.* **2014**, *43*, 901; f) C. Liu, H. Zhang, W. Shi, A. Lei, *Chem. Rev.* **2011**, *111*, 1780.

[4] a) J. F. Hartwig, in: *Handbook of Organopalladium Chemistry for Organic Synthesis*, (Ed.: E. Negishi), Wiley-Interscience, New York, **2002**, p 1051; b) L. Jiang, S. L. Buchwald, *Metal-Catalyzed Cross-Coupling Reactions*, 2nd edn., Wiley-VCH, Weinheim, **2004**, Vol. 2, p. 699; c) A. R. Muci, S. L. Buchwald, *Top. Curr. Chem.* **2002**, *219*, 131; d) J. F. Hartwig, *Synlett* **2006**, 1283; e) J. F. Hartwig, *Acc. Chem. Res.* **2008**, *41*, 1534; f) D. S. Surry, S. L. Buchwald, *Chem. Sci.* **2011**, *2*, 27; g) J. Kim, H. J. Kim, S. Chang, *Eur. J. Org. Chem.* **2013**, 3201.

[5] a) F. Ullmann, J. Bielecki, *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 2174; b) F. Ullmann, *Justus Liebigs Ann. Chem.* **1904**, *332*, 38; c) G. Evano, N. Blanchard, M. Toumi, *Chem. Rev.* **2008**, *108*, 3054; d) R. Giri, J. F. Hartwig, *J. Am. Chem. Soc.* **2010**, *132*, 15860; e) D. S. Surry, S. L. Buchwald, *Chem. Sci.* **2010**, *1*, 13.

[6] a) K. Shin, H. Kim, S. Chang, *Acc. Chem. Res.* **2015**, *48*, 1040; b) A. R. Dick, M. S. Remy, J. W. Kampf, M. S. Sanford, *Organometallics* **2007**, *26*, 1365; c) R. Shrestha, P. Mukherjee, Y. Tan, Z. C. Litman, J. F. Hartwig, *J. Am. Chem. Soc.* **2013**, *135*, 8480; d) L. Wang, D. L. Priebbenow, W. Dong, C. Bolm, *Org. Lett.* **2014**, *16*, 2661; e) H. Xu, X. Quiao, S. Yang, Z. Shen, *J. Org. Chem.* **2014**, *79*, 4414.

[7] Selected recent work: a) G. B. Boursalian, M.-Y. Ngai, K. N. Hojczyk, T. Ritter, *J. Am. Chem. Soc.* **2013**, *135*, 13278; b) A. M. Martínez, N. Rodriguez, R. G. Arrayás, J. C. Carretero, *Chem. Commun.* **2014**, *50*, 2801; c) A. A. Kantak, L. Marchetti, B. DeBoef, *Chem. Commun.* **2015**, *51*, 3574; d) D. Zhu, G. Yang, J. He, L. Chu, G. Chen, W. Gong, K. Chen, M. D. Eastgate, J.-Q. Yu, *Angew. Chem.* **2015**, *127*, 2527; *Angew. Chem. Int. Ed.* **2015**, *54*, 2497; e) C. J. Park, S. Chang, *Angew. Chem.* **2015**, *127*, 14309; *Angew. Chem. Int. Ed.* **2015**, *54*, 14103; f) Y. Park, S. Jee, J. G. Kim, S. Chang, *Org. Process Res. Dev.* **2015**, *19*, 1024; g) Y. Park, K. T. Park, J. G. Kim, S. Chang, *J. Am. Chem. Soc.* **2015**, *137*, 4534; h) K. Shin, H. Kim, S. Chang, *Acc. Chem. Res.* **2015**, *48*, 1040.

[8] For pertinent reviews on iodine(III) reagents: a) V. V. Zhdankin, *Hypervalent Iodine Chemistry Preparation, Structure and Synthetic Applications of Polyvalent Iodine Compounds*, Wiley, Chichester, **2013**; b) M. S. Yusubov, V. V. Zhdankin, *Resource-Efficient Technologies* **2015**, *1*, 49; c) V. V. Zhdankin, *J. Org. Chem.* **2011**, *76*, 1185; d) A. Duschek, S. F. Kirsch, *Angew. Chem.* **2011**, *123*, 1562; *Angew. Chem. Int. Ed.* **2011**, *50*, 1524; e) S. Schäfer, T. Wirth, *Angew. Chem.* **2010**, *122*, 2846; *Angew. Chem. Int. Ed.* **2010**, *49*, 2786; f) M. Ngatimin, D. W. Lupton, *Aust. J. Chem.* **2010**, *63*, 653; g) M. S. Yusubov, A. V. Maskaev, V. V. Zhdankin, *Arkivoc* **2009**, *1*, 370; h) V. V. Zhdankin, P. J. Stang, *Chem. Rev.* **2008**, *108*, 5299; i) M. A. Ciufolini, N. A. Braun, S. Canesi, M. Ousmer, J. Chang, D. Chai, *Synthesis* **2007**, 3759; j) *Top. Curr. Chem.* Vol. 224, (Ed.: T. Wirth), Springer, Berlin, **2003**; k) V. V. Zhdankin, P. J. Stang, *Chem. Rev.* **2002**, *102*, 2523; l) P. J. Stang, V. V. Zhdankin, *Chem. Rev.* **1996**, *96*, 1123.

[9] a) S. H. Cho, J. Yoon, S. Chang, *J. Am. Chem. Soc.* **2011**, *133*, 5996; b) H. J. Kim, J. Kim, S. H. Cho, S. Chang, *J. Am. Chem. Soc.* **2011**, *133*, 16382.

[10] A. A. Kantak, S. Potavathri, R. A. Barham, K. M. Romano, B. DeBoef, *J. Am. Chem. Soc.* **2011**, *133*, 19960.

[11] R. Samanta, I. Lategahn, A. P. Antonchick, *Chem. Commun.* **2012**, *48*, 3194.

[12] Intramolecular reactions: see ref.[9a] and a) A. P. Antonchick, R. Samanta, K. Kulikov, J. Lategahn, *Angew. Chem.* **2011**, *123*, 8764; *Angew. Chem. Int. Ed.* **2011**, *50*, 8605; b) X. Ban, Y. Pan, Y. Lin, S. Wang, Y. Du, K. Zhao, *Org. Biomol. Chem.* **2012**, *10*, 3606; c) E. Malamidou-Xenikaki, S. Spyroudis, M. Tsanakopoulou, D. Hadjipavlou-Litina, *J. Org. Chem.* **2009**, *74*, 7315; d) Y. Du, R. Liu, G. Linn, K. Zhao, *Org. Lett.* **2006**, *8*, 5919; e) J. Huang, Y. He, Y. Wang, Q. Zhu, *Chem. Eur. J.* **2012**, *18*, 13964; f) S. K. Alla, R. K. Kumar, P. Sadhu, T. Punniyamurthy, *Org. Lett.* **2013**, *15*, 1334; g) Y. Chi, W.-X. Zhang, Z. Xi, *Org. Lett.* **2014**, *16*, 6274; h) S. Maiti, P. Mal, *Adv. Synth. Catal.* **2015**, *357*, 1416; i) Y. He, J. Huang, D. Liang, L. Liu, Q. Zhu, *Chem. Commun.* **2013**, *49*, 7352.

[13] Intermolecular reactions: see refs.[9b,10,11] and a) N. Itoh, T. Sakamoto, E. Miyazawa, Y. Kikugawa, *J. Org. Chem.* **2002**, *67*, 7424; b) S. Manna, P. O. Serebrennikova, I. A. Utepova, A. P. Antonchick, O. N. Chupakhin, *Org. Lett.* **2015**, *17*, 4588; c) J. A. Souto, C. Martínez, I. Velilla, K. Muñiz, *Angew. Chem.* **2013**, *125*, 1363; *Angew. Chem. Int. Ed.* **2013**, *52*, 1324; d) L. Fra, A. Millán, J. A. Souto, K. Muñiz, *Angew. Chem.* **2014**, *126*, 7477; *Angew. Chem. Int. Ed.* **2014**, *53*, 7349; e) A. Pialat, J. Bergès, A. Sabourin, R. Vinck, B. Liégault, M. Taillefer, *Chem. Eur. J.* **2015**, *21*, 10014; f) Y. Yang, X. Wu, J. Han, S. Mao, X. Quian, L. Wang, *Eur. J. Org. Chem.* **2014**, *31*, 6854.

[14] Reviews: a) R. Narayan, S. Manna, A. P. Antonchick, *Synlett* **2015**, *26*, 1785; b) R. Samanta, K. Matcha, A. P. Antonchick, *Eur. J. Org. Chem.* **2013**, 5769.

[15] a) Y. Kita, H. Tohma, K. Hatanaka, T. Takada, S. Fujita, S. Mitoh, H. Sakurai, S. Oka, *J. Am. Chem. Soc.* **1994**, *116*, 3684; b) Y. Kita, T. Takada, H. Tohma, *Pure Appl. Chem.* **1996**, *68*, 627.

[16] For general reviews on iodine(I/III) catalysis in homogeneous oxidation, see: a) R. D. Richardson, T. Wirth,

Angew. Chem. **2006**, *118*, 4510; *Angew. Chem. Int. Ed.* **2006**, *45*, 4402; b) M. Ochiai, K. Miyamoto, *Eur. J. Org. Chem.* **2008**, 4229; c) M. Ochiai, *Chem. Rec.* **2007**, *7*, 12; d) T. Dohi, Y. Kita, *Chem. Commun.* **2009**, 2073; e) M. Uyanik, K. Ishihara, *Chem. Commun.* **2009**, 2086; f) F. V. Singh, T. Wirth, *Chem. Asian J.* **2014**, *9*, 950; g) R. M. Romero, T. H. Wöste, K. Muñiz, *Chem. Asian J.* **2014**, *9*, 972.

[17] T. Dohi, A. Maruyama, Y. Minamitsuji, N. Takenaga, Y. Kita, *Chem. Commun.* **2007**, *43*, 1224.

[18] a) F. M. Beringer, S. A. Galton, S. J. Huang, *J. Am. Chem. Soc.* **1962**, *84*, 2819; b) P. Kazmierczak, L. Skulski, *Synthesis* **1995**, 1027; c) T. Dohi, N. Yamaoka, I. Itani, Y. Kita, *Aust. J. Chem.* **2011**, *64*, 529.

[19] F. Tinnis, E. Stridfeldt, H. Lundberg, H. Adolfsson, B. Olofsson, *Org. Lett.* **2015**, *17*, 2688.

[20] See the Supporting Information for details.

[21] For a previous report on copper-catalysed C–H amination with Troc-amides, see: A. John, J. Byun, K. M. Nicholas, *Chem. Commun.* **2013**, *49*, 10965.

[22] a) W. Wolf, E. Chalekson, D. Kobata, *J. Org. Chem.* **1967**, *32*, 3239; b) for the bis-tosylate analogue, see: G. F. Koser, R. H. Wettach, *J. Org. Chem.* **1980**, *45*, 1542.

[23] CCDC 1451743 (compound **7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[24] T. Dohi, N. Takenaga, K. Fukushima, T. Uchiyama, D. Kato, M. Shiro, S. Motoo, H. Fujioka, Y. Kita, *Chem. Commun.* **2010**, *46*, 7697.

[25] For general reports on reactivity and catalyst structure relationship, see: a) M. Uyanik, K. Ishihara, *J. Synth. Org. Chem. Jpn.* **2012**, *70*, 1116; b) M. Uyanik, T. Yasui, K. Ishihara, *Angew. Chem.* **2013**, *125*, 9385; *Angew. Chem. Int. Ed.* **2013**, *52*, 9215; c) S. Haubenreisser, T. H. Wöste, C. Martínez, K. Ishihara, K. Muñiz, *Angew. Chem.* **2016**, *128*, 422; *Angew. Chem. Int. Ed.* **2016**, *55*, 413.