

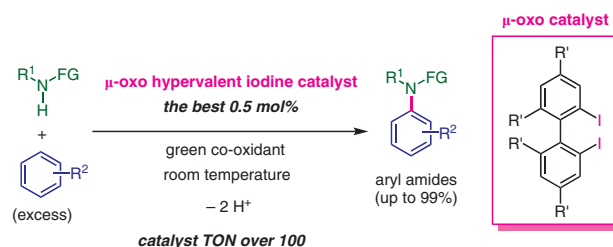
# Oxidative Coupling of *N*-Methoxyamides and Related Compounds toward Aromatic Hydrocarbons by Designer $\mu$ -Oxo Hypervalent Iodine Catalyst

Toshifumi Dohi\*<sup>a</sup>Hirotaka Sasa<sup>a</sup>Mio Dochi<sup>a</sup>Chihiro Yasui<sup>a</sup>Yasuyuki Kita\*<sup>b</sup>

<sup>a</sup> College of Pharmaceutical Sciences, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, Shiga, 525-8577, Japan  
td1203@ph.ritsume.ac.jp

<sup>b</sup> Research Organization of Science and Technology, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577, Japan  
kita@ph.ritsume.ac.jp

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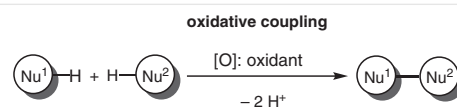
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**Abstract** Oxidative coupling strategies that can directly convert the C–H group for chemical transformations are, in theory, ideal synthetic methods to reduce the number of synthetic steps and byproduct generation. Hypervalent iodine reagents have now become one of the most promising tools in developing oxidative couplings due to their unique reactivities that are replacing metal oxidants. As part of our continuous development of oxidative coupling reactions, we describe in this report highly efficient  $\mu$ -oxo hypervalent iodine catalysts for the direct oxidative coupling of *N*-methoxyamides and related compounds with aromatic hydrocarbons. The excellent TONs, up to over 100 times, with a best catalyst loading of 0.5 mol% were determined for the oxidative C–H/N–H coupling method, which can provide the most straightforward route to obtaining these unique arylamide compounds.

**Key words** hypervalent compound, iodine, oxidative coupling, amidation, electrophilic substitution

The transition-metal-catalyzed cross-coupling strategies established in the 20th century for the reactions of unreactive organic halides with nucleophilic organic molecules, such as organometallic compounds (e.g., metal = [Zn] Negishi, [B] Suzuki, etc.)<sup>1</sup> and amines (Buchwald–Hartwig),<sup>2</sup> as the coupling partner are powerful tools in organic synthesis due to the high reliability of the reactions to construct the target structures found in pharmaceuticals and other fine chemicals. Due to their high importance in scientific fields as well as in industrial production processes,<sup>3</sup> much effort has been devoted to some improvement of the original coupling strategies; considering the recent demand for green and sustainable chemistry, a more step-economi-

cal C–H coupling route avoiding the preparation of organic halides and/or organometallic compounds has emerged in the past few decades.<sup>4</sup> In theory, the coupling reaction between two X–H bonds (X = carbon or heteroatom) present in organic molecules is ideal,<sup>5</sup> which is an important goal of the modern coupling challenge that requires the nonproduction of metal waste and byproducts during the reaction and preparation of the substrates. In this regard, the oxidative coupling between nucleophile–H bonds would principally match with the concept (Scheme 1), but early studies usually suffered from over-oxidation of the products and low reaction selectivities, such as uncontrolled homodimer formations.<sup>6</sup>



**Scheme 1** Direct oxidative coupling between nucleophilic molecules without prefunctionalization

Recently, the catalysis of oxidative C–H couplings without a prefunctionalized substrate has been quite progressive for transformations of aromatics, particularly by using transition-metal chemistry,<sup>5</sup> while the catalyst loadings in these reported cases are somewhat unsatisfactory when compared to first-generation cross-coupling methodology. Therefore, developing a new metal-catalyst-free method should be indispensable, especially in this oxidative coupling area, for further advancement of the green strategy.<sup>7</sup> Hypervalent iodine reagents have received significant attention in modern synthesis as a safe tool for oxidation reactions<sup>8</sup> and they have become promising in realizing met-

## Biographical Sketches



**Toshifumi Dohi** received his Ph.D. in 2005 (Y. Kita), subsequently became Assistant Professor at Osaka University and Ritsumeikan University, and was promoted to Associate Professor and Professor in 2014 and

2019, respectively. He received the IUPAC-ICOS 15 Poster Award for most excellent presentation, the PSJ Award for Young Scientists (2009), Banyu Chemist Award (2013), Thieme Chemistry Journal Award

(2014), and GSC Encouragement Award (2015). His current research interest is focused on reagent/catalyst design and asymmetric oxidation in hypervalent iodine chemistry.



**Hirotaka Sasa** was born and grew up in Shiga, Japan. He obtained his B.Sc. degree under the supervision of Prof. Toshifumi Dohi in 2018. Now he receives the support of the Nagai

Memorial Research Encouragement from The Pharmaceutical Society of Japan (PSJ) and works as a Ph.D. course student in the same group at the Graduate School of Pharmaceutical Sci-

ences, Ritsumeikan University. His current interest is synthetic studies using hypervalent iodine catalysts.



**Mio Dochi** was born in Fukuoka, Japan. She is an undergraduate student and studies organic

chemistry at the Fine Synthetic Chemistry Laboratory, the College of Pharmaceutical Scienc-

es, Ritsumeikan University.



**Chihiro Yasui** is an undergraduate student and lives in Shiga, Japan. She studies organic

chemistry at the Fine Synthetic Chemistry Laboratory, the College of Pharmaceutical Scienc-

es, Ritsumeikan University.

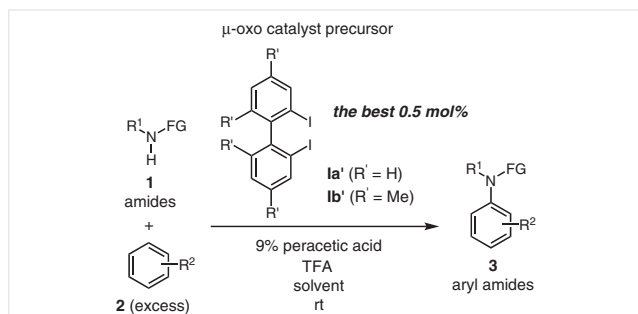


**Yasuyuki Kita** was born in 1945 in Osaka, Japan. He received his Ph.D. (1972) from Osaka University and subsequently was a member of the faculty of Pharmaceutical Sciences of the university. After two years (1975–1977) of postdoctoral work with Professor George Büchi at MIT, he moved back to Osaka University. He was promoted to Associate Professor in 1983 and to Full Professor of Osaka University in 1992. In 2008, he retired from Osaka University and joined Ritsumeikan University as the Dean

of the Faculty of Pharmaceutical Sciences. From 2011 to 2015, he held Vice-President of the Research Organization of Science and Technology, Ritsumeikan University. Since April 2015, he has been Invited Research Professor and Director of Research Center for Drug Discovery and Pharmaceutical Development Science of the same University. He has a wide range of research interest in synthetic chemistry including the development of new asymmetric synthesis, new reagents, and the total synthesis of biological-

ly active natural products. His current research interest is in hypervalent iodine chemistry. He has published more than 500 original papers. His awards include the Pharmaceutical Society of Japan (PSJ) Award for Young Scientists (1986), the PSJ Award for Divisional Scientific Contribution (1997), the PSJ Award (2002), the Japanese Society for Process Chemistry (JSPC) Award for Excellence (2005), the Society of Iodine Science (SIS) Award (2007), and the E.C. Taylor Senior Award (2017).

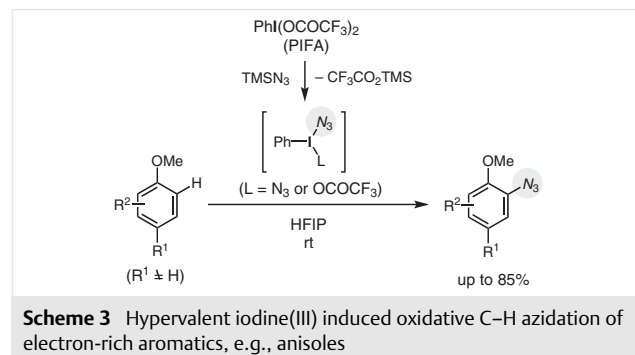
al-free oxidative coupling reactions based on our pioneering studies.<sup>9</sup> As a part of our continuous development, we now report the efficient oxidative C–H couplings of aromatic hydrocarbons toward N–H amides to easily produce functionalized arylamides using our unique  $\mu$ -oxo hypervalent iodine catalyst even at less than 1 mol% catalyst loadings at room temperature in the presence of dilute peracetic acid<sup>10</sup> (Scheme 2).



**Scheme 2** Oxidative coupling of *N*-protected amides **1** (FG = OMe, *N*-phthalimide) with aromatic hydrocarbons ( $R^2$  = alkyl, halogen) or ethers ( $R^2$  = alkoxy) by  $\mu$ -oxo hypervalent iodine organocatalyst

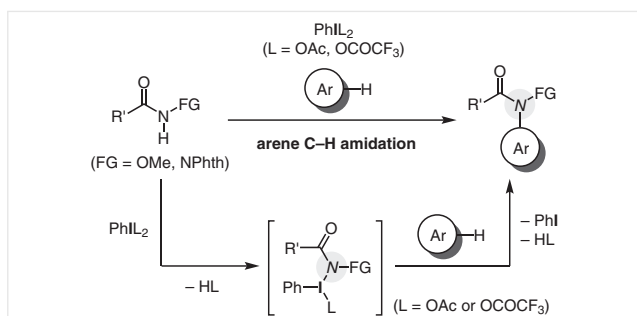
The oxidative coupling chemistry of the hypervalent iodine reagent for the conversion of aromatics has a long history since the appearances of the reactive reagents, activators, and solvents that can increase the oxidation abilities of the iodanyl groups. We first proposed the use of phenyliodine(III) bis(trifluoroacetate) (PIFA) in fluoroalcohols, i.e., hexafluoroisopropanol (HFIP) and trifluoroethanol (TFE), as an efficient oxidative coupling system for the dearomatization of phenolic substrates introducing nucleophiles (Nu–H) in the mid 1980s.<sup>11</sup> With this significant improvement as a turning point, the hypervalent iodine reagent now plays a crucial role in reproducing the biosynthetic oxidative phenolic coupling processes and syntheses of natural products.<sup>9c,h</sup> A further important contribution in the metal-free oxidative C–H coupling area is the direct activation of aromatic rings triggered by single-electron-transfer (SET) processes discovered in the early 1990s.<sup>12</sup> Phenyl ether (and alkylarene) rings, not causing oxidation unlike phenols, are smoothly SET activated by treatment with PIFA, and the introduction of an azide by ligand transfer from in situ generated  $\text{PhI}(\text{N}_3)\text{X}$  ( $\text{X} = \text{N}_3$  or  $\text{OCOCF}_3$ ) leads to the formation of aromatic C–H azidation products. Again, the highly polar, non-nucleophilic fluoroalcohol<sup>13</sup> was determined to dramatically affect the aromatic azidation process and the product yield reached 85% when employing this specific activator as a solvent (Scheme 3).<sup>12a</sup> Based on this strategy, a series of metal-free oxidative couplings of aromatic rings with nucleophiles (NuH) and that having a TMS group (Nu–TMS) has become possible;<sup>14,15</sup> we believe that these early discoveries by us were the beginning of hypervalent

iodine coupling chemistry, leading to the recent breakthrough and elucidations of the metal-free aromatic C–H functionalization strategy.



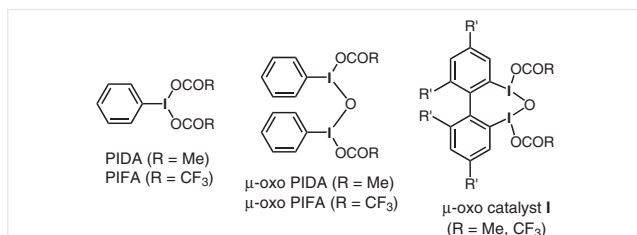
Complimentary to the Buchwald–Hartwig aryl amination procedures, substantial advances in the oxidative C–H aminations aiming at a greener goal, which can directly install amines into non-preactivated aromatic substrates to give valuable *N*-arylated molecules, have been extensively found in recent years under transition-metal catalysis and even other metal-free conditions.<sup>16</sup> The amide alternative of the hypervalent iodine induced C–H azidation involving in situ formed electrophilic amido- $\lambda^3$ -iodane species bearing a methoxy or phthalimide-substituted nitrogen group was reported in 1990 by the Kikugawa group for a few nucleophilic arenes (Scheme 4).<sup>17</sup> Later, this C–H amidation was successfully improved by using PIFA and/or by the aid of fluoroalcohols (see Scheme 3) in order to use many different substrates in an intramolecular manner.<sup>18,19</sup> For example, the optimized C–H amidative cyclization protocols have been applied to the construction of interesting compounds in the field of medicinal chemistry<sup>19a,b</sup> as well as the dearomative spirocyclizations to provide facile access to the unique spiro lactam structures known as useful precursors of some biologically active alkaloids and natural products.<sup>19c,d</sup> On the other hand, the intermolecular coupling for unreactive aromatic hydrocarbons remains relatively difficult, particularly with the catalytic use of a conventional hypervalent iodine reagent.<sup>20</sup>

Indeed, the catalytic generation of PIFA (see Figure 1) under the re-oxidizing conditions for the oxidative C–N coupling of arenes is not as effective as other hypervalent iodine mediated reactions,<sup>21</sup> and their typical turnover number (TON) for intermolecular C–H amidations is estimated to be less than only 10 times. Therefore, based on the structures of  $\mu$ -oxo PIDA and PIFA,<sup>22,23</sup> we have previously introduced the  $\mu$ -oxo catalysts **I** as more efficient tools to realize practical and greener oxidative C–N couplings.<sup>24–26</sup> These catalysts are rationally designed to steadily keep their activated forms and thus reproduce the high electrophilicity of the iodine(III) atoms caused by the strong *trans*-influence of the  $\mu$ -oxo oxygen<sup>27,28</sup> during the catalytic cycle.



**Scheme 4** Intermolecular oxidative coupling of *N*-functionalized amides with aromatic hydrocarbons by using hypervalent iodine reagent (NPhth = phthalimido)

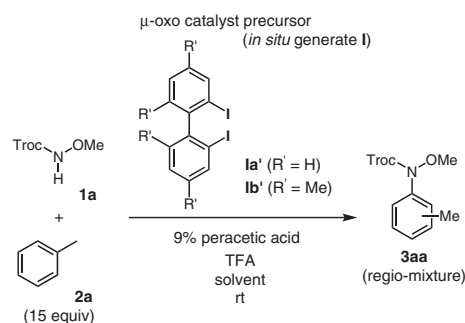
However, the suggested conditions for the intermolecular direct C–H coupling of toluene (**2a**) toward the *N*-methoxyamide N–H bond using peracetic acid as a stoichiometric oxidant in an ordinary solvent<sup>29</sup> failed and produced very low TONs for our  $\mu$ -oxo catalysts **I** (see Table 1). Thus, the reaction of *N*-methoxyamide **1a** with toluene (**2a**; 15 equiv) performed using 4 mol% of the pre-catalysts **Ia'** ( $R' = H$ ) with 1.5 equiv of peracetic acid (9% solution in acetic acid) and trifluoroacetic acid (5 equiv) in 1,2-dichloroethane (DCE, 0.3 M of amide **1a**) resulted in the formation of the corresponding C–N coupling product **3aa** in only 13% yield as a mixture of regioisomers, with a TON of ca. 3 after 2 hours at room temperature; and a large amount of amide **1a** remained unreacted in this case (Table 1, entry 1).



**Figure 1** Hypervalent iodine reagents, PIDA, PIFA, and their  $\mu$ -oxo dimers and designer  $\mu$ -oxo reagent **I**

On the other hand, our reported catalytic conditions of a mixed fluoroalcohol solvent system (HFIP/DCE 10:1)<sup>24</sup> were found to dramatically improve the TON of the catalyst **Ia'** as well as its turnover frequency (TOF) (Table 1, entry 2); this is probably because the fluoroalcohol not only accelerates the generation of the active  $\mu$ -oxo species **I** by enhancing the re-oxidation ability of peracetic acid<sup>30</sup> by powerful hydrogen bondings,<sup>13</sup> but also facilitates the smooth generation of the cationic nitrenium (or pseudo-nitrenium) species.<sup>18</sup> In a short reaction time, the target products **3aa** were thus obtained in 76% yield by simply changing the solvent in which the addition of trifluoroacetic acid takes place to produce active  $\mu$ -oxo species **Ia** ( $R = CF_3$  in Figure 1) and this was essential for this catalytic coupling (entry 3). Regarding the catalyst, the derivative **Ib'** ( $R' = Me$ ) showed similar catalytic efficiencies for the coupling of amide **1a** (entry 4). It

**Table 1** Optimization: Hypervalent Iodine Induced C–H Amidation of Toluene by  $\mu$ -Oxo Catalysts **Ia'** and **Ib'**<sup>a</sup>



Entry	$\mu$ -Oxo catalyst	Solvent	Time (h)	Yield of <b>3a</b> <sup>b,c</sup>
1	<b>Ia'</b> (4 mol%)	DCE	2 <sup>d</sup>	13% (2.6:1:2.8)
2	<b>Ia'</b> (4 mol%)	HFIP/DCE (10:1)	2	76% (2.6:1:2.6)
3 <sup>e</sup>	<b>Ia'</b> (4 mol%)	HFIP/DCE (10:1)	2	66% (3.7:1:3.4)
4	<b>Ib'</b> (4 mol%)	HFIP/DCE (10:1)	2	78% (2.1:1:2.2)
5	<b>Ib'</b> (4 mol%)	HFIP/DCE (10:1) <sup>f</sup>	2	67% (2.2:1:2.3)
6 <sup>g</sup>	<b>Ib'</b> (4 mol%)	HFIP/DCE (10:1)	2	61% (2.7:1:1.8)
7	<b>Ib'</b> (2 mol%)	HFIP/DCE (10:1)	2	81% (2.3:1:2.4)
8	<b>Ib'</b> (1 mol%)	HFIP/DCE (10:1)	6	80% (2.3:1:2.4)
9	<b>Ib'</b> (0.5 mol%)	HFIP/DCE (10:1)	12	68% (2.3:1:2.7)
10	none	HFIP/DCE (10:1)	16	– <sup>h</sup>

<sup>a</sup> Reaction conditions: amide **1a**, toluene (**2a**; 15 equiv), catalyst, peracetic acid (9% solution in AcOH, 1.5 equiv), TFA (5 equiv), solvent (0.3 M of amide **1a**), rt; unless otherwise stated.

<sup>b</sup> The product yields after purification were calculated basis on the amide **1a** used.

<sup>c</sup> The regioisomeric ratio (*ortho/meta/para*) is indicated in parentheses (calculated value by <sup>1</sup>H NMR measurement).

<sup>d</sup> Large amount of amide **1a** was recovered.

<sup>e</sup> Using TFA (1 equiv).

<sup>f</sup> Higher concentration (0.6 M of amide **1a**).

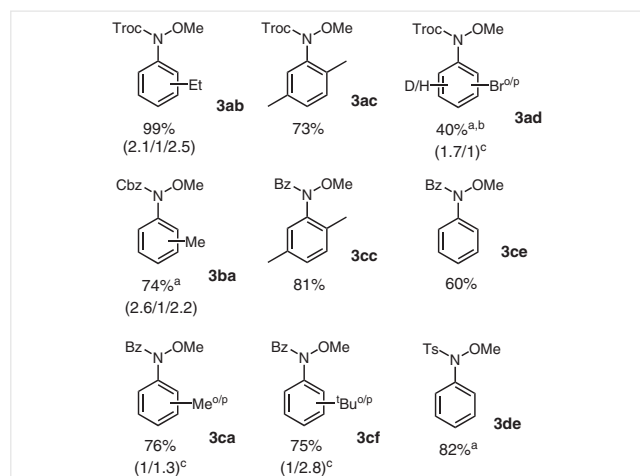
<sup>g</sup> Using toluene (**2a**; 5 equiv).

<sup>h</sup> Not determined.

also appears that the slight modification of the concentration affects the TON value (entry 5). In this reaction, the molar balance of the substrates is rather important, and the yield of the products **3aa** decreased by using 5 equiv of toluene (**2a**) relative to the amide **1a** (entry 6). Subsequently, we then examined the reaction to further lower the catalyst loading. To our delight, a comparable result was obtained in regard to the yield of the product when using a 2 mol% amount of the catalyst **Ib'** with a higher catalyst TON (entry 7). The coupling reactions proceeded at room temperature, and the robustness of our catalyst **Ib'** under the reaction conditions maintained the original activity for prolonged times (entry 8). Thus, the TON giving the product **3aa** in an acceptable yield reached 136 times for the 0.5 mol% catalyst loading after a 12 h reaction (entry 9). To the best of our knowledge, this observed TON score for the catalyst **Ib'** is the highest among all the intermolecular C–H/N–H aromatic amidations.<sup>16</sup> Of course, the coupling product **3aa** was

not produced in the absence of the  $\mu$ -oxo catalysts (entry 10). In 2016, Muñiz and co-workers also reported a new iodine catalyst, 1,2-diiodobenzene, for this type of coupling reaction.<sup>31</sup>

We then evaluated the optimized catalytic system for the  $\mu$ -oxo catalyst **1b'** using the same-type couplings of a further series of simple non-activated aromatics **2b–f** (Scheme 5). The reactions of ethylbenzene (**2b**) and *p*-xylene (**2c**) both smoothly produced the corresponding C–N coupling products **3ab** and **3ac** within 2 hours using 2 mol% of the catalyst. Although bromobenzene (**2d**) is less reactive during the coupling (see product **3ad**), the method can provide an aryl-deuterated amine with an aromatic halogen functionality in a single step from the isotopic aromatic substrate (i.e., bromobenzene-*d*<sub>5</sub>), which is beneficial for further elaboration of the structure and scalable synthesis. Other aliphatic and aromatic amides **1b** and **1c** and sulfonamide **1d** were applicable for the couplings with benzene **2e** and other aromatic hydrocarbons. The *N*-methoxy groups found in anilides are known to show unique reactivities, and new reactions utilizing cleavage between the heteroatom bond as a driving force have been reported by several research groups.<sup>32</sup>



**Scheme 5** Catalytic C–H amidation of arenes **2a–f** using  $\mu$ -oxo catalyst **1b'**. Reagents and conditions: amide **1a–d**, arene **2a–f** (15 equiv), peracetic acid (9% solution in AcOH, 1.5 equiv), TFA (5 equiv), catalyst (2 mol%), HFIP/DCE (10:1), rt, 2 h, unless otherwise stated. The *ortho/meta/para* ratio calculated by <sup>1</sup>H NMR is indicated in parentheses.

<sup>a</sup> Catalyst: 3 mol%. <sup>b</sup> Overnight. <sup>c</sup> *ortho/para* ratio.

For *N*-(acetylamino)phthalimide (**1e**), the catalyst **1b'** (R' = Me) and the steric nitrogen group are quite mismatched;<sup>26c</sup> the rates of the product formation were quite slow in comparison to that for the *N*-methoxyamides **1a–d**, and the amide **1e** was not completely consumed within 2 hours (Scheme 6). As a result, the longer reaction time of 12 hours was required in order to achieve the full conversion of the substrate. Interestingly, the more flexible  $\mu$ -oxo catalyst **1a'** (R' = H) was somewhat preferred in terms of the

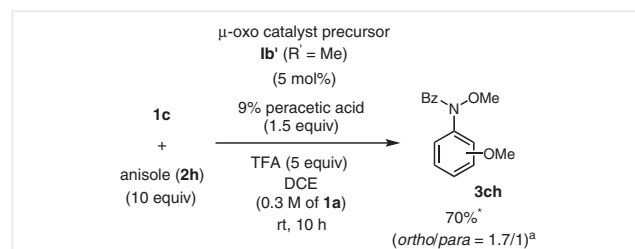
TOFs for the reactions. The bulky *N*-phthalimido group (NPhth) of the amide **1e** strongly directed the regioselectivities at the aromatic rings to *para* over the *ortho* positions.

Catalyst	Time	Product			
		<b>3ee</b>	<b>3ea</b>	<b>3ed</b>	<b>3eg</b>
$\mu$ -oxo <b>1b'</b> (2 mol%)	2 h	—	50% (1/1.9) <sup>a</sup>	55%	70%
	12 h	quant	91% (1/2.5) <sup>a</sup>	99% <sup>b</sup>	92% <sup>b</sup>
$\mu$ -oxo <b>1a'</b> (3 mol%)	2 h	—	88% (1/2.4) <sup>a</sup>	94% (1/4.7) <sup>c</sup>	96% (1/3.1) <sup>c</sup>

**Scheme 6** Steric influence of  $\mu$ -oxo catalysts **1a'** (R' = H) and **1b'** (R' = Me) in the coupling of *N*-phthalimide **1e**. Reagents and conditions: amide **1e**, arene **2a,e,d,g** (15 equiv), peracetic acid (9% solution in AcOH, 1.5 equiv), TFA (5 equiv), catalyst (2–3 mol%), HFIP/DCE (10:1), rt, unless otherwise stated.

<sup>a</sup> The *ortho* and *para* products are separable. <sup>b</sup> Exclusively *para*. <sup>c</sup> *ortho/para* ratio of the mixture, calculated by <sup>1</sup>H NMR.

The reaction of anisole (**2h**) with *N*-methoxybenzamide (**1c**) unexpectedly did not occur using either of the  $\mu$ -oxo iodine catalysts **1a'** and **1b'** under the conditions in a fluoro alcohol (see the note for Scheme 7). Obviously, a competitive diaryliodonium salt forming path for condensation with anisole **2h** to prevent the catalytic cycle was dominant in this electron-rich aromatic case in a fluoroalcohol<sup>33,34</sup> compared to the rate of the generation of the amide- $\lambda^3$ -iodane intermediate for the C–N coupling. Therefore, the use of DCE only as a solvent was plausible for this coupling combination. Interestingly, the formation of an *ortho*-coupling product of anisole **2h** over the *para* isomer was preferred by specific control of the methoxy group.<sup>35</sup>

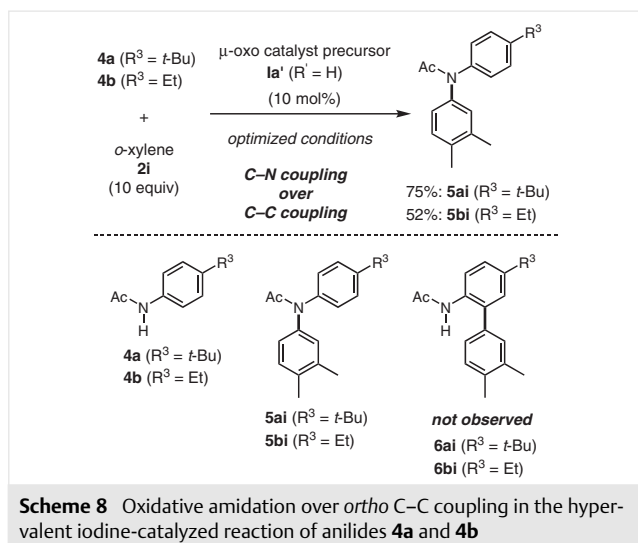


**Scheme 7** Alternative solvent for the oxidative C–H amidation of electron-rich aromatic substrate. Product yield when using catalyst **1b'** (2 mol%) in HFIP/DCE (10:1) for 2 hours was less than 5%. <sup>a</sup> The regioisomeric ratio is calculated by <sup>1</sup>H NMR.

As a complement to the transition-metal-catalyzed amination of halogenated aryls, Hartwig and co-workers proposed in 2013 the intermolecular direct coupling of simple



arenes with phthalimide by employing the hypervalent iodine reagent as the oxidant for the palladium catalyst.<sup>36a</sup> Similarly, the metal-catalyzed intermolecular amidations by converting the C–H group of aromatic hydrocarbons not having a directing group typically required the hypervalent iodine reagent as a stoichiometric activator.<sup>36b–d</sup> In addition, enhancing the TON was difficult in these catalyses.<sup>36e,f</sup> Thus, the fact that the direct couplings between the amide N–H group and aromatic C–H bond can proceed by using such a small amount of hypervalent iodine catalyst without adding any transition-metal element in our case is particularly noteworthy. The differences in the chemoselectivity during the C–H amidations were also found during the couplings of the anilides **4a** and **4b** (see Scheme 8). It was reported by the Buchwald group that *ortho* C–C bond-forming arylations leading to the formation of biaryl compounds **6ai** and **6bi** would exclusively occur for these anilide substrates under their conditions using a palladium catalyst,<sup>37</sup> rather than the coupling at the nitrogen group. In clear contrast, our organocatalytic conditions based on the use of the  $\mu$ -oxo catalyst **I'** instead afforded the C–N coupling products **5ai** and **5bi** in moderate to good yields (see experimental section).<sup>38</sup>



In this study, we have clarified the extremely high catalytic efficiencies of our designer  $\mu$ -oxo hypervalent iodine catalysts **I** for the intermolecular direct oxidative coupling of suitable amides with aromatic hydrocarbons. The C–H and N–H coupling methods can provide the most straightforward route to these arylamide compounds with excellent TONs of over 100 times with a 0.5 mol% catalyst loading. This allows many new direct amination strategies to extend the scopes recently developed on the basis of the stoichiometric hypervalent iodine chemistry,<sup>39–41</sup> and our idea for the catalyst design might contribute to the developments of practical catalysts for these transformations. In

addition, the use of related chiral hypervalent iodine catalysts based on the  $\mu$ -oxo structures<sup>42</sup> has a significant potential for the asymmetric oxidative C–N coupling reactions under metal-free conditions.<sup>43</sup>

In general, melting points were measured using a Büchi B 545 apparatus and are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Jeol JMN-300 spectrometer operating at 400 MHz and 100 MHz in CDCl<sub>3</sub> at 25 °C with TMS ( $\delta = 0$ ) as the internal standard. Infrared spectra were recorded by using a Hitachi 270-50 spectrometer. Flash column chromatography and analytical TLC were carried out on Merck silica gel 60 (230–400 mesh) and Merck silica gel F<sub>254</sub> plates (0.25 mm), respectively. The spots and bands were detected by UV irradiation (254, 365 nm) or by staining with 5% phosphomolybdic acid followed by heating.

All arenes **2** employed for the coupling reactions are commercially available and used without further purification. The amides **1a–d**,<sup>31,44a–c</sup> **1e**,<sup>44d</sup> **4a**, and **4b** were prepared from *O*-methylhydroxylamine, acetohydrazide, and corresponding anilines according to the literature. Solvents were purchased from commercial suppliers and used as received for the reactions, extraction, and eluent for column chromatography and TLC.

Regarding the  $\mu$ -oxo hypervalent iodine catalysts **1a'** and **1b'**, 2,2'-diiodobiphenyl (**1a'**) is commercially available, while 2,2'-diiodo-4,4',6,6'-tetramethylbiphenyl (**1b'**) was prepared from 1-iodo-3,5-dimethylbenzene in one step by our method.<sup>45</sup>

#### 2,2'-Diiodo-4,4',6,6'-tetramethylbiphenyl (**1b'**)

Under N<sub>2</sub> atmosphere at –78 °C, to a stirred solution of 1-iodo-3,5-dimethylbenzene (1.62 g, 7.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8.75 mL) was added dropwise a mixture of PIFA (1.51 g, 3.5 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (0.88 mL, 7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8.75 mL) over a few minutes. The mixture was stirred at this temperature for 5 h. When the reaction was complete, the mixture was quenched with sat. aq NaHCO<sub>3</sub> and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with brine and dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane/EtOAc) to give **1b'**<sup>45b</sup> (1.02 g, 2.21 mmol, 63%) as a white powder; mp 111–113 °C.

IR (KBr): 3014, 1599, 1541, 1035 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.95 (s, 6 H), 2.31 (s, 6 H), 7.06 (s, 2 H), 7.62 (s, 2 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 20.4, 21.2, 100.7, 130.7, 136.9, 137.0, 139.0, 144.3.

#### 2,2,2-Trichloroethyl Methoxy(tolyl)carbamate **3aa**; Typical Procedure for Oxidative Coupling Using a Combination of Diiodobiphenyl Catalyst **1b'** with Stoichiometric Peracetic Acid (Schemes 5 and 6)

2,2,2-Trichloroethyl carbamate (**1a**; 111.2 mg, 0.50 mmol, 1 equiv), toluene (691 mg, 7.5 mmol, 15 equiv), and catalyst **1b'** (4.6 mg, 0.010 mmol, 0.02 equiv) were dissolved in HFIP/DCE (10:1, 1.6 mL) in a round-bottomed flask at rt. Peracetic acid (9% solution in AcOH, 0.6 mL, 0.75 mmol, 1.5 equiv), and TFA (285 mg, 2.5 mmol, 5 equiv) were added sequentially. The mixture was then stirred at rt for 2 h. When the reaction was complete, the resulting solution was washed with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the combined organic extracts were dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After removal of the solvents by a rotary

evaporator, the residue was subjected to flash column chromatography (silica gel (hexane/EtOAc) to give pure **3aa**<sup>31</sup> (127.5 mg, 0.408 mmol, 81%) as a pale yellow oil; ratio *ortho/meta/para* 2.3:1:2.4 (<sup>1</sup>H NMR).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 2.30 (s, 3 H, *ortho*), 2.31 (s, 3 H, *para*), 2.33 (s, 3 H, *meta*), 3.74 (s, 3 H, *ortho*), 3.76 (s, 3 H, *para*), 3.77 (s, 3 H, *meta*), 4.78 (s, 2 H, *ortho*), 4.81 (s, 2 H, *para*), 4.83 (s, 2 H, *meta*), 6.99–7.03 (m, 1 H, *meta*), 7.12–7.35 (m, 11 H, *ortho*, *meta*, *para*).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 18.0, 21.1, 21.6, 62.1, 62.4, 62.6, 75.2, 75.3, 75.4, 95.2, 95.3 (2 ×), 119.7, 123.1, 123.3, 126.6, 127.5, 128.2, 128.9, 129.4, 129.6, 131.2, 136.2, 136.7, 136.9, 137.2, 138.6, 139.0, 152.6, 152.7, 153.5.

The analytical data of all the products **3** are listed below. The physical and spectral data of all these compounds well matched those previously reported.<sup>29,31,32d,38</sup>

### 3,3,3-Trichloro-*N*-(ethylphenyl)-*N*-methoxypropanamide **3ab**

Yellowish oil; yield: 164.5 mg (99%); ratio *ortho/meta/para* 2.1:1:2.5 (<sup>1</sup>H NMR).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.20–1.30 (m, 9 H), 2.61–2.76 (m, 6 H), 3.80 (s, 3 H), 3.82 (s, 3 H), 3.83 (s, 3 H), 4.81–4.90 (m, 6 H), 7.05–7.11 (m, 1 H, *meta*), 7.19–7.44 (m, 11 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 15.5, 15.6, 28.5, 28.9, 62.4, 62.5, 75.3, 95.2, 95.3, 119.9, 122.2, 123.0, 126.3, 128.4, 128.8, 136.3, 138.7, 143.1, 145.3, 152.6, 152.7.

### 3,3,3-Trichloro-*N*-(2,5-dimethylphenyl)-*N*-methoxypropanamide (**3ac**)

Pale yellow oil; yield: 119.2 mg (73%); mixture of rotamers.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 2.29 (s, 3 H), 2.30 (s, 3 H), 2.33 (s, 3 H), 2.34 (s, 3 H), 3.77 (s, 3 H), 3.79 (s, 3 H), 4.83 (m, 2 H), 7.03–7.05 (m, 1 H), 7.09–7.13 (m, 3 H), 7.15–7.19 (m, 2 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 17.4, 17.7, 20.8, 21.2, 61.8, 62.0, 75.1, 95.3, 127.2, 128.0, 128.5, 130.1, 130.8, 131.8, 133.3, 134.5, 136.3, 136.8, 139.4, 153.4, 153.5.

### *N*-(Bromophenyl)-3,3,3-trichloro-*N*-methoxypropanamide **3ad**

Following the typical procedure for **3aa** using **1b'** (3 mol%), reaction time: overnight; pale yellow oil; yield: 81.0 mg (40%); ratio *ortho/para* 1.7:1 (<sup>1</sup>H NMR).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 3.81 (s, 3 H, *para*), 3.83 (s, 3 H, *ortho*), 4.82–4.88 (m, 4 H), 7.22–7.29 (m, 1 H), 7.36–7.43 (m, 4 H, *ortho* and *para*), 7.46–7.53 (m, 2 H, *para*), 7.68 (dd, *J* = 8.1, 1.4 Hz, 1 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 62.8, 63.0, 75.5 (2 ×), 95.0 (2 ×), 119.6, 123.4, 123.6, 128.4, 129.2, 130.1, 133.7, 138.0, 138.1, 152.3, 153.2.

### Benzyl Methoxy(tolyl)carbamate **3ba**

Following the typical procedure for **3aa** using **1b'** (3 mol%) gave **3ba** which was separated by column chromatography to give *ortho*-**3ba** and a mixture of *meta*-**3ba** and *para*-**3ba**; ratio *ortho/meta/para* 2.6:1:2.2 (<sup>1</sup>H NMR).

### Benzyl Methoxy(2-tolyl)carbamate (*ortho*-**3ba**)

Colorless oil; yield: 38.3 mg (33%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 2.23 (s, 3 H), 3.71 (s, 3 H), 5.20 (s, 2 H), 7.16–7.38 (m, 9 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 17.7, 61.9, 67.7, 126.4, 127.9, 128.1, 128.5, 128.9, 131.0, 136.0, 136.5, 138.0, 155.2.

### Benzyl Methoxy(3-tolyl)carbamate (*meta*-**3ba**) and Benzyl Methoxy(4-tolyl)carbamate (*para*-**3ba**)

Yellowish oil; yield: 61.5 mg (41%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 2.32 (s, 3 H, *para*), 2.34 (s, 3 H, *meta*), 3.72 (s, 3 H, *para*), 3.73 (s, 3 H, *meta*), 5.24 (s, 2 H, *para*), 5.25 (s, 2 H, *meta*), 6.95–7.07 (m, 1 H, *meta*), 7.12–7.42 (m, 17 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 21.0, 21.5, 62.2, 62.4, 67.9 (2 ×), 119.3, 122.7, 122.9, 126.9, 128.2 (2 ×), 128.3 (2 ×), 128.6 (2 ×), 129.4, 136.1 (2 ×), 136.2, 137.0, 138.7, 139.4, 154.2, 154.5, 155.4.

### *N*-(2,5-Dimethylphenyl)-*N*-methoxybenzamide (**3cc**)

Colorless oil; yield: 103.7 mg (81%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 2.22 (s, 6 H), 3.50–3.85 (br s, 3 H), 6.93–7.71 (m, 8 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 17.7, 20.9, 61.0, 128.0, 128.4, 128.5, 130.2 (2 ×), 130.8, 131.2, 133.5, 133.6, 136.5.

### *N*-Methoxy-*N*-phenylbenzamide (**3ce**)

Light yellow oil; yield: 69.5 mg (60%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 3.69 (s, 3 H), 7.20–7.52 (m, 8 H), 7.56–7.64 (m, 2 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 61.8, 124.5, 127.2, 128.1, 128.6, 129.1, 130.8, 134.7, 139.4, 168.3.

### *N*-Methoxy-*N*-tolylbenzamide (**3ca**)

Light yellow oil; yield: 91.1 mg (76%); ratio *ortho/para* 1:1.3 (<sup>1</sup>H NMR).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 2.25 (s, 3 H, *para*), 2.28 (s, 3 H, *ortho*), 3.62 (s, 6 H), 7.03–7.62 (m, 18 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 18.2, 21.2, 61.0, 61.5, 125.1, 126.6, 128.1 (2 ×), 128.5, 128.6, 129.3, 130.0, 130.7, 130.8, 131.4, 134.5, 134.8, 136.8, 136.9, 137.5, 168.1.

### *N*-(*tert*-Butylphenyl)-*N*-methoxybenzamide (**3cf**)

Light yellow oil; yield: 107.6 mg (75%); ratio *ortho/para* 1:2.8 (<sup>1</sup>H NMR).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.27 (s, 9 H, *ortho*), 1.35 (s, 9 H, *para*), 3.72 (s, 3 H, *para*), 3.78 (s, 3 H, *ortho*), 7.10–7.65 (m, 18 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 31.0, 31.2, 34.5, 34.6, 61.4, 121.5, 122.2, 124.0, 125.8, 127.9, 128.3, 128.5, 129.6, 130.4, 130.5, 134.6, 134.7, 136.4, 138.9, 150.2, 152.0, 167.8, 168.0.

### *N*-Methoxy-4-methyl-*N*-phenylbenzenesulfonamide (**3de**)

Following the typical procedure for **3aa** using **1b'** (3 mol%) gave **3de**; yellowish oil; yield: 113.0 mg (82%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 2.39 (s, 3 H), 3.86 (s, 3 H), 7.05–7.13 (m, 2 H), 7.15–7.45 (m, 7 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 21.8, 64.4, 123.7, 127.6, 128.4, 129.1, 129.8, 130.2, 141.0, 144.8.

### *N*-(1,3-Dioxoisindolin-2-yl)-*N*-phenylacetamide (**3ee**)

Following the typical procedure for **3aa** using catalyst **1b'** for 12 h gave **3ee**; yellowish solid; yield: 56.8 mg (quant.); mixture of rotamers.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 2.09 (s, 3 H), 7.38–7.49 (m, 3 H), 7.64–7.91 (m, 6 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 21.8, 124.1, 129.0, 129.7, 130.0, 130.2, 134.8, 140.8, 165.0, 168.5.

#### *N*-(1,3-Dioxoisindolin-2-yl)-*N*-(tolyl)acetamide (**3ea**)

Following the typical procedure for **3aa** using catalyst **Ib'** for 12 h gave a mixture of *para/ortho* isomers 2.5:1 that were separated by column chromatography.

#### *N*-(1,3-Dioxoisindolin-2-yl)-*N*-(4-tolyl)acetamide (*para*-**3ea**)

White amorphous; yield: 85.9 mg (65%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 2.08 (s, 3 H), 2.36 (s, 3 H), 7.19–7.29 (m, 2 H), 7.54 (d, *J* = 8.3 Hz, 2 H), 7.74 (dd, *J* = 5.9, 2.9 Hz, 2 H), 7.86 (dd, *J* = 5.4, 3.0 Hz, 2 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 21.4, 21.8, 124.1, 128.8, 130.3, 130.6, 134.7, 138.3, 139.6, 165.0, 168.7.

#### *N*-(1,3-Dioxoisindolin-2-yl)-*N*-(2-tolyl)acetamide (*ortho*-**3ea**)

White amorphous; yield: 34.4 mg (26%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 2.02 (s, 3 H), 2.63 (s, 3 H), 7.23–7.35 (m, 3 H), 7.71–7.95 (m, 5 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 18.2, 21.0, 124.1, 124.4, 127.6, 129.8, 129.9, 131.9, 134.7, 134.9, 135.3, 137.6, 139.6, 165.8, 166.1, 168.9.

#### *N*-(4-Bromophenyl)-*N*-(1,3-dioxoisindolin-2-yl)acetamide (*para*-**3ed**)

Following the typical procedure for **3aa** using catalyst **Ib'** for 12 h gave *para*-**3ed**; brownish solid; yield: 169.0 mg (99%); mp 169–171 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 2.09 (s, 3 H), 7.43–7.95 (m, 8 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 21.8, 123.9, 124.2, 130.1, 130.7, 133.3, 134.9, 139.8, 165.0, 168.1.

#### *N*-(4-Chlorophenyl)-*N*-(1,3-dioxoisindolin-2-yl)acetamide (*para*-**3eg**)

Following the typical procedure for **3aa** using catalyst **Ib'** gave *para*-**3eg**; yellowish solid; yield: 57.9 mg (92%); mp 138–140 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 2.09 (s, 3 H), 7.30–7.49 (m, 2 H), 7.55–7.66 (m, 2 H), 7.69–7.95 (m, 4 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 21.8, 124.2, 130.1, 130.3, 130.4, 134.9, 135.8, 139.3, 165.0, 168.2.

#### *N*-Methoxy-*N*-(methoxyphenyl)benzamide (**3ch**)

Following the typical procedure for **3aa**, but using DCE instead of the mixed fluoroalcohol solvent (Scheme 7) and μ-oxo catalyst **Ib'** (5 mol%) gave **3ch**; light yellow oil; yield: 91.3 mg (70%); ratio *ortho/para* 1.7:1.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 3.71 (s, 3 H, *ortho*), 3.72 (s, 3 H, *para*), 3.81 (s, 3 H, *para*), 3.85 (s, 3 H, *ortho*), 6.74–6.89 (m, 4 H), 7.07–7.64 (m, 14 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 55.6, 55.7, 61.3, 61.6, 112.3, 114.4, 121.0, 127.5, 127.7, 128.1, 128.4, 128.7, 129.3, 130.2, 130.5, 130.7, 130.9, 132.3, 134.7, 134.8, 155.2, 159.0, 168.1, 169.7.

#### *N*-(4-*tert*-Butylphenyl)-*N*-(3,4-dimethylphenyl)acetamide (**5ai**)

Following to the typical procedure for **3aa**, but using the μ-oxo catalyst **Ia'** (10 mol%) in TFE/CH<sub>2</sub>Cl<sub>2</sub> (2:1, 0.067 M) (Scheme 8) and wet MCPBA (69% purity, 1.5 equiv) instead of 9% peracetic acid solution for 3 h gave **5ai**; yellowish oil; yield: 44.4 mg (75%).

IR (KBr): 2966, 2869, 1675, 1608, 1509, 1369, 1308, 1024 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 50 °C): δ = 1.28 (s, 9 H), 2.01 (s, 3 H), 2.22 (s, 6 H), 6.97 (dd, *J* = 7.8, 2.0 Hz, 1 H), 7.03 (d, *J* = 1.9 Hz, 1 H), 7.09 (d, *J* = 7.8 Hz, 1 H), 7.16 (d, *J* = 8.3 Hz, 2 H), 7.32 (d, *J* = 8.8 Hz, 2 H).

HRMS (DART): *m/z* [M + H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>26</sub>ON: 296.2009; found: 296.2009.

#### *N*-(4-Ethylphenyl)-*N*-(3,4-dimethylphenyl)acetamide (**5bi**)

Following to the typical procedure for **3aa**, but using the μ-oxo catalyst **Ia'** (10 mol%) in TFE/CH<sub>2</sub>Cl<sub>2</sub> (2:1, 0.067 M) (Scheme 8) and wet MCPBA (69% purity, 1.5 equiv) instead of 9% peracetic acid solution for 3 h gave **5bi**; yellowish oil; yield: 27.6 mg (52%).

IR (KBr): 3025, 2964, 2928, 2873, 1671, 1608, 1509, 1454, 1369, 1305, 1121, 1024 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 50 °C): δ = 1.21 (t, *J* = 7.8 Hz, 3 H), 2.02 (s, 3 H), 2.22 (s, 6 H), 2.61 (q, *J* = 7.8 Hz, 2 H), 6.97 (dd, *J* = 8.3, 2.0 Hz, 1 H), 7.03 (d, *J* = 2.0 Hz, 1 H), 7.10–7.28 (m, 5 H).

HRMS (DART): *m/z* [M + H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>22</sub>ON: 268.1696; found: 268.1696.

#### 5,7-Diacetoxy-5,7-dihydro-1,3,9,11-tetramethylidibenzo[*d,f*][1,3,2]dioxepin (**Ib**) (Figure 1)

To a stirred solution of peracetic acid (9% solution in AcOH, 6.1 mL, 7.6 mmol) in MeCN (47.5 mL) was successively added AcOH (17.1 mL) and 2,2'-diiodo-4,4',6,6'-tetramethylbiphenyl (**Ib'**; 0.88 g, 1.9 mmol), and the mixture was stirred overnight at rt. After removal of MeCN under reduced pressure, the resulting residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and then the organic solution was dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). After evaporation of the solvent, the crude solid, that is, **Ib**, was dissolved in minimal amount of CH<sub>2</sub>Cl<sub>2</sub>, which was then added dropwise to stirred hexane. The resulting suspension was filtered and dried to give pure μ-oxo-bridged hypervalent iodine(III) diacetate **Ib**<sup>24</sup> as a white powder; yield: quant (1.13 g); mp 157 °C.

IR (KBr): 1649, 1559, 1018, 750 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.85 (s, 6 H), 2.16 (s, 6 H), 2.46 (s, 6 H), 7.38 (s, 2 H), 7.86 (s, 2 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 21.2 (2 ×), 21.4, 127.0, 133.4, 135.2, 137.7, 139.2, 142.8, 177.6.

A pure sample compatible for the X-ray crystallographic analysis was obtained by recrystallization from MeCN/hexane solution. For crystallographic data of **Ib** in CIF format, see CCDC 779814.

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## References

- (1) For selected reviews, accounts, and publications, see: (a) Anastasia, L.; Negishi, E. *Handbook of Organopalladium Chemistry for Organic Synthesis*; Wiley: New York, **2002**, 311–334. (b) *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F.; Stang, P. J., Ed.; Wiley-VCH: Weinheim, **2004**. (c) Negishi, E. *Angew. Chem. Int. Ed.* **2011**, *50*, 6738, Nobel Lecture. (d) Suzuki, A. *Angew. Chem. Int. Ed.* **2011**, *50*, 6722; Nobel Lecture. (e) *Science of Synthesis: Cross Coupling and Heck-Type Reactions 1*; Molander, G. A.; Wolfe, J. P.; Larhed, M., Eds.; Thieme: Stuttgart, **2013**.
- (2) For reviews, see: (a) Yang, B. H.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125. (b) Hartwig, J. F. *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E.-i., Ed.; Wiley: New York, **2002**, 1051. (c) Janey, J. M. *Name Reactions for Functional Group Transformations*; Li, J. J.; Corey, E. J., Ed.; John Wiley & Sons: Hoboken, **2007**, 564–609. (d) Ruiz-Castillo, P.; Buchwald, S. L. *Chem. Rev.* **2016**, *116*, 12564. (e) Heravi, M. M.; Kheilkordi, Z.; Zadsirjan, V.; Heydari, M.; Malmir, M. *J. Organomet. Chem.* **2018**, *861*, 17.
- (3) For selected summarizations, see: (a) Torborg, C.; Beller, M. *Adv. Synth. Catal.* **2009**, *351*, 3027. (b) Biffis, A.; Centomo, P.; Del Zotto, A.; Zecca, M. *Chem. Rev.* **2018**, *118*, 2249. (c) *Palladium-Catalyzed Coupling Reactions: Practical Aspects and Future Developments*; Molnár, A., Ed.; Wiley-VCH: Weinheim, **2013**. (d) Cooper, T.; Campbell, I.; Macdonald, S. *Angew. Chem. Int. Ed.* **2010**, *49*, 8082. (e) Brown, D. G.; Bostrom, J. J. *Med. Chem.* **2016**, *59*, 4443. (f) Cernak, T.; Dykstra, K. D.; Tyagarajan, S.; Vachalb, P.; Krska, S. W. *Chem. Soc. Rev.* **2016**, *45*, 546. (g) Devendar, P.; Qu, R.; Kang, W.-M.; He, B.; Yang, G.-F. *J. Agric. Food Chem.* **2018**, *66*, 8914.
- (4) Heck reaction is an early pioneer for the C–H coupling toward organic halides. See: (a) Heck, R. F. *Org. React.* **1982**, *27*, 345. For the trials reported in 2000s for other types of C–H coupling reactions, see: (b) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (c) Seregin, I. Y.; Gevorgyan, V. *Chem. Soc. Rev.* **2007**, *36*, 1173. (d) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem. Int. Ed.* **2009**, *48*, 5094. (e) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (f) Zhang, Y.-F.; Shi, Z.-J. *Acc. Chem. Res.* **2019**, *52*, 161.
- (5) For recent summaries, see: (a) *From C–H to C–C Bonds: Cross-Dehydrogenative-Coupling*; Li, C.-J., Ed.; RSC Green Chemistry Series: Cambridge, **2015**. (b) Tang, S.; Zeng, L.; Lei, A. *J. Am. Chem. Soc.* **2018**, *140*, 13128. (c) Yang, Y.; Lan, J.; You, J. *Chem. Rev.* **2017**, *117*, 8787. (d) Varun, B. V.; Dhineshkumar, J.; Bettadapur, K. R.; Siddaraju, Y.; Alagiri, K.; Prabhu, K. R. *Tetrahedron Lett.* **2017**, *58*, 803. (e) He, K.-H.; Li, Y. *ChemSusChem* **2014**, *7*, 2788.
- (6) For early discussions, see: (a) Dhingra, O. P. *Oxidation in Organic Chemistry*, In *Organic Chemistry, Part D, Vol. 5*; Trahanovsky, W. S., Ed.; Academic Press: New York, **1982**, 207. (b) Brunow, G.; Kilpeläinen, I.; Sipilä, J.; Syrjänen, K.; Karhunen, P.; Setälä, H.; Rummakko, P. *Lignin and Lignan Biosynthesis*; Lewis, N. G.; Sarkanen, S., Ed.; ACS Symposium Series 687; American Chemical Society: Washington, **1998**, 131. (c) Lessene, G.; Feldman, K. S. *Modern Arene Chemistry*; Astruc, D., Ed.; Wiley-VCH: Weinheim, **2002**, 479–538.
- (7) For recent interest of metal-free couplings and the use of hypervalent iodine reagent, see the following reviews: (a) Sun, C.-L.; Shi, Z.-J. *Chem. Rev.* **2014**, *114*, 9219; and references therein. (b) Chan, T. L.; Wu, Y.; Choy, P. Y.; Kwong, F. Y. *Chem. Eur. J.* **2013**, *19*, 15802. (c) Mehta, V. P.; Punji, B. *RSC Adv.* **2013**, *3*, 11957. (d) Mousseau, J. J.; Charette, A. B. *Acc. Chem. Res.* **2013**, *46*, 412. (e) Narayan, R.; Manna, S.; Antonchick, A. P. *Synlett* **2015**, *26*, 1785. (f) Narayan, R.; Matcha, K.; Antonchick, A. P. *Chem. Eur. J.* **2015**, *21*, 14678. (g) Rossi, R.; Lessi, M.; Manzini, C.; Marianetti, G.; Bellina, F. *Adv. Synth. Catal.* **2015**, *357*, 3777. (h) Qin, Y.; Zhu, L.; Luo, S. *Chem. Rev.* **2017**, *117*, 9433.
- (8) For recent comprehensive reviews and publications, see: (a) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2016**, *116*, 3328. (b) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2008**, *108*, 5299. (c) Zhdankin, V. V. *J. Org. Chem.* **2011**, *76*, 1185. (d) Silva, L. F. Jr.; Olofsson, B. *Nat. Prod. Rep.* **2011**, *28*, 1722. (e) *The Chemistry of Hypervalent Halogen Compounds*; Marek, I.; Olofsson, B.; Rappoport, Z., Ed.; John Wiley & Sons: Chichester, **2018**. (f) *Hypervalent Iodine Chemistry*, In *Topics in Current Chemistry*, Vol. 373; Wirth, T., Ed.; Springer: Switzerland, **2016**. (g) *Hypervalent Iodine Chemistry: Modern Developments in Organic Synthesis*, In *Topics in Current Chemistry*, Vol. 224; Wirth, T., Ed.; Springer: Berlin, **2003**.
- (9) For our reviews and accounts, see: (a) Kita, Y.; Tohma, H.; Yakura, T. *Trends Org. Chem.* **1992**, *3*, 113. (b) Kita, Y.; Takada, T.; Tohma, H. *Pure Appl. Chem.* **1996**, *68*, 627. (c) Tohma, H.; Kita, Y. *Top. Curr. Chem.* **2003**, *224*, 209. (d) Dohi, T.; Ito, M.; Yamaoka, N.; Morimoto, K.; Fujioka, H.; Kita, Y. *Tetrahedron* **2009**, *65*, 10797. (e) Kita, Y.; Dohi, T.; Morimoto, K. *J. Synth. Org. Chem. Jpn.* **2011**, *69*, 1241. (f) Kita, Y.; Dohi, T. *Chem. Rec.* **2015**, *15*, 886. (g) Dohi, T.; Kita, Y. *Curr. Org. Chem.* **2016**, *20*, 580. (h) Dohi, T.; Kita, Y. *Top. Curr. Chem.* **2016**, *373*, 1. (i) Morimoto, K.; Dohi, T.; Kita, Y. *Synlett* **2017**, *28*, 1680.
- (10) Dilute peracetic acid is known as a safe and environmentally friendly oxidant that releases nontoxic acetic acid as the co-product. It is commercially available and frequently employed in industrial-scale oxidations, such as epoxidation. Furthermore, its aqueous 0.2–0.3% solution is widely used as a disinfectant in medical situations.
- (11) For early studies, see: (a) Tamura, Y.; Yakura, T.; Haruta, J.; Kita, Y. *J. Org. Chem.* **1987**, *52*, 3927. (b) Tamura, Y.; Yakura, T.; Tohma, H.; Kikuchi, K.; Kita, Y. *Synthesis* **1989**, 126. (c) Kita, Y.; Yakura, T.; Tohma, H.; Kikuchi, K.; Tamura, Y. *Tetrahedron Lett.* **1989**, *30*, 1119. (d) Kita, Y.; Tohma, H.; Kikuchi, K.; Inagaki, M.; Yakura, T. *J. Org. Chem.* **1991**, *56*, 435. (e) Kita, Y.; Tohma, H.; Inagaki, M.; Hatanaka, K.; Kikuchi, K.; Yakura, T. *Tetrahedron Lett.* **1991**, *32*, 2035. (f) Kita, Y.; Tohma, H.; Inagaki, M.; Hatanaka, K.; Yakura, T. *J. Am. Chem. Soc.* **1992**, *114*, 2175.
- (12) (a) Kita, Y.; Tohma, H.; Inagaki, M.; Hatanaka, K.; Yakura, T. *Tetrahedron Lett.* **1991**, *32*, 4321. (b) Kita, Y.; Tohma, H.; Hatanaka, K.; Takada, T.; Fujita, S.; Mitoh, S.; Sakurai, H.; Oka, S. *J. Am. Chem. Soc.* **1994**, *116*, 3684.
- (13) For the utility of fluoroalcohol solvents, see ref. 9b and the following reviews and accounts: (a) Ebersson, L.; Hartshorn, M. P.; Persson, O.; Radner, F. *Chem. Commun.* **1996**, 2105. (b) Bégué, J. P.; Bonnet-Delpon, D.; Crousse, B. *Synlett* **2004**, 18. (c) Shuklov, I. A.; Dubrovina, N. V.; Boerner, A. *Synthesis* **2007**, 2925. (d) Khaksar, S. J. *Fluorine Chem.* **2015**, *172*, 51.
- (14) Intramolecular cyclizations of azides: (a) Kita, Y.; Egi, M.; Okajima, A.; Ohtsubo, M.; Takada, T.; Tohma, H. *Chem. Commun.* **1996**, 1491. (b) Kita, Y.; Watanabe, H.; Egi, M.; Saiki, T.; Fukuoka, Y.; Tohma, H. *J. Chem. Soc., Perkin Trans. 1* **1998**, 635. (c) Kita, Y.; Egi, M.; Tohma, H. *Chem. Commun.* **1999**, 143. (d) Kita, Y.; Egi, M.; Ohtsubo, M.; Saiki, T.; Okajima, A.; Takada, T.; Tohma, H. *Chem. Pharm. Bull.* **1999**, *47*, 241. (e) Kita, Y.; Egi, M.; Takada, T.; Tohma, H. *Synthesis* **1999**, 885.

- (15) See ref. 9b and selected examples for introducing heteroatoms: (a) Kita, Y.; Takada, T.; Mihara, S.; Tohma, H. *Synlett* **1995**, 211. (b) Kita, Y.; Takada, T.; Mihara, S.; Whelan, B. A.; Tohma, H. *J. Org. Chem.* **1995**, *60*, 7144. (c) Kita, Y.; Egi, M.; Ohtsubo, M.; Saiki, T.; Takada, T.; Tohma, H. *Chem. Commun.* **1996**, 2225. (d) Hamamoto, H.; Hata, K.; Nambu, H.; Shiozaki, Y.; Tohma, H.; Kita, Y. *Tetrahedron Lett.* **2004**, *45*, 2293. (e) Hata, K.; Hamamoto, H.; Shiozaki, Y.; Cämmerer, S. B.; Kita, Y. *Tetrahedron* **2007**, *63*, 4052; and references cited therein.
- (16) Recent reviews on dehydrogenative aromatic C–H aminations: (a) Louillat, M.-L.; Patureau, F. W. *Chem. Soc. Rev.* **2014**, *43*, 901. (b) Subramanian, P.; Rudolf, G. C.; Kaliappan, K. P. *Chem. Asian J.* **2016**, *11*, 168. (c) Jiao, J.; Murakami, K.; Itami, K. *ACS Catal.* **2016**, *6*, 610. (d) Kim, H.; Chang, S. *ACS Catal.* **2016**, *6*, 2341. (e) Henry, M. C.; Mostafa, M. A. B.; Sutherland, A. *Synthesis* **2017**, *49*, 4586. (f) Park, Y.; Kim, Y.; Chang, S. *Chem. Rev.* **2017**, *117*, 9247. (g) Timsina, Y. N.; Gupton, B. F.; Ellis, K. C. *ACS Catal.* **2018**, *8*, 5732. Metal-free hypervalent iodine strategy: (h) Samanta, R.; Matcha, K.; Antonchick, A. P. *Eur. J. Org. Chem.* **2013**, 5769. (i) Samanta, R.; Antonchick, A. P. *Synlett* **2012**, 23, 809.
- (17) Kikugawa, Y.; Kawase, M. *Chem. Lett.* **1990**, 581.
- (18) (a) Kikugawa, Y.; Nagashima, A.; Sakamoto, T.; Miyazawa, E.; Shiiya, M. *J. Org. Chem.* **2003**, *68*, 6739. (b) Miyazawa, E.; Sakamoto, T.; Kikugawa, Y. *Heterocycles* **2003**, *59*, 149. (c) Serna, S.; Tellitu, I.; Dominguez, E.; Moreno, I.; SanMartin, R. *Tetrahedron* **2004**, *60*, 6533.
- (19) For other early applications, see: (a) Romero, A. G.; Darlington, W. H.; McMillan, M. W. *J. Org. Chem.* **1997**, *62*, 6582. (b) Correa, A.; Tellitu, I.; Dominguez, E.; Moreno, I.; SanMartin, R. *J. Org. Chem.* **2005**, *70*, 2256. (c) Wardrop, D. J.; Basak, A. *Org. Lett.* **2001**, *3*, 1053. (d) Wardrop, D. C.; Zhang, W. *Org. Lett.* **2001**, *3*, 2353.
- (20) For reviews on catalytic utilizations of hypervalent iodine reagents, see: (a) Richardson, R. D.; Wirth, T. *Angew. Chem. Int. Ed.* **2006**, *45*, 4402. (b) Ochiai, M.; Miyamoto, K. *Eur. J. Org. Chem.* **2008**, 4429. (c) Dohi, T.; Kita, Y. *Chem. Commun.* **2009**, 2073. (d) Yusubov, M. S.; Zhdkankin, V. V. *Mendeleev Commun.* **2010**, *20*, 2073. (e) Singh, F. V.; Wirth, T. *Chem. Asian J.* **2014**, *9*, 950.
- (21) For the first report of C–N bond-forming reaction using a catalytic amount of hypervalent iodine, see: (a) Dohi, T.; Maruyama, A.; Minamitsuji, Y.; Takenaga, N.; Kita, Y. *Chem. Commun.* **2007**, 1224. (b) Moroda, A.; Togo, H. *Synthesis* **2008**, 1257.
- (22) For early studies, see: (a) Alcock, N. W.; Waddington, T. C. *J. Chem. Soc.* **1963**, 4103. (b) Gallos, J.; Varvoglis, A.; Alcock, N. W. *J. Chem. Soc., Perkin Trans. 1* **1985**, 757.
- (23) We have recently met the notably high reactivity of  $\mu$ -oxo-bridged PIFA dimer in organic solvents as well as in water, see: (a) Dohi, T.; Uchiyama, T.; Yamashita, D.; Washimi, N.; Kita, Y. *Tetrahedron Lett.* **2011**, *52*, 2212. (b) Takenaga, N.; Uchiyama, T.; Kato, D.; Fujioka, H.; Dohi, T.; Kita, Y. *Heterocycles* **2011**, *82*, 1327. (c) Dohi, T.; Nakae, T.; Takenaga, N.; Uchiyama, T.; Fukushima, K.; Fujioka, H.; Kita, Y. *Synthesis* **2012**, *44*, 1183.
- (24) Dohi, T.; Takenaga, N.; Fukushima, K.; Uchiyama, T.; Kato, D.; Shiro, M.; Fujioka, H.; Kita, Y. *Chem. Commun.* **2010**, 46, 7697.
- (25) For utilizations of our  $\mu$ -oxo catalysts in other reactions, see: Ito, M.; Kubo, H.; Itani, I.; Morimoto, K.; Dohi, T.; Kita, Y. *J. Am. Chem. Soc.* **2013**, *135*, 14078; see also ref. 26.
- (26) (a) Dohi, T.; Nakae, T.; Ishikado, Y.; Kato, D.; Kita, Y. *Org. Biomol. Chem.* **2011**, *9*, 6899. (b) Dohi, T.; Kato, D.; Hyodo, R.; Yamashita, D.; Shiro, M.; Kita, Y. *Angew. Chem. Int. Ed.* **2011**, *50*, 3784. (c) Dohi, T.; Mochizuki, E.; Yamashita, D.; Miyazaki, K.; Kita, Y. *Heterocycles* **2014**, *88*, 245.
- (27) X-ray crystal structure data of PIFA: (a) Stergioudis, G. A.; Kokkou, S. C.; Bozopoulos, A. P.; Rentzeperis, P. J. *Acta Crystallogr., Sect. C* **1984**, *40*, 877. PIDA: (b) Lee, C.-K.; Mak, T. C. W.; Li, W.-K. *Acta Crystallogr., Sect. B* **1977**, *33*, 1620. (c) The reported bond lengths of iodine(III) ligands in the hypervalent iodine reagents, PIDA and PIFA as well as  $\mu$ -oxo-bridged PIFA dimer and our biaryl alternative **1b** (see Figure 1 for the structures), are summarized in Table 2 below.

Table 2 Bond Lengths<sup>a</sup>

Reagent	I–X [Å]	I–O* [Å]
PhI(OAc) <sub>2</sub>	2.16 (X = OAc)	–
PhI(OCOCF <sub>3</sub> ) <sub>2</sub>	2.16 (X = OCOCF <sub>3</sub> )	–
$\mu$ -oxo-bridged PIFA dimer (R = CF <sub>3</sub> )	2.27 (X = OCOCF <sub>3</sub> )	2.02
our $\mu$ -oxo catalyst <b>1b</b> <sup>b</sup> (R = R' = Me)	2.23 (X = OAc)	2.06

<sup>a</sup> Averaged bond length for the reagents; O\*: bridged oxygen.<sup>b</sup> For the crystallographic data in CIF, see CCDC 779814.

- (28) The existence of strong secondary bondings between the iodine atoms and the ligand's carbonyl oxygens appears in the structure, which was confirmed by the lower shift of carbonyl frequencies for the  $\mu$ -oxo PIFA in the infrared resonance spectra compared to that of PIFA. These observations clearly account for the enhanced cationic character of the iodine center, see: (a) Alcock, N. W.; Countryman, R. M.; Esperas, S.; Sawyer, J. F. *J. Chem. Soc., Dalton Trans.* **1979**, 854. (b) Alcock, N. W.; Harrison, W. D. *J. Chem. Soc., Dalton Trans.* **1984**, 1709. (c) Bell, R.; Morgan, K. J. *J. Chem. Soc.* **1960**, 1209.
- (29) Samanta, R.; Bauer, J. O.; Strohmann, C.; Antonchick, A. P. *Org. Lett.* **2012**, *14*, 5518.
- (30) (a) Minamitsuji, Y.; Kato, D.; Fujioka, H.; Dohi, T.; Kita, Y. *Aust. J. Chem.* **2009**, *62*, 648. (b) Dohi, T.; Yamaoka, N.; Itani, I.; Kita, Y. *Aust. J. Chem.* **2011**, *64*, 529.
- (31) The TON of a catalyst, 1,2-diiodobenzene, at the 4 mol% loading reached 18 times for the reaction between the same substrates (toluene 2a, 15 equiv) in HFIP/DCE (1:1), see: Lucchetti, N.; Scalone, M.; Fantasia, S.; Muñiz, K. *Adv. Synth. Catal.* **2016**, *358*, 2093.
- (32) For utilities of *N*-methoxy anilides for unique transformations, see: (a) Kikugawa, Y.; Shimada, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1450. (b) Matsumoto, K.; Kato, M.; Sakamoto, T.; Kikugawa, Y. *J. Chem. Res., Synop.* **1995**, 34. (c) Nakamura, I.; Jo, T.; Ishida, Y.; Tashiro, H.; Terada, M. *Org. Lett.* **2017**, *19*, 3059. (d) Ishida, Y.; Nakamura, I.; Terada, M. *J. Am. Chem. Soc.* **2018**, *140*, 8629; and references cited therein.
- (33) See ref 9d and: (a) Dohi, T.; Ito, M.; Morimoto, K.; Minamitsuji, Y.; Takenaga, N.; Kita, Y. *Chem. Commun.* **2007**, 4152. (b) Ito, M.; Ogawa, C.; Yamaoka, N.; Fujioka, H.; Dohi, T.; Kita, Y. *Molecules* **2010**, *15*, 1918. (c) Ito, M.; Itani, I.; Toyoda, Y.; Morimoto, K.; Dohi, T.; Kita, Y. *Angew. Chem. Int. Ed.* **2012**, *51*, 12555.

- (34) For the reactivities of diaryliodonium(III) salt, see: (a) Merritt, E. A.; Olofsson, B. *Angew. Chem. Int. Ed.* **2009**, *48*, 9052. (b) Yusubov, M. S.; Maskhev, A. V.; Zhdankin, V. V. *ARKIVOC* **2011**, (i), 370. (c) Olofsson, B. *Top. Curr. Chem.* **2016**, *373*, 135. (d) Stuart, D. R. *Chem. Eur. J.* **2017**, *23*, 15852. (e) Yoshimura, A.; Saito, A.; Zhdankin, V. V. *Chem. Eur. J.* **2018**, *24*, 15156. (f) Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123. (g) Müller, U. *Trends Photochem. Photobiol.* **1999**, *5*, 117.
- (35) For *ortho*-directing effect of amide-containing reagent involving pseudo-cyclic intermediate in electrophilic aromatic substitutions, see: Shen, H.; Vollhardt, K. P. C. *Synlett* **2012**, 23, 208.
- (36) Transition-metal-catalyzed oxidative amidations for aromatic hydrocarbons with stoichiometric hypervalent iodine reagent, see: (a) Shrestha, R.; Mukherjee, P.; Tan, Y.; Litman, Z. C.; Harwig, J. F. *J. Am. Chem. Soc.* **2013**, *135*, 8480. (b) Marchetti, L.; Katak, A.; Davis, R.; DeBoef, B. *Org. Lett.* **2015**, *17*, 358. (c) Berzina, B.; Sokolovs, I.; Suna, E. *ACS Catal.* **2015**, *5*, 7008. (d) Ito, E.; Fukushima, T.; Kawakami, T.; Murakami, K.; Itami, K. *Chem* **2017**, *2*, 383. The combination of transition metal ([Co]) with photocatalyst: (e) Niu, L.; Yi, H.; Wang, S.; Liu, T.; Liu, J.; Lei, A. *Nat. Commun.* **2017**, *8*, 14226. The use of 0.5 mol% amount of iridium-based photocatalyst was reported, while the product yields was up to 52% in this case: (f) Kim, H.; Kim, T.; Lee, D. G.; Roh, S. W.; Lee, C. *Chem. Commun.* **2014**, *50*, 9273.
- (37) (a) Brasche, G.; García-Fortanet, J.; Buchwald, S. L. *Org. Lett.* **2008**, *10*, 2207. For a recent review of transition-metal-catalyzed *ortho* C–H functionalizations of aniline derivatives, see: (b) Leitch, J. A.; Frost, C. G. *Synthesis* **2018**, *50*, 2693.
- (38) Antonchick reported this type of coupling reaction using PIDA as a stoichiometric amount: Antonchick, A. P.; Samanta, R.; Kulikov, K.; Lategahn, J. *Angew. Chem. Int. Ed.* **2011**, *50*, 8605.
- (39) Representative examples: (a) Kim, H. J.; Kim, J.; Cho, S. H.; Chang, S. *J. Am. Chem. Soc.* **2011**, *133*, 16382. (b) Katak, A. A.; Potavathri, S.; Barham, R. A.; Romano, K. M.; DeBoef, B. *J. Am. Chem. Soc.* **2011**, *133*, 19960. (c) Samanta, R.; Lategahn, J.; Antonchick, A. P. *Chem. Commun.* **2012**, *48*, 3194. (d) Manna, S.; Serebrennikova, P. O.; Utepova, I. A.; Antonchick, A. P.; Chupakhin, O. N. *Org. Lett.* **2015**, *17*, 4588. (e) Pialat, A.; Bergès, J.; Sabourin, A.; Vinck, R.; Liégault, B.; Taillefer, M. *Chem. Eur. J.* **2015**, *21*, 10014. (f) Mondal, S.; Samanta, S.; Jana, S.; Hajra, A. *J. Org. Chem.* **2017**, *82*, 4504. (g) Zhao, F.; Sun, T.; Sun, H.; Xi, G.; Sun, K. *Tetrahedron Lett.* **2017**, *58*, 3132. (h) Maiti, S.; Mal, P. *J. Org. Chem.* **2018**, *83*, 1340.
- (40) For diaryliodonium(III) salt mediated C–N coupling strategies, see: (a) Carroll, M. A.; Wood, R. A. *Tetrahedron* **2007**, *63*, 11349. (b) Riedmueller, S.; Nachtsheim, B. J. *Synlett* **2015**, 26, 651. (c) Yang, Y.; Wu, X.; Han, J.; Mao, S.; Quian, X.; Wang, L. *Eur. J. Org. Chem.* **2014**, 6854. (d) Tinnis, F.; Stridfeldt, E.; Lundberg, H.; Adolfsson, H.; Olofsson, B. *Org. Lett.* **2015**, *17*, 2688. (e) Lucchetti, N.; Scalone, M.; Fantasia, S.; Muñiz, K. *Angew. Chem. Int. Ed.* **2016**, *55*, 13335. (f) Sandtorv, A. H.; Stuart, D. R. *Angew. Chem. Int. Ed.* **2016**, *55*, 15812. (g) Basu, S.; Sandtorv, A. H.; Stuart, D. R. *Beilstein J. Org. Chem.* **2018**, *14*, 1034. (h) Purkait, N.; Kervefors, G.; Linde, E.; Olofsson, B. *Angew. Chem. Int. Ed.* **2018**, *57*, 11427.
- (41) (a) Morimoto, K.; Ohnishi, Y.; Nakamura, A.; Sakamoto, K.; Dohi, T.; Kita, Y. *Asian J. Org. Chem.* **2014**, *3*, 382. (b) Morimoto, K.; Ogawa, R.; Koseki, D.; Takahashi, Y.; Dohi, T.; Kita, Y. *Chem. Pharm. Bull.* **2015**, *63*, 819.
- (42) Related  $\mu$ -oxo-bridged chiral hypervalent iodine catalysts: (a) Dohi, T.; Maruyama, A.; Takenaga, N.; Senami, K.; Minamitsuji, Y.; Fujioka, H.; Cämmerer, S.; Kita, Y. *Angew. Chem. Int. Ed.* **2008**, *47*, 3787. (b) Dohi, T.; Takenaga, N.; Nakae, T.; Toyoda, Y.; Yamasaki, M.; Shiro, M.; Fujioka, H.; Maruyama, A.; Kita, Y. *J. Am. Chem. Soc.* **2013**, *135*, 4558. (c) Suzuki, S.; Kamo, T.; Fukushi, K.; Hiramatsu, T.; Tokunaga, E.; Dohi, T.; Kita, Y.; Shibata, N. *Chem. Sci.* **2014**, *5*, 2754. (d) Ogasawara, M.; Sasa, H.; Hu, H.; Amano, Y.; Nakajima, H.; Takenaga, N.; Nakajima, K.; Kita, Y.; Takahashi, T.; Dohi, T. *Org. Lett.* **2017**, *19*, 4102. (e) Dohi, T.; Sasa, H.; Miyazaki, K.; Fujitake, M.; Takenaga, N.; Kita, Y. *J. Org. Chem.* **2017**, *82*, 11954.
- (43) Utilizing our spirobiindane catalysts (see refs 42a and 42b), Cai and co-workers recently developed intramolecular oxidative C–N cyclizations accompanying asymmetric desymmetrization of the substrates, see: Ding, Q.; He, H.; Cai, Q. *Org. Lett.* **2018**, *20*, 4554.
- (44) (a) Kawase, M.; Kitamura, T.; Kikugawa, Y. *J. Org. Chem.* **1989**, *54*, 3394. (b) Miyata, O.; Koizumi, T.; Asai, H.; Iba, R.; Naito, T. *Tetrahedron* **2004**, *60*, 3893. (c) Xie, W.; Yang, J.; Wang, B.; Li, B. *J. Org. Chem.* **2014**, *79*, 8278. (d) Brosse, N.; Pinto, M.; Jamart-Gregoire, B. *Eur. J. Org. Chem.* **2003**, 4757.
- (45) (a) Tohma, H.; Morioka, H.; Takizawa, S.; Arisawa, M.; Kita, Y. *Tetrahedron* **2001**, *57*, 345. (b) Tohma, H.; Iwata, M.; Maegawa, T.; Kita, Y. *Tetrahedron Lett.* **2002**, *43*, 9241.