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# Organo-Iodine(III)-Catalyzed Oxidative Phenol–Arene and Phenol–Phenol Cross-Coupling Reaction

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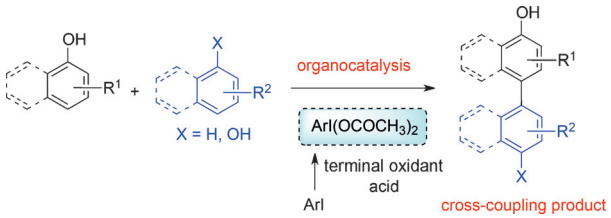
***Abstract:*** *The direct oxidative coupling reaction has been an attractive tool for environmentally benign chemistry. Reported herein is that the hypervalent iodine catalyzed oxidative metal-free cross-coupling reaction of phenols can be achieved using Oxone as a terminal oxidant in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). This method features a high efficiency and regioselectivity, as well as functional-group tolerance under very mild reaction conditions without using metal catalysts.*

The biaryl unit including phenol is an important structural motif for a wide range of functional molecules such as bioactive natural products, liquid crystals, and ligands for transition-metal catalysts.[1] The common approaches to the syntheses of these structures involve cross-couplings between aryl halides and organometallic reagents.[2] In these cases of multistep syntheses, such as Suzuki or Stille coupling, the phenol moiety usually has to be protected. Recently, transition-metal-catalyzed direct functionalization of the C–H bonds on aromatic compounds, involving the activation of the aromatic C–H bond, has attracted much attention in terms of synthetic efficiency and minimization of atomic waste.[3,4]

In contrast, the oxidative cross-coupling of unprotected phenols has received considerable attention because of the atom-economical and environmentally friendly processes.[5] Although various kinds of homocoupling reactions of unprotected phenols involving the use of Fe, Cu, Mn, and Ti salts have been developed,[6] the catalytic oxidative cross-coupling reaction of phenols by C–H/C–H′ coupling has remained challenging.[7] This reaction is a challenge because, when simple phenols are employed in oxidative cross-couplings, the desired products are often concomitantly formed along with homocoupling by-products. Moreover, the formation of higher-molecular-weight polymers or C,O-connected phenol portions, for example, quinol ethers, might also occur depending on the oxidant and the reaction conditions.[2b] A major reason for this side reaction is the difficulty associated with the tunable reactivity of phenols by controlling their oxidation potential using a protecting group for the phenol hydroxy group. Therefore, the development of an efficient catalytic cross-coupling of unprotected phenols for the construction of biaryl compounds is still highly desirable. Recently, Waldvogel and co-workers reported an electrochemical phenol–arene cross-coupling reaction using boron-doped diamond electrodes.[8] Very recently, the iron-catalyzed oxidative cross-coupling reaction of phenols with arenes was successfully achieved.[9] While recent metal-catalyzed cross-couplings of phenols have been studied, the organocatalytic cross-coupling reaction still remains particularly challenging. Recently, we developed the oxidative cross-coupling reaction of aromatic compounds using hypervalent iodine reagents.[10–15] Inspired by these studies, we now report a broadly applicable organo-iodine(III)-catalyzed oxidative cross-coupling reaction of phenols using Oxone as a terminal oxidant (Scheme 1).




***Scheme 1.*** The metal-free organocatalytic oxidative cross-coupling of phenols by hypervalent iodine catalyst.

Based on our previous research of the catalytic cross-coupling reaction of anilines,[14] we first examined the coupling reaction of 2,6-dimethoxyphenol (**1a**) and 1,2,4-trimethoxybenzene (**2a**) with a combination of iodoarenes and terminal oxidants, such as *m*CPBA, in HFIP (Table 1). However, these previous reaction conditions were ineffective for producing the coupling product **3aa**. Therefore, we examined other terminal oxidants for the coupling reaction of **1a** and **2a** in a fluoroalcohol at room temperature. As a result, when Oxone was used as a terminal oxidant, the desired cross-coupling product **3aa** was obtained in 34% yield without forming the homocoupling product (entry 3). To improve the yield of **3aa**, a variety of phase-transfer catalysts was evaluated. The use of 18-crown-6[16] and two equivalents of $CH_3COOH$ increased the yield of **3aa** (entry 6). With Oxone as the obvious choice of the terminal oxidant in the presence of 18-crown-6, we then screened iodine catalysts. The 4-fluoro-, 4-methyl-, and 2-methoxy-substituted iodine catalysts did not increase the yield of **3aa** (entries 7–9). The use of 4-methoxy iodobenzene increased the yield of **3aa** to 90% yield (entry 11). Other ordinary organic solvents, such as toluene, diethyl ether, DME, 1,4-dioxane, dichloromethane, and another fluoroalcohol, $CF_3CH_2OH$, were less effective

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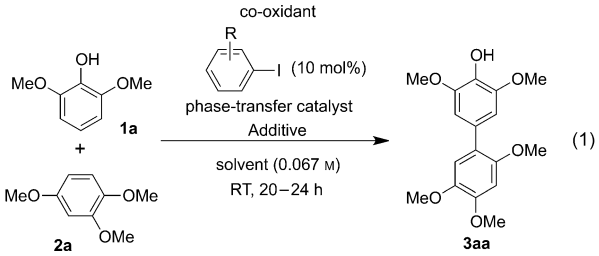
***Table 1:*** Optimization of reaction conditions [Eq. (1)].

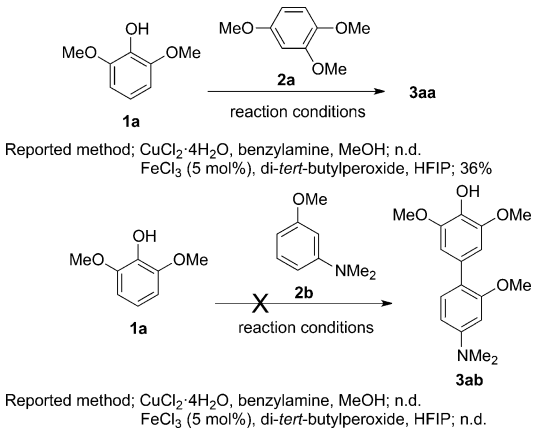



| Entry[a] | Co-Oxidant | Iodoarene | Phase-transfer catalyst | Additive | Yield [%][b] |
|---|---|---|---|---|---|
| 1 | 9% AcOOH (1 equiv) | R = H | none | none | trace |
| 2 | *m*CPBA (1 equiv) | R = H | none | none | trace |
| 3 | Oxone (1 equiv) | R = H | none | none | 34 |
| 4 | Oxone (1 equiv) | R = H | $Bu_4N^+HSO_3^-$ (0.1 equiv) | none | 27 |
| 5 | Oxone (1 equiv) | R = H | 18-crown-6 (0.4 equiv) | none | 36 |
| 6 | Oxone (1 equiv) | R = H | 18-crown-6 (0.4 equiv) | $CH_3COOH$ (2 equiv) | 41 |
| 7 | Oxone (1 equiv) | R = 4-F | 18-crown-6 (0.4 equiv) | $CH_3COOH$ (2 equiv) | 13 |
| 8 | Oxone (1 equiv) | R = 4-Me | 18-crown-6 (0.4 equiv) | $CH_3COOH$ (2 equiv) | 23 |
| 9 | Oxone (1 equiv) | R = 2-MeO | 18-crown-6 (0.4 equiv) | $CH_3COOH$ (2 equiv) | 40 |
| 10 | Oxone (1 equiv) | R = 4-MeO | 18-crown-6 (0.4 equiv) | $CH_3COOH$ (2 equiv) | 77 |
| 11 | Oxone (1.2 equiv) | R = 4-MeO | 18-crown-6 (0.4 equiv) | $CH_3COOH$ (2 equiv) | 90 |
| 12 | Oxone (1.2 equiv) | none | 18-crown-6 (0.4 equiv) | $CH_3COOH$ (2 equiv) | n.d. |

[a] Reactions were carried out by adding Oxone (0.24 mmol) to a stirred solution of the starting phenol **1a** (0.2 mmol), 1,2,4-trimethoxybenzene (**2a**; 0.3 mmol) and the additive (0.4 mmol) in HFIP (3 mL) in the presence of an iodoarene (10 mol%) at room temperature. [b] Yield of isolated product. *m*CPBA = *meta*-chloroperbenzoic acid, n.d. = not determined.

than HFIP. After the optimization process, the cross-coupling of various phenols was carried out under our standard reaction conditions, that is, 2 equivalents of $CH_3COOH$, 0.1 equivalent 4-methoxy iodobenzene, Oxone as the terminal oxidant, and HFIP as the solvent. The starting phenol **1a** was completely consumed, while the excess starting arene **2a** was recovered in almost perfect mass balance. We also confirmed the formation of unidentified by-products derived from **1a**.

In contrast, in case of using the published procedure employing a copper oxidant,[6g] the coupling reaction of **1a** with either **2a** or 3-methoxy-*N*,*N*-dimethylaniline (**2b**) did not proceed. Pappo and co-workers had shown that the iron catalyst was efficient for the oxidative cross-coupling reaction of phenols,[9] but in their cases, this procedure gave the coupling product **3aa** in a low yield and the coupling product **3ab** was not observed for the combination of the substrates **1a** and **2b** (Scheme 2).



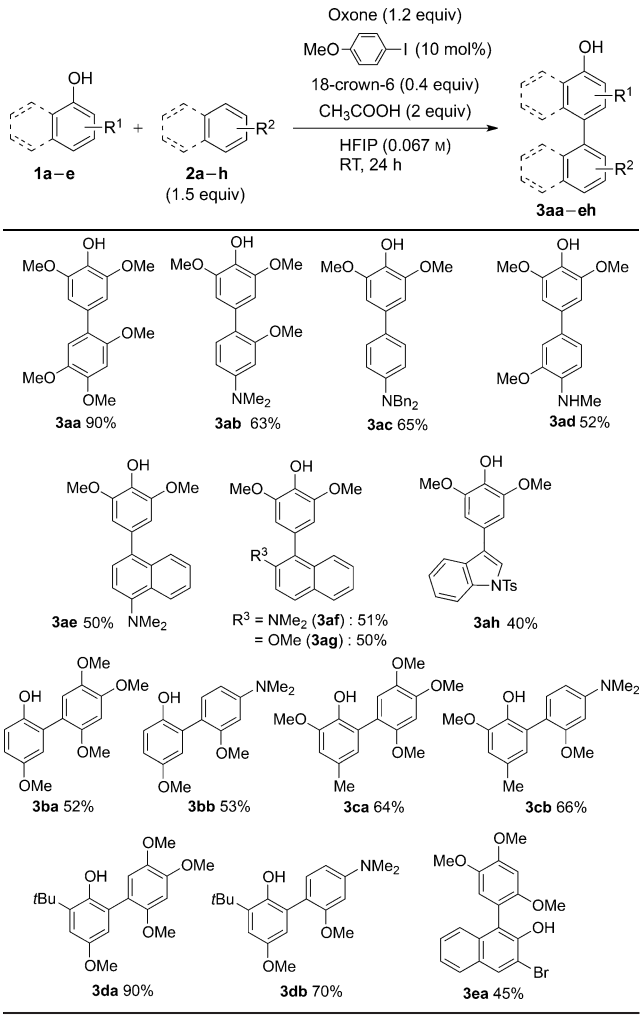

***Scheme 2.*** The cross-couplings of **1a** using metal oxidants and catalysts.

With these optimized reaction conditions (Table 1, entry 11) in hand, a number of structurally and electronically diverse arenes was subjected to the cross-coupling reactions to explore the scope and limitations. As a result, the reaction of the phenols **1** with various arenes (**2**) gave the cross-coupling products **3** in good yields upon isolation, and the results are summarized in Table 2. Electron-rich phenols smoothly reacted with various nucleophilic arenes, thus successfully providing cross-coupling products. Electron-rich aniline possessing a methoxy substituent (**2b**) coupled with **1a** and afforded the coupling product **3ab** in moderate yield. The anilines **2c** and **2d** were arylated at the *para*-position with **1a** to give the biaryls **3ac** and **3ad**, respectively, in moderate yields. Naphthalenes possessing either one dialkylamino or methoxy substituents (**2e–g**) also coupled smoothly to give the expected products **3ae–ag**. A heteroaromatic compound, such as the protected indole **2h**, was found to smoothly react with **1a** to furnish the corresponding coupling product **3ah**. In the case of *para*-substituted phenols, the coupling reaction occurred at the *ortho*-position selectively. 4-Methoxy phenol (**1b**), which often caused undesired multiple arylation reactions using a metal catalyst, afforded the biaryl products **3ba** and **3bb**. Notably, over-oxidized products, such as trimers and quinones, were not observed. Employing **2a** with *ortho*- (**1c**) and *para*-substituted phenols (**1d**) afforded the cross-coupling products **3ca** and **3da**, respectively, in good yields. The electron-rich aniline **2b** also coupled with **1c** and **1d** at the *para*-position to the amino group in good yields. One of the reasons for this selectivity of the coupling products **3cb** and **3db** is presumably the steric effect of the amino group.[12d] The bromine-substituted naphthol **1e** successfully gave the product **3ea** without cleaving the C–Br bond, which is useful for further synthetic elaboration.

In contrast, the oxidative coupling of naphthols has been introduced by stoichiometric copper oxidants or iron(salan) complexes.[17] However, the cross-coupling of various phenols is not well studied and remains challenging because of the undesired side reactions, such as homocoupling of the phenols. Recently, the cross-coupling of 2,6-dialkylphenols with various phenols was developed by using a chromium salen catalyst.[18] Waldvogel and co-workers reported an

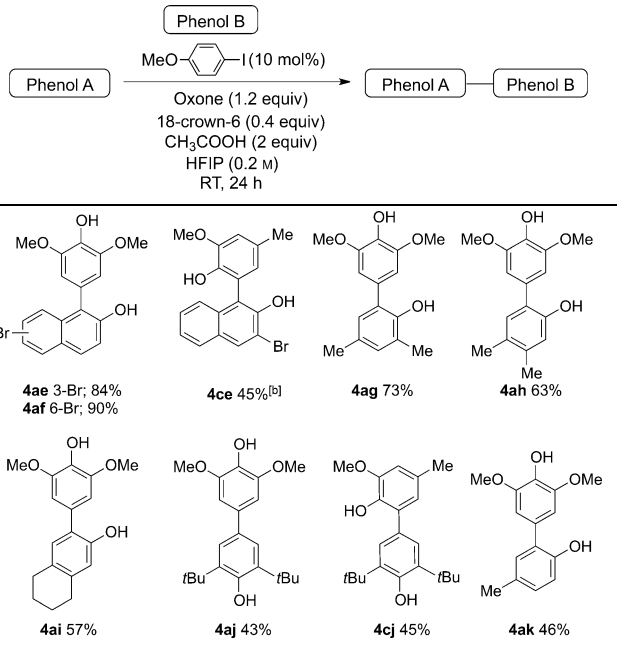
  

***Table 2:*** Reaction scope.[a,b]




[a] Reactions were carried out by adding Oxone (0.24 mmol) to a stirred solution of the starting phenol **1a–e** (0.2 mmol), arene **2a–h** (0.3 mmol), and $CH_3COOH$ (0.4 mmol) in HFIP (3 mL) in the presence of the iodoarene (10 mol%) at room temperature. [b] Yield of isolated product.

***Table 3:*** Cross-coupling reaction between two phenols.[a]




[a] Reactions were carried out by adding Oxone (0.24 mmol) to a stirred solution of the starting phenol (**1a** or **1c** = (0.2 mmol), the phenols **1e–k** (0.2 mmol), and $CH_3COOH$ (0.4 mmol) in HFIP (1 mL) in the presence of iodoarene (10 mol%) at room temperature. [b] Reactions were carried out by adding Oxone (0.24 mmol) to a stirred solution of the starting phenol **1c** (0.2 mmol), phenol **1e** (0.2 mmol) and $CH_3COOH$ (0.4 mmol) in HFIP (3 mL) in the presence of the iodoarene (10 mol%) at room temperature.

electrochemical oxidative cross-coupling reaction of phenols.[19] Jeganmohan and co-workers also described an oxidative cross-coupling of two different phenols using $K_2S_2O_8$ and $Bu_4N^+HSO_3^-$ (10 mol%) in $CF_3COOH$.[20] More recently, the iron-catalyzed oxidative cross-coupling reaction of two different phenols was achieved by the group of Pappo,[21] in which the cross-coupling selectivities of two different phenols are nicely controlled.

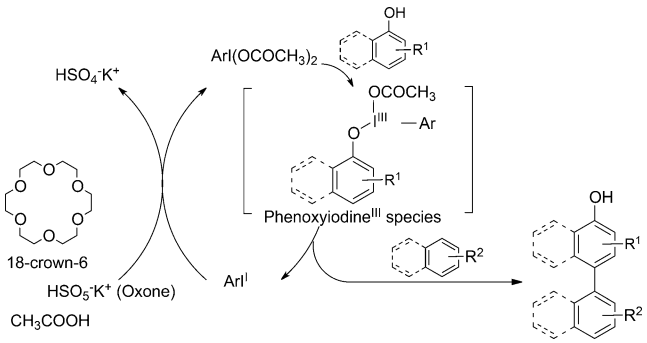
To increase the generality of our cross-coupling, we next considered extending the cross-coupling methods to phenol–phenol combinations. As a result, the reaction of **1a** with the bromo-substituted naphthols **1e** and **1f** gave the cross-coupling products **4ae** and **4af**, respectively, in good yields without affecting the C–Br bond (Table 3). Similarly, **1e** reacted with **1c**, thus affording the cross-coupling product **4ce** in moderate yield. Trisubstituted phenols such as 2,4-dimethylphenol (**1g**), 3,4-dimethylphenol (**1h**), and 5,6,7,8-tetrahydronaphthalen-2-ol (**1i**), reacted efficiently with **1a**, thus giving the corresponding biphenols **4ag–ai** in 73, 63, and 57% yields. 2,6-Di-*tert*-butyl phenol (**1j**) reacted with either **1a** or **1c** to give the corresponding cross-coupling products **4aj** (43%) and **4cj** (45%). Treatment of the disubstituted 4-methyl phenol (**1k**) with **1a** gave the coupling product **4ak** in 46% yield. The group of Jeganmohan tried the oxidative cross-coupling for the synthesis the biphenols **4ag** and **4ah**, thus giving the products in 48% and 56% yields, respectively.[20] In another example, the group of Pappo reported the oxidative coupling of **1a** with various phenols (**1e**, **1f**, **1h,** and **1k**) in 40–96% yields.[21]

A plausible catalytic cycle for the present iodine-catalyzed oxidative coupling of phenols is illustrated in Scheme 3.

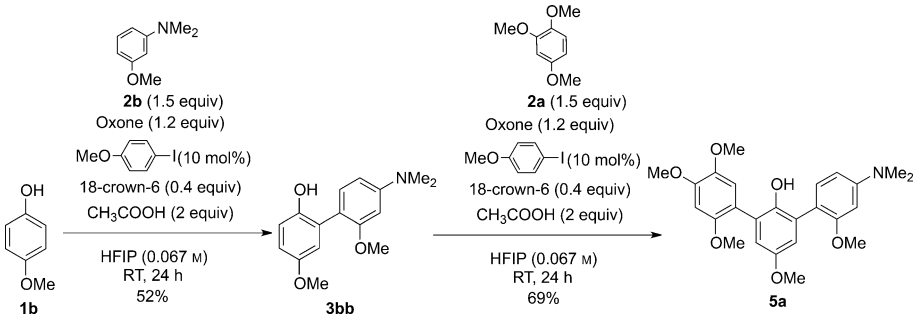
With our cross-coupling protocol, we investigated the sequential C–H arylation reactions of phenol as a way to add two different arenes through an iterative process (Scheme 4). 4-Methoxy phenol (**1b**) first underwent *ortho* arylation to give **3bb** in 52% yield as shown in Table 2. We then attempted to perform a second arylation reaction with **2a** as a coupling partner under our coupling conditions. As a result, we found that the reaction could smoothly proceed to give the diarylated product **5a** in 69% yield.

In summary, the hypervalent iodine(III)-catalyzed[22] intermolecular oxidative cross-coupling reaction of electron-rich aromatic compounds has been successfully developed using a catalytic amount of an iodoarene and an inorganic oxidant. This reaction demonstrates a broad substrate scope and precludes the over-oxidation of the coupling products. Not requiring metal catalysts and functionalization of the




***Scheme 3.*** Plausible catalytic cycle.




***Scheme 4.*** Sequential arylation of phenol.

starting materials for the reaction conditions are also advantageous. This catalytic method is valuable for the synthesis of phenol biaryls with interesting functions and biological activities.

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[1] a) W. Schuehly, J. M. V. Paredes, J. Kleyer, A. Huefner, S. Anavi-Goffer, S. Raduner, K.-H. Altmann, J. Gertsch, *Chem. Biol.* **2011**, *18*, 1053; b) G. Bringmann, T. Gulder, T. M. Gulder, M. Breuning, *Chem. Rev.* **2011**, *111*, 563; c) D. Parmar, E. Sugiono, S. Raja, M. Rueping, *Chem. Rev.* **2014**, *114*, 9047.

[2] a) J. M. Brunel, *Chem. Rev.* **2005**, *105*, 857; b) M. C. Kozlowski, B. J. Morgan, E. C. Linton, *Chem. Soc. Rev.* **2009**, *38*, 3193; c) J. A. Ashenhurst, *Chem. Soc. Rev.* **2010**, *39*, 540; d) H. Wang, *Chirality* **2010**, *22*, 827; e) A. E. Wendlandt, A. M. Suess, S. S. Stahl, *Angew. Chem. Int. Ed.* **2011**, *50*, 11062; *Angew. Chem.* **2011**, *123*, 11256.

[3] a) T. Satoh, Y. Kawamura, M. Miura, M. Nomura, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1740; *Angew. Chem.* **1997**, *109*, 1820; b) T. Satoh, Y. Kawamura, M. Miura, M. Nomura, *Chem. Lett.* **1998**, 931; c) S. Saito, T. Kano, H. Muto, M. Nakadai, H. Yamamoto, *J. Am. Chem. Soc.* **1999**, *121*, 8943; d) R. B. Bedford, S. J. Coles, M. B. Hursthouse, M. E. Limmert, *Angew. Chem. Int. Ed.* **2003**, *42*, 112; *Angew. Chem.* **2003**, *115*, 116; e) R. B. Bedford, M. E. Limmert, *J. Org. Chem.* **2003**, *68*, 8669; f) S. Oi, S. Watanabe, S. Fukita, Y. Inoue, *Tetrahedron Lett.* **2003**, *44*, 8665; g) A. Wetzel, G. Pratsch, R. Kolb, M. R. Heinrich, *Chem. Eur. J.* **2010**, *16*, 2547.

[4] a) C. Huang, V. Gevorgyan, *J. Am. Chem. Soc.* **2009**, *131*, 10844; b) R. Bedford, R. L. Webster, C. J. Mitchell, *Org. Biomol. Chem.* **2009**, *7*, 4853; c) X. Zhao, C. S. Yeung, V. M. Dong, *J. Am. Chem. Soc.* **2010**, *132*, 5837; d) B. Xiao, Y. Fu, J. Xu, T.-J. Gong, J.-J. Dai, J. Yi, L. Liu, *J. Am. Chem. Soc.* **2010**, *132*, 468; e) C.-L. Ciana, R. J. Phipps, J. R. Brandt, F.-M. Meyer, M. J. Gaunt, *Angew. Chem. Int. Ed.* **2011**, *50*, 458; *Angew. Chem.* **2011**, *123*, 478; f) L. Ackermann, E. Diers, A. Manvar, *Org. Lett.* **2012**, *14*, 1154; Tritylaniline *o*-arylation by benzynes: g) T. Pirali, F. Zhang, A. H. Miller, J. L. Head, D. McAusland, M. F. Greaney, *Angew. Chem. Int. Ed.* **2012**, *51*, 1006; *Angew. Chem.* **2012**, *124*, 1030.

[5] a) Z. Rappoport, *The Chemistry of Phenols*, Wiley, Chichester, **2003**; b) I. M. Malkowsky, C. E. Rommel, K. Wedeking, R. Frchlich, K. Bergander, M. Nieger, C. Quaiser, U. Griesbach, H. Pütter, S. R. Waldvogel, *Eur. J. Org. Chem.* **2006**, 241; c) A. Kirste, S. Hayashi, G. Schnakenburg, I. M. Malkowsky, F. Stecker, A. Fischer, T. Fuchigami, S. R. Waldvogel, *Chem. Eur. J.* **2011**, *17*, 14164, see also Ref. [2].

[6] a) M. J. S. Dewar, T. Nakaya, *J. Am. Chem. Soc.* **1968**, *90*, 7134; b) B. Feringa, H. Wynberg, *Tetrahedron Lett.* **1977**, *18*, 4447; c) B. Feringa, H. Wynberg, *J. Org. Chem.* **1981**, *46*, 2547; d) K. Yamamoto, H. Fukushima, Y. Okamoto, K. Hatada, M. Nakazaki, *J. Chem. Soc. Chem. Commun.* **1984**, 1111; e) F. Toda, K. Tanaka, S. Iwata, *J. Org. Chem.* **1989**, *54*, 3007; f) M. Hovorka, J. Günterová, J. Závada, *Tetrahedron Lett.* **1990**, *31*, 413; g) M. Smrčina, M. Lorenc, V. HanuŠ, P. Kočovský, *Synlett* **1991**, 231; h) H. Nishino, N. Itoh, M. Nagashima, K. Kurosawa, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 620; i) K. Ding, Y. Wang, L. Zhang, Y. Wu, *Tetrahedron* **1996**, *52*, 1005; j) J. Doussot, A. Guy, C. Ferroud, *Tetrahedron Lett.* **2000**, *41*, 2545.

[7] a) K. Yamamoto, H. Fukushima, M. Nakazaki, *J. Chem. Soc. Chem. Commun.* **1984**, 1490; b) K. Yamamoto, H. Yumioka, Y. Okamoto, H. Chikamatsu, *J. Chem. Soc. Chem. Communm.* **1987**, 168; c) M. Smrcina, J. Poláková, Š. Vyskocil, P. Kocovský, *J. Org. Chem.* **1993**, *58*, 4534; d) M. Smrcina, J. Poláková, Š. Vyskocil, P. Kocovský, *J. Org. Chem.* **1994**, *59*, 2156; e) Š. Vyskočil, M. Smrčina, M. Lorenc, P. Kočovský, Š. Vyskočil, M. Lorenc, V. HanuŠ, M. PolášEk, *Chem. Commun.* **1998**, 585; f) X. Li, J. B. Hewgley, C. A. Mulrooney, J. Yang, M. C. Kozlowski, *J. Org. Chem.* **2003**, *68*, 5500.

[8] a) A. Kirste, G. Schnakenburg, F. Stecker, A. Fischer, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2010**, *49*, 971; *Angew. Chem.* **2010**, *122*, 983; b) A. Kirste, B. Elsler, G. Schnakenburg, S. R. Waldvogel, *J. Am. Chem. Soc.* **2012**, *134*, 3571; c) B. Elsler, D. Schollmeyer, K. M. Dyballa, R. Franke, S. R. Waldvogel, *Chem. Eur. J.* **2015**, *21*, 12321.

  

[9] E. Gaster, Y. Vainer, A. Regev, S. Narute, K. Sudheendran, A. Werbeloff, H. Shalit, D. Pappo, *Angew. Chem. Int. Ed.* **2015**, *54*, 4198; *Angew. Chem.* **2015**, *127*, 4272.

[10] For recent reviews and publications, see: a) P. J. Stang, V. V. Zhdankin, *Chem. Rev.* **1996**, *96*, 1123; b) Y. Kita, T. Takada, H. Tohma, *Pure Appl. Chem.* **1996**, *68*, 627; c) A. Varvoglis, *Hypervalent Iodine in Organic Synthesis*, Academic Press, San Diego, CA, **1997**; d) H. Tohma, Y. Kita, *Top. Curr. Chem.* **2003**, *224*, 209; e) H. Tohma, Y. Kita, *Adv. Synth. Catal.* **2004**, *346*, 111; f) V. V. Zhdankin, P. J. Stang, *Chem. Rev.* **2008**, *108*, 5299; g) E. A. Merritt, B. Olofsson, *Angew. Chem. Int. Ed.* **2009**, *48*, 9052; *Angew. Chem.* **2009**, *121*, 9214; h) T. Dohi, Y. Kita, *Chem. Commun.* **2009**, 2073; i) A. Duschek, S. F. Kirsch, *Angew. Chem. Int. Ed.* **2011**, *50*, 1524; *Angew. Chem.* **2011**, *123*, 1562; j) E. A. Merritt, B. Olofsson, *Synthesis* **2011**, 517; k) D. F. González, F. Benfatti, J. Waser, *ChemCatChem* **2012**, *4*, 955; l) M. S. Yusubov, V. V. Zhdankin, *Curr. Org. Synth.* **2012**, *9*, 247, and references therein.

[11] K. Morimoto, K. Sakamoto, Y. Ohnishi, T. Miyamoto, M. Ito, T. Dohi, Y. Kita, *Chem. Eur. J.* **2013**, *19*, 8726.

[12] a) T. Dohi, M. Ito, K. Morimoto, M. Iwata, Y. Kita, *Angew. Chem. Int. Ed.* **2008**, *47*, 1301; *Angew. Chem.* **2008**, *120*, 1321; b) Y. Kita, K. Morimoto, M. Ito, C. Ogawa, A. Goto, T. Dohi, *J. Am. Chem. Soc.* **2009**, *131*, 1668; c) T. Dohi, M. Ito, N. Yamaoka, K. Morimoto, H. Fujioka, Y. Kita, *Angew. Chem. Int. Ed.* **2010**, *49*, 3334; *Angew. Chem.* **2010**, *122*, 3406; d) T. Dohi, M. Ito, I. Itani, N. Yamaoka, K. Morimoto, H. Fujioka, Y. Kita, *Org. Lett.* **2011**, *13*, 6208; review: e) Y. Kita, T. Dohi, K. Morimoto, *J. Synth. Org. Chem. Jpn.* **2011**, *69*, 1241.

[13] a) A. Jean, J. Cantat, D. Bèrard, D. Brochu, S. Canesi, *Org. Lett.* **2007**, *9*, 2553; recently, Canesi et al. have improved the coupling reaction at the *ortho* position of phenols by the introduction of the substituents to stabilize the intermediate. b) G. Jacquemot, M.-A. Ménard, C. L'Homme, S. Canesi, *Chem. Sci.* **2013**, *4*, 1287.

[14] M. Ito, H. Kubo, I. Itani, K. Morimoto, T. Dohi, Y. Kita, *J. Am. Chem. Soc.* **2013**, *135*, 14078.

[15] Our Hypervalent iodine catalyzed oxidation reactions: a) T. Dohi, A. Maruyama, M. Yoshimura, K. Morimoto, H. Tohma, Y. Kita, *Angew. Chem. Int. Ed.* **2005**, *44*, 6193; *Angew. Chem.* **2005**, *117*, 6349; b) T. Dohi, A. Maruyama, Y. Minamitsuji, N. Takenaga, Y. Kita, *Chem. Commun.* **2007**, 1224; c) T. Dohi, Y. Minamitsuji, A. Maruyama, S. Hirose, Y. Kita, *Org. Lett.* **2008**, *10*, 3559; d) T. Dohi, T. A. Maruyama, N. Takenaga, K. Senami, Y. Minamitsuji, H. Fujioka, S. B. Caemmerer, Y. Kita, *Angew. Chem. Int. Ed.* **2008**, *47*, 3787; *Angew. Chem.* **2008**, *120*, 3847; e) T. Dohi, N. Takenaga, K. Fukushima, T. Uchiyama, D. Kato, S. Motoo, H. Fujioka, Y. Kita, *Chem. Commun.* **2010**, *46*, 7697; f) T. Dohi, N. Takenaga, T. Nakae, Y. Toyoda, M. Yamasaki, M. Shiro, H. Fujioka, A. Maruyama, Y. Kita, *J. Am. Chem. Soc.* **2013**, *135*, 4558.

[16] R. Curci, M. Fiorentino, L. Troisi, J. O. Edwards, R. H. Pater, *J. Org. Chem.* **1980**, *45*, 4758.

[17] a) H. Egami, T. Katsuki, *J. Am. Chem. Soc.* **2009**, *131*, 6082; b) H. Egami, K. Matsumoto, T. Oguma, T. Kunisu, T. Katsuki, *J. Am. Chem. Soc.* **2010**, *132*, 13633; c) M. Holtz-Mulholland, M. de Leseleuc, S. K. Collins, *Chem. Commun.* **2013**, *49*, 1835.

[18] Y. Eun Lee, T. Cao, C. Torruellas, M. C. Kozlowsk, *J. Am. Chem. Soc.* **2014**, *136*, 6782.

[19] B. Elsler, D. Schollmeyer, K. M. Dyballa, R. Franke, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2014**, *53*, 5210; *Angew. Chem.* **2014**, *126*, 5311.

[20] N. Y. More, M. Jeganmohan, *Org. Lett.* **2015**, *17*, 3042. In our hands using this procedure, the coupling reaction of **1a** and **2a** did not give the coupling product **3aa**, but the homocoupling product of **2a** was observed in 58%. The coupling reaction of **1a** with **2b** did not proceed and resulted in a complex mixture under the reaction conditions reported by the group of Jeganmohan.

[21] A. Libman, H. Shalit, Y. Vainer, S. Narute, S. Kozuch, D. Pappo, *J. Am. Chem. Soc.* **2015**, *137*, 11453.

[22] Hypervalent iodine oxidation using a catalytic amount of an iodine reagent and Oxone as a terminal oxidant: a) A. P. Thottumkara, M. S. Bowsher, T. K. Vinod, *Org. Lett.* **2005**, *7*, 2933; b) T. Yakura, M. Omoto, Y. Yamauchi, Y. Tian, A. Ozono, *Tetrahedron* **2010**, *66*, 5833.

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