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Communication

Biaryls

Ligand- and Base-Free Access to Diverse Biaryls by the Reductive Coupling of Diaryliodonium Salts

V. Arun,[a] P. O. Venkataramana Reddy,[a] Meenakshi Pilania,[a] and Dalip Kumar*[a]

Abstract: A ligand- and base-free, Pd-catalyzed protocol to access a wide range of symmetrical and unsymmetrical biaryls from stable diaryliodonium salts was developed. The reaction involved the use of an effective and recyclable Pd/polyethylene glycol-400 catalyst system to harness the aryl moieties of two diaryliodonium salts; the ensuing biaryls may be utilized to synthesize an array of useful compounds, including 5-aryluracils, carbazoles, chromenones, fluorenones, phenathridines, and boscalid analogues.

Introduction

The biaryl framework is an important scaffold that is present in various natural products, valuable drug candidates, chiral ligands, agrochemical agents, and advanced materials (Figure 1).[1] The most common approaches to prepare biaryls include traditional cross-coupling reactions (Scheme 1) involving preactivated precursors, namely, aryl pseudohalides and aryl metal reagents (e.g., Stille, Kumada, Suzuki, and Negishi reactions).[2] However, some of these classical couplings often require over-stoichiometric amounts of the precursors that need to be prepared in additional synthetic steps, the use of relatively unfavorable solvents, and generate homocoupled byproducts and waste salts. In the recent past, these methods have been supplanted by emerging and attractive C–H functionalization strategies, namely, directing group (DG)-assisted arylation,[3] cross-dehydrogenative coupling,[4] and transition-metal (TM)-free cross-coupling reactions (Scheme 1).[5] Cross-dehydrogenative couplings require activated arenes, excess amounts of the arenes (as solvent), metal catalysts, oxidants, high temperatures (>100 °C), and prolonged reaction times (20–48 h). Generally, poor regioselectivities of the C–H arylations and the use of excess amounts of the arenes are the major obstacles associated with dehydrogenative coupling reactions. TM-free cross-couplings employ aryl halides (1.0 equiv.), excess amounts of the arenes (10.0 equiv.), a radical initiator (2–3 equiv.), elevated temperatures (>140 °C), and long reaction times (24–72 h). However, simple and atom-economical protocols to prepare valuable biaryls from easily available starting materials are highly desirable.

In recent years, tremendous efforts have been directed towards the chemistry of diaryliodonium salts because they have high intrinsic electrophilicity relative to the corresponding aryl halides.[6] They are stable solids, inert to air and moisture, and are also mild and nontoxic arylating agents that are easily prepared from commercially available starting materials.[7] Owing to their increasing significance, diaryliodonium salts have been extensively studied for various TM-catalyzed and metal-free ary-

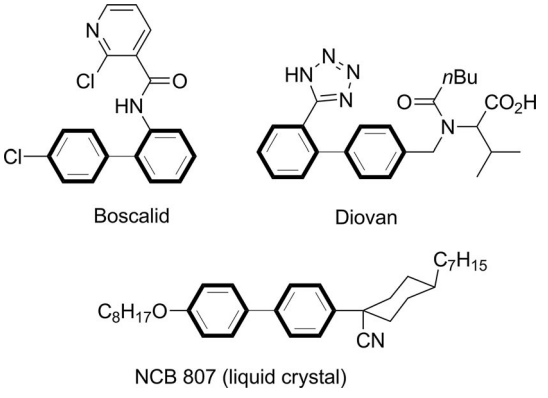
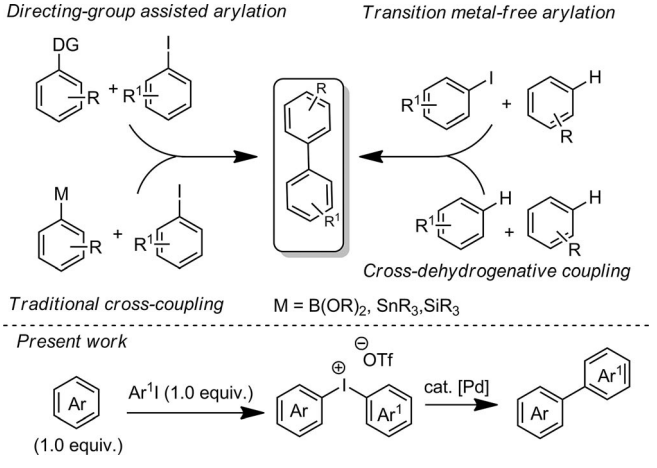


Figure 1. Some important molecules containing the biaryl motif.



Scheme 1. Existing and present strategies to prepare biaryls.

[a] Department of Chemistry, Birla Institute of Technology and Science, Pilani 333031, Rajasthan, India
E-mail: dalipk@pilani.bits-pilani.ac.in
http://universe.bits-pilani.ac.in/pilani/dalipk/profile

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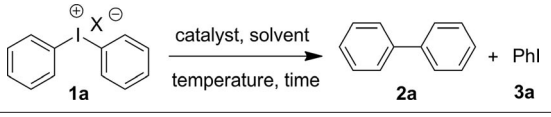
lations and also in the construction of heterocycles.[8] Research originating from the groups of Sanford, Macmilian, and Gaunt demonstrates the synthetic utilities of diaryliodonium salts through copper- and palladium-mediated carbon–carbon bond formation.[9] To the best of our knowledge, there are a few reports involving the reductive coupling of diaryliodonium salts to access biaryls involving the use of stoichiometric amounts of methylmagnesium iodide and anhydrous nickel chloride under an inert atmosphere[10] and activated Zn in the presence of a palladium catalyst[10b] in combination with diethylzinc and $Pd(OAc)_2$[10c] and indium with $Pd(OAc)_2$ under a N_2 environment.[10d] Besides the limited substrate scope and the formation of a mixture of biaryls in some cases, these reaction conditions involve the use of stoichiometric amounts of ligands, metals, and sensitive reagents. Sodium tetraarylborates, organoboranes, organostannanes, and arenes have also been coupled with diaryliodonium salts by using $PdCl_2$, $Pd(PPh_3)_4$, CuI, and Pd complexes to prepare diverse biaryls.[11]

As a result of our ongoing research directed towards the synthetic utilities of hypervalent iodine reagents,[12] we envisioned an operationally simple $Pd(OAc)_2$/polyethylene glycol-400 (PEG-400) catalysis system to prepare biaryls by harnessing the aryl moieties of two easily accessible and stable diaryliodonium salts. This protocol proceeds under neutral conditions without the use of any activating metal reagent, ligand, or base to generate an array of biaryls in good to excellent yields. Despite an additional synthetic step required to obtain the diaryliodonium salts, the present protocol provides a convenient route to prepare biaryls in view of the associated drawbacks of the direct coupling of aryl halides and arenes in C–H functionalization strategies.[5]

Results and Discussion

At the outset of this study, we chose diphenyliodonium triflate (**1a**) as a model substrate to identify the optimum reaction conditions. Initially, the coupling reaction was performed in the presence of CuI (0.5 equiv.) at 140 °C for 24 h, but desired biphenyl (**2a**) was not obtained (Table 1, entry 1). Trials with various copper catalysts including CuI, copper(II) trifluoromethanesulfonate [$Cu(OTf)_2$], CuCl, CuBr, $Cu(OAc)_2$, and $CuBr_2$ in 1,2-dichloroethane (DCE) or dioxane at 80 °C for 12 h were also unsuccessful (Table 1, entries 2–7). We further explored the reaction of **1a** in the presence of a Pd catalyst by using microwave irradiation. Microwave irradiation is a greener method to activate reactions than conventional heating, because it drives the chemical transformations very rapidly, and the desired products are obtained in high yields.[13] Reaction of **1a** in the presence of $Pd(OAc)_2$ (10 mol-%) in DCE and DMF under microwave irradiation at 50 °C for 30 min also failed to deliver **2a**. Surprisingly, under similar reaction conditions, upon changing the solvent from DMF to dioxane, anticipated product **2a** was obtained in 60 % yield (Table 1, entry 11). Notably, if the reaction of **1a** was conducted in PEG-400, **2a** was formed in 90 % yield within 10 min. PEG-400 as a reaction medium has received great attention owing to its appealing and ecofriendly features.[14] No change in the yield was observed upon reducing the loading of $Pd(OAc)_2$ from 10 to 5 mol-%. Under conventional heating (50 °C) conditions, the Pd-catalyzed reductive coupling of **1a** failed to produce **2a** (Table 1, entry 14); however, upon raising the reaction temperature to 100 °C, **2a** was obtained in 75 % yield (Table 1, entry 15). During optimization of the reaction conditions, we also screened diphenyliodonium salts bearing

Table 1. Optimization of the reaction conditions to prepare biphenyl (**2a**).



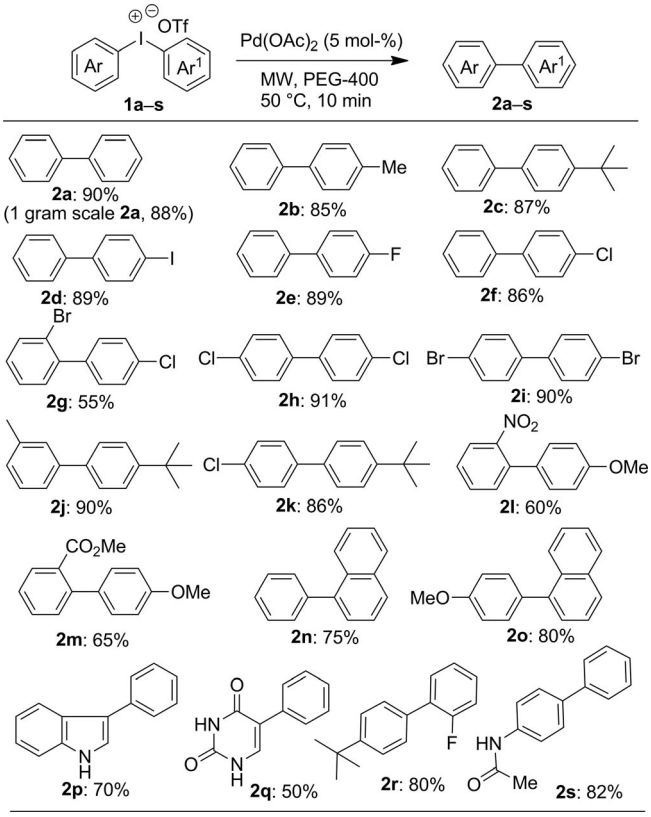
1a **2a** **3a**

Entry	Catalyst (mol-%)	X	Solvent	Microwave irradiation [W]	*T* [°C]	Time [min]	Yield [%][a] **2a**	Yield [%][a] **3a**
1	CuI (50)	OTf	DMF	–	140	1440	–	–
2	CuI (50)	OTf	dioxane	–	80	720	–	–
3	$Cu(OTf)_2$ (50)	OTf	DCE	–	80	720	–	–
4	CuCl (50)	OTf	dioxane	–	80	720	–	70
5	CuBr(50)	OTf	dioxane	–	80	720	–	10
6	$CuBr_2$ (50)	OTf	dioxane	–	80	720	–	70
7	$Cu(OAc)_2$ (50)	OTf	dioxane	–	80	30	–	60
8	$Pd(OAc)_2$(10)	OTf	DCE	50	50	30	–	–
9	$Pd(OAc)_2$(10)	OTf	DMF	50	50	30	–	–
10	$Pd(OAc)_2$ (10)	OTf	water	50	50	30	–	–
11	$Pd(OAc)_2$ (10)	OTf	dioxane	50	50	30	60	10
12	$Pd(OAc)_2$ (10)	OTf	PEG-400	50	50	10	90	–
13	$Pd(OAc)_2$ (5)	OTf	PEG-400	50	50	10	90	–
14	$Pd(OAc)_2$ (5)	OTf	PEG-400	–	50	10	n.r.[b]	
15	$Pd(OAc)_2$ (5)	OTf	PEG-400	–	100	120	75	
16	$Pd(OAc)_2$(5)	OTs	PEG-400	50	50	10	–	90
17	$Pd(OAc)_2$ (5)	Br	PEG-400	50	50	10	–	90
18	$Pd(OAc)_2$(5)	BF_4	PEG-400	50	50	10	40	50

[a] Yield of isolated product. [b] n.r.: no reaction.

different counterions (e.g., $^{-}$OTf, $^{-}BF_4$, Br^{-}, and $^{-}$OTs) and found that diphenyliodonium triflate (**1a**) was the most suitable salt to obtain biaryls **2** in high yields. Diphenyliodonium tetrafluoroborate was better than the salts bearing bromide and tosylate ($^{-}$OTs) counterions (Table 1, entries 16–18). The scope of the protocol was investigated by treating various symmetrical and unsymmetrical diaryliodonium salts under the catalytic system. Diaryliodonium salts **1a**–**z** were prepared by known protocols involving easily available arenes and iodoarenes.[7a] Iodonium salts containing electron-donating groups such as methyl (see compound **1b**) and *tert*-butyl (see compounds **1c**, **1j**, **1k**, and **1r**) were successfully coupled to afford corresponding biaryls **2b**, **2c**, **2j**, **2k**, and **2r** in good to excellent yields (85–90 %, Table 2). Iodonium salts **1d**–**i** possessing halogen atoms (i.e., F, Cl, Br, and I) were well tolerated under the optimal reaction conditions and delivered corresponding biaryls **2d**–**i** in good yields (55–90 %). Halogen-bearing biaryls **2d**, **2g**, and **2i** can serve as useful precursors for various cross-coupling reactions to give useful molecules in addition to their interesting organic luminogen properties.[15] Gratifyingly, fused-ring naphthyl derivatives **2n** and **2o** were prepared in yields of 75 and 80 %, respectively. Diaryliodonium salts possessing nitro (see compound **1l**), ester (see compound **1m**), and amide (see compound **1s**) functional groups were successfully prepared and converted into corresponding biaryls **2l**, **2m**, and **2s** in good yields (60–82 %). To our delight, indolyl(phenyl)iodonium salt **1p** gave anticipated 3-phenylindole (**2p**) in 70 % yield. The developed strategy was successfully extended to prepare an arylated pyrimidine base by using the 5-phenyluracil iodonium salt (**1q**), which afforded 5-phenyluracil (**2q**) in 50 % yield. Arylated uracils are well known for their interesting medicinal properties.[16]

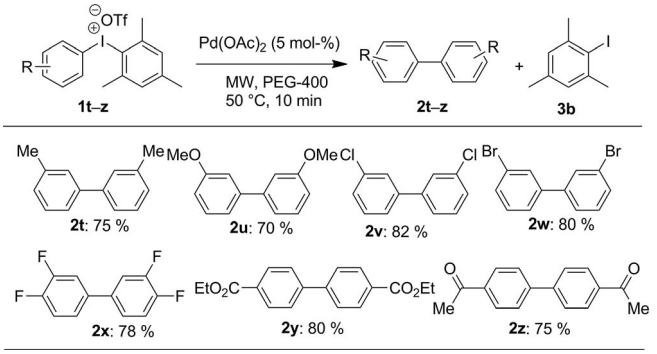
Table 2. Substrate scope of diaryliodonium salts **1a**–**s**.[a,b]



[a] Reaction conditions: **1a**–**s** (1 mmol), $Pd(OAc)_2$ (5 mol-%), PEG-400 (2 mL), microwave irradiation (50 W), 50 °C, 10 min. [b] Yields of isolated products are shown.

Phenyl(mesityl)iodonium triflate with a bulky mesityl moiety led to biphenyl **2a** rather than expected phenyl–mesityl coupled product. This interesting observation motivated us to prepare various symmetrical biaryls **2t**–**z** (Table 3). In these reactions, iodomesitylene (**3b**) behaved as a leaving group and another aryl partner underwent self-coupling to deliver symmetrical biaryls **2t**–**z**. Released **3b** was easily recovered from the reaction mixture by hexane wash, and resulting **3b** was successfully reused to prepare diaryliodonium salts **1t**–**z**. Notably, various aryl(mesityl) iodonium salts bearing methyl (see compound **1t**), methoxy (see compound **1u**), halo (see compounds **1v**–**x**), ester (see compound **1y**), and acetyl (see compound **1z**) substituents were well tolerated under the reaction conditions and produced symmetrical biaryls **2t**–**z** in good to excellent yields (70–82 %). Though the protocol is fairly general, it may not be suitable to prepare highly oxygenated or amino-substituted biphenyls owing to inaccessibility of the corresponding diaryliodonium salts.

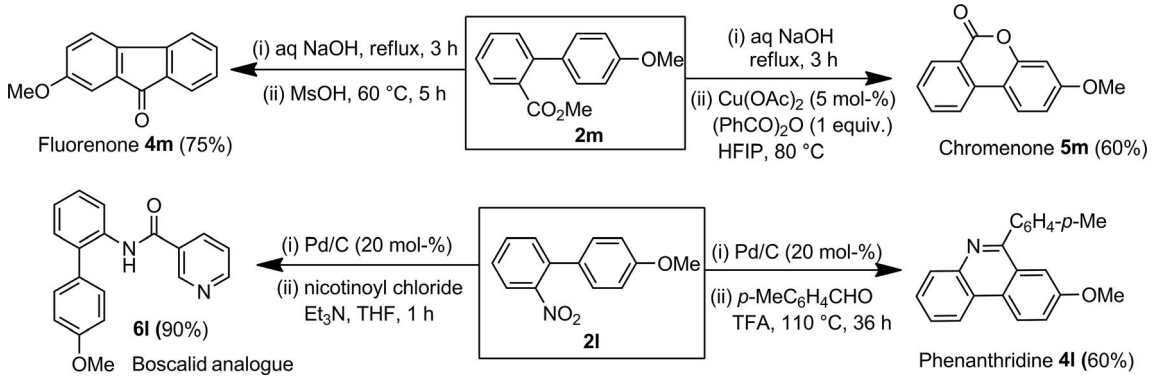
Table 3. Substrate scope of aryl(mesityl)iodonium triflates.[a,b]



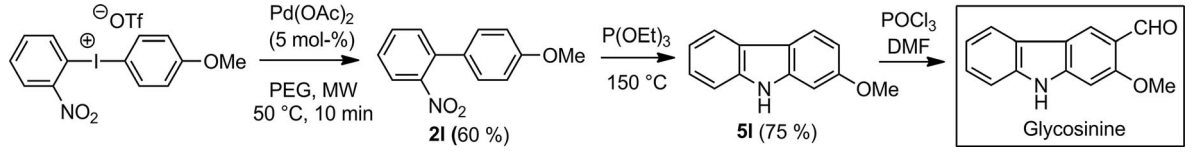
[a] Reaction conditions: **1t**–**z** (1 mmol), $Pd(OAc)_2$ (5 mol-%), PEG-400 (2 mL), microwave irradiation (50 W), 50 °C, 10 min. [b] Yields of isolated products are shown.

The synthetic usefulness and prowess of the methodology was clear by the successful preparation of *o*-functionalized biaryls **2l**–**m** from corresponding iodonium salts **1l**–**m** within 10 min (Scheme 2). Biaryl **2m** was utilized to obtain fluorenone **4m** (75 %) and chromenone **5m** (60 %). Similarly, a useful precursor, *o*-nitro biaryl **2l** was smoothly converted into phenanthiridine **4l** (75 %) and boscalid analogue **6l** (90 %) in good to excellent yields.[17] Interestingly, biaryl **2l** also provided a simple and efficient route to the carbazole alkaloid glycosinine (Scheme 3).[18] To demonstrate scalability (1 gram) of the developed protocol, we prepared **2a** in 88 % yield from **1a** under the optimized reaction conditions (Table 2).

The recyclability of the Pd/PEG catalyst system was demonstrated by the reaction of **1a** under the optimized conditions. Gratifyingly, the Pd/PEG system was successfully recovered and reused six times without any loss of catalytic activity (see the Supporting Information).[19]

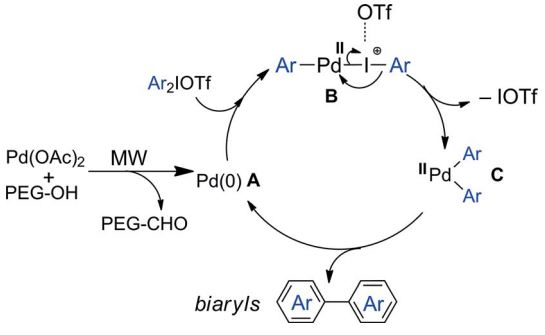


Scheme 2. Synthesis of druglike molecules; MsOH = methanesulfonic acid, HFIP = hexafluoroisopropanol, TFA = trifluoroacetic acid.



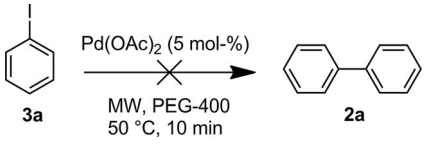
Scheme 3. Rapid access to the carbazole alkaloid glycosinine.

Additional experiments such as TEM analysis of the reaction mixture and analysis of Pd^{II} in the PEG-400 solution exposed to microwave irradiation by ^1H NMR spectroscopy indicated the formation of in situ Pd nanoparticles (see the Supporting Information).[19] On the basis of our results and literature reports,[19] a plausible mechanism for the formation of biaryls is depicted in Scheme 4. It is believed that initial microwave irradiation of a solution of palladium acetate in PEG-400 (reducing species) generates Pd^0 species **A**, which upon oxidative addition to the diaryliodonium salt is believed to give arylpalladium species **B**.[8d] This species is likely to rearrange into Pd^{II} species **C**. Subsequently, reductive elimination of **C** generates the biaryl compound and Pd^0.



Scheme 4. Plausible mechanism.

Under the optimized reaction conditions, iodobenzene (**3a**) did not lead to biphenyl (Scheme 5); furthermore, biphenyl was not produced upon reductive coupling of **3a** (see the Supporting Information). These observations suggest that the aryl iodide may not be involved in any stage in the reductive coupling of the diaryliodonium salts to biaryls **2**. However, formation of symmetrical biaryls **2t**–**z** by reductive coupling of aryl(mesityl)-iodonium triflates **1t**–**z** needs further mechanistic investigation.



Scheme 5. Reaction of **3a** under optimized conditions.

Conclusions

In summary, we successfully developed a ligand- and base-free Pd-catalyzed synthesis of useful biaryls from easily accessible and stable diaryliodonium salts. The highlights of the present protocol include operational simplicity, mild reaction conditions, broad substrate scope for symmetrical and unsymmetrical biaryls, scalability, and the use of a recyclable Pd catalyst. The potential utility of the developed method was demonstrated by preparing valuable heterocycles such as 5-aryluracils, carbazoles, chromenones, fluorenones, phenanthiridines, and boscalid analogues. Hopefully, this methodology will find application in diverse fields of synthetic organic chemistry. Further mechanistic investigation and exploration of this transformation to other heterocyclic systems are currently underway in our laboratory, and the results will be disclosed in due course.

Experimental Section

Typical Procedure for the Synthesis of Biaryls: A 10 mL microwave vial was charged with a magnetic stir bar, diphenyliodonium triflate (**1a**; 0.1 g, 0.232 mmol), $Pd(OAc)_2$ (2.6 mg, 5 mol-%), and PEG-400 (2 mL). The vial was kept under microwave irradiation for 10 min at 50 °C (power: 50 W, pressure: 345 kPa). Completion of the reaction was confirmed by TLC (hexane), and the resulting contents were taken into water and extracted with ethyl acetate (3 × 3 mL). The combined organic layer was dried with anhydrous sodium sulfate. After removal of the organic solvent, the residue was

purified by column chromatography (hexane) to afford product **2a** (32 mg, 90 %).

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Keywords: Synthetic methods · Microwave chemistry · C–C coupling · Biaryls · Hypervalent compounds · Iodine · Palladium

[1] a) J. Wencel-Delord, A. Panossian, F. R. Leroux, F. Colobert, *Chem. Soc. Rev.* **2015**, *44*, 3418–3430; b) I. Hussain, T. Singh, *Adv. Synth. Catal.* **2014**, *356*, 1661–1696, and references cited therein.

[2] a) C. C. C. Johansson Seechurn, M. O. Kitching, T. J. Colacot, V. Snieckus, *Angew. Chem. Int. Ed.* **2012**, *51*, 5062–5085; *Angew. Chem.* **2012**, *124*, 5150–5174; b) C. Cordovilla, C. Bartolomé, J. M. Martínez-Ilarduya, P. Espinet, *ACS Catal.* **2015**, *5*, 3040–3053; c) B.-T. Guan, X.-Y. Lu, Y. Zheng, D.-G. Yu, T. Wu, K.-L. Li, B.-J. Li, Z.-J. Shi, *Org. Lett.* **2010**, *12*, 396–399; d) Q. Liang, P. Xing, Z. Huang, J. Dong, K. B. Sharpless, X. Li, B. Jiang, *Org. Lett.* **2015**, *17*, 1942–1945, and references cited therein.

[3] a) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem. Int. Ed.* **2009**, *48*, 9792–9826; *Angew. Chem.* **2009**, *121*, 9976–10011; b) J. Yamaguchi, A. D. Yamaguchi, K. Itami, *Angew. Chem. Int. Ed.* **2012**, *51*, 8960–9009; *Angew. Chem.* **2012**, *124*, 9092–9142, and references cited therein.

[4] a) C. Liu, J. Yuan, M. Gao, S. Tang, W. Li, R. Shi, A. Lei, *Chem. Rev.* **2015**, *115*, 12138–12204; b) L. Grigorjeva, O. Daugulis, *Org. Lett.* **2015**, *17*, 1204–1207; c) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord, F. Glorius, *Angew. Chem. Int. Ed.* **2012**, *51*, 10236–10254; *Angew. Chem.* **2012**, *124*, 10382–10401, and references cited therein.

[5] a) C.-L. Sun, Z.-J. Shi, *Chem. Rev.* **2014**, *114*, 9219–9280; b) A. Kumar, B. A. Shah, *Org. Lett.* **2015**, *17*, 5232–5235; c) Z. Xu, L. Gao, L. Wang, M. Gong, W. Wang, R. Yuan, *ACS Catal.* **2015**, *5*, 45–50; d) S. Senaweera, J. D. Weaver, *J. Am. Chem. Soc.* **2016**, *138*, 2520–2523, and references cited therein.

[6] a) V. V Zhdankin, *Hypervalent Iodine Chemistry Preparation, Structure and Synthetic Applications of Polyvalent Iodine Compounds*, Wiley, Chichester, UK, **2014**; b) M. S. Yusubov, A. V. Maskaev, V. V. Zhdankin, *ARKIVOC (Gainesville, FL, U.S.)* **2011**, *1*, 370–409; c) E. A. Merritt, B. Olofsson, *Angew. Chem. Int. Ed.* **2009**, *48*, 9052–9070; *Angew. Chem.* **2009**, *121*, 9214–9234.

[7] a) M. Bielawski, M. Zhu, B. Olofsson, *Adv. Synth. Catal.* **2007**, *349*, 2610–2618; b) M. D. Hossain, T. Kitamura, *Tetrahedron* **2006**, *62*, 6955–6960; c) J.-H. Chun, S. Lu, V. W. Pike, *Eur. J. Org. Chem.* **2011**, 4439–4447.

[8] For selected reactions on diaryliodonium salts, see: a) T. Kasahara, Y. J. Jang, L. Racicot, D. Panagopoulos, S. H. Liang, M. A. Ciufolini, *Angew. Chem. Int. Ed.* **2014**, *53*, 9637–9639; *Angew. Chem.* **2014**, *126*, 9791–9793; b) N. Miralles, R. M. Romero, E. Fernandez, K. Muniz, *Chem. Commun.* **2015**, *51*, 14068–14071; c) Á. Sinai, D. Vangel, T. Gáti, P. Bombicz, Z. Novák, *Org. Lett.* **2015**, *17*, 4136–4139; d) X. Wu, Y. Yang, J. Han, L. Wang, *Org. Lett.* **2015**, *17*, 5654–5657; e) C. Dey, E. Lindstedt, B. Olofsson, *Org. Lett.* **2015**, *17*, 4554–4557; f) S. K. Sundalam, D. R. Stuart, *J. Org. Chem.* **2015**, *80*, 6456–6466; g) N. Margraf, G. Manolikakes, *J. Org. Chem.* **2015**, *80*, 2582–2600; h) D. Wang, B. Ge, L. Li, J. Shan, Y. Ding, *J. Org. Chem.* **2014**, *79*, 8607–8613; i) M. Iyanaga, Y. Aihara, N. Chatani, *J. Org. Chem.* **2014**, *79*, 11933–11939; j) L. Qin, B. Hu, K. D. Neumann, E. J. Linstad, K. McCauley, J. Veness, J. J. Kempinger, S. G. DiMagno, *Eur. J. Org. Chem.* **2015**, 5919–5924; k) R. Edwards, A. D. Westwell, S. Daniels, T. Wirth, *Eur. J. Org. Chem.* **2015**, 625–630.

[9] a) S. Zhu, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2012**, *134*, 10815–10818; b) N. R. Deprez, M. S. Sanford, *Inorg. Chem.* **2007**, *46*, 1924–1935; c) E. Cahard, H. P. J. Male, M. Tissot, M. J. Gaunt, *J. Am. Chem. Soc.* **2015**, *137*, 7986–7989, and references cited therein.

[10] a) Y. Tamura, M. W. Chun, K. Inoue, J. Minamikawa, *Synthesis* **1978**, 822–822; b) M. Uchiyama, T. Suzuki, Y. Yamazaki, *Chem. Lett.* **1983**, *12*, 1165–1166; c) S.-K. Kang, R.-K. Hong, T.-H. Kim, S.-J. Pyun, *Synth. Commun.* **1997**, *27*, 2351–2356; d) Zhou, Z.-C. Chen, *J. Chem. Res. Synop.* **2001**, 153–155.

[11] a) S.-K. Kang, H.-W. Lee, S.-B. Jang, P.-S. Ho, *J. Org. Chem.* **1996**, *61*, 4720–4724; b) S.-K. Kang, T. Yamaguchi, T.-H. Kim, P.-S. Ho, *J. Org. Chem.* **1996**, *61*, 9082–9083; c) T. E. Storr, M. F. Greaney, *Org. Lett.* **2013**, *15*, 1410–1413; d) J. Yan, W. Hu, G. Rao, *Synthesis* **2006**, 943–945.

[12] a) D. Kumar, V. B. Reddy, *Synthesis* **2010**, 1687–1691; b) D. Kumar, V. Arun, M. Pilania, K. P. C. Shekar, *Synlett* **2013**, *24*, 831–836; c) D. Kumar, M. Pilania, V. Arun, S. Pooniya, *Org. Biomol. Chem.* **2014**, *12*, 6340–6344; d) M. K. Mehra, M. P. Tantak, I. Kumar, D. Kumar, *Synlett* **2016**, *27*, 604–610.

[13] a) R. S. Varma, *Green Chem.* **2014**, *16*, 2027–2041; b) D. Dallinger, C. O. Kappe, *Chem. Rev.* **2007**, *107*, 2563–2591, and references cited therein.

[14] J. Chen, S. K. Spear, J. G. Huddleston, R. D. Rogers, *Green Chem.* **2005**, *7*, 64–82.

[15] W. Z. Yuan, X. Y. Shen, H. Zhao, J. W. Y. Lam, L. Tang, P. Lu, C. Wang, Y. Liu, Z. Wang, Q. Zheng, J. Z. Sun, Y. Ma, B. Z. Tang, *J. Phys. Chem. C* **2010**, *114*, 6090–6099.

[16] V. Gayakhe, Y. S. Sanghvi, I. J. S. Fairlamb, A. R. Kapdi, *Chem. Commun.* **2015**, *51*, 11944–11960.

[17] a) S. Aki, Y. Haraguchi, H. Sakikawa, M. Ishigami, T. Fujioka, T. Furuta, J.-i. Minamikawa, *Org. Process Res. Dev.* **2001**, *5*, 535–538; b) J. Gallardo-Donaire, R. Martin, *J. Am. Chem. Soc.* **2013**, *135*, 9350–9353; c) S. W. Youn, J. H. Bihn, *Tetrahedron Lett.* **2009**, *50*, 4598–4601; d) T. N. Glasnov, C. O. Kappe, *Adv. Synth. Catal.* **2010**, *352*, 3089–3097.

[18] a) Y. Qiu, D. Ma, C. Fu, S. Ma, *Org. Biomol. Chem.* **2013**, *11*, 1666–1671; b) J. T. Kuethe, K. G. Childers, *Adv. Synth. Catal.* **2008**, *350*, 1577–1586.

[19] a) C. Luo, Y. Zhang, Y. Wang, *J. Mol. Catal. A* **2005**, *229*, 7–12; b) Z. Du, W. Zhou, L. Bai, F. Wang, J.-X. Wang, *Synlett* **2011**, 369–372; c) W. Han, C. Liu, Z.-L. Jin, *Org. Lett.* **2007**, *9*, 4005–4007; d) Q. Zhou, S. Wei, W. Han, *J. Org. Chem.* **2014**, *79*, 1454–1460.

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