JOC The Journal of Organic Chemistry

Article

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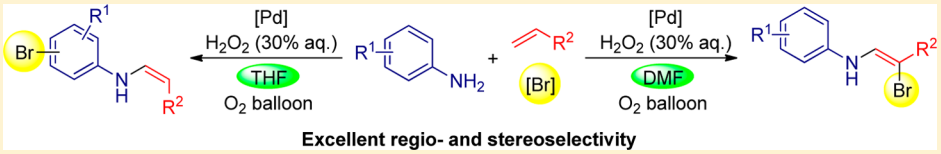
Palladium-Catalyzed Oxidative C–N Bond Coupling Involving a Solvent-Controlled Regioselective Bromination Process

Xiaochen Ji,[†] Huawen Huang,[†] Wenfang Xiong,[†] Kunbo Huang,[†] Wanqing Wu,[†] and Huanfeng Jiang*[,†,‡]

[†]School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

[‡]State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

Supporting Information



ABSTRACT: Stereoselective palladium-catalyzed oxidative C–N bond coupling reactions between aromatic amines and alkenes involving a solvent-controlled regioselective bromination process under 1 atm of oxygen atmosphere are disclosed, providing easy access to two different brominated enamines. The addition of hydrogen peroxide (30% aq) as a co-oxidant in the system is crucial for the dehydrogenative aminohalogenation under molecular oxygen (1 atm), and in such a case, the C–N bond coupling/electrophilic bromination reaction cascade is proposed. Furthermore, the different reaction media leads to a switched regioselectivity of the process.

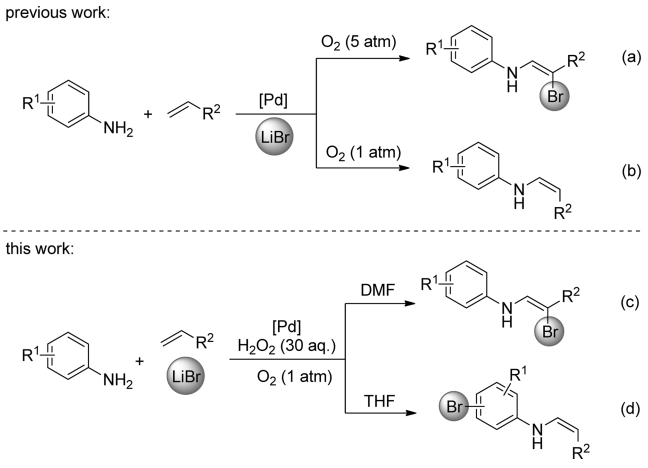
INTRODUCTION

Palladium-catalyzed transformations are powerful tools to efficiently construct complex molecules from easily available starting materials under mild conditions, with high chemo-, regio-, and stereoselectivity and great functional group tolerance generally observed.[1−4] Oxidants are usually involved in these processes, such as Cu^{II}, $PhI(OAc)_2$, BQ, DDQ, etc. In view of sustainable and green chemistry, molecular oxygen and hydrogen peroxide are undoubtedly ideal oxidants, with only nontoxic water released after the reaction. Moreover, the inexpensive and highly atom-efficient properties make these environmentally friendly oxidants particularly attractive, with broad academic and industrial application prospects.[5−8] Therefore, palladium-catalyzed reactions with molecular oxygen or hydrogen peroxide as the oxidant have received considerable attention over the past few decades and continue to be one of the research hotspots in organic synthesis.[9−12]

The enamine skeleton is ubiquitous in a wide range of pharmaceuticals and natural products, and its derivatives are also valuable and flexible precursors in synthetic chemistry, particularly in building a variety of biologically and synthetically important nitrogen-containing heterocycles, such as pyrroles, pyridines, and indoles.[13−26] Enamines could also be used for the asymmetric synthesis of various secondary or tertiary chiral amines.[27−32] Consequently, varieties of methods have been developed to construct diversified enamine compounds over the past years.[33−46]

Recently, our group has reported the first example of palladium-catalyzed dehydrogenative aminohalogenation of alkenes with molecular oxygen as the sole oxidant, with simple aromatic amines as the nitrogen source (Scheme 1a).[47] This approach leads to (*Z*)-brominated enamine products with excellent regio- and stereoselectivity which are difficult to prepare by traditional methods. However, high pressure (5 atm) of O_2 as the oxidant is indispensible to achieve high efficiency of this transformation. While this process hardly occurred under 1 atm of O_2, the direct oxidative C–N bond coupling between aromatic amines and alkenes proceeded smoothly to give (*Z*)-enamines in good to excellent yields with exclusive stereoselectivity (Scheme 1b).[48] Further studies revealed that the dehydrogenative aminohalogenation of alkenes could be achieved efficiently under 1 atm of O_2 by

Scheme 1. Palladium-Catalyzed Oxidative Transformations Involving Aromatic Amines and Alkenes



Received: May 26, 2014
Published: July 10, 2014

   dx.doi.org/10.1021/jo501171c | J. Org. Chem. 2014, 79, 7005−7011

simply adding a co-oxidant into the catalytic system. As part of our continuing interest in palladium-catalyzed aerobic reactions,[49−53] herein we disclose a solvent-controlled highly selective palladium-catalyzed oxidative transformation involving aromatic amines and alkenes under molecular oxygen (1 atm) with hydrogen peroxide (30% aq) as the co-oxidant. With DMF as the solvent, the dehydrogenative aminohalogenation of alkenes selectively occurs (Scheme 1c), while in the THF system, the reaction proceeds via selective bromination of aromatic amines and subsequent oxidative C−N bond coupling with alkenes (Scheme 1d).

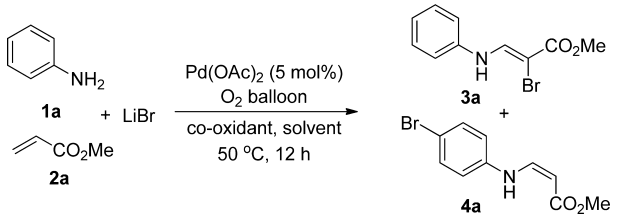
RESULTS AND DISCUSSION

In our previous report, the requirement of high pressure (5 atm) of molecular oxygen limited the practical applications of the dehydrogenative aminohalogenation of alkenes to some extent.[47] We hypothesized that it would be preferable to develop an efficient catalytic system to facilitate this transformation under 1 atm of O_2. Thus, we started to optimize the reaction conditions by investigating the Pd-catalyzed oxidative transformations between aniline (**1a**) and methyl acrylate (**2a**) in the presence of LiBr (4 equiv) under molecular oxygen (1 atm), as summarized in Table 1. Notably, the addition of a co-oxidant appeared to have a strong impact on this transformation, and several co-oxidants were examined. While the employment of $Cu(OAc)_2$, $PhI(OAc)_2$, DDQ, Oxone, or $K_2S_2O_8$ as the co-oxidant did not afford the desired product (entries 1−6), BQ could enhance the efficiency, giving (*Z*)-brominated enamine product (**3a**) in 27% yield (entry 7). To our delight, the addition of 30% aqueous H_2O_2 (2 equiv) to the catalytic system could greatly promote this transformation with DMF as the solvent, providing **3a** in 93% yield with good stereoselectivity (dr >10:1) (entry 8). As for the solvents, DMF was proved to be superior over DMSO, CH_3CN, or toluene (entry 8 versus entries 10−12).

Intriguingly, a switched selectivity was observed when using THF as the solvent, and (*Z*)-enamine product (**4a**), brominated at the *para* position of the aniline motif, was given in 71% yield with excellent stereoselectivity, which was further improved to 87% with an increased dosage (3 equiv) of 30% aqueous H_2O_2 (entries 13−14). It was noteworthy that molecular oxygen was indispensible to the success of these reactions, since only a very low yield of product (**3a** or **4a**) was obtained with 30% aqueous H_2O_2 as the sole oxidant under N_2 atmosphere (entries 9 and 15), thus highlighting the significance of the co-oxidants in the catalytic system.

Next, we evaluated the substrate scope of the Pd-catalyzed dehydrogenative aminohalogenation of alkenes under 1 atm of O_2 with 30% aqueous H_2O_2 as the co-oxidant (Scheme 2). In general, this catalytic system was more efficient than that with 5 atm of O_2 as the sole oxidant in our previous report, and mostly a complete consumption of the substrates was observed within 12 h, giving (*Z*)-brominated enamine products (**3**) with similar yields and stereoselectivity. A series of aromatic amines, with various substituents at the *ortho*, *meta*, and *para* positions of the phenyl ring, reacted smoothly with methyl acrylate (**2a**) to give the corresponding products (**3a−j**) in good to excellent yields. Prolonged reaction time (20 h) was required for *ortho*-substituted anilines, probably due to the steric interference in the process. In addition, α-naphthylamine worked well to

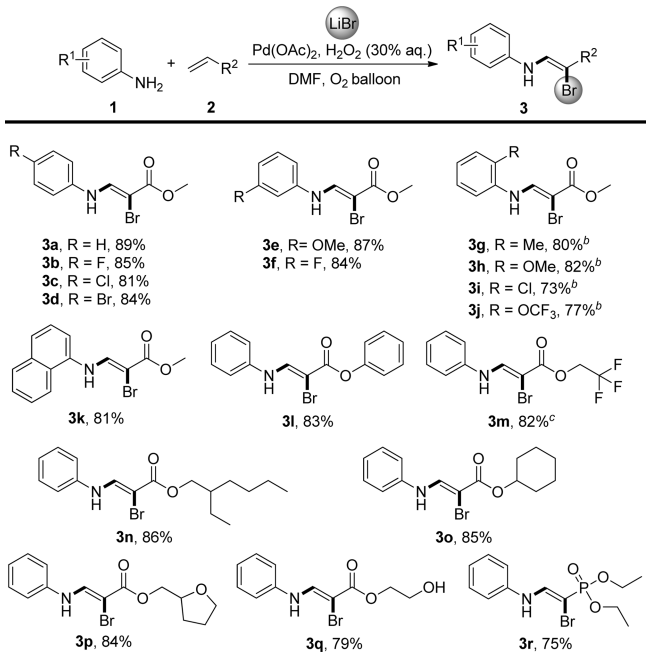
Table 1. Optimization of the Reaction Conditions under 1 atm of O_2[a]



entry	co-oxidant	solvent	yield[b] (%)	3a:4a
1		DMF	7	>10:1
2	$Cu(OAc)_2$	DMF	trace	
3	$PhI(OAc)_2$	DMF	trace	
4	DDQ	DMF	trace	
5	Oxone	DMF	trace	
6	$K_2S_2O_8$	DMF	trace	
7	BQ	DMF	27	>10:1
8	H_2O_2 (30% aq)	DMF	93 (89)	>10:1
9[c]	H_2O_2 (30% aq)	DMF	8	
10	H_2O_2 (30% aq)	DMSO	23	>10:1
11	H_2O_2 (30% aq)	CH_3CN	19	>10:1
12	H_2O_2 (30% aq)	toluene	trace	
13	H_2O_2 (30% aq)	THF	71	<1:10
14[d]	H_2O_2 (30% aq)	THF	87 (81)	<1:10
15[c]	H_2O_2 (30% aq)	THF	9	

[a]Reaction conditions: aniline **1a** (0.5 mmol), methyl acrylate **2a** (0.8 mmol), $Pd(OAc)_2$ (5 mol %), LiBr (4 equiv), co-oxidant (2 equiv), solvent (2 mL), with an O_2 balloon, at 50 °C for 12 h. [b]GC yield. Isolated yield is given in parentheses. [c]Under N_2 atmosphere. [d]The reaction was performed using 3 equiv of 30% aqueous H_2O_2 for 10 h.

Scheme 2. Palladium-Catalyzed Dehydrogenative Aminohalogenation of Alkenes under O_2 (1 atm)[a]



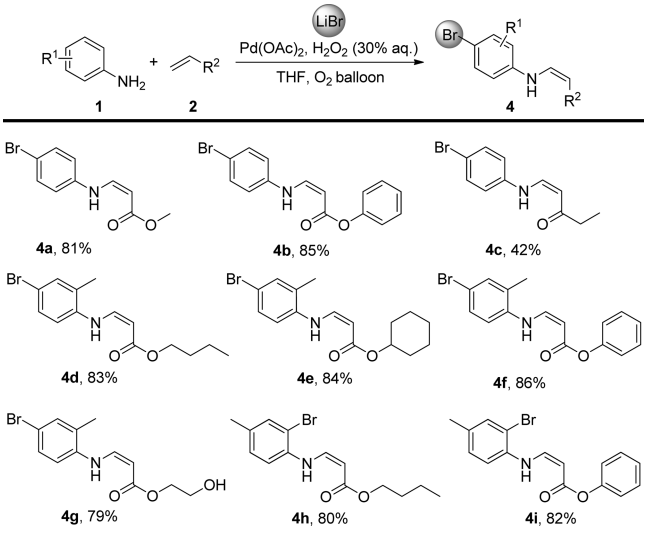
[a]Reaction conditions: aromatic amine **1** (0.5 mmol), alkene **2** (0.8 mmol), $Pd(OAc)_2$ (5 mol %), LiBr (4 equiv), 30% aqueous H_2O_2 (2 equiv), DMF (2 mL), with an O_2 balloon, 50 °C for 12 h. dr > 10:1 unless otherwise noted. [b]The reaction time was prolonged to 20 h. [c]dr = 5:1.

dx.doi.org/10.1021/jo501171c | J. Org. Chem. 2014, 79, 7005−7011

furnish **3k** in 81% yield. On the other hand, other acrylates bearing diverse functional groups, such as phenyl, trifluoromethyl, cyclohexyl, tetrahydrofuran, and even free hydroxyl, performed well in the present catalytic system, affording respective products (**3l**–**q**) in good yields. Delightedly, diethyl vinylphosphonate was also productive, leading to the desired product (**3r**) in 75% yield.

When THF was used as the solvent, the reaction exclusively led to (*Z*)-enamine products **4** with bromination at the benzene ring of anilines (Scheme 3). Further examination of this

Scheme 3. Solvent-Switched Selectivity on the Reaction[a]

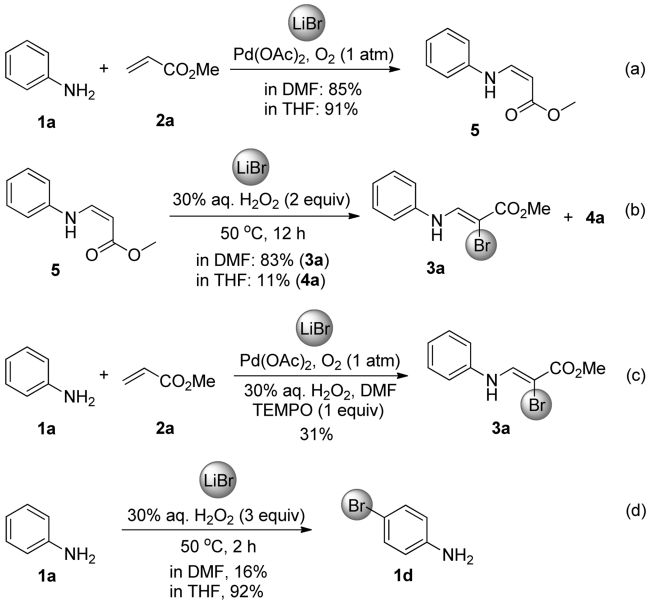


[a]Reaction conditions: aromatic amine **1** (0.5 mmol), alkene **2** (0.8 mmol), $Pd(OAc)_2$ (5 mol %), LiBr (4 equiv), 30% aqueous H_2O_2 (3 equiv), 2 mL of THF, with an O_2 balloon, 50 °C for 10 h. Exclusive *Z* selectivities of the products were obtained.

transformation revealed that the electronic nature of the substituents on the phenyl ring of aniline component could greatly affect the efficiency of this reaction, since anilines substituted with electron-withdrawing functional groups, such as fluoro, chloro, or trifluoromethyl, afforded the corresponding products in significantly decreased yields. Aniline and *o*-toluidine reacted well with various acrylates in this catalytic system, providing the corresponding 4-brominated enamine products (**4a**,**b**,**d**–**g**) in good to excellent yields with complete stereoselectivity. In addition, pent-1-en-3-one was also a suitable substrate to undergo this transformation, albeit affording the product (**4c**) in moderate yield (42%). When *p*-toluidine was employed as the substrate, *ortho*-brominated enamine products (**4h**,**i**) were obtained in good yields. It was noteworthy that the vinyl amine and the aryl bromine functionalities in the resultant products enabled them to undergo various transformations, thus providing ample opportunity for further derivatization to construct more complicated organic architectures.

Mechanism Investigations. In order to gain insight into the reaction mechanism of these co-oxidative catalytic systems, several control experiments were conducted (Scheme 4). The reaction of aniline (**1a**) and methyl acrylate (**2a**) using molecular oxygen (1 atm) as the sole oxidant proceeded smoothly with either DMF or THF as the solvent, giving (*Z*)-enamine **5** in excellent yields (85% and 91%, respectively, Scheme 4a). The (*Z*)-enamine **5** was successfully converted

Scheme 4. Control Experiments



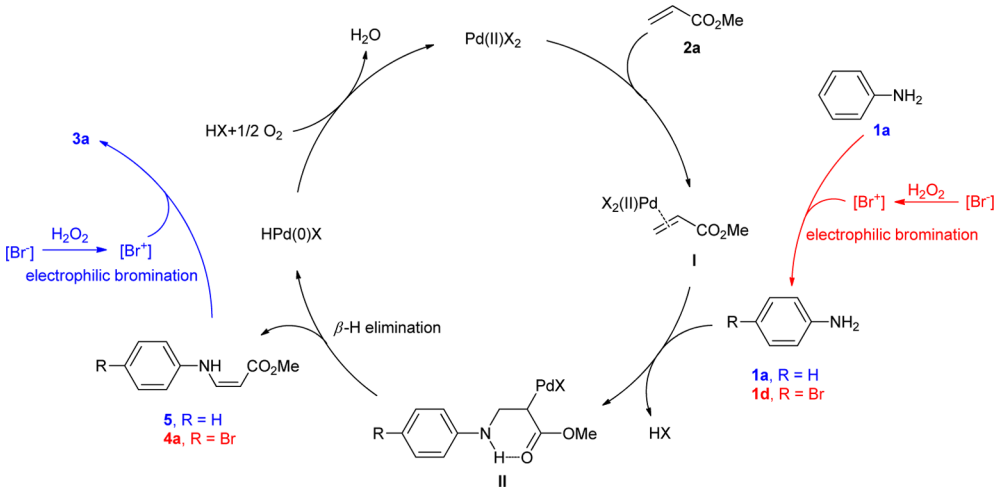
into brominated enamine **3a** in the presence of LiBr with 30% aqueous H_2O_2 in DMF, while could hardly be transformed into product **4a** with THF as the solvent under similar conditions (Scheme 4b). Then the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added to the reaction of aniline (**1a**) and methyl acrylate (**2a**) in the presence of LiBr under the standard conditions of the dehydrogenative aminohalogenation of alkenes, and product (**3a**) was obtained in 31% yield (Scheme 4c). The switched regioselectivity in THF could be clarified by the fact that the bromination of aniline (**1a**) efficiently occurred in the presence of 30% aqueous H_2O_2 within 2 h, delivering 4-bromoaniline (**1d**) in 92% yield, while only 16% yield of **1d** was obtained with DMF as the solvent (Scheme 4d).[54,55]

As for the Pd-catalyzed dehydrogenative aminohalogenation of alkenes, the above results were inconsistent with those when 5 atm of O_2 was used as the sole oxidant in our previous report, illustrating that different mechanisms might be involved in these two reaction systems. We speculated that (*Z*)-enamine (**5**) might be a key intermediate of the transformation in this co-oxidative catalytic system. A plausible mechanism is proposed to illustrate the reaction process of the dehydrogenative aminohalogenation of alkenes in the present catalytic system (Scheme 5). Initially, the complex **I**, formed by the coordination of methyl acrylate (**2a**) to Pd(II) catalyst, underwent nucleophilic attack by aniline (**1a**) to give the *σ*-alkylpalladium species **II**. Subsequent *β*-hydride elimination of complex **II** afforded the enamine intermediate (**5**) in exclusive *Z* stereoselectivity, probably due to the existence of the intramolecular hydrogen bond either in complex **II** or in enamine **5**. The Pd(0) species was oxidized by molecular oxygen to regenerate the active Pd(II) catalyst. Then the electrophilic substitution of the (*Z*)-enamine intermediate (**5**) with [Br^+], arising from the oxidation of [Br^-] with 30% aqueous H_2O_2,[56,57] resulted in the final product **3a**.

When THF was used as the solvent, we found that the efficiency of the reaction was highly dependent on the electronic nature of the amine partner, and electron-deficient amines could not efficiently converted into the desired products. Combined with the results of the control experi-

dx.doi.org/10.1021/jo501171c | J. Org. Chem. 2014, 79, 7005–7011

Scheme 5. Plausible Mechanism for These Transformations



ments, it was suggested that the electrophilic substitution at the *para* position of aniline **1a** with [Br^+], generated by the oxidation of [Br^-] with 30% aqueous H_2O_2, preferentially occurred in this case to provide 4-bromoaniline (**1d**), which underwent subsequent Pd-catalyzed oxidative C−N bond coupling with methyl acrylate (**2a**) in THF to deliver the final products **4a**.

CONCLUSION

In summary, we have developed two regio- and stereoselective palladium-catalyzed aerobic transformations involving aromatic amines and alkenes in the co-oxidative catalytic system. The reaction media played a crucial role in determining the regioselectivity of these processes. With 30% aqueous H_2O_2 as the co-oxidant, the Pd-catalyzed dehydrogenative amino-halogenation of alkenes was achieved in DMF under 1 atm of O_2, providing easy access to (*Z*)-brominated enamines. When THF was employed as the solvent, the electrophilic bromination of anilines and subsequent oxidative C−N bond coupling with alkenes selectively occurred instead. The two oxidants performed their respective duties in this system: the role of molecular oxygen lies in the regeneration of Pd(II) species in the process of oxidative C−N bond coupling, whereas H_2O_2 (30% aq) served for the oxidation of [Br^-] to [Br^+] in the bromination process. Moreover, the employment of readily available starting materials as well as environmentally friendly oxidants makes these atom-economical transformations particularly attractive and practical.

EXPERIMENTAL SECTION

General Methods. All commercial materials and solvents were used without further purification. ^1H and ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C), and the broadband decoupling of carbon data was proton-decoupled $^{13}C\{^1H\}$. The chemical shifts were referenced to signals at 7.26 and 77.0 ppm, respectively, and $CDCl_3$ was used as the solvent with TMS as the internal standard. Melting points were uncorrected. High-resolution mass spectra were obtained with a maXis impact (UHR-TOF) mass spectrometer.

Typical Procedure for Pd-Catalyzed Dehydrogenative Aminohalogenation of Alkenes under O_2 (1 atm). A 25 mL Schlenk tube was charged with a solution of $Pd(OAc)_2$ (0.025 mmol, 5.6 mg), LiBr (2 mmol, 174 mg), amine **1** (0.5 mmol), and alkene **2** (0.8 mmol) in DMF (2 mL), and then 30% aqueous H_2O_2 (2 equiv) was added. The tube was equipped with an O_2 balloon, and the mixture was heated at 50 °C under magnetic stirring for 12 h. The reaction was then quenched with water, and the mixture was extracted with ethyl acetate (15 mL × 3). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to afford the corresponding products **3**.

*(Z)-Methyl 2-bromo-3-(phenylamino)acrylate (**3a**).*[47] Light yellow oil (0.114 g, 89%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.25 (d, J = 13.2 Hz, 1H), 7.33 (t, J = 7.8 Hz, 2H), 7.07 (t, J = 7.4 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 13.2 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.3, 139.6, 138.6, 129.8, 123.5, 116.0, 87.1, 52.5.

*(Z)-Methyl 2-Bromo-3-((4-fluorophenyl)amino)acrylate (**3b**).*[47] Light yellow solid (0.116 g, 85%). Mp: 68−70 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.14 (dd, J = 13.2, 2.0 Hz, 1H), 7.05−6.97 (m, 4H), 6.83 (d, J = 12.0 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.3, 159.1, 139.1, 136.0, 117.7, 116.5, 87.0, 52.5.

*(Z)-Methyl 2-Bromo-3-((4-chlorophenyl)amino)acrylate (**3c**).*[47] Light yellow solid (0.118 g, 81%). Mp: 124−125 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.17 (d, J = 13.2 Hz, 1H), 7.28 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 12.8 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.1, 138.3, 138.2, 129.8, 128.4, 117.2, 87.7, 52.5.

*(Z)-Methyl 2-Bromo-3-((4-bromophenyl)amino)acrylate (**3d**).*[47] Light yellow solid (0.141 g, 84%). Mp: 137−138 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.16 (d, J = 13.2 Hz, 1H), 7.42 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 12.4 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.1, 138.8, 138.0, 132.7, 117.5, 115.8, 88.0, 52.6.

*(Z)-Methyl 2-Bromo-3-((3-methoxyphenyl)amino)acrylate (**3e**).*[47] Light yellow oil (0.124 g, 87%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.22 (d, J = 13.2 Hz, 1H), 7.22 (t, J = 8.2 Hz, 1H), 6.83 (d, J = 13.2 Hz, 1H), 6.61 (dd, J = 8.2, 2.2 Hz, 2H), 6.55 (t, J = 2.4 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.3, 161.0, 140.9, 138.5, 130.7, 108.7, 108.5, 102.3, 87.2, 55.4, 52.5.

*(Z)-Methyl 2-Bromo-3-((3-fluorophenyl)amino)acrylate (**3f**).*[47] Light yellow solid (0.115 g, 84%). Mp: 97−99 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.18 (d, J = 13.2 Hz, 1H), 7.30−7.24 (m, 1H), 6.88 (d, J = 12.8 Hz, 1H), 6.80−6.73 (m, 3H), 3.82 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.1, 163.7, 141.3, 138.0, 131.2, 111.6, 110.1, 103.3, 88.3, 52.6.

*(Z)-Methyl 2-Bromo-3-(o-tolylamino)acrylate (**3g**).*[47] Light yellow oil (0.108 g, 80%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.25 (d, J = 13.2 Hz, 1H), 7.20 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.0 Hz, 1H), 7.00 (t, J = 7.4 Hz, 1H), 6.80 (d, J = 12.8 Hz, 1H), 3.82 (s, 1H), 2.31 (s, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.3, 139.0, 138.0, 131.1, 127.5, 125.3, 123.4, 114.9, 87.6, 52.4, 17.1.

dx.doi.org/10.1021/jo501171c | J. Org. Chem. 2014, 79, 7005−7011

*(Z)-Methyl 2-Bromo-3-((2-methoxyphenyl)amino)acrylate (**3h**).*[47] Light yellow oil (0.117 g, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28 (d, J = 13.6 Hz, 1H), 7.48 (d, J = 13.2 Hz, 1H), 7.12 (dd, J = 7.8, 1.4 Hz, 1H), 7.00−6.94 (m, 2H), 6.90 (dd, J = 8.0, 1.2 Hz, 1H), 3.92 (s, 3H), 3.82 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.5, 147.7, 137.7, 129.2, 122.9, 121.3, 113.2, 110.9, 87.4, 55.8, 52.4.

*(Z)-Methyl 2-Bromo-3-((2-chlorophenyl)amino)acrylate (**3i**).* Light yellow oil (0.106 g, 73%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.26 (d, J = 13.2 Hz, 1H), 7.45 (d, J = 12.4 Hz, 1H), 7.39 (dd, J = 8.0, 1.2 Hz, 1H), 7.28−7.25 (m, 1H), 7.18 (d, J = 7.2 Hz, 1H), 6.98 (td, J = 7.8, 1.4 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.1, 137.2, 136.3, 130.0, 128.2, 123.4, 121.9, 114.7, 89.5, 52.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{10}H_{10}BrClNO_2$ 289.9578, found 289.9586.

*(Z)-Methyl 2-Bromo-3-((2-(trifluoromethoxy)phenyl)amino)-acrylate (**3j**).* Light yellow oil (0.131 g, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (d, J = 13.2 Hz, 1H), 7.29−7.22 (m, 4H), 7.04 (td, J = 7.6, 1.6 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.0, 137.6, 137.1, 132.6, 128.1, 123.0, 121.6, 120.6, 115.2, 89.7, 52.6. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{11}H_9BrF_3NNaO_3$ 361.9610, found 361.9606.

*(Z)-Methyl 2-Bromo-3-(naphthalen-1-ylamino)acrylate (**3k**).*[47] Light yellow oil (0.124 g, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.37 (d, J = 13.2 Hz, 1H), 7.90 (dd, J = 12.6, 8.6 Hz, 2H), 7.64−7.53 (m, 4H), 7.44 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 7.6 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.3, 140.2, 135.4, 134.3, 128.8, 126.6, 126.6, 125.9, 125.0, 124.3, 119.8, 112.9, 88.3, 52.5.

*(Z)-Phenyl 2-Bromo-3-(phenylamino)acrylate (**3l**).* Light yellow solid (0.132 g, 83%). Mp: 122−124 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.42 (d, J = 13.6 Hz, 1H), 7.39−7.31 (m, 4H), 7.22 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 7.6 Hz, 2H), 7.10−7.03 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.4, 151.1, 140.0, 139.3, 129.8, 129.3, 125.6, 123.8, 121.7, 116.3, 86.4. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{12}BrNNaO_2$ 339.9944, found 339.9936.

*(Z)-2,2,2-Trifluoroethyl 2-Bromo-3-(phenylamino)acrylate (**3m**).*[47] Light yellow solid (0.133 g, 82%). Mp: 60−62 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.30 (d, J = 13.6 Hz, 1H), 7.36 (dd, J = 8.4, 7.6 Hz, 2H), 7.12 (t, J = 7.4 Hz, 1H), 7.05−7.00 (m, 3H), 4.60 (q, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.1, 140.3, 139.1, 129.9, 125.4, 124.1, 116.4, 85.1, 60.9.

*(Z)-2-Ethylhexyl 2-Bromo-3-(phenylamino)acrylate (**3n**).*[47] Light yellow oil (0.152 g, 86%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.24 (d, J = 13.2 Hz, 1H), 7.33 (t, J = 7.8 Hz, 2H), 7.06 (t, J = 7.4 Hz, 1H), 7.01 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 13.2 Hz, 1H), 4.14 (d, J = 5.6 Hz, 2H), 1.68−1.64 (m, 1H), 1.42 (t, J = 7.6 Hz, 2H), 1.36−1.32 (m, 6H), 0.95−0.89 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.0, 139.7, 138.2, 129.8, 123.3, 115.9, 87.7, 67.8, 38.9, 30.6, 29.0, 24.0, 23.0, 14.0, 11.1.

*(Z)-Cyclohexyl 2-Bromo-3-(phenylamino)acrylate (**3o**).*[47] Light yellow oil (0.138 g, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (d, J = 13.2 Hz, 1H), 7.33 (t, J = 8.0 Hz, 2H), 7.06 (t, J = 7.4 Hz, 1H), 7.01 (d, J = 7.6 Hz, 2H), 6.84 (d, J = 13.2 Hz, 1H), 4.94−4.88 (m, 1H), 1.91−1.87 (m, 2H), 1.78−1.75 (m, 2H), 1.59−1.50 (m, 3H), 1.47−1.36 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.2, 139.8, 138.0, 129.8, 123.3, 116.0, 88.4, 73.5, 31.7, 25.5, 23.6.

*(Z)-(Tetrahydrofuran-2-yl)methyl 2-Bromo-3-(phenylamino)-acrylate (**3p**).*[47] Light yellow oil (0.137 g, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (d, J = 13.2 Hz, 1H), 7.29 (t, J = 7.8 Hz, 2H), 7.05−6.94 (m, 4H), 4.27−4.13 (m, 3H), 3.92−3.87 (m, 1H), 3.82−3.77 (m, 1H), 2.05−1.83 (m, 3H), 1.71−1.62 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.7, 139.5, 138.7, 129.6, 123.3, 116.0, 87.0, 76.5, 68.4, 67.2, 27.9, 25.6.

*(Z)-2-Hydroxyethyl 2-Bromo-3-(phenylamino)acrylate (**3q**).*[47] Light yellow oil (0.113 g, 79%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28 (d, J = 13.6 Hz, 1H), 7.33 (t, J = 8.0 Hz, 2H), 7.07 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 13.6 Hz, 1H), 4.37−4.34 (m, 2H), 3.90−3.88 (m, 2H), 2.23 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.4, 139.4, 139.2, 129.8, 123.7, 116.2, 86.7, 67.1, 61.5.

*(Z)-Diethyl (1-Bromo-2-(phenylamino)vinyl)phosphonate (**3r**).* Light yellow oil (0.125 g, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 (dd, J = 13.0, 9.0 Hz, 1H), 7.30 (t, J = 7.6 Hz, 2H), 7.04−6.99 (m, 3H), 6.85 (d, J = 13.2 Hz, 1H), 4.16−4.03 (m, 4H), 1.37−1.33 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.2, 140.9, 139.7, 129.7, 123.0, 115.7, 62.4, 62.3, 16.2, 16.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{18}BrNO_3P$ 334.0202, found 334.0198.

Typical Procedure for the Solvent-Switched Selectivity on the Reaction. A 25 mL Schlenk tube was charged with a solution of amine **1** (0.5 mmol), LiBr (2 mmol, 174 mg) in THF (2 mL), and 30% aqueous H_2O_2 (3 equiv), and the mixture was heated at 50 °C under magnetic stirring for 2 h. Then $Pd(OAc)_2$ (0.025 mmol, 5.6 mg) and alkene **2** (0.8 mmol) were added. The tube was equipped with an O_2 balloon, and the mixture was heated at 50 °C under magnetic stirring for another 8 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc/Et_3N) to afford the corresponding products **4**.

*(Z)-Methyl 3-((4-Bromophenyl)amino)acrylate (**4a**).* Light yellow oil (0.104 g, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.88 (d, J = 12.0 Hz, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.17 (dd, J = 12.4, 8.4 Hz, 1H), 6.83 (d, J = 8.8 Hz, 2H), 4.88 (d, J = 8.4 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.6, 142.6, 139.8, 132.5, 116.9, 114.8, 87.9, 50.7.

*(Z)-Phenyl 3-((4-Bromophenyl)amino)acrylate (**4b**).* Light yellow solid (0.135 g, 85%). Mp: 93−95 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.94 (d, J = 12.4 Hz, 1H), 7.43−7.39 (m, 4H), 7.33 (dd, J = 12.8, 8.0 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 5.12 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.8, 150.7, 144.3, 139.3, 132.6, 129.3, 125.5, 121.8, 117.0, 115.4, 87.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{13}BrNO_2$ 318.0124, found 318.0125.

*(Z)-1-((4-Bromophenyl)amino)pent-1-en-3-one (**4c**).* Light yellow solid (0.053 g, 42%). Mp: 90−92 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.57 (d, J = 10.4 Hz, 1H), 7.40 (d, J = 8.4 Hz, 2H), 7.15 (dd, J = 12.2, 7.8 Hz, 1H), 6.88 (d, J = 8.4 Hz, 2H), 5.32 (d, J = 7.6 Hz, 1H), 2.43 (q, J = 7.4 Hz, 2H), 1.13 (t, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 202.8, 142.3, 139.6, 132.6, 117.4, 115.5, 97.2, 35.5, 9.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{13}BrNO$ 254.0175, found 254.0175.

*(Z)-Butyl 3-((4-Bromo-2-methylphenyl)amino)acrylate (**4d**).* Light yellow oil (0.129 g, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.97 (d, J = 12.0 Hz, 1H), 7.28−7.25 (m, 2H), 7.22 (dd, J = 12.2, 8.2 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 4.90 (d, J = 8.0 Hz, 1H), 4.13 (t, J = 6.6 Hz, 2H), 2.29 (s, 3H), 1.69−1.62 (m, 2H), 1.46−1.37 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.6, 142.6, 138.3, 133.6, 129.9, 127.3, 114.4, 114.2, 88.5, 63.4, 30.9, 19.2, 17.3, 13.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{19}BrNO_2$ 312.0594, found 312.0585.

*(Z)-Cyclohexyl 3-((4-Bromo-2-methylphenyl)amino)acrylate (**4e**).* Light yellow oil (0.142 g, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.97 (d, J = 12.0 Hz, 1H), 7.28−7.26 (m, 2H), 7.21 (dd, J = 12.4, 8.4 Hz, 1H), 6.87 (d, J = 8.8 Hz, 1H), 4.89 (d, J = 8.4 Hz, 1H), 4.85−4.81 (m, 1H), 2.29 (s, 3H), 1.92−1.90 (m, 2H), 1.77−1.74 (m, 2H), 1.58−1.55 (m, 1H), 1.47−1.37 (m, 4H), 1.29−1.24 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.0, 142.4, 138.4, 133.5, 129.9, 127.2, 114.3, 114.1, 89.2, 71.6, 31.9, 25.4, 23.9, 17.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{21}BrNO_2$ 338.0750, found 338.0741.

*(Z)-Phenyl 3-((4-Bromo-2-methylphenyl)amino)acrylate (**4f**).* Light yellow solid (0.143 g, 86%). Mp: 105−106 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.98 (d, J = 12.0 Hz, 1H), 7.47−7.42 (m, 3H), 7.37 (d, J = 15.2 Hz, 1H), 7.34 (s, 1H), 7.29 (d, J = 6.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.0 Hz, 1H), 5.19 (d, J = 8.0 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.9, 150.7, 144.6, 137.9, 133.6, 130.0, 129.4, 127.8, 125.5, 121.9, 115.2, 114.7, 87.3, 17.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{15}BrNO_2$ 332.0281, found 332.0285.

*(Z)-2-Hydroxyethyl 3-((4-Bromo-2-methylphenyl)amino)acrylate (**4g**).* Light yellow oil (0.119 g, 79%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.94 (d, J = 12.0 Hz, 1H), 7.29−7.23 (m, 3H), 6.89 (d, J = 8.8 Hz, 1H), 4.95 (d, J = 8.0 Hz, 1H), 4.29−4.27 (m, 2H), 3.87−3.85 (m, 2H), 2.29−2.22 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.7, 143.5, 138.1, 133.6, 130.0, 127.5, 114.8, 114.5, 87.7, 65.3, 61.6, 17.2.

dx.doi.org/10.1021/jo501171c | J. Org. Chem. 2014, 79, 7005−7011

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{15}BrNO_3$ 300.0230, found 300.0221.

*(Z)-Butyl 3-((2-Bromo-4-methylphenyl)amino)acrylate (**4h**).* Light yellow oil (0.125 g, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.23 (d, J = 12.0 Hz, 1H), 7.35 (s, 1H), 7.18 (dd, J = 12.4, 8.4 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 4.91 (d, J = 8.4 Hz, 1H), 4.16 (t, J = 6.6 Hz, 2H), 2.27 (s, 3H), 1.70−1.62 (m, 2H), 1.46−1.39 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.0, 141.7, 136.3, 133.5, 132.8, 129.1, 113.5, 111.8, 89.0, 63.4, 30.9, 20.2, 19.2, 13.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{19}BrNO_2$ 312.0594, found 312.0593.

*(Z)-Phenyl 3-((2-Bromo-4-methylphenyl)amino)acrylate (**4i**).* Light yellow oil (0.136 g, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.18 (d, J = 12.4 Hz, 1H), 7.37 (t, J = 7.8 Hz, 2H), 7.33−7.28 (m, 2H), 7.20 (t, J = 8.0 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.4 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H), 5.13 (d, J = 8.4 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.2, 150.7, 143.6, 136.0, 133.5, 133.5, 129.3, 129.1, 125.4, 121.9, 114.0, 112.1, 87.7, 20.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{15}BrNO_2$ 332.0281, found 332.0282.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jianghf@scut.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Basic Research Program of China (973 Program) (2011CB808600), the National Nature Science Foundation of China (21172076 and 21202046), the Guangdong Natural Science Foundation (10351064101000000 and S2012040007088), and the Fundamental Research Funds for the Central Universities (2014ZP0004 and 2014ZZ0046).

■ REFERENCES

(1) McDonald, R. I.; Liu, G.; Stahl, S. S. *Chem. Rev.* **2011**, *111*, 2981.
(2) Beccalli, E. M.; Broggini, G.; Martinelli, M.; Sottocornola, S. *Chem. Rev.* **2007**, *107*, 5318.
(3) Zeni, G.; Larock, R. C. *Chem. Rev.* **2006**, *106*, 4644.
(4) Cacchi, S.; Fabrizi, G. *Chem. Rev.* **2011**, *111*, PR215.
(5) Anastas, P.; Eghbali, N. *Chem. Soc. Rev.* **2010**, *39*, 301.
(6) Piera, J.; Bäckvall, J.-E. *Angew. Chem., Int. Ed.* **2008**, *47*, 3506.
(7) Vedernikov, A. N. *Acc. Res. Chem.* **2012**, *45*, 803.
(8) ten Brink, G.-J.; Arends, I. W. C. E.; Sheldon, R. A. *Chem. Rev.* **2004**, *104*, 4105.
(9) Stahl, S. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 3400.
(10) Stahl, S. S. *Science* **2005**, *309*, 1824.
(11) Gligorich, K. M.; Sigman, M. S. *Chem. Commun.* **2009**, 3854.
(12) Campbell, A. N.; Stahl, S. S. *Acc. Res. Chem.* **2012**, *45*, 851.
(13) Stanovnik, B.; Svete, J. *Chem. Rev.* **2004**, *104*, 2433.
(14) Toh, K. K.; Wang, Y.-F.; Ng, E. P. J.; Chiba, S. *J. Am. Chem. Soc.* **2011**, *133*, 13942.
(15) Toh, K. K.; Biswas, A.; Wang, Y.-F.; Tan, Y. Y.; Chiba, S. *J. Am. Chem. Soc.* **2014**, *136*, 6011.
(16) Rakshit, S.; Patureau, F. W.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 9585.
(17) Neumann, J. J.; Suri, M.; Glorius, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 7790.
(18) Bernini, R.; Fabrizi, G.; Sferrazza, A.; Cacchi, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 8078.
(19) Würtz, S.; Rakshit, S.; Neumann, J. J.; Dröge, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2008**, *47*, 7230.
(20) Ke, J.; He, C.; Liu, H.; Li, M.; Lei, A. *Chem. Commun.* **2013**, *49*, 7549.
(21) Wang, C.; Dong, C.; Kong, L.; Li, Y.; Li, Y. *Chem. Commun.* **2014**, *50*, 2164.
(22) Muthusaravanan, S.; Sasikumar, C.; Bala, B. D.; Perumal, S. *Green Chem.* **2014**, *16*, 1297.
(23) Yang, M.; Tang, J.; Fan, R. *Org. Lett.* **2013**, *15*, 3464.
(24) Zhao, M.; Wang, F.; Li, X. *Org. Lett.* **2012**, *14*, 1412.
(25) Xiang, D.; Xin, X.; Liu, X.; Zhang, R.; Yang, J.; Dong, D. *Org. Lett.* **2012**, *14*, 644.
(26) Jiang, B.; Li, Y.; Tu, M.-S.; Wang, S.-L.; Tu, S.-J.; Li, G. *J. Org. Chem.* **2012**, *77*, 7497.
(27) Liu, G.; Liu, X.; Cai, Z.; Jiao, G.; Xu, G.; Tang, W. *Angew. Chem., Int. Ed.* **2013**, *52*, 4235.
(28) Ager, D. J.; de Vries, A. H. M.; de Vries, J. G. *Chem. Soc. Rev.* **2012**, *41*, 3340.
(29) Etayo, P.; Vidal-Ferran, A. *Chem. Soc. Rev.* **2013**, *42*, 728.
(30) Arribas, I.; Álvarez, E.; Pizzano, A. *Organometallics* **2013**, *32*, 2497.
(31) Verendel, J. J.; Pàmies, O.; Diéguez, M.; Andersson, P. G. *Chem. Rev.* **2014**, *114*, 2130.
(32) Burk, M. J. *Acc. Chem. Res.* **2000**, *33*, 363.
(33) Chuprakov, S.; Worrell, B. T.; Selander, N.; Sit, R. K.; Fokin, V. V. *J. Am. Chem. Soc.* **2014**, *136*, 195−202.
(34) Jin, X.; Yamaguchi, K.; Mizuno, N. *Angew. Chem., Int. Ed.* **2014**, *53*, 455.
(35) Liang, H.; Ren, Z.-H.; Wang, Y.-Y.; Guan, Z.-H. *Chem.—Eur. J.* **2013**, *19*, 9789.
(36) Yamagishi, M.; Nishigai, K.; Ishii, A.; Hata, T.; Urabe, H. *Angew. Chem., Int. Ed.* **2012**, *51*, 6471.
(37) Li, M.; Yuan, H.; Zhao, B.; Liang, F.; Zhang, J. *Chem. Commun.* **2014**, *50*, 2360.
(38) Evano, G.; Gaumont, A.-C.; Alayrac, C.; Wrona, I. E.; Giguere, J. R.; Delacroix, O.; Bayle, A.; Jouvin, K.; Theunissen, C.; Gatignol, J.; Silvanus, A. C. *Tetrahedron* **2014**, *70*, 1529.
(39) Ueno, S.; Shimizu, R.; Kuwano, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 4543.
(40) Mizuta, Y.; Yasuda, K.; Obora, Y. *J. Org. Chem.* **2013**, *78*, 6332.
(41) Kotov, V.; Scarborough, C. C.; Stahl, S. S. *Inorg. Chem.* **2007**, *46*, 1910.
(42) Lee, J. M.; Ahn, D.-S.; Jung, D. Y.; Lee, J.; Do, Y.; Kim, S. K.; Chang, S. *J. Am. Chem. Soc.* **2006**, *128*, 12954.
(43) Timokhin, V. I.; Stahl, S. S. *J. Am. Chem. Soc.* **2005**, *127*, 17888.
(44) Gooßen, L. J.; Salih, K. S. M.; Blanchot, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 8492.
(45) Bolshan, Y.; Batey, R. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 2109.
(46) Selander, N.; Worrell, B. T.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2012**, *51*, 13054.
(47) Ji, X.; Huang, H.; Wu, W.; Jiang, H. *J. Am. Chem. Soc.* **2013**, *135*, 5286.
(48) Ji, X.; Huang, H.; Wu, W.; Li, X.; Jiang, H. *J. Org. Chem.* **2013**, *78*, 11155.
(49) Wu, W.; Jiang, H. *Acc. Res. Chem.* **2012**, *45*, 1736.
(50) Yu, Y.; Huang, L.; Wu, W.; Jiang, H. *Org. Lett.* **2014**, *16*, 2146.
(51) Liu, B.; Gao, H.; Yu, Y.; Wu, W.; Jiang, H. *J. Org. Chem.* **2013**, *78*, 10319.
(52) Wang, Q.; Huang, L.; Wu, X.; Jiang, H. *Org. Lett.* **2013**, *15*, 5940.
(53) Zheng, M.; Huang, L.; Wu, W.; Jiang, H. *Org. Lett.* **2013**, *15*, 1838.
(54) Bora, U.; Bose, G.; Chaudhuri, M. K.; Dhar, S. S.; Gopinath, R.; Khan, A. T.; Patel, B. K. *Org. Lett.* **2000**, *2*, 247.
(55) Islam, S. M.; Roy, A. S.; Mondal, P.; Tuhina, K.; Mobarak, M.; Mondal, J. *Tetrahedron Lett.* **2012**, *53*, 127.

(56) Chen, A.-J.; Wong, S.-T.; Hwang, C.-C.; Mou, C.-Y. *ACS Catal.* **2011**, *1*, 786.
(57) Sharma, R. K.; Sharma, C. *Tetrahedron Lett.* **2010**, *51*, 4415.