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Hypervalent iodine-mediated aminobromination of olefins in water

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ABSTRACT

The PhI(OAc)$_2$-catalyzed aminobromination of electron-deficient olefins has been achieved in pure water with TsNH$_2$ and NBS as nitrogen and bromine sources, respectively. With a catalytic amount of PhI(OAc)$_2$, various olefins including α,β-unsaturated ketones, cinnamates, and cinnamides could be aminobrominated efficiently, giving the vicinal bromoamines in good yields and high regio- and diastereoselectivities. Utilizing water as solvent was crucial to realize this aminobromination reaction catalytically. The regioselectivity for the aminobromination of styrenes under the present aqueous conditions was also dramatically improved.

1. Introduction

Vicinal haloamines have elicited attention from the chemical sciences owing to their utility as key intermediates in the synthesis of biologically and pharmaceutically relevant molecules.[1] These important functionalities could be installed by the aminohalogenation of carbon–carbon double bond. Many reagent systems including *N*,*N*-dihalo sulfonamides,[2] *N*,*N*-dihalo carbamates,[3] *N*-halo carbamates,[4] *N*-bromoacetamide,[5] *N*,*N*-dibromo phosphoramidate,[6] *S*,*S*-dimethyl-*N*-(*p*-toluenesulfonyl)-sulfilimine/NBS,[7] and cyanamide/NBS[8] are employed in this subject and these methodologies represent useful routes to synthesize vicinal haloamine moieties during the past few decades. However, considerable drawbacks such as severe reaction conditions, tedious manipulation, and low reaction efficiency plagued these reactions. As a result, the convenient and selective aminohalogenation of olefins is highly desirable.

Li and co-workers developed the first catalytic aminochlorination reaction of electron-deficient olefins with Cu(I) salts,[9a,b,d–i,10] ZnCl$_2$,[9a] and Pd complex[9c,j] as efficient catalysts. By employment of several different nitrogen/chlorine sources, such as 4-TsNCl$_2$,[9a,c,e–g,i,j,10] 2-NsNNaCl,[9d] or the combination of 2-NsNCl$_2$ and 2-NsNHNa,[9b,h] various olefins including α,β-unsaturated esters,[9a–e] ketones,[9g,h] amides,[9f,j] nitriles,[9i] and β-nitrostyrenes[10] could be aminochlorinated to produce vicinal chloroamine derivatives with good yields and excellent regio- and diastereoselectivities.[11,12] Later, the double bonds of methylenecyclopropanes were also aminobrominated efficiently.[13] Furthermore, the combination of sulfonamides and NBS has been found to be very efficient in the aminobromination of various olefins by Sudalai,[14] Doyle,[15] Fu,[16] Wei,[17] and their co-workers with CuI, MnSO$_4$, V$_2$O$_5$, Mn(III)–salen, Rh complex, FeCl$_2$, or copper powder as catalysts.

Among the myriad of works devoted to this chemistry, those on developing new methods that make use of mild reaction conditions, simple manipulation, atom-economy, and environmentally-friendly catalysts have become very topical. The metal-free aminochlorination of chalcones[18] and β-nitrostyrenes[10] has been realized by Li and co-workers. The reversed regioselectivity of these reactions suggested a different pathway. We found that the aminohalogenation reaction of electron-deficient olefins could be promoted by hypervalent iodine compounds under solvent-free conditions[19] or in organic solvent,[20] giving a similar regioselectivity as metal-catalyzed reactions. Hypervalent iodine compounds such as PhI(OAc)$_2$ are usually used as clean and efficient oxidants in various organic transformations.[21] Surprisingly, only 50–75 mol % of PhI(OAc)$_2$ was required in our methods. However, further decreasing the loading of PhI(OAc)$_2$ was unsuccessful and the aminohalogenation reaction with catalytic amount of PhI(OAc)$_2$ still remains challenging. Recently, the first Brønsted acid-promoted aminochlorination reaction utilizing pure water as the solvent was realized by our group. Water was revealed to represent as a privileged solvent to this reaction.[22] We envisioned that water may hold promise as an efficient reaction medium for the PhI(OAc)$_2$-promoted aminobromination reaction. In our continuous interest on the aminohalogenation of olefins, herein we report the first PhI(OAc)$_2$-catalyzed aminobromination of olefins in pure water with TsNH$_2$ and NBS as nitrogen and bromine sources, respectively.

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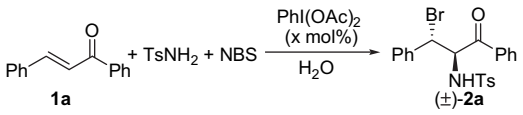
2. Results and discussion

In the preliminary study, we chose chalcone **1a** as a model substrate to probe the feasibility of this reaction. The results are summarized in Table 1. Much to our delight, when chalcone **1a**, $TsNH_2$, and NBS were mixed with $PhI(OAc)_2$ (75 mol%) in H_2O at 20 °C for 60 min, vicinal bromoamine **2a** was obtained in moderate yield yet with high regioselectivity and diastereoselectivity (Table 1, entry 1). This result suggested that the hypervalent iodine-promoted aminobromination reaction could, indeed, be performed in pure water. Elevating the temperature to 50 °C accelerated the reaction significantly; the aminobromination completed in 20 min, giving the final product in good yield of 80% (entry 2). Intrigued by this nice result, we next reduced the loading of $PhI(OAc)_2$. To our satisfaction, this aminobromination reaction could proceed efficiently with only 20 mol% of $PhI(OAc)_2$, and haloamine **2a** could still be isolated in 81% yield within 30 min (entries 3–5). Compared with the reaction in the solid state and organic solvent, this remarkable outcome indicated that water was an optimal reaction medium and was crucial to realize the aminobromination reaction catalytically. $PhI(OAc)_2$, in the true sense, played the role of catalyst in this aminobromination process. Further reducing the loading of $PhI(OAc)_2$ compromised the yield obviously; however, with 5 mol% of $PhI(OAc)_2$ the product was still obtained in 41% yield (entries 6 and 7). Without the promotion of $PhI(OAc)_2$, no expected product was observed (entry 8). The reaction yield would decrease to some extent no matter the reaction temperature was elevated or reduced (entries 9–11). Reducing the amount of $TsNH_2$ was harmful; the yield dropped visibly when 1 equiv of $TsNH_2$ was employed (entries 12 and 13). To further demonstrate the unique property of water in this reaction, ethanol was added as a cosolvent. The reaction carried out in H_2O/EtOH 1:2 afforded only a trace amount of the bromoamine, and no product was observed in pure ethanol (entries 14 and 15).

Table 1
Aminobromination of chalcone **1a** in pure water promoted by $PhI(OAc)_2$[a]



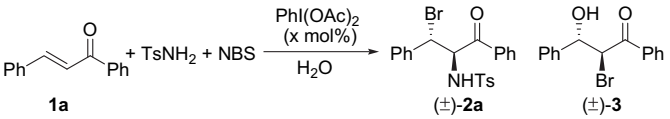
1a (±)-**2a**

Entry	*x*	*T* (°C)	*t* (min)	Yield[b] (%)	dr[c] (*anti*/*syn*)
1	75	20	60	61	90:10
2	75	50	20	80	89:11
3	50	50	25	81	90:10
4	30	50	25	80	89:10
5	20	50	30	81	88:12
6	10	50	40	63	90:10
7	5	50	60	41	89:11
8	0	50	60	0	—
9	20	40	50	78	90:10
10	20	70	30	75	89:11
11	20	100	20	73	87:13
12[d]	20	50	30	79	90:10
13[e]	20	50	40	70	89:11
14[f]	75	20	120	Trace	nd
15[g]	75	20	120	0	—

[a] Unless otherwise specified, all reactions were performed with 0.2 mmol of chalcone **1a**, 0.3 mmol of $TsNH_2$, and 0.3 mmol of NBS in 2 mL of water.
[b] Isolated yield of (±)-**2a**.
[c] Determined by the analysis of ^1H NMR spectra.
[d] 0.24 mmol of $TsNH_2$ and 0.3 mmol of NBS were employed.
[e] 0.2 mmol of $TsNH_2$ and 0.3 mmol of NBS were employed.
[f] Reaction was performed in H_2O/EtOH 1:2.
[g] Reaction was performed in EtOH.

The bromohydroxylation of electron-deficient olefins with NBS in aqueous media is known.[23] In our aminobromination system, the bromohydroxylation was an obvious competition reaction. Bromohydrine **3** could be observed as a minor product, as shown in Table 2. In the absence of $PhI(OAc)_2$, bromohydrine was obtained as a major product in good yield (entries 1–3). Once 5 mol% of $PhI(OAc)_2$ was added, the bromohydroxylation was suppressed, and bromoamine **2a** was isolated in 41% yield together with 34% yield of bromohydrine **3** (entry 4). This result demonstrated the remarkable catalytic efficiency of $PhI(OAc)_2$. Increasing the loading of $PhI(OAc)_2$ could further reduce the generation of **3** (entries 5–7). However, this side reaction could not be completely inhibited, and the bromohydrine was observed as a minor product throughout this research, but could be easily separated out from the desired bromoamine by flash chromatography.

Table 2
The aminobromination and bromohydroxylation of chalcone **1a** in water[a]



1a (±)-**2a** (±)-**3**

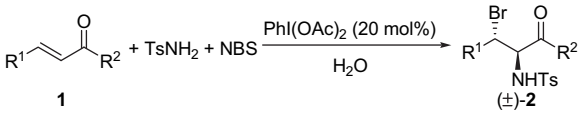
Entry	*x*	*T* (°C)	*t* (min)	Yield[b] of **2a**	Yield[b] of **3**
1	0	100	30	0	68
2	0	50	30	0	65
3[c]	0	50	30	0	71
4	5	50	60	41	34
5	10	50	60	61	28
6	15	50	50	71	14
7	20	50	30	81	5

[a] All reactions were performed with 0.2 mmol of chalcone **1a**, 0.3 mmol of $TsNH_2$, and 0.3 mmol of NBS in 2 mL of water.
[b] Isolated yield.
[c] Reaction was performed without $TsNH_2$.

Compelled by the significance of this reaction together with the importance of the vicinal bromoamine products, we next embarked on exploring the substrate scope of this $PhI(OAc)_2$-catalyzed aminobromination reaction. Various electron-deficient olefins were investigated and the results are listed in Table 3. Our method was successfully amenable to a variety of chalcones with different substituents on the phenyl rings, giving the final products in good to high yields ranging from 61% to 81%. It is worth mentioning that the reaction system was very efficient and the reactions were completed within 30–90 min (entries 1–9). When the enone with 3,4-Cl_2 substituted on the phenyl ring attached with the double bond and the enone with 4-Cl substituted on both phenyl rings were employed as substrates, the reactions were performed at elevated temperature to get higher conversion (entries 4 and 9). 4-Nitro substituted chalcone was less reactive, affording the bromoamine in reduced yield even by increasing the catalyst loading and reaction temperature (entry 5). The scope of this method could be successfully extended to the enone with methyl attached to the carbonyl group, which furnished the product in good yield as a single diastereoisomer within 25 min (entry 10). The cinnamates and cinnamides were also tolerated, giving the α-amino derivatives in moderate yields (entries 11–14). The 4-Cl substituted reactants were less reactive; higher catalyst loading was necessary to achieve reasonable yields (entries 12 and 14). Compared with the reaction in the solid state and dichloromethane, the efficiency of the present system improved obviously.[19b,20] Most of these reactions could be completed within 1 h. The diastereoselectivity of the present catalytic aqueous system is generally comparable to that in the solid state[19b] and in dichloromethane.[20a] Nevertheless, a much better diastereoselectivity in cases of **1e** and **1j** was observed by our present protocol, and only one pure diastereoisomer was obtained (entries 5 and 10).

The $PhI(OAc)_2$-promoted aminobromination of styrenes was observed under ball milling conditions. The corresponding products were obtained in moderate yields together with poor

Table 3
$PhI(OAc)_2$-catalyzed aminobromination of electron-deficient olefins in water[a]



1 (±)-2

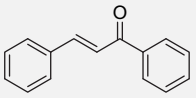
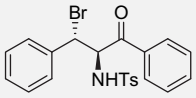
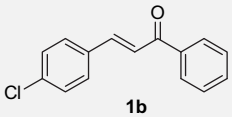
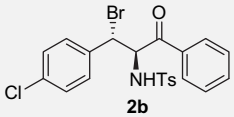
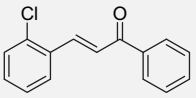
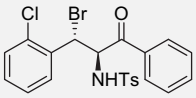
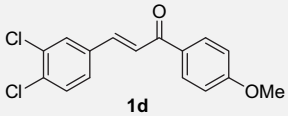
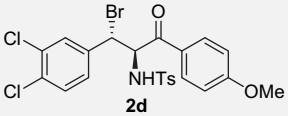
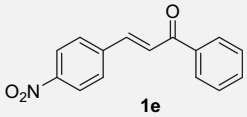
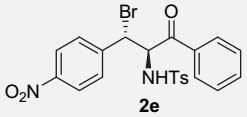
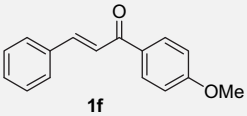
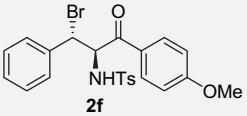
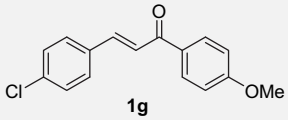
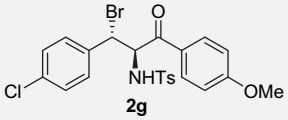
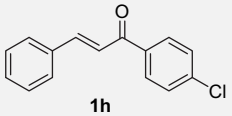
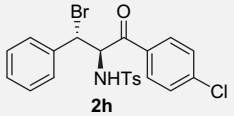
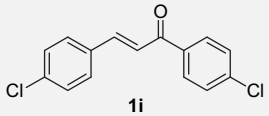
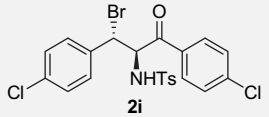
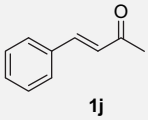
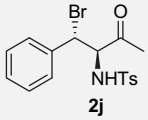
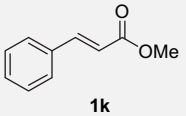
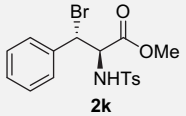
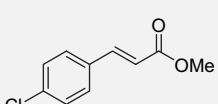
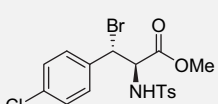
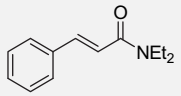
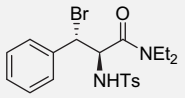
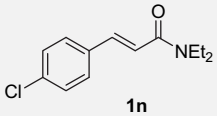
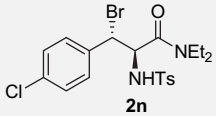
Entry	1	T (°C)	t (min)	2	Yield[b] (%)	dr[c] (*anti*/*syn*)
1	 **1a**	50	30	 **2a**	81	88:12
2	 **1b**	50	40	 **2b**	72	91:9
3	 **1c**	50	30	 **2c**	75	95:5
4	 **1d**	70	40	 **2d**	73	96:4
5[d]	 **1e**	70	90	 **2e**	61	>99:1
6	 **1f**	50	30	 **2f**	69	90:10
7	 **1g**	50	60	 **2g**	73	93:7
8	 **1h**	50	50	 **2h**	71	96:4
9	 **1i**	70	40	 **2i**	68	91:9
10	 **1j**	50	25	 **2j**	71	>99:1
11	 **1k**	50	60	 **2k**	67	90:10
12[d]	 **1l**	50	60	 **2l**	52	97:3

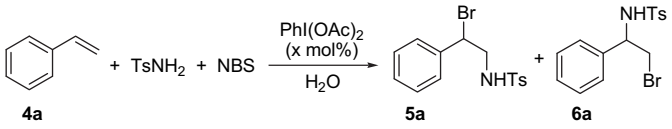
Table 3 (*continued*)

Entry	1	T (°C)	t (min)	2	Yield[b] (%)	dr[c] (*anti*/*syn*)
13	 **1m**	50	90	 **2m**	67	>99:1
14[d]	 **1n**	50	80	 **2n**	54	>99:1

[a] Unless otherwise specified, all reactions were performed with 0.2 mmol of olefin, 0.3 mmol of $TsNH_2$, 0.3 mmol of NBS, and 0.04 mmol of $PhI(OAc)_2$ in 2 mL of water.
[b] Isolated yield.
[c] Determined by the analysis of ^1H NMR spectra.
[d] 30 mol % of $PhI(OAc)_2$ was employed.

regioselectivities (from 2.0:1 to 2.6:1).[19b] We next examined the feasibility of aminobromination of styrenes in the current system. The results are listed in Table 4. When styrene **4a** was stirred with $TsNH_2$ and NBS in water at 50 °C for 45 min, the vicinal bromoamine was isolated in 47% yield (Table 4, entry 1). On the basis of ^1H NMR spectra, we were pleased to find that only a small amount of unwanted regioisomer **6a** was observed and the regioisomeric ratio of **5a**/**6a** was 95:5. While performing the reaction at lower temperature decreased the yield, elevating the reaction temperature was also not helpful to this reaction (entries 2–4). Then we commenced to increase the catalyst loading. With 40 mol % of $PhI(OAc)_2$ the bromoamine could be isolated in 60% yield (entries 5–7). Unfortunately, further increasing the loading of $PhI(OAc)_2$ did not give an obvious increase in yield (entry 8). The excellent regioselectivity nicely demonstrated the efficiency of the current $PhI(OAc)_2$-mediated aminobromination system.

Table 4
Aminobromination of styrene in water[a]



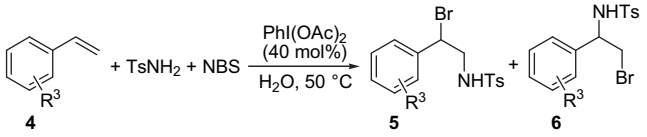
4a **5a** **6a**

Entry	x	T (°C)	t (min)	Yield[b] (%)
1	20	50	45	47
2	20	25	120	31
3	20	70	40	45
4	20	100	30	41
5	25	50	45	50
6	30	50	45	55
7	40	50	45	60
8	50	50	45	61

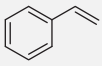
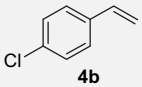
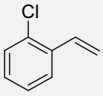
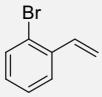
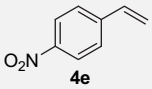
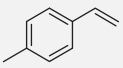
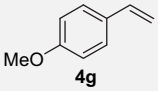
[a] All reactions were performed with 0.5 mmol of styrene, 0.75 mmol of $TsNH_2$, and 0.75 mmol of NBS in 2 mL of water.
[b] Combined yields of **5a** and **6a**; the regioisomeric ratio of **5a**/**6a** was 95:5 on the basis of ^1H NMR spectra.

With the optimized conditions in hand, various styrenes were examined in this aminobromination process (Table 5). 4-Cl-styrene was less reactive, furnishing 57% yield with prolonged reaction time. The regioselectivity was still excellent, and only a negligible amount of regioisomer **6b** was formed (entry 2). When 2-Cl-styrene and 2-Br-styrene were employed as substrates, the corresponding vicinal bromoamine was obtained as single isomers (entries 3 and 4). Unfortunately, 4-nitrostyrene and 4-OMe-styrene gave very complex reaction mixtures and the bromoamine products failed to be isolated (entries 5 and 7). The aminobromination of 4-Me-styrene indeed occurred, yet the regioselectivity was reversed (entry 6).

Table 5
$PhI(OAc)_2$-catalyzed aminobromination of styrenes in water[a]



4 **5** **6**

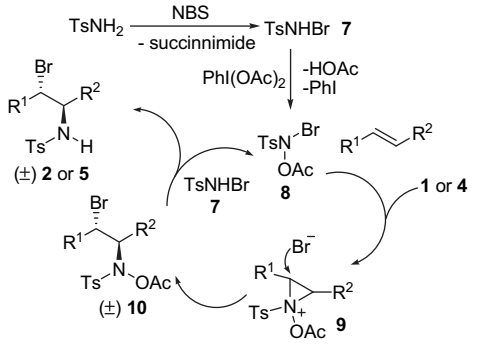
Entry	4	t (min)	Yield[b] (%)	5/6[c]
1	 **4a**	45	60	95:5
2	 **4b**	70	57	97:3
3	 **4c**	50	50	>99:1
4	 **4d**	30	51	>99:1
5	 **4e**	90	nd[d]	nd[d]
6	 **4f**	80	31	23:77
7	 **4g**	90	nd[d]	nd[d]

[a] All reactions were performed with 0.5 mmol of styrene, 0.75 mmol of $TsNH_2$, and 0.75 mmol of NBS with 0.2 mmol of $PhI(OAc)_2$ in 2 mL of water.
[b] Combined yields of **5** and **6**.
[c] The regioisomeric ratio was determined by the analysis of ^1H NMR spectra.
[d] Not determined because of complex reaction mixture.

According to the previous work,[9,19,20,22] the current $PhI(OAc)_2$-catalyzed reaction was believed to go through an aziridinium cation intermediate. The detailed reaction mechanism is shown in Scheme 1, which is similar to our previously proposed one,[19b,20a] and can explain the high regio- and diastereoselectivity.

The unusual rate acceleration and better selectivity of organic reactions in water compared to the same reactions in organic solvents have been known for many years.[24] In comparison with our earlier

investigated aminobromination under solvent-free conditions[19b] or in organic solvent,[20a] water exhibited as a superior reaction medium to facilitate the reaction with high efficiency. The amount of $PhI(OAc)_2$ could be decreased up to 20 mol % from previous 75 mol %, successfully realizing the aminobromination catalytically.



Scheme 1. Possible reaction mechanism.

3. Conclusion

In summary, we have demonstrated a highly efficient aminobromination reaction of electron-deficient olefins catalyzed by $PhI(OAc)_2$ in pure water with $TsNH_2$ and NBS as the nitrogen and bromine sources, respectively. Besides guaranteeing a clean and eco-friendly reaction condition, this aqueous reaction allows the aminobromination of olefins to proceed smoothly and efficiently, giving the useful vicinal bromoamines with high yields and selectivities. Catalytic amount of $PhI(OAc)_2$ was used to facilitate this reaction for the first time. Employing water as solvent was crucial to realize this aminobromination reaction catalytically. The diastereoselectivity for the current catalytic aqueous reaction of olefins was generally comparable to, even much better in cases of **1e** and **1j** than, that in the solid state and in dichloromethane. Furthermore, the regioselectivity for styrenes under the present aqueous conditions was also dramatically improved.

4. Experimental

4.1. General

All reagents were obtained from commercial sources and used without further purification. Chromatographic purification of products was accomplished using flash column chromatography on silica gel. ^1H and ^{13}C NMR spectra were recorded with a Bruker AV300 spectrometer; chemical shifts are expressed in parts per million (δ) and are referenced to the carbon and residual proton signals of the NMR solvent ($CHCl_3$: δ=7.26 ppm for ^1H NMR, δ=77.0 ppm for ^{13}C NMR). Infrared spectra were obtained with a VECTOR-12 infrared spectrometer; data are presented in wavenumbers (cm^{-1}). HRMS data were recorded with a BRUKER VPEXII spectrometer with EI mode.

4.2. General procedure for the $PhI(OAc)_2$-catalyzed aminobromination of electron-deficient olefins in water

To a 25 mL round-bottom flask were added electron-deficient olefin **1a** (**1b**–**n**, 0.2 mmol), $TsNH_2$ (51.3 mg, 0.3 mmol), NBS (53.4 mg, 0.3 mmol), and $PhI(OAc)_2$ (12.9 mg, 0.04 mmol) (19.4 mg, 0.06 mmol for **1e**, **1l**, and **1n**). Then 2 mL of water was added and the resulting mixture was allowed to stir vigorously at 50 °C (70 °C in cases of **1d**, **1e**, and **1i**) for an appropriate time (monitored by TLC). Upon completion, ethyl acetate (3 mL×2) was added to extract the product. The organic layer was dried with $MgSO_4$ and then evaporated to dryness in vacuo. The residual was separated on a silica gel column with petroleum ether/ethyl acetate 5:1 as the eluent to get the desired product **2a** (**2b**–**n**).

4.3. General procedure for the aminobromination of styrene in water

To a 25 mL round-bottom flask were added styrene **4a** (**4b**–**g**, 0.5 mmol), $TsNH_2$ (128.3 mg, 0.75 mmol), NBS (133.5 mg, 0.75 mmol), and $PhI(OAc)_2$ (64.5 mg, 0.2 mmol). Then 2 mL of water was added and the resulting mixture was allowed to stir vigorously at 50 °C for an appropriate time (monitored by TLC). Upon completion, ethyl acetate (3 mL×2) was added to extract the product. The organic layer was dried with $MgSO_4$ and then evaporated to dryness in vacuo. The residual was separated on a silica gel column with petroleum ether/ethyl acetate 6:1 as the eluent to get the desired product.

Products **2a**–**n**,[14,19b] **3**,[23b] **5a**,[14] and **5f**[7] have previously been synthesized and characterized. The mixture of compound **5b** and its regioisomer **6b** has been characterized,[19b] and the IR, ^1H NMR, and ^{13}C NMR spectra data of pure **5b** were given here. Physical and spectroscopic data of the newly synthesized compounds are given below.

*4.3.1. 1-(4-Chlorophenyl)-1-bromo-2-(tosylamino)ethane (**5b**).* White solid; mp 129–131 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, J=8.4 Hz, 2H), 7.33–7.21 (m, 6H), 4.90 (t, J=7.2 Hz, 1H), 4.80 (t, J=6.0 Hz, 1H), 3.57–3.51 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, all 1C unless indicated) δ 144.0, 137.0, 136.9, 135.0, 130.0 (2C), 129.25 (2C), 129.17 (2C), 127.1 (2C), 51.5, 50.1, 21.7; IR (KBr) ν_{max} 3277, 1597, 1494, 1429, 1323, 1154, 1092, 852, 817, 677, 552, 516 cm^{-1}; HRMS (EI–TOF, m/z $[M+H]^+$) calcd for $C_{15}H_{16}NO_2S^{35}Cl^{81}Br$ 389.9753, found 389.9749.

*4.3.2. 1-(2-Chlorophenyl)-1-bromo-2-(tosylamino)ethane (**5c**).* White solid; mp 67–69 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J=8.4 Hz, 2H), 7.47–7.24 (m, 6H), 5.38 (dd, J=7.8, 6.3 Hz, 1H), 4.90 (t, J=6.3 Hz, 1H), 3.65–3.58 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, all 1C unless indicated) δ 143.9, 137.1, 135.7, 133.3, 130.2, 130.1, 130.0 (2C), 129.1, 127.7, 127.2 (2C), 49.0, 48.2, 21.6; IR (KBr) ν_{max} 3292, 3262, 1477, 1437, 1324, 1158, 1088, 849, 812, 739, 673, 553 cm^{-1}; HRMS (EI–TOF, m/z $[M+H]^+$) calcd for $C_{15}H_{16}NO_2S^{35}Cl^{81}Br$ 389.9753, found 389.9751.

*4.3.3. 1-(2-Bromophenyl)-1-bromo-2-(tosylamino)ethane (**5d**).* White solid; mp 80–82 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J=8.4 Hz, 2H), 7.53 (dd, J=8.1, 1.3 Hz, 1H), 7.46 (dd, J=7.8, 1.3 Hz, 1H), 7.33–7.28 (m, 3H), 7.16 (td, J=7.8, 1.5 Hz, 1H), 5.37 (dd, J=8.1, 6.0 Hz, 1H), 4.88 (t, J=6.0 Hz, 1H), 3.65–3.57 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, all 1C unless indicated) δ 143.9, 137.3, 137.1, 133.4, 130.5, 130.0 (2C), 129.2, 128.3, 127.2 (2C), 123.7, 51.0, 49.1, 21.7; IR (KBr) ν_{max} 3290, 1427, 1327, 1156, 1093, 1039, 1026, 851, 818, 762, 730, 668, 551 cm^{-1}; HRMS (EI–TOF, m/z $[M+H]^+$) calcd for $C_{15}H_{16}NO_2S^{79}Br_2$ 431.9268, found 431.9266.

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References and notes

1. Kemp, J. E. G. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 7, p 469.
2. (a) Kharasch, M. S.; Priestley, H. M. *J. Am. Chem. Soc.* **1939**, *61*, 3425; (b) Ueno, Y.; Takemura, S.; Ando, Y.; Terauchi, H. *Chem. Pharm. Bull.* **1967**, *15*, 1193.

3. (a) Chabrier, P. *Ann. Chim.* **1942**, *17*, 353; (b) Foglia, T. A.; Swern, D. *J. Org. Chem.* **1966**, *31*, 3625; (c) Schrage, K. *Tetrahedron Lett.* **1966**, *7*, 5795; (d) Daniher, F. A.; Butler, P. E. *J. Org. Chem.* **1968**, *33*, 2637; (e) Klepacz, A.; Zwierzak, A. *Tetrahedron Lett.* **2001**, *42*, 4539; (f) Śliwińska, A.; Zwierzak, A. *Tetrahedron Lett.* **2003**, *44*, 9323; (g) Śliwińska, A.; Zwierzak, A. *Tetrahedron* **2003**, *59*, 5927.
4. (a) Lessard, J.; Driguez, H.; Vermes, J.-P. *Tetrahedron Lett.* **1970**, *11*, 4887; (b) Driguez, H.; Vermes, J.-P.; Lessard, J. *Can. J. Chem.* **1978**, *56*, 119.
5. (a) Yeung, Y.-Y.; Gao, X.; Corey, E. J. *J. Am. Chem. Soc.* **2006**, *128*, 9644; (b) Yeung, Y.-Y.; Hong, S.; Corey, E. J. *J. Am. Chem. Soc.* **2006**, *128*, 6310.
6. Osowska-Pacewicka, K.; Zwierzak, A. *Tetrahedron* **1985**, *41*, 4717.
7. Raghavan, S.; Reddy, S. R.; Tony, K. A.; Kumar, C. N.; Nanda, S. *Synlett* **2001**, 851.
8. (a) Ponsold, K.; Ihn, W. *Tetrahedron Lett.* **1970**, *11*, 1125; (b) Kohn, H.; Jung, S. H. *J. Am. Chem. Soc.* **1983**, *105*, 4106; (c) Jung, S. H.; Kohn, H. *J. Am. Chem. Soc.* **1985**, *107*, 2931.
9. (a) Li, G.; Wei, H.-X.; Kim, S. H.; Neighbors, M. *Org. Lett.* **1999**, *1*, 395; (b) Li, G.; Wei, H.-X.; Kim, S. H. *Org. Lett.* **2000**, *2*, 2249; (c) Wei, H.-X.; Kim, S. H.; Li, G. *Tetrahedron* **2001**, *57*, 3869; (d) Li, G.; Wei, H.-X.; Kim, S. H. *Tetrahedron* **2001**, *57*, 8407; (e) Kotti, S. R. S. S.; Xu, X.; Wang, Y.; Headley, A. D.; Li, G. *Tetrahedron Lett.* **2004**, *45*, 7209; (f) Xu, X.; Kotti, S. R. S. S.; Liu, J.; Cannon, J. F.; Headley, A. D.; Li, G. *Org. Lett.* **2004**, *6*, 4881; (g) Chen, D.; Timmons, C.; Chao, S.; Li, G. *Eur. J. Org. Chem.* **2004**, 3097; (h) Liu, J.; Wang, Y.; Li, G. *Eur. J. Org. Chem.* **2006**, 3112; (i) Han, J.-L.; Zhi, S.-J.; Wang, L.-Y.; Pan, Y.; Li, G. *Eur. J. Org. Chem.* **2007**, 1332; (j) Wang, Y.-N.; Kattuboina, A.; Ai, T.; Banerjee, D.; Li, G. *Tetrahedron Lett.* **2007**, *48*, 7894.
10. Zhi, S.; Han, J.; Lin, C.; An, G.; Pan, Y.; Li, G. *Synthesis* **2008**, 1570.
11. For publications of other groups on transition metal-catalyzed aminohalogenations, see: (a) Bach, T.; Schlummer, B.; Harms, K. *Chem. Commun.* **2000**, 287; (b) Helaja, J.; Gottlich, R. *Chem. Commun.* **2002**, 720; (c) Qi, X.; Lee, S. H.; Kwon, J. Y.; Kim, Y.; Kim, S. J.; Lee, Y. S.; Yoon, J. *J. Org. Chem.* **2003**, *68*, 9140; (d) Nadir, U. K.; Singh, A. *Synth. Commun.* **2004**, *34*, 1337; (e) Ye, C.; Shreeve, J. M. *J. Org. Chem.* **2004**, *69*, 8561; (f) Lei, A.; Lu, X.; Liu, G. *Tetrahedron Lett.* **2004**, *45*, 1785; (g) Manzoni, M. R.; Zabawa, T. P.; Kasi, D.; Chemler, S. R. *Organometallics* **2004**, *23*, 5618; (h) Minakata, S.; Yoneda, Y.; Oderaotoshi, Y.; Komatsu, M. *Org. Lett.* **2006**, *8*, 967; (i) Fan, R.; Wen, F.; Qin, L.; Pu, D.; Wang, B. *Tetrahedron Lett.* **2007**, *48*, 7444; (j) Michael, F. E.; Sibbald, P. A.; Cochran, B. M. *Org. Lett.* **2008**, *10*, 793; (k) Hövelmann, C. H.; Streuff, J.; Brelot, L.; Muñiz, K. *Chem. Commun.* **2008**, 2334.
12. For a recent review on the aminohalogenation of olefins, see: Li, G.; Kotti, S. R. S. S.; Timmons, C. *Eur. J. Org. Chem.* **2007**, 2745.
13. (a) Li, Q.; Shi, M.; Timmons, C.; Li, G. *Org. Lett.* **2006**, *8*, 625; (b) Huang, X.; Fu, W.-J. *Synthesis* **2006**, 1016.
14. Thakur, V. V.; Talluri, S. K.; Sudalai, A. *Org. Lett.* **2003**, *5*, 861.
15. Catino, A. J.; Nichols, J. M.; Forslund, R. E.; Doyle, M. P. *Org. Lett.* **2005**, *7*, 2787.
16. Wang, Z.; Zhang, Y.; Fu, H.; Jiang, Y.; Zhao, Y. *Synlett* **2008**, 2667.
17. Chen, Z.-G.; Wei, J.-F.; Li, R.-T.; Shi, X.-Y.; Zhao, P.-F. *J. Org. Chem.* **2009**, *74*, 1371.
18. Wang, Y.-N.; Ni, B.; Headley, A. D.; Li, G. *Adv. Synth. Catal.* **2007**, *349*, 319.
19. (a) Wang, G.-W.; Wu, X.-L. *Adv. Synth. Catal.* **2007**, *349*, 1977; (b) Wu, X.-L.; Xia, J.-J.; Wang, G.-W. *Org. Biomol. Chem.* **2008**, *6*, 548.
20. (a) Wu, X.-L.; Wang, G.-W. *Eur. J. Org. Chem.* **2008**, 6239; (b) Xia, J.-J.; Wu, X.-L.; Wang, G.-W. *ARKIVOC* **2008**, *xvi*, 22.
21. For selected recent reviews on hypervalent iodine chemistry, see: (a) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523; (b) Müller, P.; Fruit, C. *Chem. Rev.* **2003**, *103*, 2905; (c) Moriarty, R. M. *J. Org. Chem.* **2005**, *70*, 2893; (d) Wirth, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 3656; (e) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2008**, *108*, 5299.
22. Wu, X.-L.; Wang, G.-W. *J. Org. Chem.* **2007**, *72*, 9398.
23. (a) Rodebaugh, R.; Fraser-Reid, B. *Tetrahedron* **1996**, *52*, 7663; (b) Urankar, D.; Rutar, I.; Modec, B.; Dolenc, D. *Eur. J. Org. Chem.* **2005**, 2349; (c) Hajra, S.; Bhowmick, M.; Karmakar, A. *Tetrahedron Lett.* **2005**, *46*, 3073; (d) Hajra, S.; Karmakar, A.; Bhowmick, M. *Tetrahedron* **2005**, *61*, 2279; (e) Phukan, P.; Chakraborty, P.; Kataki, D. *J. Org. Chem.* **2006**, *71*, 7533.
24. For reviews, see: (a) Li, C.-J. *Chem. Rev.* **1993**, *93*, 2023; (b) Li, C.-J. *Chem. Rev.* **2005**, *105*, 3095; (c) Grieco, P. A. *Organic Synthesis in Water*; Blackie Academic and Professional: London, 1998; (d) Beletskaya, I. P.; Cheprakov, A. V. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley: New York, NY, 2002; Vol. 2, p 2957.