

# ORGANIC CHEMISTRY

FRONTIERS

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

# 1,2-Alkylarylation of Activated Alkenes with Dual C-H Bonds of Arenes and Alkyl Halides Toward Polyhalo-Substituted Oxindoles

Yu Liu,<sup>a</sup> Jia-Ling Zhang,<sup>a</sup> Ren-Jie Song,<sup>a</sup> and Jin-Heng Li\*<sup>a</sup>

Received (in XXX, XXX) Xth XXXXXXXXXX 200X, Accepted Xth XXXXXXXXXX 200X

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

We describe here a new visible light facilitated radical strategy for 1,2-alkylarylation of activated alkenes with a C(sp<sup>2</sup>)-H bond of arenes and a C(sp<sup>3</sup>)-H bond of alkyl halides. This method achieves selective scission of the C(sp<sup>3</sup>)-H bond adjacent to halide atoms leading to an halo-substituted alkyl radical, and provides a new synthetic utilization of aryl halides toward polyhalo-substituted oxindoles in good to excellent yields. Moreover, the concise transformation of the products, polyhalo-substituted oxindoles, into vinyl halides and alkynyl halides was also illustrated.

Polyhalogenated hydrocarbons, a class of organic compounds with multiple substitutions of halogens, are of particular importance in organic synthesis and chemical industries (particular pharmaceuticals and materials), albeit arousing controversy for their effects of these compounds on the environment and on human and animal health.<sup>1</sup> For example, the polychloromethyl unit is a structural feature presented in numerous bioactive natural products and pharmaceutical drugs wherein it usually plays the key component for potent activity role in these compounds (Figure 1).<sup>1-3</sup> As a result, the introduction of the polychloromethyl groups into the known bioactive molecules remains an active area.<sup>2,3</sup> Generally, the synthesis of polyhalogenated hydrocarbons from organohalides (often alkyl halides) are performed by thermo- or photo-initiated scission of the carbon-halogen bonds in organohalides leading to the carbon-centered radicals, in which radical initiators, such as AIBN (azobis(isobutyronitrile)) and organotin (often Bu<sub>3</sub>SnH), are usually used to accomplish these transformations.<sup>4</sup> However, methods for the carbon-centered radical formation from organohalides by selectively splitting carbon-hydrogen bond, not the carbon-halogen bond, are quite rare.<sup>5</sup> The reason is that in organohalides the reactivity of the carbon-halogen bond is far higher than that of the carbon-hydrogen bond under thermo- or photo-initiation.

Recently, a new radical strategy for the oxidative cyclization of *N*-arylmethacrylamides with alkyl C(sp<sup>3</sup>)-H bonds to access functionalized oxindoles has been developed (Schemes 1a and 1b).<sup>6,7</sup> We have first reported a Fe-catalyzed oxidative 1,2-alkylarylation of activated alkenes with an aryl C(sp<sup>2</sup>)-H bond and a C(sp<sup>3</sup>)-H bond adjacent to a heteroatom for building oxindoles using TBHP oxidant, in which proceeds via a radical process (Scheme 1a).<sup>6a</sup> Subsequently, the Guo/Duan group,<sup>7a-d</sup> Liang group,<sup>7e</sup> Liu group<sup>7f</sup> and our group<sup>7b</sup> have independently developed the other new radical cyclization of *N*-

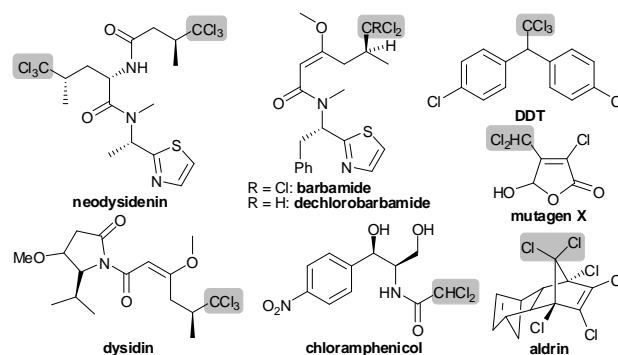
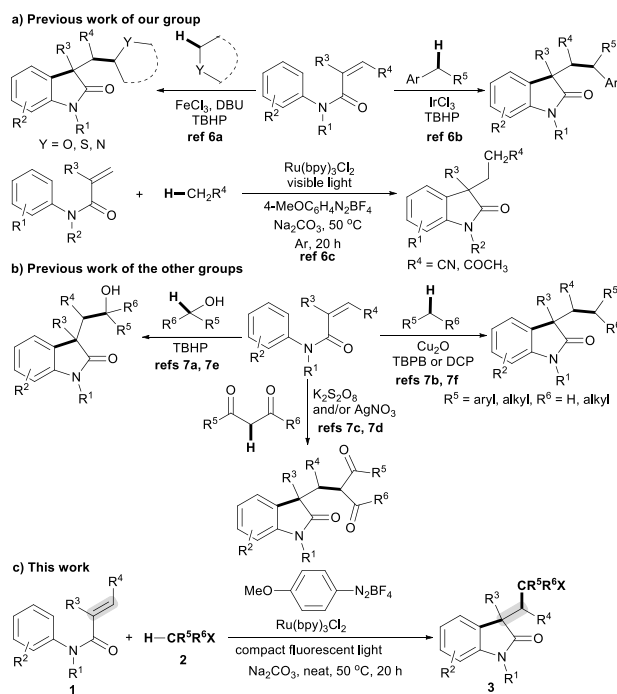


Figure 1. Important Compounds with Polychloro Groups.

arylmethacrylamides with alkyl C(sp<sup>3</sup>)-H bonds, including the C(sp<sup>3</sup>)-H bonds adjacent to an aryl,<sup>6b,7b,7f</sup> a hydroxyl<sup>7a,7e</sup> or dicarbonyl groups<sup>7c-d</sup> and the C(sp<sup>3</sup>)-H bonds in simple alkanes<sup>7i</sup> (Schemes 1a and 1b). However, these methods required unfriendly radical initiators including peroxides and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> under harsh conditions (often at over 100 °C), thereby greatly restricting their applications in synthesis and industry.<sup>5b,6-8</sup> Thus, a new mild radical strategy avoiding the use of unfriendly radical initiators for the cyclization of *N*-arylmethacrylamides with alkyl C(sp<sup>3</sup>)-H bonds is highly desirable. Very recently, we described a visible light catalysis strategy for the cyclization of *N*-arylmethacrylamides alkyl C(sp<sup>3</sup>)-H bonds adjacent to a carbonyl group, which proceeds under mild conditions.<sup>6c</sup> Inspired by these results, we reasoned that the visible light catalysis strategy might be a better alternative for the cyclization of *N*-arylmethacrylamides with various alkyl C(sp<sup>3</sup>)-H bonds.<sup>9,10</sup>

We began with our investigation on the reaction between *N*-methyl-*N*-phenylmethacrylamide (**1a**) and dichloromethane (DCM, **2a**) in the presence of visible light catalysts and 4-methoxybenzenediazonium tetrafluoroborate (Table 1). In the presence of 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub>, the desired oxindole **3aa** was obtained in 55% yield from substrate **1a** with DCM **2a** (entry 1). It has been reported that the visible light catalysis strategy could promote the 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub>-based reaction.<sup>5a,6c,10,11</sup> As expected, treatment of substrate **1a** with DCM **2a**, Ru(bpy)<sub>3</sub>Cl<sub>2</sub>, 4-methoxybenzenediazonium tetrafluoroborate and 36 W compact fluorescent light increased the yield of oxindole **3aa** from 55% to 96% yield (entry 2). The results showed that bases played an important role in the reaction, and Na<sub>2</sub>CO<sub>3</sub> was the most effective (entries 2-5). While Na<sub>2</sub>CO<sub>3</sub> as the base gave 96% yield of oxindole **3aa** (entry 2), Et<sub>3</sub>N as the base decreased the yield to only 31% (entry 3), Cs<sub>2</sub>CO<sub>3</sub> as the



Scheme 1. 1,2-Alkylarylation of Activated Alkenes.

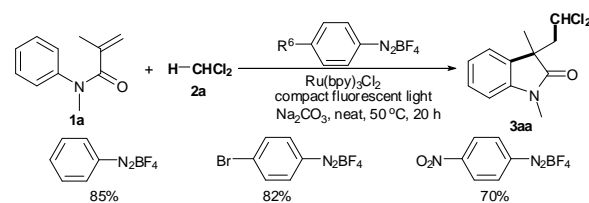
base to 37% (entry 4) and the absence of bases to trace (entry 5). Among the reaction temperature examined, it turned out that 50 °C was preferred for the reaction (entries 2 and 6-7). Gratifyingly, good yield was still achieved even at 2 mol % Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (entry 8). It is noteworthy that the reaction proceeds in MeCO<sub>2</sub><sup>n</sup>Bu smoothly, albeit with slightly lowering the yield (entry 9). Two other visible light photoredox catalysts, Ir(ppy)<sub>3</sub> and Eosin Y, were found to effect the reaction (entries 1 vs. 10-11). These results also suggest that role of both Ru and visible light is mainly used to improve the reaction. Extensive screening revealed that the amount of 4-methoxyphenyldiazonium tetrafluoroborate has a fundamental influence on the reaction: the yield decreased from 96% (entry 2) to 59% at 1 equiv diazonium salt (entry 12), and the absence of diazonium salts resulted in no detectable product **3aa** (entry 13).

Table 1 Screening of Optimal Conditions<sup>a</sup>

Entry	[M] [mol%]	base	T [°C]	Isolated Yield [%]
1 <sup>b</sup>	—	Na <sub>2</sub> CO <sub>3</sub>	50	55
2	Ru(bpy) <sub>3</sub> Cl <sub>2</sub> (5)	Na <sub>2</sub> CO <sub>3</sub>	50	96
3	Ru(bpy) <sub>3</sub> Cl <sub>2</sub> (5)	Et <sub>3</sub> N	50	31
4	Ru(bpy) <sub>3</sub> Cl <sub>2</sub> (5)	Cs <sub>2</sub> CO <sub>3</sub>	50	37
5	Ru(bpy) <sub>3</sub> Cl <sub>2</sub> (5)	—	50	trace
6	Ru(bpy) <sub>3</sub> Cl <sub>2</sub> (5)	Na <sub>2</sub> CO <sub>3</sub>	25	8
7	Ru(bpy) <sub>3</sub> Cl <sub>2</sub> (5)	Na <sub>2</sub> CO <sub>3</sub>	80	83
8	Ru(bpy) <sub>3</sub> Cl <sub>2</sub> (5)	Na <sub>2</sub> CO <sub>3</sub>	50	80
9 <sup>c</sup>	Ru(bpy) <sub>3</sub> Cl <sub>2</sub> (5)	Na <sub>2</sub> CO <sub>3</sub>	50	75
10	Ir(ppy) <sub>3</sub> (5)	Na <sub>2</sub> CO <sub>3</sub>	50	95
11	Eosin Y (5)	Na <sub>2</sub> CO <sub>3</sub>	50	68
12 <sup>d</sup>	Ru(bpy) <sub>3</sub> Cl <sub>2</sub> (5)	Na <sub>2</sub> CO <sub>3</sub>	50	59
13 <sup>e</sup>	Ru(bpy) <sub>3</sub> Cl <sub>2</sub> (5)	Na <sub>2</sub> CO <sub>3</sub>	50	0

<sup>a</sup> Reaction conditions: **1a** (0.3 mmol), **2a** (15 mmol), [M], 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> (2 equiv) and base (2 equiv) with 36 W compact fluorescent light for 20 h under argon atmosphere. <sup>b</sup> Without additional light. <sup>c</sup> **2a** (6 mmol) and MeCO<sub>2</sub><sup>n</sup>Bu (anhydrous, 0.5 mL). <sup>d</sup> 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> (1 equiv). <sup>e</sup> Without 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub>.

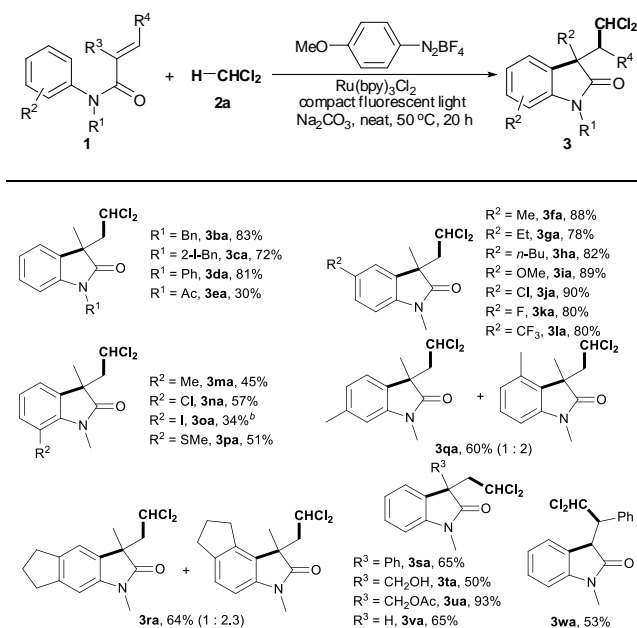
Encouraged by these results, we next set out to examine the effect of diazonium salts (Scheme 2).<sup>[11]</sup> The results demonstrated that three other aryldiazonium salts showed high reactivity, but they were less effective than 4-methoxybenzenediazonium tetrafluoroborate (Scheme 2 vs. entry 2 in Table 1).



Scheme 2. Screening of Effect of Diazonium Salts.

With the optimal conditions in hand, we first employed *N*-arylacrylamides **1** to exploit the scope of the above radical cyclization protocol in the presence of DCM **2a** (Table 2). While analogous amides with *N*-Bn, *N*-(2-iodobenzyl) or *N*-Ph were found to be viable substrates for the reaction (Products **3ba-3da**), changing to *N*-Ac resulted in a lower reactivity (Product **3ea**). Gratifyingly, we found that a number of substituents, including alkyl, MeO, Cl, F, CF<sub>3</sub>, I and SME groups, on the aromatic ring of the *N*-aryl moiety were tolerated well (Products **3fa-ra**), and the reactive order is as follow: *para*- > *meta*- > *ortho*-substituents. For example, *para*-Me-substituted substrate **1f** afforded oxindole **3fa** in 88% yield under the optimized conditions. Good yields were still achieved from substrates **1g-1i** with other electron-rich groups, such as Et, *n*-Bu and MeO groups (Products **3ga-ia**). The reaction was not constrained by an electron-withdrawing CF<sub>3</sub> group, giving product **3la** in 80% yield. However, the yields of oxindoles **3ma-pa** from the corresponding *ortho*-substituted substrates **1m-1p** decreased to moderate. It was noted that *meta*-substituted substrates **1q** or **1r** gave a mixture of two regioselective oxindoles (Products **3qa** and **3ra**). Most importantly, halo groups, I, Cl and F groups, could be perfectly tolerated, thereby facilitating additional modifications at the halogenated position (Products **3ca**, **3ja**, **3ka**, **3na**, and **3oa**). Screening disclosed that substrates **1s-1u** bearing substituents, Ph, CH<sub>2</sub>OH or CH<sub>2</sub>OAc, at the 2 position of the acrylamide moiety were consistent with the optimal conditions (Products **3sa-ua**). Free CH<sub>2</sub>OH-substituted substrate **1t**, for instance, was converted into product **3ta** in 50% yield. However, substrate **1v** with a hydrogen atom at the 2 position had no reactivity for the reaction (Product **3va**). Interestingly, *N*-methyl-*N*-phenylcinnamamide (**1w**), an internal alkene, could also be cyclized toward oxindole **3wa** in 53% yield.

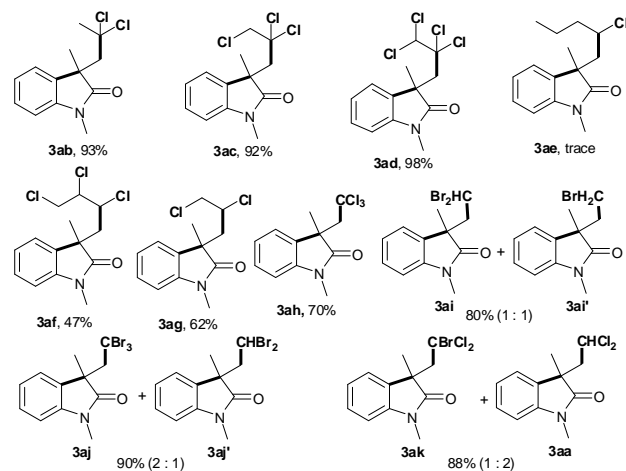
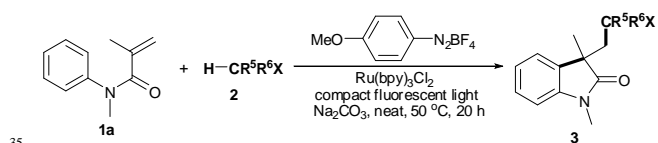
As shown in Table 3, a variety alkyl halides **2** was next investigated in the presence of *N*-methyl-*N*-phenylmethacrylamide (**1a**), Ru(bpy)<sub>3</sub>Cl<sub>2</sub>, 4-methoxybenzenediazonium tetrafluoroborate, Na<sub>2</sub>CO<sub>3</sub> and

**Table 2** Screening Scope of N-Arylacrylamides (**1**)<sup>a</sup>

<sup>a</sup> Reaction conditions: **1** (0.3 mmol), **2a** (15 mmol), Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (5 mol%), 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> (2 equiv) and Na<sub>2</sub>CO<sub>3</sub> (2 equiv) with 36 W compact fluorescent light at 50 °C for 20 h under argon atmosphere. <sup>b</sup> A side de-I product **3aa** was isolated in 36% yield.

36 W compact fluorescent light. Using 1,1-dichloroethane (**2b**), the C(sp<sup>3</sup>)-H bond adjacent to two chloride atoms was selectively cleaved, giving product **3ab** in 93% yield. The results indicate that halo groups are necessary for selective scission of the C(sp<sup>3</sup>)-H bond. Indeed, both 1,1,2-trichloroethane (**2c**) and 1,1,2,2-tetrachloroethane (**2d**) were suitable substrates; moreover, the C(sp<sup>3</sup>)-H bond adjacent to dichloride atoms, not the C(sp<sup>3</sup>)-H bond adjacent to monochloride atoms, was selected to react with substrate **1a** (Product **3ac** and **3ad**). However, no reaction was observed using 1-chlorobutane (**2e**), a monochloro-substituted substrate (Product **3ae**). Gratifyingly, using 1,2,3-trichloropropane (**2f**) and 1,2-dichloroethane (**2g**) to build the corresponding products **3af** and **3ag** was successful in moderate yields. For chloroform (**2h**), good yield of the desired oxindole **3ah** was also obtained under the optimal conditions.

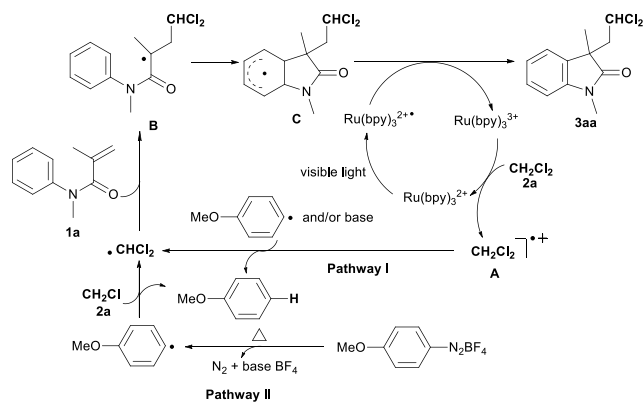
However, this reaction was dependent on the leaving nature of the halo group: both C-H bond and C-Br bond cleavage took place using alkyl bromides (Products **3ai**/**3ai'** and **3ak**/**3ak'**). For example, treatment of CH<sub>2</sub>Br<sub>2</sub> (**2i**) with substrate **1a** afforded a mixture of C-H bond cleavage and C-Br bond cleavage oxindoles **3ai** and **3ai'** in 80% total yield with 1:1 ratio. For bromoform (**2j**), however, ratio of C-H/C-Br cleavage is 2:1. Using bromodichloromethane (**2k**), however, the reactivity of the C-Br bond is higher than the C-H bond in view of the ratio of products **3ak** and **3aa**.

**Table 3** Screening Scope of Alkyl Halides (**2**)<sup>a</sup>

<sup>a</sup> Reaction conditions: **1a** (0.3 mmol), **2** (15 mmol), Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (5 mol%), 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> (2 equiv) and Na<sub>2</sub>CO<sub>3</sub> (2 equiv) with 36 W compact fluorescent light at 50 °C for 20 h under argon atmosphere.

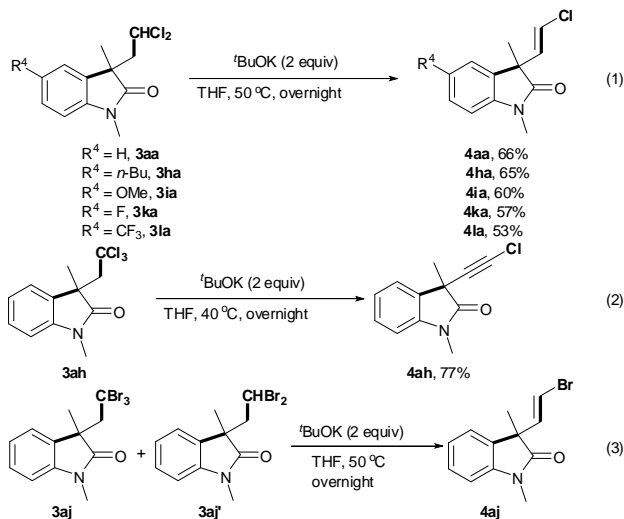
To understand the current radical reaction, the mechanisms outlined in Scheme 3 are proposed on the basis of the present results<sup>13</sup> and the literature reports.<sup>5-11</sup> Initially, ·CHCl<sub>2</sub> radical may be generated via two pathways: (1) Single-electron oxidation of DCM **2a** by Ru(bpy)<sub>3</sub><sup>3+</sup> gives a carbocation **A**, followed by deprotonation leading to the ·CHCl<sub>2</sub> radical (Pathway I), and/or (2) hydrogen abstraction of DCM **2a** by a phenyl radical which was generated from the diazonium salt forms the ·CHCl<sub>2</sub> radical (Pathway I).<sup>6c,10,11</sup> Subsequently, addition of ·CHCl<sub>2</sub> radical to alkene produces radical intermediate **B**, followed by intramolecular cyclization of radical intermediate **B** with an arene gives rise to radical intermediate **C**. Hydrogen atom abstraction of radical intermediate **C** by Ru(bpy)<sub>3</sub><sup>2+</sup> takes place to yield product **3aa** and Ru(bpy)<sub>3</sub><sup>3+</sup>. Notably, This photoinduced mechanism is supported by the quantum yield (Φ<sub>x</sub> = 0.056).<sup>13,14</sup>

On the basis of the results in Table 1, the ·CHCl<sub>2</sub> radical can also be directly formed from the reaction between CH<sub>2</sub>Cl<sub>2</sub> (**2a**) and 4-methoxyphenyl radical in the presence of a base under heating conditions. Thus, there are two key roles of base in the present reaction: initiation of the radical reaction and neutralization of the *in-situ* formed BF<sub>4</sub><sup>-</sup>.

**Scheme 3** Possible Mechanisms.



Vinyl halides or alkynyl halides are important intermediates in organic synthesis. Having established a hydrogen abstraction-cyclization tandem method for the preparation of polyhalo-substituted oxindoles **3**, we finally explored their concise transformation into vinyl halides or alkynyl halides (Scheme 4).<sup>15</sup> After brief screening of bases, <sup>t</sup>BuOK was employed to dehalogenation of dichloro-substituted oxindoles **3aa**, **3ha**, **3ia**, **3ka** and **3la**, exclusively providing the corresponding (*Z*)-vinyl chlorides **4** in moderate yields (Eq 1). Interestingly, dehalogenation of trichloro-substituted oxindole **3ah** resulted in alkynyl chloride **4ah** in good yield (Eq 2). Using a mixture of bromo-substituted oxindoles **3aj** and **3aj'**, (*Z*)-vinyl bromide **4aj** was formed alone in 61% yield (Eq 3).



Scheme 4 Utilizations of Products 3.

In summary, selective scission of the C-H bond adjacent to halide atoms in alkyl halides under visible light photoredox catalysts-facilitated conditions has been illustrated for the synthesis of polyhalo-substituted oxindoles. Importantly, the polyhalo-substituted oxindoles could be further converted into (*Z*)-vinyl halides or alkynyl halides simply by treatment with <sup>t</sup>BuOK.

This research was supported by the Hunan Provincial Natural Science Foundation of China (No. 13JJ2018), Natural Science Foundation of China (No. 21172060), and Specialized Research Fund for the Doctoral Program of Higher Education (No. 20120161110041).

## Notes and references

<sup>a</sup> State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China. Fax: 0086731 8871 3642; Tel: 0086731 8882 2286; E-mail: [jhli@hnu.edu.cn](mailto:jhli@hnu.edu.cn)

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

1 (a) D. J. Faulkner, *Nat. Prod. Rep.* 1997, **14**, 259; (b) S. L. Neidleman and J. Geigert, *Biohalogenation: Principles, Basic Roles and Applications*, Wiley, New York, 1986; (c) G. W. Gribble, *J. Chem. Educ.* 2004, **81**, 1441; (d) C. N. Albers, P. E. Hansen and O. S. Jacobsen, *Sci. Total Environ.* 2010, **408**, 6223; (e) N. Clarke, M.

Gryndler, H.-H. Liste, R. Schroll, P. Schröder and M. Matucha, in *Organic Xenobiotics and Plants: From Mode 17 of Action to Ecophysiology*, P. Schröder and C. D. Collins, Eds., Springer, Heidelberg, 2011.

2 (a) X. Fu, M. L. G. Ferreira, F. J. Schmitz and M. Kelly-Borges, *J. Nat. Prod.* 1998, **61**, 1226; (b) P. N. Sitachitta, J. Rossi, M. A. Roberts, W. H. Gerwick, M. D. Fletcher and C. L. Willis, *J. Am. Chem. Soc.* 1998, **120**, 7131; (c) J. B. MacMillan, E. K. Trousdale and T. F. Molinski, *Org. Lett.* 2000, **2**, 2721; (d) M. D. Unson, C. B. Rose, D. J. Faulkner, L. S. Brinen, J. R. Steiner and J. Clardy, *J. Org. Chem.* 1993, **58**, 6336; (e) J. O. Orjala and W. H. Gerwick, *J. Nat. Prod.* 1996, **59**, 427; (f) D. P. Galoni, E. W. Barr, C. T. Walsh, J. M. Bollinger, Jr and C. Krebs, *Nat. Chem. Biol.* 2007, **3**, 113; (g) G. W. Gribble, *Chemosphere* 2003, **52**, 289; (h) C. Wagner, M. El Omari and G. M. König, *J. Nat. Prod.* 2009, **72**, 540; (i) M. Rich, R. Ritterhoff and R. Hoffmann, *Ann. Intern. Med.* 1950, **33**, 1459; (j) S. J. Singer, F. Spengler, J. T. Chavez and T. Kusmierek, *Carcinogenesis* 1987, **8**, 745; (k) K. C. Cheng, D. S. Preston, M. K. Cahill, B. Dossanjh and L. A. Singer, *Proc. Natl. Acad. Sci. U.S.A.* 1991, **88**, 9974. (l) L. M. Werbel, E. F. Elslager, C. Hess and M. P. Hutt, *J. Med. Chem.* 1987, **30**, 1943.

65 3 For selected reviews and papers: (a) F. I. Luknitskii, *Chem. Rev.* 1975, **75**, 259; (b) A. Butler and J. V. Walker, *Chem. Rev.* 1993, **93**, 1937; (c) A. Butler, *Curr. Opin. Chem. Biol.* 1998, **2**, 279; (d) P. Verhaeghe, P. Rathelot, A. Gellis, S. Rault and P. Vanelle, *Tetrahedron* 2006, **62**, 8173; (e) A. Guirado, B. Martiz and R. Andreu, *Tetrahedron Lett.* 2004, **45**, 8523; (f) A. Guirado, B. Martiz, R. Andreu and D. Bautista, *Tetrahedron* 2009, **65**, 5958; (g) A. Guirado, B. Martiz, R. Andreu and D. Bautista, *Tetrahedron* 2011, **67**, 5811; (h) H.-F. Wang, P. Li, H.-F. Cui, X.-W. Wang, J.-K. Zhang, W. Liu, G. Zhao, *Tetrahedron* 2011, **67**, 1774; (i) P. Verhaeghe, N. Azas, S. Hutter, C. Castera-Ducros, M. Laget, A. Dumâtre, M. Gasquet, J.-P. Reboul, S. Rault, P. Rathelot and P. Vanelle, *Bioorg. Med. Chem.* 2009, **17**, 4313; (j) S. E. Brantley and T. F. Molinski, *Org. Lett.* 1999, **1**, 2165; (k) H. Morimoto, G. Lu, N. Aoyama, S. Matsunaga and M. Shibasaki, *J. Am. Chem. Soc.* 2007, **129**, 9588; (l) S. Beaumont, E. A. Iardi, L. R. Monroe and A. Zakarian, *J. Am. Chem. Soc.* 2010, **132**, 1482.

4 For selected reviews, see: (a) D. P. Curran, in *Comprehensive Organic Synthesis*, Vol. 4; B. M. Trost, I. Fleming and M. F. Semmelhack, Eds.; Pergamon: Oxford, 1991, pp. 715-779; (b) I. Ryu, N. Sonoda and D. P. Curran, *Chem. Rev.* 1996, **96**, 172; (c) *Radicals in Organic Synthesis*, 1st ed.; P. Renaud and M. P. Sibi, Eds., Wiley-VCH: Weinheim, 2001; (d) *Encyclopedia of Radicals in Chemistry, Biology and Materials*, C. Chatgililoglu and A. Studer, Eds., Wiley: Hoboken, 2012.

90 5 (a) Y. Liu, J.-L. Zhang, R.-J. Song and J.-H. Li, *Eur. J. Org. Chem.*, 2014, 1177; During our preparation of this paper, a paper has been reported on the oxidative radical cyclization of *N*-arylacrylamides with only CH<sub>2</sub>Cl<sub>2</sub> or CCl<sub>4</sub> toward chloro-containing oxindoles using FeCl<sub>2</sub> catalyst, Ph<sub>2</sub>IOTf oxidant and Et<sub>3</sub>N base at 100 °C: (b) M.-Z. Lu and T.-P. Loh, *Org. Lett.*, 2014, **16**, 4698.

6 (a) W.-T. Wei, M.-B. Zhou, J.-H. Fan, W. Liu, R.-J. Song, Y. Liu, M. Hu, P. Xie and J.-H. Li, *Angew. Chem. Int. Ed.* 2013, **52**, 3638; (b) M.-B. Zhou, C.-Y. Wang, R.-J. Song, Y. Liu, W.-T. Wei and J.-H. Li, *Chem. Commun.*, 2013, 49, 10817; (c) J.-L. Zhang, Y. Liu, R.-J. Song, G.-F. Jiang and J.-H. Li, *Synlett*, 2014, **25**, 1031.

7 (a) Y. Meng, L.-N. Guo, H. Wang and X.-H. Duan, *Chem. Commun.*, 2013, **49**, 7540; (b) S.-L. Zhou, L.-N. Guo, H. Wang and X.-H. Duan, *Chem. Eur. J.*, 2013, **19**, 12970; (c) H. Wang, L.-N. Guo and X.-H. Duan, *Chem. Commun.*, 2013, **49**, 10370; (d) H. Wang, L.-N. Guo and X.-H. Duan, *Org. Lett.*, 2013, **15**, 5254; (e) Z.-Z. Zhou, H.-L. Hua, J.-Y. Luo, Z.-S. Chen, P.-X. Zhou, X.-Y. Liu and Y.-M. Liang, *Tetrahedron*, 2013, **69**, 10030; (f) Z. Li, Y. Zhang, L. Zhang and Z.-Q. Liu, *Org. Lett.*, 2014, **16**, 382.

8 For papers on the other oxidative cyclization of *N*-arylacrylamides: (a) S. Jaegli, J. Dufour, H.-L. Wei, T. Piou, X.-H. Duan, J.-P. Vors, L. Neuville and J. Zhu, *Org. Lett.*, 2010, **12**, 4498; (b) T. Wu, X. Mu and G.-S. Liu, *Angew. Chem. Int. Ed.*, 2011, **50**, 12578; (c) T. Wu, H. Zhang and G.-S. Liu, *Tetrahedron*, 2012, **68**, 5229; (d) H. Zhang, P. Chen and G.-S. Liu, *Synlett*, 2012, **23**, 2749; (e) M.-B. Zhou, R.-J. Song, X.-H. Ouyang, Y. Liu, W.-T. Wei, G.-B. Deng and J.-H. Li, *Chem. Sci.*, 2013, **4**, 2690; (f) Q. Zhang, F. Yang and Y.-J. Wu, *Tetrahedron*, 2013, **69**, 4908; (g) Y.-M. Li, M. Sun, H.-L. Wang, Q.-P. Tian and S.-D. Yang, *Angew. Chem. Int. Ed.*, 2013, **52**, 3972; (h) F. Jia, K.-S. Liu, H. Xi, S.-L. Lu and Z.-P. Li, *Tetrahedron Lett.*, 2013, **54**, 6337; (i) X.-H. Wei, Y.-M. Li, A.-X. Zhou, T.-T. Yang and S.-D. Yang, *Org. Lett.*, 2013, **15**, 4158; (j) K. Matcha, R. Narayan and A. P. Antonchick, *Angew. Chem. Int. Ed.*, 2013, **52**, 7985; (k) H. Wang, L.-N. Guo and X.-H. Duan, *Adv. Synth. Catal.*, 2013, **355**, 2222; (l) S.-L. Zhou, L.-N. Guo, S. Wang and X.-H. Duan, *Chem. Commun.*, 2014, **50**, 3589; (m) Q. Dai, J. Yu, Y. Jiang, S. Guo, H. Yang and J. Cheng, *Chem. Commun.*, 2014, **50**, 3865; (n) J.-H. Fan, M.-B. Zhou, Y. Liu, W.-T. Wei, X.-H.

Ouyang, R.-J. Song and J.-H. Li, *Synlett*, 2014, **25**, 657; (o) X.-H. Ouyang, R.-J. Song and J.-H. Li, *Eur. J. Org. Chem.*, 2014, 3395; (p) X. Li, X. Xu, P. Hu, X. Xiao and C. Zhou, *J. Org. Chem.*, 2013, **78**, 7343; (q) G. Wang, S. Wang, J. Wang, S.-Y. Chen and X.-Q. Yu, *Tetrahedron* 2014, **70**, 3466; (r) Y.-M. Li, X.-H. Wei, X.-A. Li and S.-D. Yang, *Chem. Commun.*, 2013, **49**, 11701; (s) Y.-M. Li, Y. Shen, K.-J. Chang and S.-D. Yang, *Tetrahedron Lett.*, 2014, **55**, 2119; (t) T. Shen, Y. Yuan and N. Jiao, *Chem. Commun.*, 2014, **50**, 554; (u) W. Fu, F. Xu, Y. Fu, C. Xu, S. Li and D. Zou, *Eur. J. Org. Chem.*, 2014, 709; (v) J. Liu, S. Zhuang, Q. Gui, X. Chen, Z. Yang and Z. Tan, *Eur. J. Org. Chem.*, 2014, 3196; (w) F. Yin and X.-S. Wang, *Org. Lett.*, 2014, **16**, 1128; (x) B. Zhou, W. Hou, Y. Yang, H. Feng and Y. Li, *Org. Lett.*, 2014, **16**, 1322; (y) W. Wei, J. Wen, D. Yang, X. Liu, M. Guo, R. Dong and H. Wang, *J. Org. Chem.* 2014, **79**, 4225.

9 For papers on the cyclization of *N*-arylacrylamides using visible light photoredox catalysis: (a) P. Xu, J. Xie, Q. Xue, C. Pan, Y. Cheng and C. Zhu, *Chem. Eur. J.*, 2013, **19**, 14039; (b) J. Xie, P. Xu, H. Li, Q. Xue, H. Jin, Y. Cheng and C. Zhu, *Chem. Commun.*, 2013, **49**, 5672; (c) W. Fu, F. Xu, Y. Fu, M. Zhu, J. Yu, C. Xu and D. Zou, *J. Org. Chem.* 2013, **78**, 12202; (d) X.-J. Tang, C. S. Thomason and W. R. Dolbier, Jr., *Org. Lett.*, **2014**, **16**, 4594.

10 For selective reviews on the visible light photoredox catalysis, see: (a) P. Melchiorre, *Angew. Chem. Int. Ed.*, 2009, **48**, 1360; (b) K. Zeitler, *Angew. Chem. Int. Ed.*, 2009, **48**, 9785; (c) T. P. Yoon, M. A. Ischay and J. Du, *Nat. Chem.*, 2010, **2**, 527; (d) J. M. R. Narayanan and C. R. J. Stephenson, *Chem. Soc. Rev.*, 2011, **40**, 102; (e) F. Teplý, *Collect. Czech. Chem. Commun.*, 2011, **76**, 859; (f) J. Xuan and W.-J. Xiao, *Angew. Chem. Int. Ed.*, 2012, **51**, 6828; (g) D. P. Hari and B. König, *Angew. Chem. Int. Ed.*, 2013, **52**, 4734.

11 For representative papers on the use of aryldiazonium salts in organic synthesis including the Sandmeyer reaction: (a) T. Sandmeyer, *Ber. Dtsch. Chem. Ges.*, 1884, **17**, 1633; (b) T. Sandmeyer, *Ber. Dtsch. Chem. Ges.*, 1884, **17**, 2650; (c) H. H. Hodgson, *Chem. Rev.*, 1947, **40**, 251; the Pschorr reaction: (d) R. Pschorr, *Ber.*, 1896, **29**, 496; (e) P. H. Leake, *Chem. Rev.*, 1956, **56**, 27; the visible light photoredox catalysis: (f) H. Cano-Yelo and A. Deronzier, *J. Chem. Soc., Perkin Trans.*, 2 1984, 1093; (g) H. Cano-Yelo and A. Deronzier, *J. Chem. Soc., Faraday Trans. 1*, 1984, 3011; (h) H. Cano-Yelo and A. Deronzier, *Tetrahedron Lett.*, 1984, **25**, 5517; (i) D. P. Hari, P. Schroll and B. König, *J. Am. Chem. Soc.*, 2012, **134**, 2958; (j) P. Schroll, D. P. Hari and B. König, *ChemistryOpen*, 2012, **1**, 130; (k) T. Hering, D. P. Hari and B. König, *J. Org. Chem.*, 2012, **77**, 10347; (l) T. Xiao, X. Dong, Y. Tang and L. Zhou, *Adv. Synth. Catal.*, 2012, **354**, 3195.

12 For reviews: (a) B. S. Jensen, *CNS Drug Rev.* 2002, **8**, 353; (b) C. Marti and E. M. Carreira, *Eur. J. Org. Chem.* 2003, 2209; (c) H. Lin and S. J. Danishefsky, *Angew. Chem. Int. Ed.* 2003, **42**, 36; (d) C. V. Galliford and K. A. Scheidt, *Angew. Chem. Int. Ed.* 2007, **46**, 8748; (e) A. Millemaggi and R. J. K. Taylor, *Eur. J. Org. Chem.* 2010, 4527; (f) F. Zhou, Y.-L. Liu and J. Zhou, *Adv. Synth. Catal.* 2010, **352**, 1381; (g) S. R. S. Rudrangi, V. K. Bontha, V. R. Manda and S. Bethi, *Asian J. Research Chem.* 2011, **4**, 335; For selected papers: (h) G. Deak, M. Doda, L. Gyorgy, L. Hazai and L. Sterk, *J. Med. Chem.* 1977, **20**, 1384; (i) A. Numata, P. Yang, C. Takahashi, R. Fujiki, M. Nabae and E. Fujita, *Chem. Pharm. Bull.* 1989, **37**, 648; (j) S. Hibino and T. Choshi, *Nat. Prod. Rep.* 2001, **18**, 66; (k) A. S. Ratnayake, W. Y. Yoshida, S. L. Mooberry and T. K. Hemscheidt, *J. Org. Chem.* 2001, **66**, 8717; (l) M. Kuriyama, S. Tanigawa, Y. Kubo, Y. Demizu and O. Onomura, *Tetrahedron: Asymmetry* 2010, **21**, 1370.

13 The detailed data, including kinetic isotope effect experiments (Scheme S1) and the quantum yield (Figure S1), are summarized in of Supporting Information.

65 14 (a) H. Gerner and H. J. Khun, *J. Chem. Soc., Perkin Trans. 2* 1999, 2671; (b) A. P. Pelliccioli and J. Wirz, *Photochem. Photobiol. Sci.* 2002, **1**, 441.

15 (a) C. Hanekamp and P. A. A. Klusener, *Synth. Commun.* 1989, **19**, 2677; (b) Z.-Q. Wang, Y. Lei, M.-B. Zhou, G.-X. Chen, R.-J. Song, Y.-X. Xie, J.-H. Li, *Org. Lett.* 2011, **13**, 14; (c) R. Bejot, S. Tisserand, L. M. Reddy, D. K. Barma, R. Baati, J. R. Falck and C. Mioskowski, *Angew. Chem. Int. Ed.* 2005, **44**, 2008.