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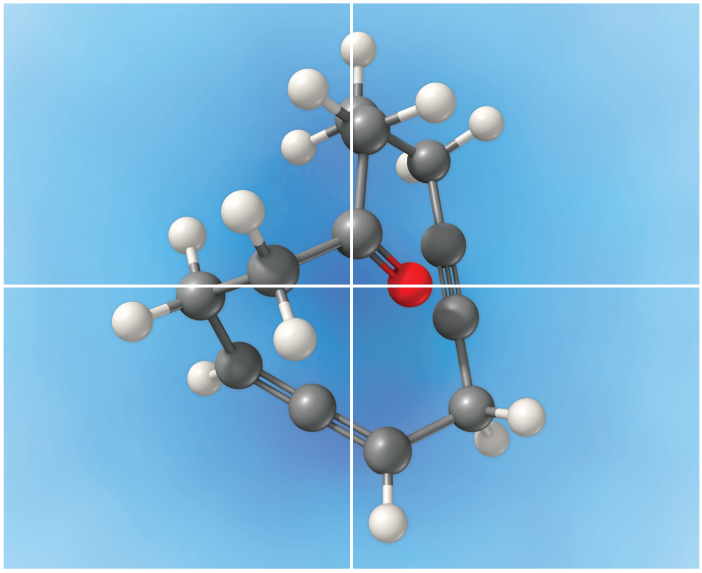

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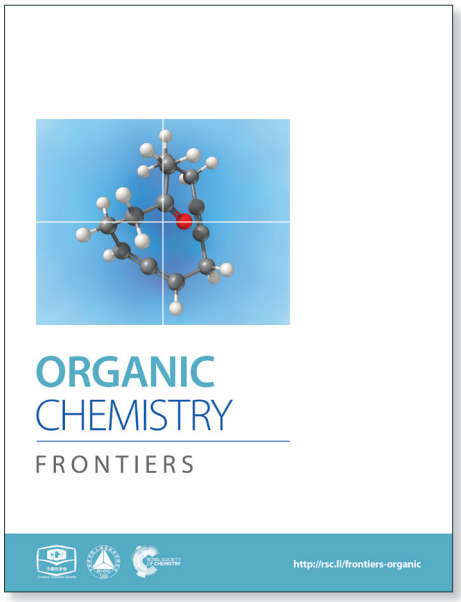

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1,2-Alkylarylation of Activated Alkenes with Dual C-H Bonds of Arenes and Alkyl Halides Toward Polyhalo-Substituted Oxindoles

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We describe here a new visible light facilitated radical strategy for 1,2-alkylarylation of activated alkenes with a C(sp^2)-H bond of arenes and a C(sp^3)-H bond of alkyl halides. This method achieves selective scission of the C(sp^3)-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 pharmaceticals and materials), albeit arousing controversy for their effects of these compounds on the environment and on human and animal health.[1] 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).[1-3] As a result, the introduction of the polychloromethyl groups into the known bioactive molecules remains an active area.[2,3] 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 organotins (often Bu_3SnH), are usually used to accomplish these transformations.[4] However, methods for the carbon-centered radical formation from organohalides by selectively splitting carbon-hydrogen bond, not the carbon-halogen bond, are quite rare.[5] 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^3)-H bonds to access functionalized oxindoles has been developed (Schemes 1a and 1b).[6,7] We have first reported a Fe-catalyzed oxidative 1,2-alkylarylation of activated alkenes with an aryl C(sp^2)-H bond and a C(sp^3)-H bond adjacent to a heteroatom for building oxindoles using TBHP oxidant, in which proceeds via a radical process (Scheme 1a).[6a] Subsequently, the Guo/Duan group,[7a-d] Liang group,[7e] Liu group[7f] and our group[7b] have independently developed the other new radical cyclization of *N*-arylmethacrylamides with alkyl C(sp^3)-H bonds, including the C(sp^3)-H bonds adjacent to an aryl,[6b,7b,7f] a hydroxyl[7a,7e] or dicarbonyl groups[7c-d] and the C(sp^3)-H bonds in simple alkanes [7f](Schemes 1a and 1b). However, these methods required unfriendly radical initiators including peroxides and $K_2S_2O_8$ under harsh conditions (often at over 100 °C), thereby greatly restricting their applications in synthesis and industry.[5b,6-8] Thus, a new mild radical strategy avoiding the use of unfriendly radical initiators for the cyclization of *N*-arylmethacrylamides with alkyl C(sp^3)-H bonds is highly desirable. Very recently, we described a visible light catalysis strategy for the cyclization of *N*-arylmethacrylamides alkyl C(sp^3)-H bonds adjacent to a carbonyl group, which proceeds under mild conditions.[6c] 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^3)-H bonds.[9,10]

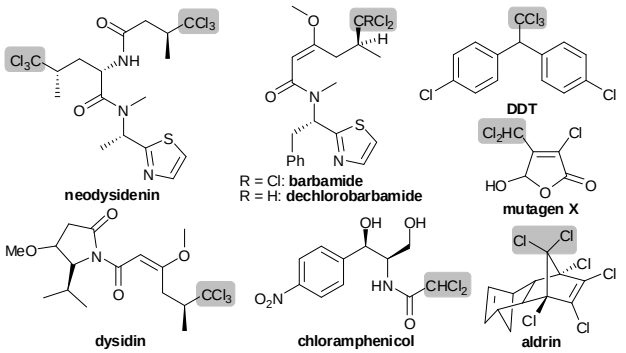
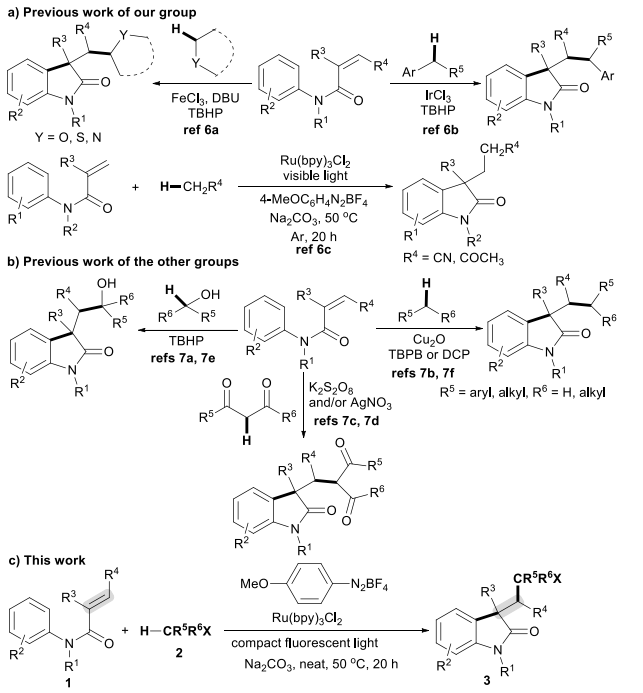


Figure 1. Important Compounds with Polychloro Groups.

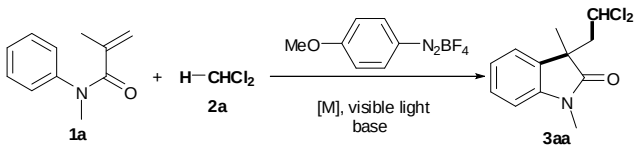
We began with our investigation on the reaction between *N*-methyl-*N*-phenylmethacrylamide (**1a**) and dichloromethane (DCM, **2a**) in the presence of visible light catalysts and 4-methoxybenzenediazonium tetrafluorobrorate (Table 1). In the presence of 4-$MeOC_6H_4N_2BF_4$ and Na_2CO_3, the desired 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 promoted the 4-$MeOC_6H_4N_2BF_4$-based reaction.[5a,6c,10,11] As expected, treatment of substrate **1a** with DCM **2a**, $Ru(bpy)_3Cl_2$, 4-methoxybenzenediazonium tetrafluorobrorate 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_2CO_3 was the most effective (entries 2-5). While Na_2CO_3 as the base gave 96% yield of oxindole **3aa** (entry 2), Et_3N as the base decreased the yield to only 31% (entry 3), Cs_2CO_3 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 % $Ru(bpy)_3Cl_2$ (entry 8). It is noteworthy that the reaction proceeds in $MeCO_2{}^nBu$ smoothly, albeit with slightly lowering the yield (entry 9). Two other visible light photoredox catalysts, $Ir(ppy)_3$ 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 tetrafluorobrorate 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).

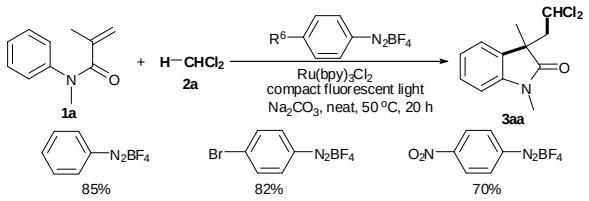
Table 1 Screening of Optimal Conditions[a]



Entry	[M] [mol%]	base	T [°C]	Isolated Yield [%]
1[b]	—	Na_2CO_3	50	55
2	$Ru(bpy)_3Cl_2$ (5)	Na_2CO_3	50	96
3	$Ru(bpy)_3Cl_2$ (5)	Et_3N	50	31
4	$Ru(bpy)_3Cl_2$ (5)	Cs_2CO_3	50	37
5	$Ru(bpy)_3Cl_2$ (5)	—	50	trace
6	$Ru(bpy)_3Cl_2$ (5)	Na_2CO_3	25	8
7	$Ru(bpy)_3Cl_2$ (5)	Na_2CO_3	80	83
8	$Ru(bpy)_3Cl_2$ (5)	Na_2CO_3	50	80
9[c]	$Ru(bpy)_3Cl_2$ (5)	Na_2CO_3	50	75
10	$Ir(ppy)_3$ (5)	Na_2CO_3	50	95
11	Eosin Y (5)	Na_2CO_3	50	68
12[d]	$Ru(bpy)_3Cl_2$ (5)	Na_2CO_3	50	59
13[e]	$Ru(bpy)_3Cl_2$ (5)	Na_2CO_3	50	0

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (15 mmol), [M], 4-$MeOC_6H_4N_2BF_4$ (2 equiv) and base (2 equiv) with 36 W compact fluorescent light for 20 h under argon atmosphere. [b] Without additional light. [c] **2a** (6 mmol) and $MeCO_2{}^nBu$ (anhydrous, 0.5 mL). [d] 4-$MeOC_6H_4N_2BF_4$ (1 equiv). [e] Without 4-$MeOC_6H_4N_2BF_4$.

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

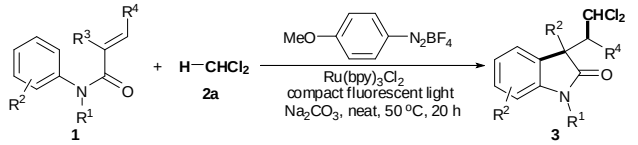


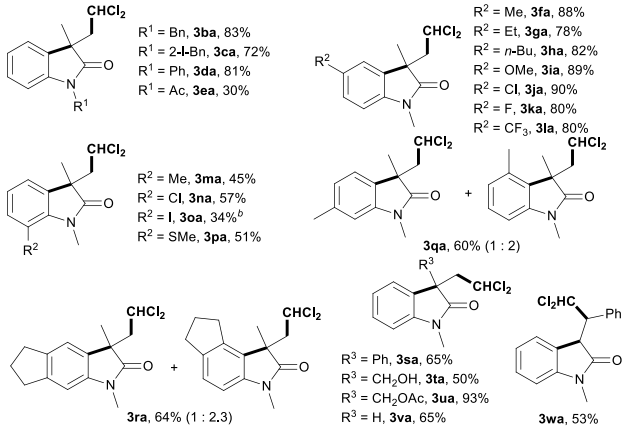
Scheme 2. Screening of Effect of Diazonium Salts.

With the optimal conditions in hand, we first employed *N*-arylacrylamides **1** to exploit the scope of 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_3, 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_3 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_2OH or CH_2OAc, at the 2 position of the acrylamide moiety were consistent with the optimal conditions (Products **3sa-ua**). Free CH_2OH-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**), $Ru(bpy)_3Cl_2$, 4-methoxybenzenediazonium tetrafluorobrorate, Na_2CO_3 and

Table 2 Screening Scope of N-Arylacrylamides **(1)** [a]



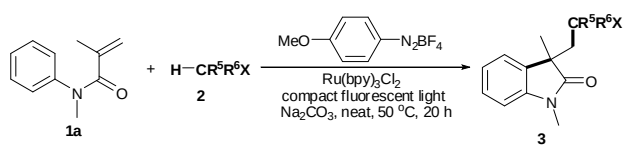


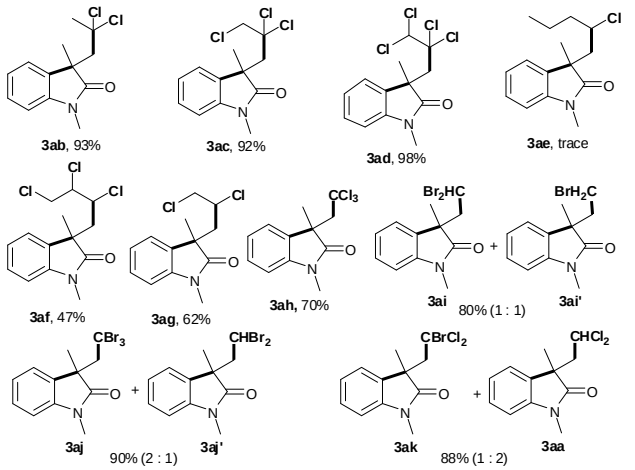
[a] Reaction conditions: **1** (0.3 mmol), **2a** (15 mmol), $Ru(bpy)_3Cl_2$ (5 mol%), 4-$MeOC_6H_4N_2BF_4$ (2 equiv) and Na_2CO_3 (2 equiv) with 36 W compact fluorescent light at 50 °C for 20 h under argon atmosphere. [b] A side de-I product **3aa** was isolated in 36% yield.

36 W compact fluorescent light. Using 1,1-dichloroethane (**2b**), the C(sp^3)-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^3)-H bond. Indeed, both 1,1,2-trichloroethane (**2c**) and 1,1,2,2-tetrachloroethane (**2d**) were suitable substrates; moreover, the C(sp^3)-H bond adjacent to dichloride atoms, not the C(sp^3)-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_2Br_2 (**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**)[a]

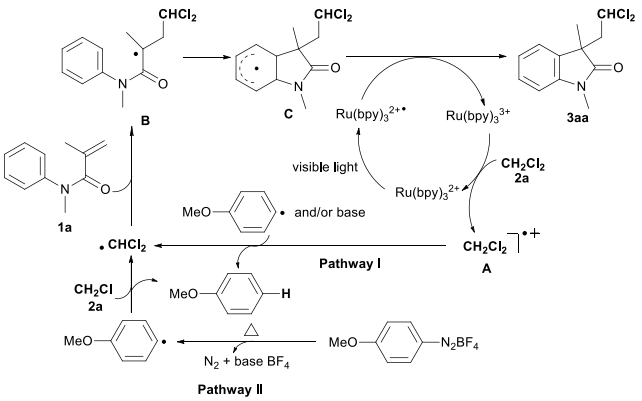




[a] Reaction conditions: **1a** (0.3 mmol), **2** (15 mmol), $Ru(bpy)_3Cl_2$ (5 mol%), 4-$MeOC_6H_4N_2BF_4$ (2 equiv) and Na_2CO_3 (2 equiv) with 36 W compact fluorescent light at 50 °C for 20 h under argon atmosphere.

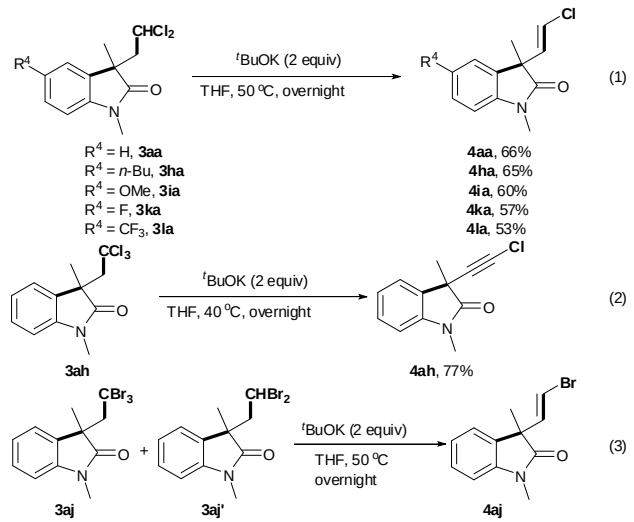
To understand the current radical reaction, the mechanisms outlined in Scheme 3 are proposed on the basis of the present results[13] and the literature reports.[5-11] Initially, $\cdot CHCl_2$ radical may be generated via two pathway: (1) Single-electron oxidation of DCM **2a** by $Ru(bpy)_3^{3+\cdot}$ gives a carbocation **A**, followed by deprotonation leading to the $\cdot CHCl_2$ radical (Pathway I), and/or (2) hydrogen abstraction of DCM **2a** by a phenyl radical which was generated from the diazonium salt forms the $\cdot CHCl_2$ radical (Pathway I).[6c,10,11] Subsequently, addition of $\cdot CHCl_2$ 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 $Ru(bpy)_3^{2+\bullet}$ takes place to yield product **3aa** and $Ru(bpy)_3^{3+}$. Notably, This photoinduced mechanism is supported by the quantum yield ($\Phi x = 0.056$).[13,14]

On the basis of the results in Table 1, the $\cdot CHCl_2$ radical can also be directly formed from the reaction between CH_2Cl_2 (**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_4^-.



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).[15] After brief screening of bases, ^{t}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 **4ai** 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 ^{t}BuOK.

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

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