Visible light photocatalysis has received considerable attention in recent years owing to the mild reaction conditions, green and sustainable chemistry features, and high atom-economy. As reported in the literature, two different activation modes are commonly used. Most of the photochemical reactions proceed through a single-electron transfer (SET) process from the excited photosensitizers to the organic substrates or reagents. The other activation mode is an energy transfer (EnT) process in which no charge separation is involved in the whole process. This EnT activation pathway mainly depends on the triplet-state energies of the photosensitizers and the organic substrates. Synthetically useful visible light-induced organic transformation reactions through the EnT process have been successfully developed in the past decades.

The synthesis of multisubstituted alkenes is an important reaction because of their versatile utility as synthetic building blocks for organic synthesis and as structural elements contributing to the significant biological properties of natural products and pharmaceuticals. Unlike E-alkenes, the strategies for synthesis of thermodynamically less stable Z-alkenes are not readily accessible. Hammond and Arai developed pioneering photochemical $E \rightarrow Z$ isomerisations of stilbenes and styrenes and delineated the reaction mechanisms. Inspired by these mechanistic studies, visible light induced $E \rightarrow Z$ isomerization has attracted great interest. In 2014, Weaver and co-workers reported Ir(ppy)$_3$ catalyzed $E$ to $Z$ isomerization of allylamines proceeding via an EnT mechanism. In 2015, the Gilmour group developed photoisomerization of activated alkenes using (-)-riboflavin as an EnT photocatalyst. Furthermore, Gilmour and co-workers have reported photoisomerization of styrenyl boron species and selective isomerization of $\beta$-borylacrylates. In 2020, the same group reported a synthetic procedure for $E \rightarrow Z$ isomerization of $\beta$-borylacrylates via EnT using thioxanthone as the sensitizer eliminating the need of an aryl unit for alkene isomerization, and the inert aryl rings were replaced by a traceless BPin handle.

Arylvinyl halides are versatile synthetic intermediates for organic synthesis. In particular, transition metal-catalyzed cross couplings of vinyl halides with organometallics, such as, organoboronic and organozinc reagents, are efficient methods for synthesis of multisubstituted alkenes. However, synthesis of the thermodynamically less stable Z-isomer still poses a great challenge. In 2019, Yu’s group demonstrated a synthetically useful $E \rightarrow Z$ photocatalytic isomerization of styrenyl halides (Scheme 1). On the other hand, decarboxylation of $\alpha,\beta$-unsaturated arylvinyl acids accompanied by simultaneous replacement by halogen is a useful reaction for the synthesis of styrenyl halides. Considering the importance of Z-arylvinyl halides in the synthesis of multisubstituted alkenes, we hypothesize that it would be interesting to combine the halodecarboxylation of $\alpha,\beta$-unsaturated arylvinyl acids and photoisomerization of E-arylvinylhalides in a one pot sequential catalytic process. Herein, we report a novel method to synthesize Z-arylvinyl halides by visible

![Scheme 1](image)

Scheme 1  Photocatalytic synthesis of multisubstituted alkenes.
light Ir-photocatalyzed reaction of \(E\)-arylvinyl acids with \(N\)-halosuccinimide.

Our group has synthesized a series of new fluorescent quinolizinium compounds from quinolines and alkyne substrates.\(^{11}\) Due to the high tunability and high excited state reduction potentials of the fluorescent quinolizinium compounds, we proposed that the quinolizinium compounds could be used as photocatalysts for the synthesis of \(Z\)-arylhalides from \(\alpha,\beta\)-unsaturated arylvinyl acids.

With this idea in mind, we started the initial investigation by treatment of \((Z/E)-3\)-phenyl-2-butenoic acid (1a) with 2 equiv. of \(N\)-bromosuccinimide (NBS) in the presence of 5 mol% of photocatalyst 3a in \(\text{CH}_3\text{CN}\) at room temperature under 30 W blue LEDs irradiation. 36% NMR yield of the desired product \((Z/E)\)-3-phenyl-2-butenoic acid (2a) was obtained with modest selectivity \((Z/E = 44:56)\). Next, we optimized the reaction conditions by varying the additives. Adding \(K_2\text{CO}_3\) and TBAI, \(E\)-2a was obtained only (entries 2–3, Table 1). Interestingly, adding 1.0 equiv. of acetic acid as the additive, improvement in the \(Z/E\) ratio (52 : 48) (entry 1, Table 2). When the reaction was conducted with metal photocatalysts (\(0.3\) equiv. of K\text{CO}_3\)), the reaction solvent was \(\text{CH}_3\text{CN}\). No light irradiation.

Table 1. Optimization of the reaction conditions using quinoliziniums as photocatalyst

| Entry | Photocatalyst (PC) | Additive | Yield\(^a\) | \(Z/E\) |
|-------|-------------------|----------|-------------|--------|
| 1     | 3a                | —        | 45          | 44/56  |
| 2     | 3a                | 1 eq. \(K_2\text{CO}_3\) | 88         | 0/100  |
| 3     | 3a                | 1 eq. TBAI | 75         | 0/100  |
| 4     | 3a                | 1 eq. \(\text{CH}_3\text{CO}_2\text{H}\) | 43         | 56/44  |
| 5     | 3a                | 2 eq. \(\text{CH}_3\text{CO}_2\text{H}\) | 35         | 77/23  |
| 6     | 3a                | 3 eq. \(\text{CH}_3\text{CO}_2\text{H}\) | 58         | 66/34  |
| 7     | 3a                | 2 eq. \(\text{PhCO}_2\text{H}\) | 21         | 99/1   |
| 8     | 3a                | 0.3 eq. \(\text{PhCO}_2\text{H}\) | 32         | 94/6   |
| 9     | 3b                | 0.3 eq. \(\text{PhCO}_2\text{H}\) | 29         | 86/14  |
| 10    | 3c                | 0.3 eq. \(\text{PhCO}_2\text{H}\) | 22         | 91/9   |
| 11    | 3d                | 0.3 eq. \(\text{PhCO}_2\text{H}\) | 38         | 84/16  |
| 12    | 3e                | 0.3 eq. \(\text{PhCO}_2\text{H}\) | 24         | 88/12  |
| 13    | 3f                | 0.3 eq. \(\text{PhCO}_2\text{H}\) | 33         | 94/6   |
| 14    | 3g                | 0.3 eq. \(\text{PhCO}_2\text{H}\) | 35         | 86/14  |
| 15    | 3h                | 0.3 eq. \(\text{PhCO}_2\text{H}\) | 49         | 69/31  |
| 16    | 3i                | 0.3 eq. \(\text{PhCO}_2\text{H}\) | 63         | 60/40  |

\(^a\) Reaction conditions: treatment of \(E\)-1a (0.2 mmol), NBS (0.4 mmol) and photocatalyst (5 mol\%) in 2 mL of \(\text{CH}_3\text{CN}\) under \(N_2\) and blue LEDs light for 17 hours at room temperature. \(^b\) Yield was determined by \(^1\text{H}\) NMR using dibromomethane as internal standard. \(^c\) The Z/E ratio was determined by \(^1\text{H}\) NMR spectroscopy.

Then, we screened the reaction conditions with metal photocatalyst Ir(ppy)\(_3\)). Styrenyl halide 2a was obtained in 48% NMR yield in a Z/E ratio (52 : 48) (entry 1, Table 2). When the reaction conditions of 2 mol% Ir(ppy)\(_3\) with 0.3 equiv. of \(\text{K}_2\text{CO}_3\) were used, the reaction proceeded to give the desired product 2a with 61 : 39 Z/E ratio. Increasing the base loading from 0.3 equiv. to 2 equiv. improved the NMR yield of 2a from 31% to 60% and gave a 97 : 3 Z/E ratio (entry 5, Table 2). When we further increased the loadings of the base, the yield dropped slightly (entries 6
and 7, Table 2). Next, various inorganic and organic bases were examined in this reaction, and \(\alpha,\beta\)-unsaturated arylvinyl acid \(1a\) was found to be successfully converted to \(2a\) in moderate to good \(Z/E\) ratios (entries 8–13, Table 2). Several other photocatalysts were also screened, such as, \(\text{Ir}(\text{ppy}))_3\), \(\text{Ir(}^{\text{diFppy})_3}\), \(\text{Mes-Acr-BF}_4\), \(\text{Ru(bpy})_3(\text{PF}_6)_2\) and \(\text{Ru(bpy})_3\text{Cl}_2\), but none of them gave better yields or \(Z/E\) ratios (entries 14–18, Table 2). Only \(E-2a\) was obtained in the absence of light (entry 19, Table 2), and a trace amount of \(Z-2a\) was observed without photocatalyst (entry 20, Table 2).

After optimizing the reaction conditions, we next sought to explore the scope of the reaction. The results summarized in Table 3 show that this reaction provides a straightforward route to a variety of \(Z\)-aryl halides \(2\) directly from \(E\)-arylvinyl acids \(1\). Different alkyl substitutions at the \(\alpha\) position (\(R\)), such as methyl, ethyl, propyl and butyl were compatible in the reaction, affording the corresponding \(Z\)-arylvinyl bromides in high stereoselectivities (up to >99/1 \(Z/E\) ratios). The reaction was affected by the electronic effect of the substituents on the aryl ring. Substrates bearing electron-donating group (OMe), phenyl, and halogens gave the desired \(Z-2\) in high \(Z/E\) ratios (up to >99/1) (\(2d\)–\(2j\), Table 3). However, \(E\)-arylvinyl acid \(1k\) with electron-withdrawing group \((\text{CF}_3)\) did not afford the corresponding bromide \(2k\). The efficiency of the reaction was not impeded by \(meta\)-substituents on the aryl ring (\(2l\) and \(2m\), 53% and 42% yield, respectively, 99/1 \(Z/E\) ratios). In contrast, the \(ortho\)-substituent hindered the reaction, only providing the halodecarboxylation product \(E-2n\). In addition, naphthyl ring was also compatible under these mild reaction conditions giving \(Z-2o\) (\(Z/E = 80/20\)) in 79% yield. \(N\)-Chlorosuccinimide (NCS) can also be used in this halodecarboxylation/isomerization smoothly to afford \(Z-2p\) in 96 : 4 \(Z/E\) ratios. When 1.03 g of \(1j\) was used, the corresponding styrenyl bromide \(Z-2j\) was obtained without compromising on yield and stereoselectivity, representing the robustness of this reaction.

To gain mechanistic insight on this reaction, the reaction progress was monitored under the optimized reaction conditions (Scheme 2). Complete halodecarboxylation of \(E-1c\) was observed in 1 hour to give \(E-2c\), which suggests that the isomerisation is the rate-determining step. Some product \(Z-2c\) was obtained after 2 hours. Almost complete \(E \rightarrow Z\) isomerization was observed over the course of 16 hours.

At last, we performed two \(Pd\)-catalyzed coupling reactions with styrenyl bromide \(Z-2j\) to further illustrate the synthetic utility of this cascade reaction (Scheme 3). When 4-methoxypyphenylboronic acid was treated with bromide \(Z-2j\) using \(\text{Pd(PPh}_3)_4\) as catalyst, Suzuki–Miyaura cross coupling reaction\(^{14}\) successfully afforded trisubstituted alkenes \(Z-4\) \(Z/E = 98/2\) in 78% yield. Moreover, Sonogashira coupling reaction\(^{15}\) with 1-ethyl-4-methylbenzene gave enyne \(Z-5\) \(Z/E = 98/2\) in 87% yield.

### Conclusions

In conclusion, we have developed an efficient visible light photocatalytic strategy to synthesize \(Z\)-arylvinyl halides directly from \(E\)-arylvinyl acid with \(N\)-halosuccinimide through a sequential halodecarboxylation/photoisomerization sequence with up to >99/1 \(Z/E\) ratio and 86% yield. A series of \(E\)-arylvinyl...
acids were converted to Z-arylvinyl halides with high stereoselectivity under mild reaction conditions.

Conflicts of interest
There are no conflicts to declare.

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