

## RESEARCH ARTICLE OPEN ACCESS

Photoinduced Selective *E/Z* Isomerization and Site-Selective C(sp<sup>2</sup>)-H Functionalization of Diaryl MethoximesYuki Hirata<sup>1,2</sup> | Masayuki Danjo<sup>1</sup> | Kosuke Higashida<sup>1</sup> | Tatsuhiko Yoshino<sup>1</sup>  | Shigeki Matsunaga<sup>1,2</sup> <sup>1</sup>Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto, Japan | <sup>2</sup>Faculty of Pharmaceutical Sciences, Hokkaido University, Kita-ku, Sapporo, Japan**Correspondence:** Tatsuhiko Yoshino ([yoshino.tatsuhiko.5j@kyoto-u.ac.jp](mailto:yoshino.tatsuhiko.5j@kyoto-u.ac.jp)) | Shigeki Matsunaga ([matsunaga.shigeki.5x@kyoto-u.ac.jp](mailto:matsunaga.shigeki.5x@kyoto-u.ac.jp))**Received:** 25 March 2026 | **Revised:** 19 May 2026 | **Accepted:** 22 May 2026**Keywords:** C-H functionalization | isomerization | photocatalysts | Z-selectivity

## ABSTRACT

Selective *E/Z* isomerization of diaryl oxime derivatives, in which the two isomers have similar geometric and electronic characteristics, was achieved using photosensitizers with appropriate triplet energies. We found that suitable substituents can modulate conjugation in methoximes, thereby generating a triplet energy gap between the *E* and *Z* isomers. In addition, *Z*-isomer-enriched methoximes enabled site-selective C(sp<sup>2</sup>)-H functionalization.

## 1 | Introduction

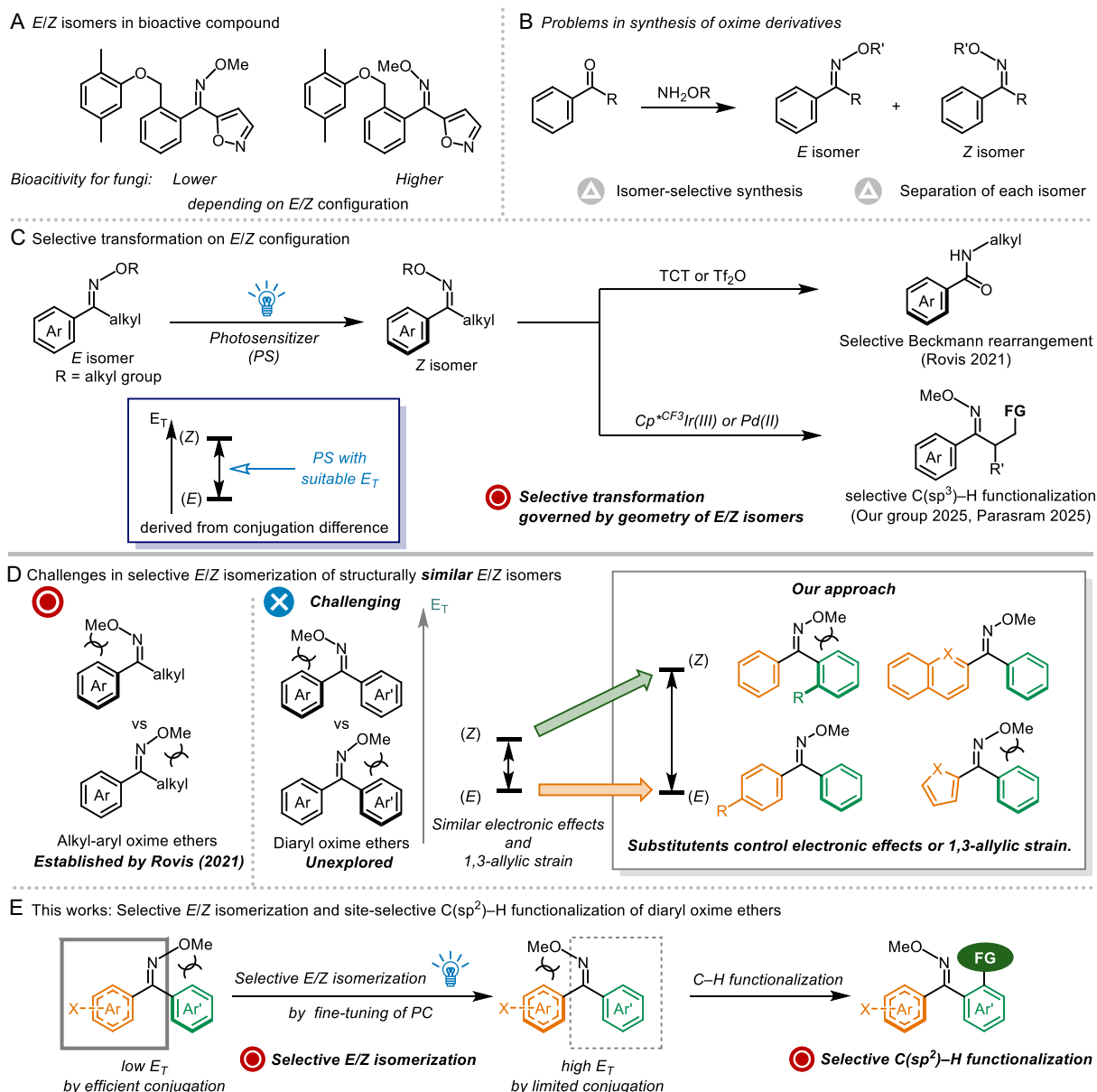
Oxime derivatives are valuable precursors to amides, amines, and other nitrogen-containing compounds in both fine and industrial chemistry [1–3]. They exist as *E/Z* isomers depending on the geometry of the imine moiety. This *E/Z* configuration can influence biologic activity (e.g., compounds against plant-pathogenic fungi in Figure 1A) [4, 5]. In organic synthesis, conventional reactions such as the Beckmann rearrangement show *E/Z*-dependent chemoselectivity [6]. These examples demonstrate that control of the *E/Z* configuration is pivotal; however, oxime derivatives are typically obtained from the corresponding ketones under thermal conditions as *E/Z* mixtures that are often inseparable (Figure 1B) [7]. To overcome this limitation, Padwa and coworkers pioneered photoinduced *E/Z* isomerization of oxime derivatives, furnishing *Z*-enriched oxime ethers [8–12]. Recently, Rovis and coworkers developed selective *E/Z* isomerization of alkyl-aryl oxime derivatives under visible light using a photosensitizer (Figure 1C, top) [13]. Under visible-light irradiation, a photosensitizer with an appropriate triplet energy preferentially sensitizes the *E* isomer, which has a lower triplet energy due to extended conjugation, thereby enriching the *Z* isomer. In this strategy, a photosensitizer with a triplet energy

between those of *E* and *Z* isomer would be suitable although the best-performing photosensitizer is not always obvious. They further investigated site-selective Beckmann rearrangement by leveraging the controlled orientation of the OH group on the imino nitrogen in oximes, which serves as the leaving group. Our group demonstrated that a biased *E/Z* configuration of alkyl-aryl oxime ethers, achieved by photoinduced *E/Z* isomerization, enables site-selective C(sp<sup>3</sup>)-H functionalization as well as switchable C(sp<sup>3</sup>)-H/C(sp<sup>2</sup>)-H and C(sp<sup>2</sup>)-H/C(sp<sup>3</sup>)-H functionalization using Cp\*CF<sub>3</sub>Ir(III) (Figure 1C, bottom) [14]. Following this work, Parasram and coworkers reported sequential C(sp<sup>2</sup>)-H/C(sp<sup>3</sup>)-H functionalization by combining a Pd(II) catalyst with an organic photosensitizer [15].

While selective *E/Z* isomerization using photosensitizers and site-selective transformations have been demonstrated for alkyl-aryl oxime derivatives (Figure 1D, left), photoinduced *E/Z* isomerization to obtain enriched diaryl oxime derivatives remains unexplored (Figure 1D, right). The selectivity of *E/Z* isomerization would depend on the difference of triplet energy between *E* and *Z* isomers, which would be derived from the conjugation gap of the isomers based on substituents and 1,3-allylic strain [16].

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**FIGURE 1** | (A) Bioactivity depending on the *E/Z* configuration. (B) Difficulties in synthesis of oxime derivatives. (C) Selective transformation of oxime derivatives by controlled configuration. (D) Difficulty of selective *E/Z* isomerization of diaryl methoximes. (E) This work: selective *E/Z* isomerization of diaryl methoximes and site-selective *E/Z* isomerization.

When diaryl oxime derivatives have structurally and electronically similar two aryl groups, it would be difficult for a photosensitizer to recognize the differences of triplet energy between the *E* and *Z* isomers. This issue is also relevant and has been investigated in the photosensitized *E/Z* isomerization of 1,1-diaryl alkenes, which are C=C analogs of oxime ethers [17–23]. Although Kawamura and coworkers reported *E/Z* isomerization of a few diaryl oxime ethers using singlet oxygen, the reaction proceeds through complicated intermediates, and the substrate scope is limited [24]. In addition, direct excitation of diaryl oxime ethers under ultraviolet irradiation would induce decomposition of an oxime ether [25]. To the best of our knowledge, an investigation of selective isomerization of diaryl oxime derivatives via simple triplet energy transfer under mild conditions has not yet been reported.

Herein, we report that photosensitizers with appropriate triplet energies enable selective *E/Z* isomerization of diaryl methoximes bearing different aryl groups that produce a triplet energy difference between the *E/Z* isomers (Figure 1D right and 1E left). Control of the degree of conjugation by substituents and 1,3-allylic strain differentiates triplet energy of *E/Z* isomers of diaryl methoximes. Various diaryl methoximes were categorized into four classes according to the characteristics of their substituents, and successfully underwent selective *E/Z* isomerization with an optimal sensitizer. We further demonstrated that selectively isomerized oxime ethers enable site-selective C(sp<sup>2</sup>)-H functionalization (Figure 1E, right). The geometry of the directing group, determined by the *E/Z* configuration, controls the site-selectivity of C-H functionalization in diaryl

methoximes, and C–H functionalization following isomerization preferentially furnishes products derived from one isomer.

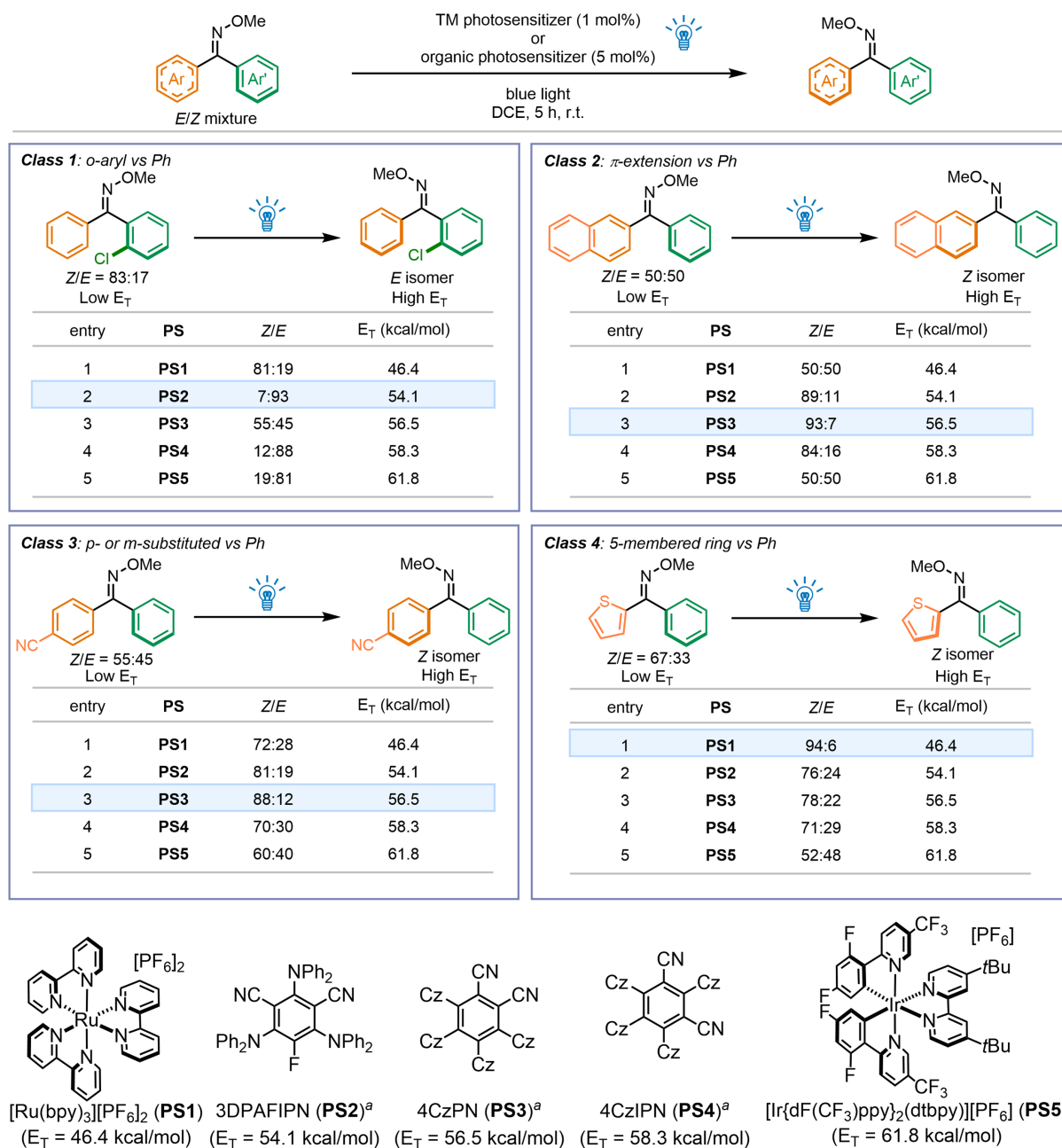
## 2 | Results and Discussion

### 2.1 | Optimized Reaction Conditions and Control Experiments

We first classified potential substrates for selective isomerization into four classes in which modification of one aryl unit was expected to modulate the triplet energy gap between the *E* and *Z* isomers. We then investigated suitable photosensitizers for selective *E/Z* isomerization (Figure 2).

#### 2.1.1 | Class 1: Methoximes Bearing an Ortho-Substituted Aryl Group with a Twisted Structure (Figure 2, Top Left)

In *Z* isomers, where the OMe moiety is oriented toward the aryl group bearing an *o*-substituent, the phenyl ring and the C=N moiety are efficiently conjugated, leading to a lower triplet energy (Class 1, left). In *E* isomers, where the OMe moiety is oriented toward the phenyl group, steric repulsion from the *o*-substituent on the aryl group and 1,3-allylic strain between the OMe moiety and phenyl group [16] induce a highly twisted conformation that inhibits conjugation and increases the triplet energy (Class 1, right). We selected *o*-chloro methoxime **1a** (*Z/E* = 83:27) as a model substrate for Class 1 and investigated selective isomerization using photosensitizers. A series of photosensitizers



**FIGURE 2** | Classified substrates and screening of photosensitizers: Cz = 9*H*-carbazol-9-yl.

spanning a range of triplet energies was screened to identify an appropriate catalyst. [Ru(bpy)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> (**PS1**) ( $E_T$ =46.4 kcal/mol) [13], 3DPAFIPN (**PS2**) ( $E_T$ =54.1 kcal/mol) [26], 4CzPN (**PS3**) ( $E_T$ =56.5 kcal/mol) [27], 4CzIPN (**PS4**) ( $E_T$ =58.3 kcal/mol) [27], and [Ir{dF(CF<sub>3</sub>)ppy}<sub>2</sub>(dtbpy)][PF<sub>6</sub>]<sub>2</sub> (**PS5**) ( $E_T$ =61.8 kcal/mol) [13] were evaluated (entries 1–5). Screening revealed that 3DPAFIPN ( $E_T$ =54.1 kcal/mol) was the optimal photosensitizer, inverting the *Z/E* ratio from 83:17 to 7:93 (entry 1). The *E/Z* configuration was determined by single-crystal X-ray diffraction analysis (See Supporting Information for details).

### 2.1.2 | Class 2: Methoximes with an $\pi$ -Extended Aryl Group (e.g., 2-Naphthyl) (Figure 2, Top Right)

In *E* isomers where the OMe group is typically oriented toward the phenyl ring, the aryl ring and the C=N moiety are efficiently conjugated (Class 2, left). They would exhibit a lower triplet energy than the corresponding *Z* isomers with less effective conjugation (Class 2, right). We examined oxime ether **1b**, bearing 2-naphthyl and phenyl groups, using photosensitizers with various triplet energies (entries 1–5). Screening disclosed that 4CzPN ( $E_T$ =56.5 kcal/mol) efficiently isomerized the substrate, shifting the *Z/E* ratio from 50:50 to 93:7 (entry 3). These results indicate that  $\pi$ -extension of the aryl group can increase the triplet energy difference between the *Z* and *E* isomers.

### 2.1.3 | Class 3: Methoximes Bearing an Aryl Group with a Functional Group for Conjugation (Figure 2, Bottom Left)

Given the applicability of the Class 2 substrate with a conjugated aryl group, we investigated a Class 3 substrate bearing a functional group that extends the conjugation. Conjugated electron-donating and electron-withdrawing groups are expected to reduce the triplet energy of the isomer in which the aryl ring with the functional group and the C=N unit are efficiently conjugated (*E* isomer; Class 3, left). Photosensitizer screening revealed that extending conjugation by a *p*-CN group in **1c** enabled selective *Z/E* isomerization (entry 3: 4CzPN,  $E_T$ =56.5 kcal/mol; *Z/E*=55:45 to 88:12).

### 2.1.4 | Class 4: Methoximes Including Five-Membered Rings (Figure 2, Bottom Right)

Five-membered rings such as a thiophene with a smaller internal angle leading to smaller 1,3-allylic strain [22], heteroatom effects, and related structural factors are expected to alter the triplet energies of the *E* (Class 4, left) and *Z* isomers (Class 4, right). Photosensitizer screening using a methoxime bearing 2-thienyl and phenyl groups (**1d**) is shown in Figure 2 (bottom, right). **PS1** ([Ru(bpy)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>,  $E_T$ =46.4 kcal/mol) facilitated selective *Z/E* isomerization (entry 1, *Z/E*=67:33 to 95:5).

## 2.2 | Substrate Scope in Selective *E/Z* Isomerization

With the results of the initial screenings in hand, we next examined methoximes bearing diverse substituents within the four classes (Figure 3). For almost all Class 1 substrates, 3DPAFIPN served as a suitable photosensitizer. Methyl-substituted substrate **1e** was well tolerated, *Z/E*=77:23 (before isomerization) to 11:89 (after isomerization), 97%. Notably, oxime ethers bearing halogen

substituents such as fluoro (**1f**), bromo (**1g**), and iodo (**1h**) substituents were also compatible with these conditions, affording the desired isomers (**1f**: *Z/E*=76:24 to 13:87, 83%; **1g**: *Z/E*=83:17 to 20:80, 96%; **1h**: *Z/E*=>95:5 to 8:92, 99%). The *o*-hydroxy substrate was also tolerated with this type of *Z/E* isomerization using DMF as the solvent (**1i**: *Z/E*=44:56 to 30:70, 98%). Furthermore, the presence of a 2-hydroxyl group on the aryl group opposite the 2-methyl phenyl moiety improved the *Z/E* ratio (**1j**: *E/Z*=89:11 to 11:89, >99%).

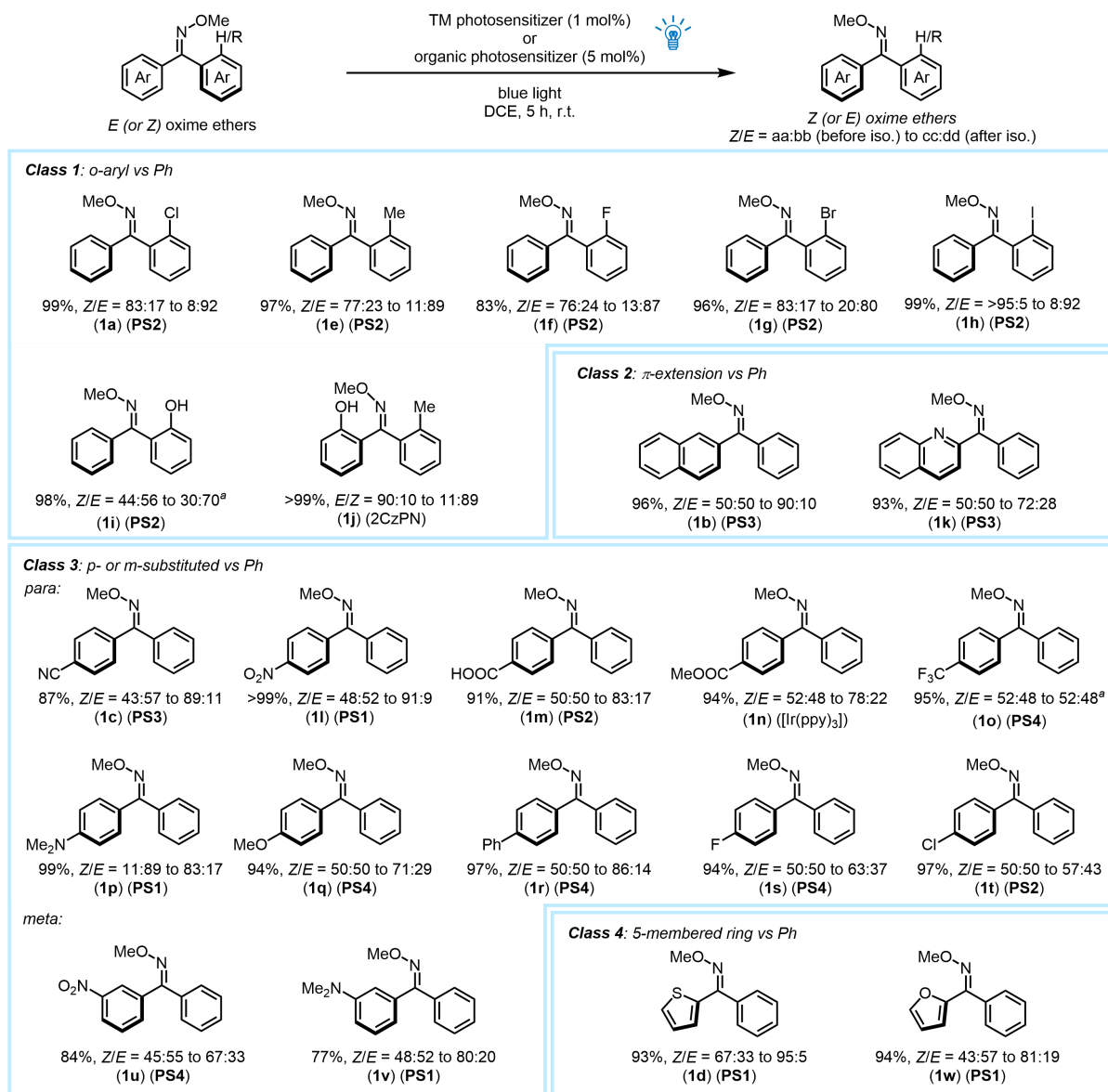
A 2-quinolyl-phenyl methoxime **1k** as a Class 2 substrate, underwent the desired selective *Z/E* isomerization using 4CzPN (**PS3**), albeit with slightly lower selectivity than the 2-naphthyl substrate **1b** (**1b**: *Z/E*=50:50 to 90:10; 96%, **1k**: *Z/E*=50:50 to 72:28, 93%).

As Class 3 substrates, methoximes bearing diverse *p*- or *m*-substituents were also investigated. The *p*-NO<sub>2</sub> substrate **1l**, featuring an electron-deficient and conjugated aryl group, underwent efficient isomerization with [Ru(bpy)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> (**PS1**,  $E_T$ =46.4 kcal/mol), affording the desired isomer (*Z/E*=48:52 to 91:9, >99%). Carboxylic acid (**1m**) and methyl ester (**1n**) substituents also promoted selective isomerization when the appropriate photosensitizers were used (**1m**: *Z/E*=50:50 to 83:17, 91%; **1n**: *Z/E*=52:48 to 78:22, 94%). In contrast, the CF<sub>3</sub>-substituted substrate **1o**, which provides little conjugation but is electron-withdrawing, showed no selectivity (**1o**: *Z/E*=52:48 to 52:48, 95%), indicating that conjugation is more crucial than electronic effects alone (See Supporting Information for results with other photosensitizers). Electron-donating substituents such as NMe<sub>2</sub> (**1p**) and OMe (**1q**) were also compatible, affording good selectivity (**1p**: *Z/E*=11:89 to 83:17, 99%; **1q**: *Z/E*=50:50 to 71:29, 94%). A *p*-phenyl substituent delivered the desired *Z* isomer with high selectivity (**1r**: *Z/E*=50:50 to 86:14, 97%), whereas *p*-halo substituents such as fluoro (**1s**) and chloro (**1t**), which are expected to minimally extend conjugation, only slightly improved the *Z* ratio (**1s**: *Z/E*=50:50 to 63:37, 94%; **1t**: *Z/E*=50:50 to 57:43, 97%). On the other hand, the *m*-NO<sub>2</sub> substrate **1u** showed only moderate selectivity using 4CzIPN (**PS4**,  $E_T$ =58.3 kcal/mol), compared with the *p*-substituted analog (*m*-NO<sub>2</sub> (**1u**): *Z/E*=45:55 to 67:33, 84% vs *p*-NO<sub>2</sub> (**1l**): *Z/E*=48:52 to 91:9, >99%). Together, these results indicate that efficient stabilization of the biradical character in the triplet state through *p*-substitution is crucial for achieving high selectivity. Similarly, the *m*-NMe<sub>2</sub> substrate **1v** afforded the desired *Z* isomer (*Z/E*=48:52 to 80:20, 77%).

A methoxime bearing a 2-thienyl group as five-membered ring **1d**, representing a Class 4 substrate, was also applicable to selective *E/Z* isomerization using [Ru(bpy)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> (**PS1**,  $E_T$ =46.4 kcal/mol) (*Z/E*=67:33 to 95:5, 93%). Likewise, 2-furyl group **1w** was also compatible with these conditions, although the selectivity was lower (*Z/E*=43:57 to 81:19, 94%).

## 2.3 | Site-Selective C(sp<sup>2</sup>)-H Functionalization

We next investigated applications of methoximes with enriched isomer ratios. We envisioned that the orientation of the lone pair on the oxime moiety could control the site-selectivity of C(sp<sup>2</sup>)-H functionalization, similarly to the previously reported site-selective C(sp<sup>3</sup>)-H functionalization [14, 15]. As



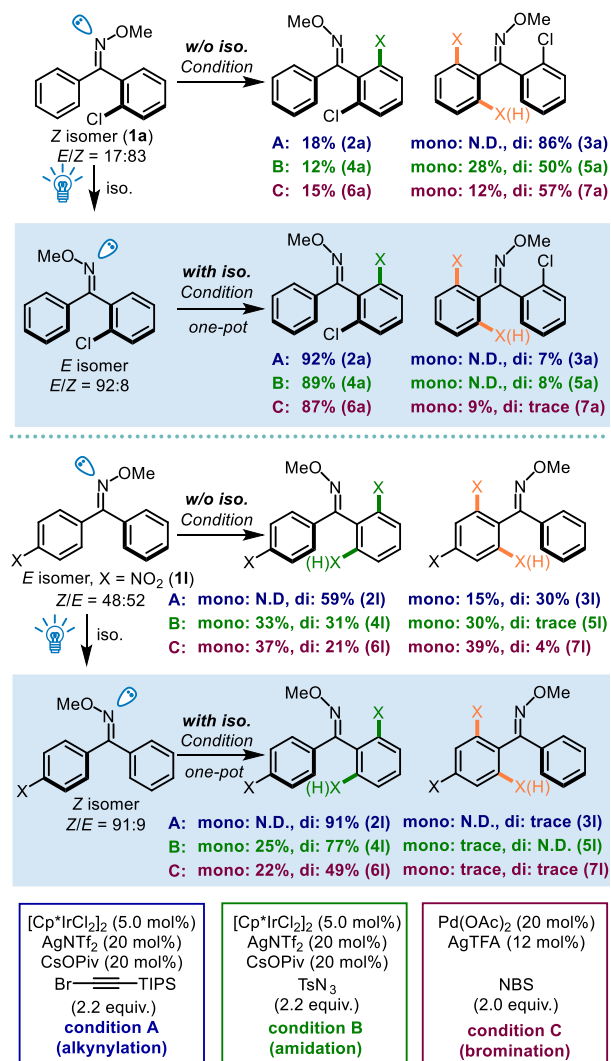
**FIGURE 3** | Substrate scope in selective *E/Z* isomerization: Z/E = aa:bb to cc:dd; aa:bb is the ratio before isomerization. cc:dd is the ratio after isomerization. (a) The reaction was performed in DMF. (b) *E/Z* configuration was not determined.

representative transformations, Cp\*Ir(III)-catalyzed C–H alkylation (Condition A) [28], Cp\*Ir(III)-catalyzed C–H amidation (Condition B) [29], and Pd(II)-catalyzed C–H bromination (Condition C) [30] were examined using **1a** and **1l** as the model substrates before or after *E/Z* isomerization (Figure 4). The yields in the following reactions are discussed based on NMR yields.

When using an *o*-chloro-substituted methoxime (**1a**), alkylation under Condition A after *E/Z* isomerization predominantly furnished **2a** with one alkynyl group on the *o*-substituted aryl group in 92% yield (<sup>1</sup>H NMR yield), whereas alkylation on the phenyl ring (**3a**) hardly proceeded (7%, <sup>1</sup>H NMR yield). The ratio of **2a** and **3a** closely corresponded to the *Z/E* ratio of **1a** after isomerization, suggesting that the *Z/E* configuration remained stable under these conditions. In contrast, without prior isomerization, the alkynylated product **3a** derived from the *Z* isomer was obtained preferentially (**2a:di-3a** = 18%:86%). These results demonstrated that selective *E/Z* isomerization of diaryl methoximes

can control site selectivity in C(sp<sup>2</sup>)–H functionalization through the geometry of the directing group. Photoinduced *E/Z* isomerization also enabled site-selective C(sp<sup>2</sup>)–H amidation using a Cp\*Ir(III) catalyst (Condition B), predominantly affording **4a** with the amide moiety on the *o*-substituted aryl group (**4a:di-5a** = 89%:8%). In contrast, amidation without isomerization mainly gave the product functionalized on the opposite phenyl ring (**4a:mono+di-5a** = 12%:28 + 50%). Pd(II)-catalyzed bromination (Condition C) showed a similar trend, with site selectivity depending on whether isomerization was performed (with isomerization: **6a:mono-7a** = 87%:9%; without isomerization: **6a:mono+di-7a** = 15%:12 + 57%).

In the case of *p*-NO<sub>2</sub> methoxime (**1l**, *Z/E* = 48:52), C(sp<sup>2</sup>)–H functionalization under Conditions A, B, and C after *E/Z* isomerization (*Z/E* = 48:52 to 91:9) afforded products predominantly functionalized on the phenyl group (A: **di-2l:3l** = 91%:trace [with iso.]; B: **mono+di-4l:mono-5l** = 25 + 77%:trace [with iso.];



**FIGURE 4** | Site-selective C(sp<sup>2</sup>)-H functionalization: the yields were determined by <sup>1</sup>H NMR analysis using dimethyl sulfone as an internal standard. For isolated yields after purification, see Supporting Information.

**C: mono+di-6l:7l** = 22 + 49%:trace [with iso.]). These results indicate that reisomerization from *Z* to *E* did not proceed under reaction conditions and that the minor *E* isomer is less reactive in C(sp<sup>2</sup>)-H functionalization than the major *Z* isomer. In contrast, C(sp<sup>2</sup>)-H functionalization without prior isomerization furnished mixtures of products functionalized on either the phenyl or the *p*-NO<sub>2</sub>-substituted aryl group (A: **di-2l:mono+di-3l** = 59%:15 + 30% [without iso.]; B: **mono+di-4l:mono-5l** = 33 + 31%:30% [without iso.]; C: **mono+di-6l:mono+di-7l** = 37 + 21%:39 + 4%). These regioisomers were difficult to separate under all conditions examined, demonstrating that *E/Z* isomerization prior to C(sp<sup>2</sup>)-H functionalization is crucial for obtaining the functionalized products in high purity.

### 3 | Conclusions

We demonstrated that careful selection of photosensitizers enabled selective *E/Z* isomerization of diaryl methoximes. The available methoximes can be categorized into four classes based on the

structural and electronic characteristics of their substituents. We also demonstrated site-selective C(sp<sup>2</sup>)-H functionalization as an application of this selective *E/Z* isomerization, affording products preferentially functionalized on one aryl group. We hope that this strategy will expand the scope of selective *E/Z* isomerization for compounds with similar triplet energies.

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### Conflicts of Interest

The authors declare no conflicts of interest.

### Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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## Supporting Information

Additional supporting information can be found online in the Supporting Information section.