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Photoswitched Stereodivergent Synthesis of Allylic Sulfones

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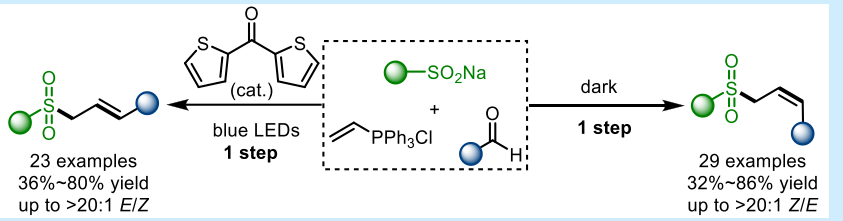
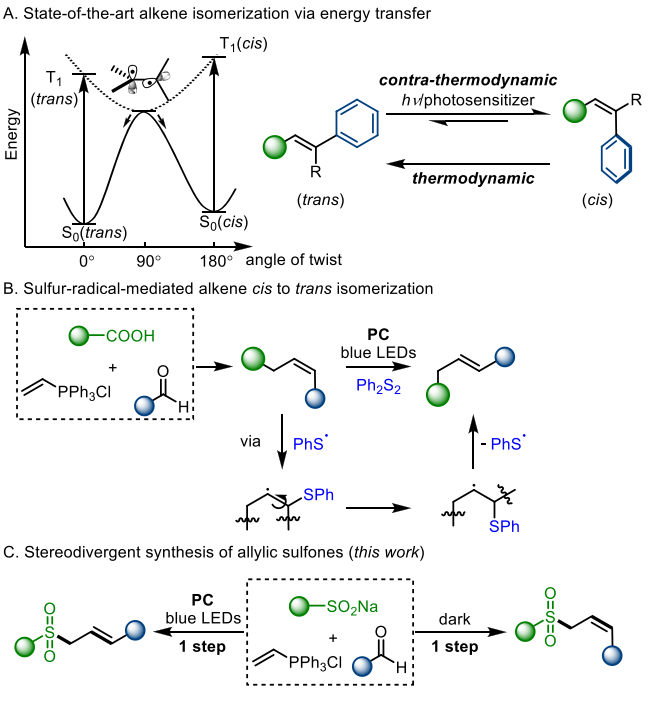


ABSTRACT: The present Letter demonstrates a photoswitched stereodivergent synthesis of allylic sulfones from sodium sulfinates, triphenylvinylphosphonium chloride, and (hetero)aromatic aldehydes in a single step. Mechanistically, *cis*-allylic sulfones, generated from the unstabilized ylide intermediates and aldehydes *in situ*, could be finally converted to *trans*-allylic sulfones via photochemical isomerization in the presence of a catalytic amount of bis(2-thienyl) ketone.

The stereodivergent formation of C=C double bonds is a long-standing concern lying in front of the synthesis of internal alkenes due to their prevalence in chemistry,[1] biology,[2] and materials science.[3] Recently, alkene isomerization via energy transfer catalysis has emerged as a powerful paradigm for providing internal alkenes with different configurations.[4] Typically, *trans*-alkenes are prone to generation under thermodynamic conditions, while *cis*-alkenes can be accessed via inversion of the configuration of the *in situ*-generated *trans*-products under contra-thermodynamic conditions to achieve the stereodivergence.[5] For the latter process, the directionality of *E* to *Z* isomerization is strategically governed through the discrimination of the triplet energies between the isomers by triplet photosensitizers. Consequently, the *cis*-alkenes with high triplet energies resulting from deconjugation between the chromophore and the double bond accumulate due to the inefficient energy transfer from the triplet photosensitizer, which is only capable of activating the *trans*-alkenes with relatively lower triplet energy (Scheme 1A).

By contrast, the opposite directionality, alkene *Z* to *E* isomerization, is thermodynamically preferred and can be promoted by strong acids,[6] halogens,[7] elemental selenium,[8] diphenyl disulfide,[9] transition metal catalysts,[10] *etc.*[11] Although a biologically typical alkene *Z* to *E* isomerization enabled by photochemistry is well-known for the transformation of 11-*cis*-retinal to all-*trans*-retinal in the mammalian visual cycle,[12] the stereoselective *Z* to *E* isomerization of simple alkenes remains underexplored with photochemical approaches except for stilbene[7,13] and highly conjugated aryl alkenes.[14] For the highly conjugated aryl alkenes, the triplet minimum is at a typically *trans*-planar geometry that leads to a one-way isomerization to give *trans*-alkenes rather than at the perpendicular structure

Scheme 1. Alkene Isomerization and Stereodivergent Synthesis of Alkenes from Vinylphosphonium Salts



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which is the energy minimum for simple alkenes and gives both *E*- and *Z*-alkenes via conical intersection. Therefore, for simple alkenes which have triplet minima at the perpendicular structure, it has remained elusive to control the directionality as *Z* to *E* rather than *E* to *Z* between the two-way isomerization by only leveraging a catalytic amount of triplet photosensitizers.

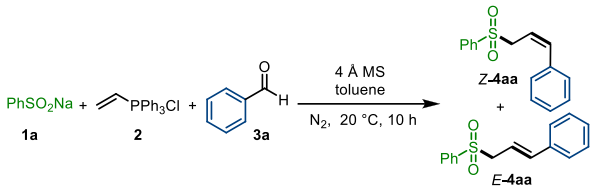
Triphenylvinylphosphonium salts generally produce internal *cis*-alkenes via tandem nucleophilic/radical addition and Wittig reaction under lithium-free conditions.[15] Recently, Filippini and Silvi reported an elegant approach that stereodivergently produced *cis*-alkenes and *trans*-alkenes from visible-light-driven reactions of aliphatic carboxylic acids, triphenylvinylphosphonium salts, and aldehydes.[16] The stereodivergence is achieved by a stepwise protocol in which *trans*-alkenes are obtained from the subsequent isomerization of *cis*-alkenes mediated by sulfur radical (Scheme 1B).

Inspired by stereodivergent synthesis of internal alkenes enabled by photochemistry and given the importance of unsaturated sulfones,[17] we herein unprecedentedly report a photoswitched stereodivergent synthesis of allylic sulfones from organic sulfinates, triphenylvinylphosphonium salt, and aldehydes. While *cis*-allylic sulfones are formed in the dark, *trans*-allylic sulfones are yielded in the presence of a catalytic amount of photocatalyst (**PC**) under the irradiation of blue LEDs. Both *cis*- and *trans*-allylic sulfones are obtained in a single-step process (Scheme 1C).

We initiated our study by examining the three-component reaction of commercially available sodium benzenesulfinate (**1a**), triphenylvinylphosphonium chloride (**2**), and benzaldehyde (**3a**). Through extensive condition optimization, we found that the desired product *Z*-**4aa** was selectively obtained in good yield when toluene was used as the solvent in the presence of 4 Å molecular sieves for removing H_2O (entry 1, Table 1). Diminished yield and *Z*:*E* ratio were observed without 4 Å molecular sieves or at a lower temperature (entries 2 and 3). Other solvents, such as MeOH, EtOH, HMPA, acetone, *etc.*, gave unsatisfactory results (see the Supporting Information). Given that both **1a** and **2** have poor solubility in toluene, 15-crown-5 was tested and found to be ineffective for the transformation (entry 4). Notably, the counteranion of the triphenylvinylphosphonium salt is vital for this reaction. Using BPh_4^- or Br^- as the counteranion failed to produce the target product (entry 5). The conditions toward synthesis of the stereoisomer *E*-**4aa** were also explored. Surprisingly, benzophenone derivatives, usually used as triplet photosensitizers for alkene *E* to *Z* isomerization, promoted the formation of *E*-**4aa**. Even though an excellent *E*:*Z* ratio resulted from the addition of **PC-1**−**7** under the irradiation with 456 nm blue LEDs, *E*-**4aa** was formed in poor to moderate yields (entries 6−12). Then our attention was turned to studying some heteroaryl ketones. The yield could be improved with dipyridin-2-ylmethanone (**PC-8**), although the *Z*:*E* ratio was compromise (21:79; entry 13). Nevertheless, when bis(2-thienyl) ketone (**PC-9**) was employed, an acceptable *E*:*Z* ratio (93:7) was observed, and pure *E*-**4aa** could be isolated in 72% yield (entry 14). The irradiation wavelength has a prominent effect on the reaction, as the reaction was hampered under the irradiation at 395 nm (entry 15). Notably, *Z*-**4aa** was the major product under irradiation without **PC-9** (entry 16).

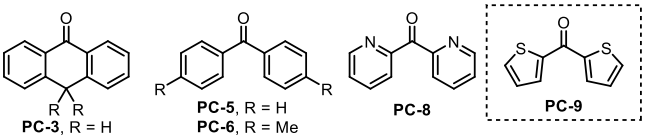
Subsequently, our method for producing *Z*-allylic sulfones was evaluated using a wide variety of sodium sulfinates and aldehydes. The results are shown in Scheme 2. Electron-donating groups (Me, *i*Pr, OMe) and electron-withdrawing

Table 1. Optimization of the Reaction Conditions[a]



entry	variation from the standard conditions[e]	yield (%)[b]	*Z*:*E*[b]
1	none	78	94:6
2	without 4 Å MS	50	88:12
3	−10 °C, 16 h	53	91:9
4	with 15-crown-5 (1.5 equiv)	22	–
5	BPh_4^- or Br^- as the counteranion of triphenylvinylphosphonium	trace	–
6[c]	fluoren-9-one (**PC-1**)	39	<1:20
7[c]	9,10-anthraquinone (**PC-2**)	43	<1:20
8[c]	**PC-3**	53	<1:20
9[c]	**PC-4**	60	<1:20
10[c]	**PC-5**	60	<1:20
11[c]	**PC-6**	60	<1:20
12[c]	**PC-7**	(56)	<1:20
13[c]	**PC-8**	(66)	21:79
14[c]	**PC-9**	(72)	7:93
15[d]	**PC-9**	trace	–
16[c]	without **PC-9**	56	89:11

[a]Reaction conditions: **1a** (0.6 mmol), **2** (0.2 mmol), **3a** (0.4 mmol), 4 Å MS (200 mg), toluene (4 mL), 10 h, N_2. [b]Yields and *Z*:*E* ratios were determined by ^1H NMR analysis of the crude mixtures using 1,3,5-trimethoxybenzene as an internal standard. Isolated yields are given in parentheses. [c]Blue LEDs (456 nm), **PC** (5 mol %), 16 h. [d]Blue LEDs (395 nm), **PC** (5 mol %), 16 h. [e]Structures of **PC-3**−**9**:



groups (halides, CF_3) were well-tolerated on the phenyl ring of sulfinates, and the desired products *Z*-**4ba** to *Z*-**4ja** were obtained in moderate to good yields with good to excellent *Z*:*E* ratios. Sodium 2-naphthalenesulfinate (**1k**) was also suitable for this protocol, although it showed no bias toward either isomer. Delightedly, the reactions of alkyl sulfinates proceeded smoothly, leading to products *Z*-**4la** and *Z*-**4ma** in moderate yields with good stereoselectivities. Next, reactions of various aldehydes with **1a** and phosphonium salt **2** were examined to further demonstrate the generality of this methodology. The reaction efficiency and stereoselectivity were satisfactory with aromatic aldehydes bearing a series of electronically diverse substituents, including halide, alkyl, ether, thioether, methoxycarbonyl, and terminal alkynyl groups (*Z*-**4ab**−*Z*-**4an**). Besides, some other (hetero)aromatic aldehydes were tested, including 1-naphthaldehyde, 9-anthraldehyde, furfural, and benzo[*b*]thiophene-3-carboxaldehyde, affording the desired products *Z*-**4ao**−*Z*-**4ar** in moderate to good yields and *Z*:*E* ratios. In addition to aryl aldehydes, cinnamaldehyde was also suitable for this transformation, resulting in the product *Z*-**4as** in a moderate yield and stereoselectivity.

Next, the substrate scope for preparing *E*-allylic sulfones was expanded, as shown in Scheme 3. Arylsulfinates bearing alkyl, alkoxyl, and halides afforded the *E*-allylic sulfones in acceptable

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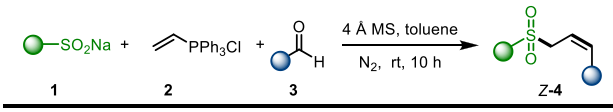
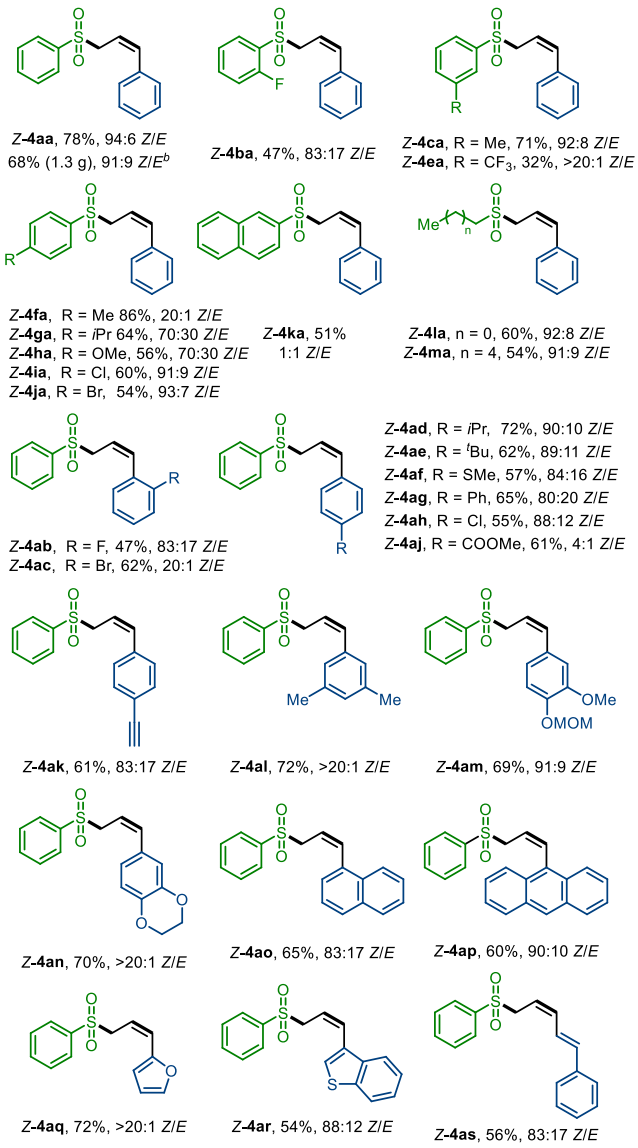
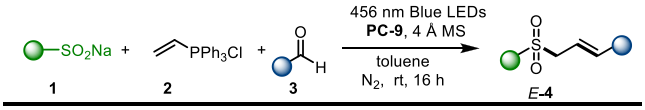
Scheme 2. Synthesis of *Z*-Allylic Sulfones[a]

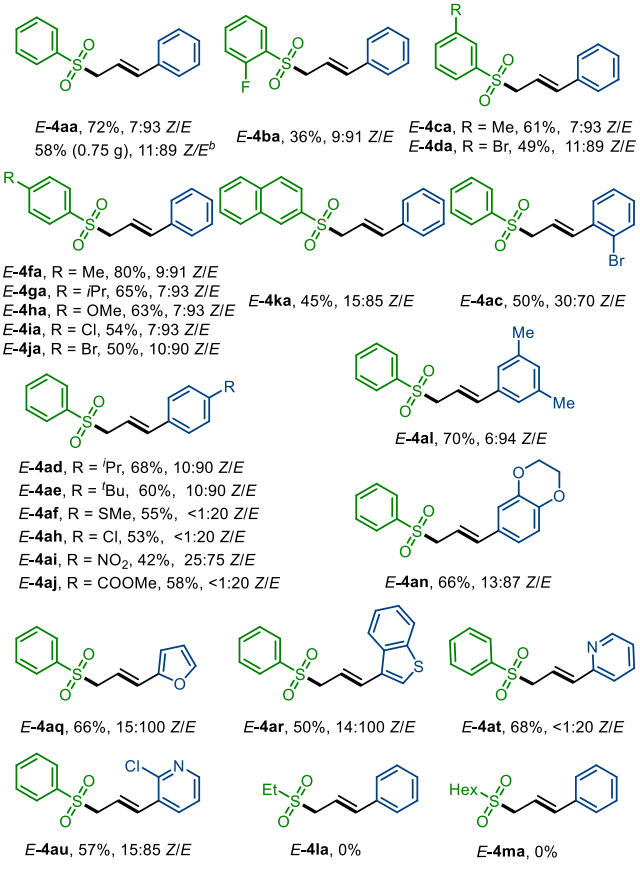




[a]Reaction conditions: **1a** (3 equiv), **2** (0.2 mmol), **3a** (2 equiv), 4 Å MS (200 mg), toluene (4 mL), 10 h, N_2. Isolated yields of pure *Z* isomer are shown. *Z*:*E* ratios were determined by ^{1}H NMR analysis of the crude mixtures. [b]7.5 mmol scale.

Scheme 3. Synthesis of *E*-Allylic Sulfones[a]





[a]Reaction conditions: **1** (3 equiv), **2** (0.2 mmol), **3** (2 equiv), **PC-9** (5 mol %), 4 Å MS (200 mg), toluene (4 mL), 16 h, 456 nm blue LEDs, N_2. Isolated yields of pure *E* isomers are shown. *Z*:*E* ratios were determined by ^{1}H NMR analysis of the crude mixtures. [b]5 mmol scale.

yields with good stereoselectivities (*E*-**4aa**−*E*-**4ja**). Though 2-naphthalenesulfinate dictated no selectivity when it was used to prepare the *Z*-allylic sulfone, moderate stereoselectivity could be observed for yielding *E*-allylic sulfone *E*-**4ka**. When the reactions of sodium benzenesulfinate were explored with benzaldehydes bearing various electron-donating and electron-withdrawing functional groups, most of them afford the *E*-allylic sulfones in moderate yields with good to excellent stereoselectivities (*E*-**4ac**−*E*-**4an**), except 2-bromobenzaldehyde (*E*-**4ac**, 30:70 *Z*:*E*) and 4-nitrobenzaldehyde (*E*-**4ai**, 25:75 *Z*:*E*). Additionally, furfural, benzo[*b*]thiophene-3-carboxaldehyde, and 2-pyridinecarboxaldehyde were well-tolerated to yield the *E*-allylic sulfones with good to excellent stereoselectivities (*E*-**4aq**−*E*-**4au**).

Surprisingly, the aforementioned alkylsulfinates which were suitable for producing *Z*-allylic sulfones could not produce any products under the conditions for preparing *E*-allylic sulfones.

To demonstrate the synthetic value of our methodology, gram-scale synthesis was conducted to afford 1.3 g of *Z*-**4aa** and 0.75 g of *E*-**4aa**, respectively. Since unsaturated sulfones are versatile building blocks, the derivatization of the allylic sulfone *Z*-**4aa** is illustrated in Scheme 4. Cyclization of *Z*-**4aa** with cinnamaldehyde readily afforded terphenyl **5a**. Catalytic hydrogenation is efficient with Pd/C, yielding alkyl aryl sulfone **5b** in excellent yield. Deprotonation of *Z*-**4aa** followed by reaction with electrophiles, like *N*-fluorobenzenesulfonimide (NFSI) or benzyl bromide, resulted in the fluorination product **5c** and benzylation product **5d** which reserved the geometry of the double bond.

To gain further insight into the reaction mechanism, control experiments were conducted (Scheme 5). Triphenylvinylphosphonium chloride **2** was completely consumed when reacted with benzenesulfinate **1a**, likely yielding the alkylphosphonium salt **6**, which could be detected by ^{31}P NMR (eq 1). After the reaction of **1a** and **2**, benzaldehyde (**3a**) was then added to the reaction mixture, affording **4aa** in moderate yield but with a poor

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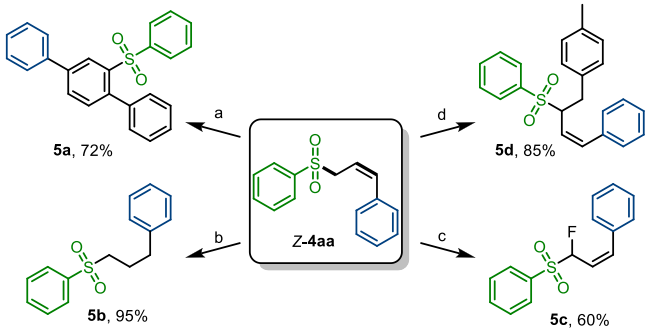
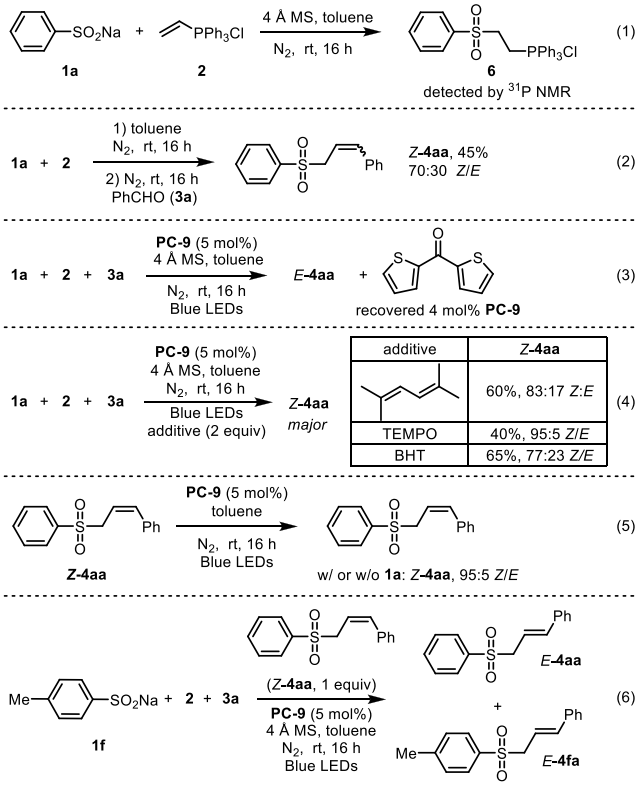
Scheme 4. Derivatization of the Allylic Sulfone[a]



[a]Reaction conditions: (a) NaH (4 equiv), cinnamaldehyde (1 equiv), rt to reflux, 3 h. (b) 5 mol % Pd/C (10% w/w), H_2 (1 atm), MeOH, 12 h. (c) LiHMDS (3 equiv), $ZnCl_2$ (2.2 equiv), THF, −78 °C, 1 h, then NFSI (2 equiv), rt, 0.5 h. (d) Under N_2 atmosphere, ^{n}BuLi (1 equiv), −78 °C, 1 h, then 4-methylbenzyl bromide, 0 °C, 2 h.

Scheme 5. Mechanistic Studies



Z:*E* ratio (eq 2). These experiments imply that the generation of the **6**-derived ylide from **1a** and **2** was probably involved. Notably, catalyst **PC-9** could be recovered after the reaction, which unveils that **PC-9** disfavors the Wittig-type reaction with the *in situ*-generated ylide in the present system. Thus, it is a genuine catalyst in the synthesis of *E*-allylic sulfones (eq 3). When 2,5-dimethyl-2,4-hexadiene was added as a triplet quencher under the standard conditions for synthesis of *E*-alkenes, *Z*-**4aa** was formed as the major product (83:17 *Z*:*E*), implying that the excited triplet state of **PC-9** was quenched by 2,5-dimethyl-2,4-hexadiene (eq 4). Moreover, the photochemical reaction for the synthesis of *E*-**4aa** is inhibited by TEMPO or BHT (eq 4), and *Z*-**4aa** is formed as the major product instead, which indicates that a radical mechanism is unlikely for the addition of sulfinate to the vinylphosphonium salt. However, alkene isomerization hampered by the radical scavenger suggests that a radical mechanism may be involved in the isomerization process. However, irradiation of *Z*-**4aa** in the presence of **PC-9** could not furnish the corresponding *trans*-alkene with or without the addition of benzenesulfinate (eq 5). Interestingly, when *Z*-**4aa** was added to the reaction mixture for preparing *E*-**4fa**, it was found that a mixture of *E*-**4aa** and *E*-**4fa** was obtained (eq 6), implying that *E*-allylic sulfones may result from the isomerization of *Z*-allylic sulfones. It is worth noting that each ingredient of the three-component mixture of benzenesulfinate, triphenylvinylphosphonium chloride, and benzaldehyde is vital for the efficiency of *Z* to *E* alkene isomerization.[18] Although it is still not clear how to govern the *Z* to *E* alkene isomerization by the three-component mixture, a mechanism for this process is proposed. Maybe the sulfonyl radical is generated from the reaction mixture and subsequently adds to the C=C double bond of the *Z*-allylic sulfone, which is a reversible process. The following elimination of the sulfonyl radical forms the thermally favored *E*-allylic sulfone.

In summary, we have developed a photoswitched stereodivergent synthesis of allylic sulfones from sodium sulfinates, triphenylvinylphosphonium chloride, and (hetero)aromatic aldehydes. Different from the usual stepwise approach, this protocol features single-step synthesis, and *Z*-allylic sulfones were obtained in the dark while *E*-allylic sulfones were formed in the presence of bis(2-thienyl) ketone as a photocatalyst under irradiation with blue LEDs. Mechanistic studies hint that the addition of sulfinates to triphenylvinylphosphonium chloride is an ionic process to form unstabilized ylides in both thermochemical and photochemical reactions. *cis*-Alkenes, generated from the unstabilized ylide intermediates and aldehydes, could be finally converted to *trans*-alkenes via photochemical isomerization which is enabled by bis(2-thienyl) ketone catalyst and the three-component mixture of sulfinate, triphenylvinylphosphonium chloride, and aldehyde.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.4c01391.

Experimental procedures, screening reaction conditions, control experiments, characterization data, and NMR spectra for the products and all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Thirsk, C.; Whiting, A. Polyene natural products. *J. Chem. Soc., Perkin Trans. 1* **2002**, 999−1023.

(2) Dugave, C.; Demange, L. Cis−Trans Isomerization of Organic Molecules and Biomolecules: Implications and Applications. *Chem. Rev.* **2003**, *103*, 2475−2532.

(3) Lan, R.; Bao, J.; Huang, R.; Wang, Z.; Zhang, L.; Shen, C.; Wang, Q.; Yang, H. Amplifying Molecular Scale Rotary Motion: The Marriage of Overcrowded Alkene Molecular Motor with Liquid Crystals. *Adv. Mater.* **2022**, *34*, No. 2109800.

(4) For a review, see: (a) Neveselý, T.; Wienhold, M.; Molloy, J. J.; Gilmour, R. Advances in the *E*→*Z* Isomerization of Alkenes Using Small Molecule Photocatalysts. *Chem. Rev.* **2022**, *122*, 2650−2694. For some selected recent examples, see: (b) Zhang, H.; Huang, C.; Yuan, X.-A.; Yu, S. Photoexcited Chiral Copper Complex-Mediated Alkene *E*→*Z* Isomerization Enables Kinetic Resolution. *J. Am. Chem. Soc.* **2022**, *144*, 10958−10967. (c) Zähringer, T. J. B.; Wienhold, M.; Gilmour, R.; Kerzig, C. Direct Observation of Triplet States in the Isomerization of Alkenylboronates by Energy Transfer Catalysis. *J. Am. Chem. Soc.* **2023**, *145*, 21576−21586. (d) Wang, J.; Gu, J.; Zou, J.-Y.; Zhang, M.-J.; Shen, R.; Ye, Z.; Xu, P.-X.; He, Y. Photocatalytic *Z*/*E* isomerization unlocking the stereodivergent construction of axially chiral alkene frameworks. *Nat. Commun.* **2024**, *15*, 3254.

(5) For a review, see: Corpas, J.; Mauleón, P.; Gómez Arrayás, R.; Carretero, J. C. *E*/*Z* Photoisomerization of Olefins as an Emergent Strategy for the Control of Stereodivergence in Catalysis. *Adv. Synth. Catal.* **2022**, *364*, 1348−1370.

(6) (a) Meek, J. S. The determination of a mechanism of isomerization of maleic acid to fumaric acid. *J. Chem. Educ.* **1975**, *52*, 541−543. (b) Hao, T.; Yang, Y.; Liang, W.; Fan, C.; Wang, X.; Wu, W.; Chen, X.; Fu, H.; Chen, H.; Yang, C. Trace mild acid-catalysed *Z*→*E* isomerization of norbornene-fused stilbene derivatives: intelligent chiral molecular photoswitches with controllable self-recovery. *Chem. Sci.* **2021**, *12*, 2614−2622.

(7) Zyubina, T. S.; Razumov, V. F. A Theoretical Study on the Mechanism of Iodine-Photocatalyzed *cis-trans* Isomerization of Stilbene. *High Energy Chem.* **2001**, *35*, 100−106.

(8) Fitzpatrick, J. D.; Orchin, M. Selenium-catalyzed Isomerization of *cis*-Stilbene. *J. Org. Chem.* **1957**, *22*, 1177−1179.

(9) Moussebois, C.; Dale, J. A method of *cis,trans*-isomerisation of non-conjugated olefins without double-bond migration. *J. Chem. Soc. C* **1966**, 260−264.

(10) Liu, H.; Xu, M.; Cai, C.; Chen, J.; Gu, Y.; Xia, Y. Cobalt-Catalyzed *Z* to *E* Isomerization of Alkenes: An Approach to (*E*)-*β*-Substituted Styrenes. *Org. Lett.* **2020**, *22*, 1193−1198.

(11) Molloy, J. J.; Morack, T.; Gilmour, R. Positional and Geometrical Isomerisation of Alkenes: The Pinnacle of Atom Economy. *Angew. Chem., Int. Ed.* **2019**, *58*, 13654−13664.

(12) Polli, D.; Altoè, P.; Weingart, O.; Spillane, K. M.; Manzoni, C.; Brida, D.; Tomasello, G.; Orlandi, G.; Kukura, P.; Mathies, R. A.; Garavelli, M.; Cerullo, G. Conical intersection dynamics of the primary photoisomerization event in vision. *Nature* **2010**, *467*, 440−443.

(13) (a) Lewis, F. D.; Petisce, J. R.; Oxman, J. D.; Nepras, M. J. One-way photoisomerization of *cis*-stilbene via a cation radical chain mechanism. *J. Am. Chem. Soc.* **1985**, *107*, 203−207. (b) Zhong, J.-J.; Liu, Q.; Wu, C.-J.; Meng, Q.-Y.; Gao, X.-W.; Li, Z.-J.; Chen, B.; Tung, C.-H.; Wu, L.-Z. Combining visible light catalysis and transfer hydrogenation for *in situ* efficient and selective semihydrogenation of alkynes under ambient conditions. *Chem. Commun.* **2016**, *52*, 1800−1803.

(14) Arai, T.; Takahashi, O.; Asano, T.; Tokumaru, K. The Effect of Substitution of 3-Perylenyl Group, an Aromatic Nucleus with a Very Low Triplet Energy, on Photochemical Isomerization of the Unsaturated Bond. Direct Observation of Triplet State Isomerization of a Styrene Derivative. *Chem. Lett.* **1994**, *23*, 205−208.

(15) (a) Catalán-Muñoz, S.; Müller, C. A.; Ley, S. V. An Asymmetric Tandem Conjugative Addition-Intramolecular Cyclisation Process to Provide Functionalised 3,6-Dihydropyrans and 4,5-Epoxytetrahydropyrans. *Eur. J. Org. Chem.* **2010**, *2010*, 183−190. (b) Ikeshita, D.; Masuda, Y.; Ishida, N.; Murakami, M. Photoinduced Hydrophosphination of Terminal Alkynes with Tri(*o*-tolyl)phosphine: Synthesis of Alkenylphosphonium Salts. *Org. Lett.* **2022**, *24*, 2504−2508. (c) Mori, H.; Yoshida, M.; Sawamura, M.; Masuda, Y. Photocatalytic Aldehyde C−H Bond Phosphonioethylation with Vinylphosphonium Bromide. *Asian J. Org. Chem.* **2024**, *13*, e202300532. (d) Yoshida, M.; Sawamura, M.; Masuda, Y. Photoinduced Alcoholic *α*-C−H Bond Anti-Markovnikov Addition to Vinylphosphonium Bromides Followed by Wittig Olefination: Two-Step Protocol for *α*-C−H Allylic Alkylation of Alcohols. *ChemCatChem* **2022**, *14*, e202200744. (e) Yoshida, M.; Sawamura, M.; Masuda, Y. Sequence-selective three-component reactions of alkyltrifluoroborates with *α*,*β*-unsaturated carbonyl compounds and vinylphosphonium salts. *Org. Chem. Front.* **2023**, *10*, 3654−3661.

(16) Filippini, D.; Silvi, M. Visible light-driven conjunctive olefination. *Nat. Chem.* **2022**, *14*, 66−70.

(17) (a) Luo, Z.; Liu, Z.-Q.; Yang, T.-T.; Zhuang, X.; Hong, C.-M.; Zou, F.-F.; Xue, Z.-Y.; Li, Q.-H.; Liu, T.-L. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP)-Assisted Catalyst-Free Sulfonation of Allylic Alcohols with Sulfinyl Amides. *Org. Lett.* **2022**, *24*, 741−745. (b) Wang, Y.; Wu, G.; Yan, K.; Qin, J.; Liu, R.; Rong, N.; Tang, Y.; Loh, T.-P.; Xie, P. Sulfination of Unactivated Allylic Alcohols via Sulfinate-Sulfone Rearrangement. *Org. Lett.* **2023**, *25*, 8895−8900. (c) Yang, Z.-X.; Lai, L.; Chen, J.; Yan, H.; Ye, K.-Y.; Chen, F.-E. Stereoselective electrochemical carboxylation of *α*,*β*-unsaturated sulfones. *Chin. Chem. Lett.* **2023**, *34*, No. 107956. (d) Zhang, K.-Y.; Long, F.; Peng, C.-C.; Liu, J.-H.; Wu, L.-J. Pd-Catalyzed Multicomponent Cross-Coupling of Allyl Esters with Alkyl Bromides and Potassium Metabisulfite: Access to Allylic Sulfones. *Org. Lett.* **2023**, *25*, 5817−5821.

(18) See the mechanistic studies section in the Supporting Information.