

Visible-light-mediated decarboxylative (*E*)-alkenylation of aliphatic carboxylic acids with aryl styryl sulfones under metal-free conditions

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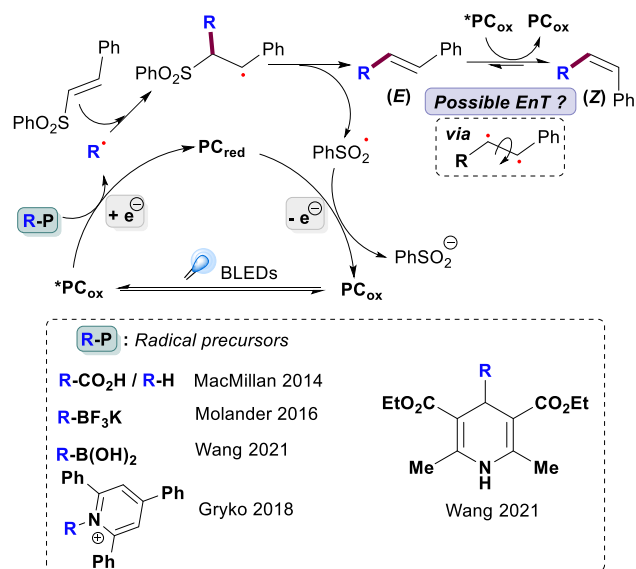
The decarboxylative alkenylation of aliphatic carboxylic acids with aryl styryl sulfones is efficiently catalyzed by riboflavin tetraacetate under visible light irradiation at room temperature. This metal-free protocol is cost-efficient, environmentally friendly and provides the corresponding olefins with excellent (*E*)-diastereocontrol. The methodology can also be used to prepare internal alkynes regioselectively by using alkynyl sulfones as radical acceptors. The suitability as building blocks of the olefins obtained was demonstrated by performing an (*E*)- to (*Z*) photoisomerization, an iron-catalyzed allylic substitution of the phenoxy group derived from the 2-phenoxy-carboxylic acids substrates, as well as *syn*-epoxidations, and diastereoselective intramolecular iodoarylations. Based on control experiments and DFT calculations, we proposed a reaction mechanism that accounts for the regio- and diastereo-selectivity observed.

Introduction

Olefins are fundamental building blocks in organic synthesis, and considerable efforts have been focused on their preparation. Cross-coupling reactions allow a modular assembly of olefins, where chemo-, regio-, and stereoselectivity are important challenges. In this context, transition-metal catalysts have played a key role, although the protocols are commonly limited by the employment of expensive or toxic reagents, low tolerance to water and air, and the frequent use of harsh conditions.^{1, 2} Among the classic cross-coupling alkenylations are the Wittig reaction,^{3, 4} the Heck-type reactions,⁵⁻⁸ and olefin metathesis.^{9, 10}

In modern organic synthesis, photoredox catalysis with visible light is one of the most frequently used approaches to obtain alkyl radicals under mild conditions.¹¹⁻¹³ In this context, aryl styryl sulfones are excellent SOMO-philes to trap alkyl radicals at the α -position.¹⁴ The reaction is usually followed by β -elimination of the sulfinyl radical to furnish the corresponding olefins.¹⁵ When this strategy is implemented using photoredox catalysis (Scheme 1), the excited photocatalyst can be reductively quenched by the radical precursor, and its turnover can take place by single-electron transfer to the sulfinyl radical (or *via* HAT catalysis) without using any sacrificial oxidant (redox-neutral process). Inoue's group made seminal parallel contributions to this area,¹⁶ using UV light and benzophenone as a HAT photocatalyst, and MacMillan's group with visible light and iridium-based photocatalysts.¹⁷ The latter work inspired similar protocols recently developed in Wang's group, where transition-metal-based photocatalysts were used to oxidize

alkyl boronic acids,¹⁸ or 4-alkyl-1,4-dihydropyridines.¹⁹ Interestingly, the group of Molander has developed a similar alkenylation protocol but using the organic dye eosin Y as the photocatalyst to oxidize the potassium α -pyrrolidiny trifluoroborate under transition-metal-free conditions.²⁰ The same catalyst was recently used for Gryko's group in the deaminative alkenylation of Katritzky salts, and it was compatible with a broad scope of substrates.²¹



Scheme 1. Literature precedents, working model, and possible *E/Z* isomerization.

Organic dyes are much less expensive and environmentally friendly than iridium-based catalysts. Furthermore, it is known that Ir(ppy)₃ and other similar photocatalysts can engage in a triplet-energy transfer to alkenes, promoting an *E/Z* isomerization of the obtained olefin.^{22, 23} With the precedents commented above, we decided to explore the performance of

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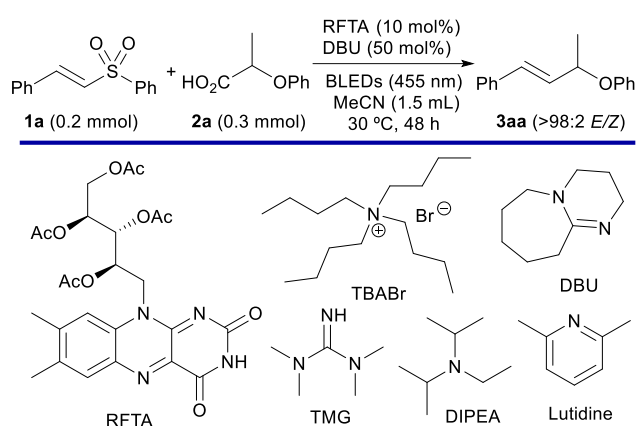
riboflavin tetraacetate (RFTA), a photocatalyst derived from vitamin B2, in the decarboxylative alkenylation of aliphatic carboxylic acids with styryl phenyl sulfone promoted by irradiation with visible light.

Results and discussion

Setting the reaction conditions.

A problem often associated with the direct oxidative decarboxylation of aliphatic carboxylic acids is that the back-electron transfer is very fast, competing with the generation of the alkyl radical. We thus selected 2-phenoxypropanoic acid as a model substrate for the reaction (**2a**, Table 1).

Table 1. Optimization of the reaction conditions



Entry	Variation from above	Yield (%) ^a
1	RFTA (5 mol%), no base	53
2	RFTA (5 mol%), no base, 2:1 DCE/H ₂ O	25
3	No base, 2:1 CH ₃ CN/H ₂ O	40
4	No base	61
5	RFTA (5 mol%), DBU (150 mol%)	79
6	K ₂ CO ₃ (150 mol%), TBABr (10 mol%)	75
7	TEA (150 mol%), TBABr (10 mol%)	50
8	none	84
9	DBU (150 mol%)	72
10	RFTA (5 mol%)	56
11	DBU (20 mol%)	56
12	24 h	56
13	Lutidine (50 mol%)	36
14	TMG (50 mol%)	66
15	DIPEA (50 mol%)	67
16	No deoxygenation	20
17	No irradiation	-
18	No RFTA	18

^a Yield of the isolated pure product after flash column chromatography.

The decarboxylation of this acid has been reported to be extremely rapid,²⁴ providing a secondary α -phenoxy radical, with high SOMO energy for a good match with an electrophilic acceptor such as the phenyl styryl sulfone **1a**. We have previously observed that RFTA can catalyze the oxidative photodecarboxylation of aliphatic carboxylic acids without an external base.^{25, 26} However, this model reaction has shown

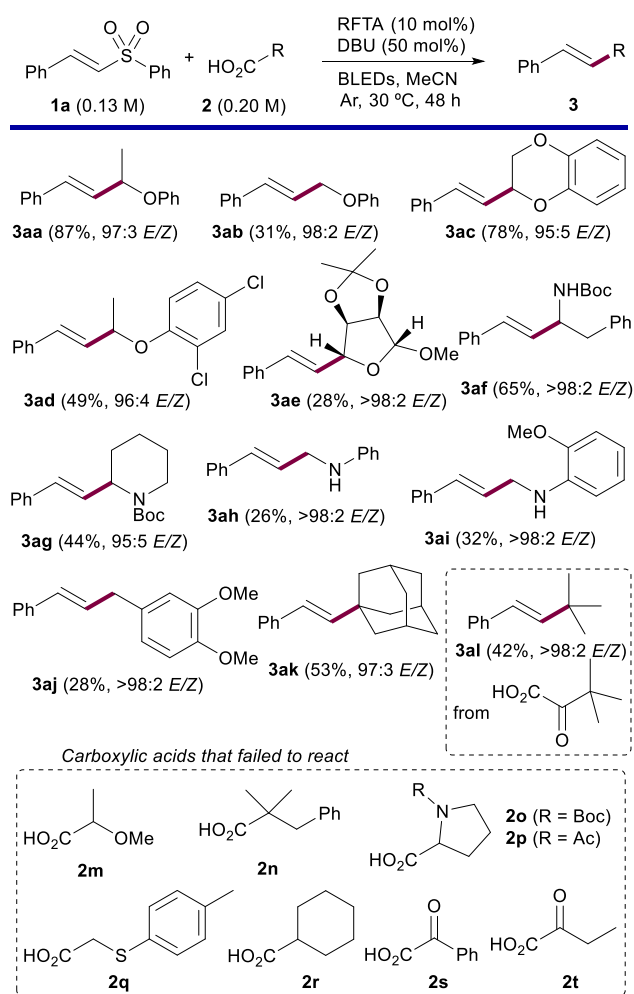
moderate results under these conditions, obtaining the best results in MeCN as solvent (entries 1-4). Upon screening different basic additives in this transformation (entries 5-15), it was found that 50 mol% of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 10 mol% of RFTA over an irradiation period of 48 h provided the best results (entry 8). Finally, control experiments revealed that deoxygenation, irradiation with Blue LEDs (BLEDs, 455 nm), and the presence of the photocatalyst are essential for the appropriate reaction performance (entries 16-18). Notably, only the *E*-isomer was detected by GC-MS and ¹H-NMR. This stereoselective formation of the *E*-olefin is in stark contrast with the results recently reported with iridium-based photocatalysts, where *E/Z* mixtures were obtained,^{18, 19} and with protocols where triplet-energy-transfer inhibitors were necessary.²⁷ It is also worth mentioning that Gilmour's group has reported that riboflavin (RF) promotes the *E*→*Z* photoisomerization of activated olefins with high 1,3-allylic strain.²⁸ A lower triplet energy for RF (209 kJ/mol) compared to Ir(ppy)₃ (231 kJ/mol) or Ir[dF(CF₃)ppy]₂(dtbpy)PF₆ (251 kJ/mol) might explain the lack of isomerization observed with our protocol.²²

Scope and limitations of the protocol.

Under our optimized conditions, we explored the scope of the reaction concerning the carboxylic acid (Scheme 2). Substrates with aryloxy substituents in the α -position were well tolerated, giving the corresponding products in good-to-moderate yields for secondary acids (**3aa**, **3ac**, and **3ad**) and a lower yield for a primary acid (**3ab**). Notably, a ribosic acid derivative afforded the desired product **3ae** as a single isomer with retention of the configuration, although in moderate yield.²⁹ α -Amino acids, either with a carbamate or an aryl protecting group, were also suitable substrates, affording the corresponding alkenes (**3af-3ai**) in moderate yields. Although heteroatoms in the adjacent position to the carboxylic group were generally required for a successful reaction, electron-rich carboxylic acids such as (3,4-dimethoxyphenyl)acetic acid and 1-adamantanoic acid (sp³ tertiary radical) also resulted suitable substrates, giving products **3aj** and **3ak**, respectively, in moderate yields. Remarkably, in most cases, only the formation of (*E*)-olefins was detected by ¹H-NMR of the crude reaction mixture (and GC-MS), the diastereoselectivity being $\geq 95:5$. Some limitations were found regarding the carboxylic acids suitable for this protocol (see failed substrates **2m – 2t**).

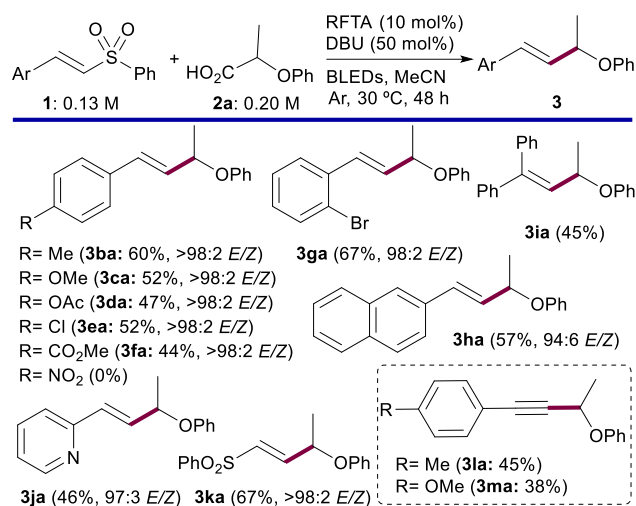
In most cases, the carboxylic acid remained unreacted, likely because the back-electron transfer of their carboxylates is extremely fast ($k_{\text{BET}} \sim 10^{11} \text{ s}^{-1}$) competing with their decarboxylation ($k_{\text{dec}} \sim 10^9 \text{ s}^{-1}$).²⁴ To overcome this issue, the decarboxylation must be sped up, such as for α -oxo benzylic carboxylic acids ($k_{\text{dec}} \sim 10^{11} \text{ s}^{-1}$),²⁴ or the resulting radical should react faster (more nucleophilic) with the acceptor sulfone. Eventually, we have found that the incorporation of simple tertiary radicals in the final olefin is possible from the corresponding α -keto carboxylic acid, obtaining the product (*E*)-**3ak** in moderate yield after decarboxylation and decarbonylation of the substrate. We hypothesized that a fast decarbonylation is needed, providing stable and nucleophilic

tertiary radicals because aromatic keto acid **2s** and primary keto acid **2t** failed as substrates.



Scheme 2. Scope of carboxylic acids on the decarboxylative alkenylation.

The reaction scope for the alkenyl sulfone was also examined under the optimized conditions, using 2-phenoxypropanoic acid as the model substrate (Scheme 3). Electron-donating and electron-withdrawing substituents in the aromatic ring of the sulfone were well tolerated, furnishing the corresponding products in good-to-moderate yields (**3ba–3ha**). The only limitation found in this case was for the nitro-substituted sulfone that failed to react under the reaction conditions. A disubstituted sulfone at the β -position was also a suitable substrate (product **3ia**), as well as a pyridinesulfone (product **3ja**). Interestingly, a 1,2-bis-sulfone was an excellent partner in this protocol, affording the corresponding product **3ka** in good yield, with a sulfone moiety that can be further elaborated.¹⁶ As previously, excellent diastereoselectivities were observed, obtaining only the *E*-isomer in all cases, except for the formation of **3ha** and **3ja**, where 94:6 and 97:3 *E/Z* ratios were respectively obtained. We were pleased to observe that alkynyl sulfones were also suitable substrates in our protocol, giving the corresponding internal alkynes (**3la** and **3ma**) in synthetically useful yields.

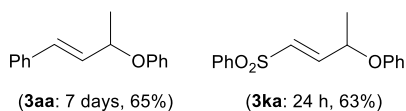


Scheme 3. Scope of sulfones on the decarboxylative alkenylation/alkynylation.

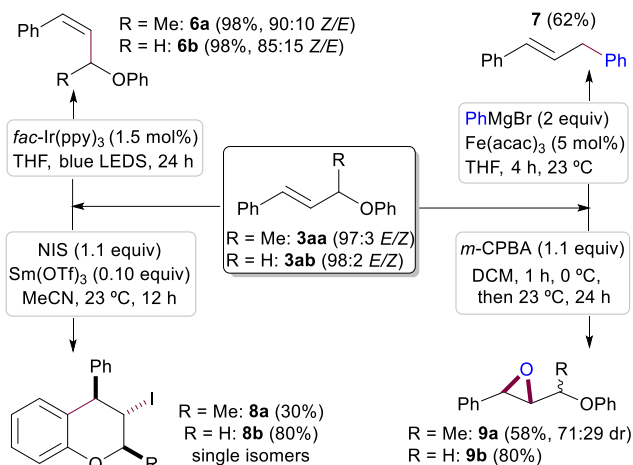
Some synthetic applications of this protocol.

To demonstrate the synthetic usefulness of this methodology, we prepared **3aa** and **3ka** at a 2-mmol scale, with good yields (Scheme 4a). Moreover, we examined the versatility of the products obtained with this protocol by exploring some follow-up reactions of **3aa** and **3ab** (Scheme 4b). Firstly, we conducted a photo-*E* to *Z* isomerization of these compounds using an iridium-based photocatalyst for triplet-energy transfer, furnishing products **6a** and **6b** with $\geq 85:15$ *Z/E* ratio.³⁰ These results exemplify that a careful selection of the photocatalyst has an essential impact on the configuration of the obtained olefin. Secondly, we capitalized on the fact that 2-phenoxypropanoic acids are suitable substrates for this method by performing an iron-catalyzed allylic substitution of the phenoxy group in **3aa** by a phenyl ring,³¹ using an excess of phenylmagnesium bromide to obtain (*E*)-**7** as a single isomer.³² This transformation allows the preparation of (*E*)-alkenes that are not accessible using our decarboxylative alkenylation approach since aromatic or primary carboxylic acids are unsuitable substrates. Moreover, the samarium catalyzed intramolecular iodoarylation of **3ab** was accomplished with *N*-iodosuccinimide (NIS), obtaining the corresponding chromane **8b** in an excellent yield and with *trans*-configuration.^{33, 34} Remarkably, when substrate **3ab** was submitted to this protocol, product **8a** was obtained as a single diastereoisomer with three new stereogenic centers (see ESI for the stereochemical assignment). Lastly, the *syn*-epoxidation of compounds **3aa** and **3ab** under conventional conditions gave rise to products **9a** and **9b** in good yields and with complete diastereocontrol at the oxirane ring.

(a) Reactions at 2 mmol scale



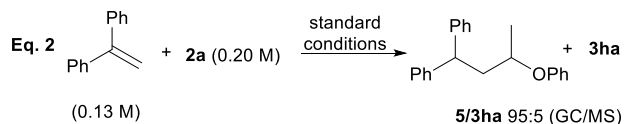
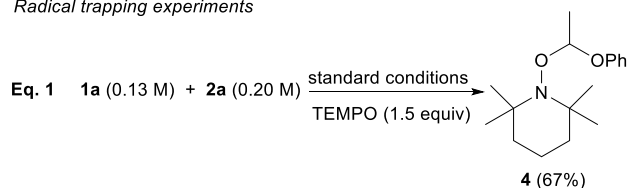
(b) Follow-up reactions



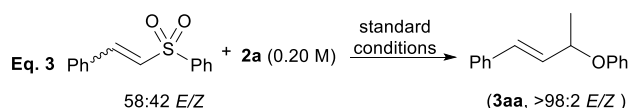
Scheme 4. Scale-up and synthetic applications

Study of the reaction mechanism.

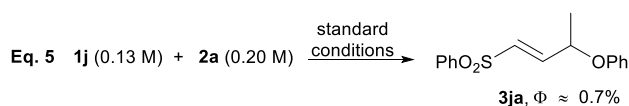
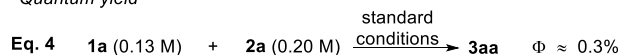
Radical trapping experiments



Diastereoconvergency



Quantum yield



Scheme 5. Mechanistic experiments.

Concerning the mechanism of the reaction, the cyclic voltammetry of carboxylic acid **2a**, in the presence of DBU, revealed that this oxidation ($E_{p/2} \sim 1.15$ V vs SCE, see ESI) is feasible with photoexcited RFTA ($E_{\text{red}} = +1.67$ V vs. SCE).³⁵ We have checked that at 450 nm the photocatalyst absorbed, but none of the reagents showed significant absorbance (see ESI). Furthermore, quenching experiments show that a 3:1 mixture

of **2a**/DBU is much more efficient as quencher of fluorescence of RFTA* than each independent reagent (**2a** or **1a**), as we observed before for other carboxylates.^{25, 26} Importantly, DBU is also an excellent quencher of RFTA*, but in the reaction mixture is protonated (3:1 acid/DBU) and the corresponding ammonium salt is not a good quencher of RFTA* (see ESI for details of quenching experiments).

In addition, when the model reaction was accomplished in the presence of TEMPO, compound **4** was obtained instead of **3aa**, in accordance with the formation of an α -phenoxy radical (Scheme 4, Eq. 1). Interestingly, when 1,1-diphenylethylene was used as the radical scavenger, compound **5** was obtained as the major product, where the radical addition is likely followed by hydrogen atom transfer (HAT, Eq. 2). Moreover, when the reaction was conducted with a diastereomeric mixture of E/Z-**1a** (Eq. 3), only compound (E)-**3aa** was obtained, suggesting that the configuration of the olefin is determined in the elimination of sulfinyl radical, regardless of the configuration of the starting styryl sulfone. Furthermore, the meager quantum yields obtained for substrates **1a** (Eq. 4) and **1j** (Eq. 5), following the general procedure with **2a**, support a closed photocatalytic cycle instead of radical chain propagation.³⁶

To gain insightful information on the reaction mechanism, we performed DFT calculations for the addition of radical PhOCH_2^{\bullet} (generated by oxidative photodecarboxylation of **2b**) to alkene **1a** and the following elimination step of radical PhSO_2^{\bullet} to give product **3ab**. Several pathways were studied for these two processes (see the ESI for details), and only the most favorable route is depicted in Figure 1.

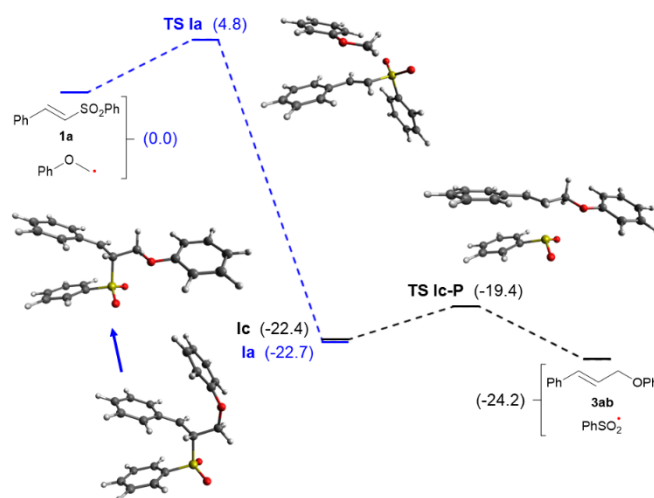


Figure 1. Relative Gibbs free energies (numbers in brackets, kcal/mol) for the addition of radical PhOCH_2^{\bullet} to **1a** and the subsequent elimination of PhSO_2^{\bullet} to give **3ab**, obtained from DFT calculations [B3LYP-D3/6-311G(d,p) in acetonitrile]. Separated **1a** and PhOCH_2^{\bullet} were taken as zero-energy.

The reaction of radical PhOCH_2^{\bullet} with alkene **1a** at the carbon atom adjacent to the sulfonyl group has a low activation barrier of 4.8 kcal/mol, and the formation of radical **1a** leads to a significant fall in the energy of 27.5 kcal/mol from transition state **TS 1a**, suggesting that this could be an irreversible step. Thus, the formation of the benzylic radical highly stabilizes the system, much more than the generation of the alternative

radical at the carbon atom bonded to the sulfonyl group (see the ESI for details), which agrees with the complete regioselectivity observed experimentally. Radical **1a** could isomerize to its conformer **1c**, which is almost isoenergetic with the former. The elimination of radical PhSO₂[•] from **1c** to give alkene **3ab** should be considerably faster than the corresponding elimination from radical **1a**, according to the calculated activation barriers for these two possibilities (3.0 and 5.1 kcal/mol, respectively. See the ESI). The Gibbs free energy of products **3ab** + PhSO₂[•] is 1.8 kcal/mol lower than that of radical **1c**. The overall addition-elimination process is highly exergonic ($\Delta G = -24.2$ kcal/mol), which implies that it should occur spontaneously.

In principle, rotation of radical **1c** 180° through the C-CS bond could take place, leading to conformer **II**, from which a similar β -elimination of PhSO₂[•] would yield the isomeric alkene product (**Z**)-**3ab** (Figure 2). We have evaluated the barrier for this change of conformation, and we obtained a value of 10.8 kcal/mol, which is much higher than the activation barrier for the formation of the *E*-alkene **3ab** from **1c** (3.0 kcal/mol), indicating that the formation of **3ab** should be faster than the conformational change. Moreover, **1c** is 2.7 kcal/mol more stable than **II**, making the transformation of **1c** to **II** thermodynamically disfavoured. These data suggest that only the *E* alkene **3ab** would be formed from radical **1c**, which matches with the excellent *E*-selectivity experimentally observed in most cases.

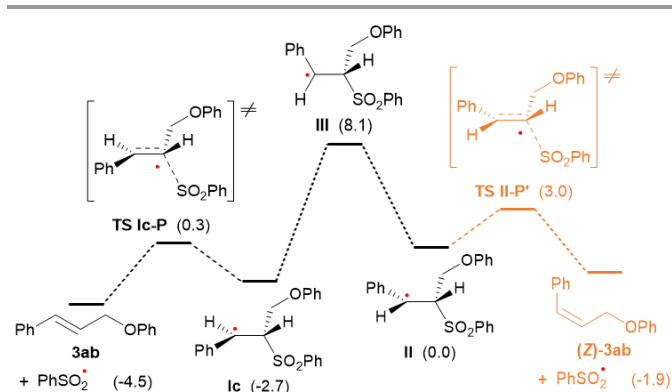


Figure 2. Relative Gibbs free energies (numbers in brackets, kcal/mol) for the transformation of radical **II** to either (*E*)-**3ab** (black profile) or (*Z*)-**3ab** (orange profile), obtained from DFT calculations [B3LYP-D3/6-311G(d,p) in acetonitrile]. Radical **II** was taken as zero-energy.

As indicated above, only the *E* alkene was formed when the reaction was performed with an *E/Z* diastereomeric mixture of substrate **1a** (Scheme 5, Eq. 3). Data shown in Figure 2 can also help to find a possible reason for this result. We have just seen that the calculated Gibbs free energies support the exclusive formation of the *E* alkene from radical **1c**. On the other hand, we have done a computational study for the addition of PhOCH₂[•] to (*Z*)-**1a**, leading to radical **II**, and for the following β -elimination of PhSO₂[•] to afford product (*Z*)-**3ab** (see the ESI for details). As can be seen in Figure 2, the latter transformation should be very fast since its activation barrier is 3.0 kcal/mol. However, in principle, the barriers for the reverse reaction (4.9

kcal/mol) and for the change of conformation from **II** to **1c** (8.1 kcal/mol) could also be overcome at room temperature and this is an overall exergonic process. The formed radical **1c** could rapidly evolve to the (*E*)-**3ab**. This means that, finally, a thermodynamic control could be established, and the ratio between the *E* and *Z* alkenes could be determined by the difference in their Gibbs free energies. The calculated value of ΔG between (*E*)-**3ab** and (*Z*)-**3ab** is -2.5 kcal/mol, which represents a theoretical diastereomeric ratio (*E*)-**3ab**:(*Z*)-**3ab** of ca. 99:1. This agrees with the experimentally observed diastereoconvergence.

Experimental

See detailed experimental procedures in the ESI.

Conclusions

In conclusion, we have demonstrated that (*E*)-olefins can be regio- and diastereo-selectively formed by riboflavin tetraacetate photocatalyzed decarboxylative coupling of aliphatic carboxylic acids and aryl styryl sulfones. This reaction is promoted by visible light at room temperature, in the absence of toxic and expensive noble metals, and can be adapted to prepare internal alkynes by using alkynyl sulfones as radical acceptors. Moreover, we were able to prepare (*Z*)-alkenes by photoisomerization of the (*E*)-olefins, using Ir(ppy)₃ as an efficient triplet-energy transfer photosensitizer. Furthermore, we took advantage of the fact that 2-phenoxy-carboxylic acids are privileged substrates for this protocol, substituting the phenoxy group with an aryl one by an iron-catalyzed allylic substitution with Grignard reagents. Eventually, the stereochemical information of the obtained (*E*)-olefins proved useful in stereospecific epoxidations and intramolecular iodoarylations. Concerning the reaction mechanism, our control experiments show that a closed photoredox cycle should be operative with the decarboxylative generation of alkyl radicals. Finally, DFT calculations supported the observed regio- and diastereo-selectivity, and the diastereoconvergence from an *E/Z*-sulfone mixture.

Author Contributions

The experiments and data analysis were conducted by S.-J. B. and I. B. The computational studies were performed by D. G. The conceptualization and supervision of the project were performed by J. C. G.-G. and R. C. The original draft of the manuscript was written by J. C. G.-G. and D. G. All authors discussed the results and approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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