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1,2-Bis(phenylsulfonyl)ethylene (BPSE). A Potent Radical C2 Synthon Available in the Radical and Electron-Transfer-Based Organic Synthesis

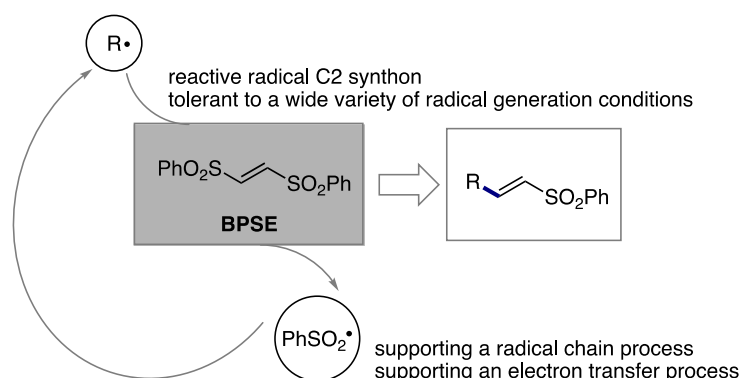
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Abstract In this short review, we discuss radical reactions using 1,2-bis(phenylsulfonyl)ethylene (BPSE), which has drawn significant attention as a versatile building block for (phenylsulfonyl)ethenylation. Regardless of its *E* or *Z* form, BPSE exhibits reliable reactivity towards the attack of alkyl and aryl radicals in order to function as a reliable radical C₂ synthon.

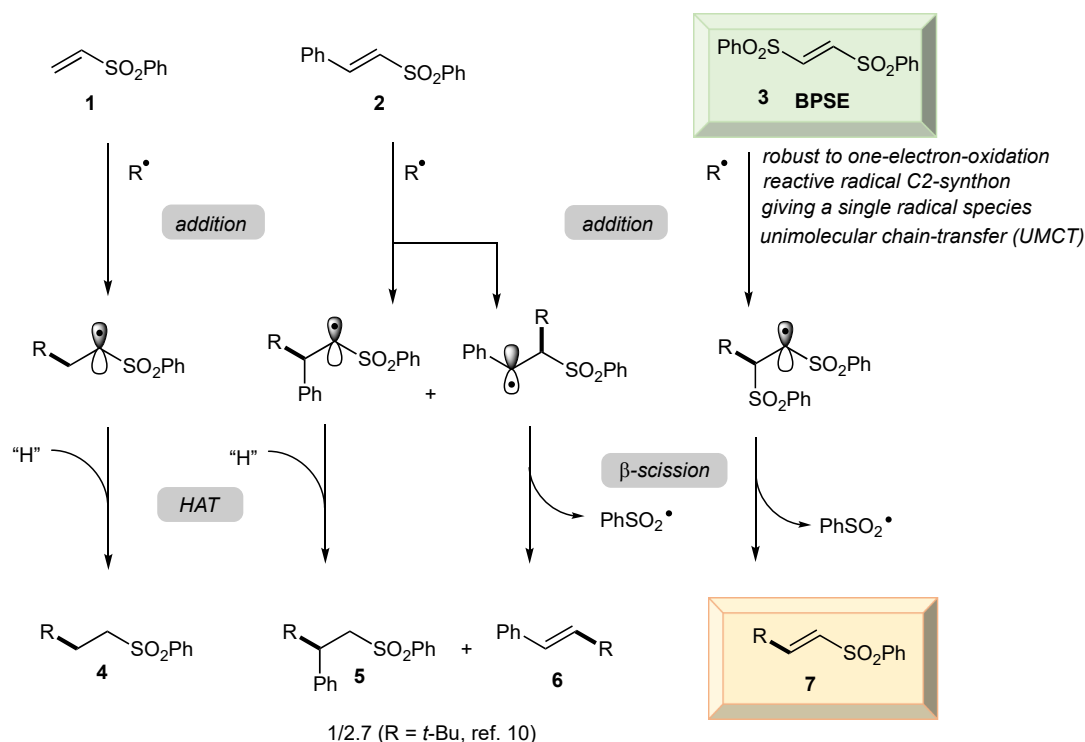
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2. Use in the Radical Chain Reactions
3. Use in the Reactions Utilizing Electron Transfer Process
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Key words 1,2-bis(phenylsulfonyl)ethylene, radical C₂ synthon, β-scission, phenylsulfonyl radical, radical alkenylation

1. Introduction

Unfunctionalized alkyl, alkenyl, and aryl radicals are classified as nucleophilic carbon radicals. In early 1980s, Giese investigated a polarity-matched trapping of these carbon-centered radicals by testing a series of alkenes.¹ The effective radical addition step coupled with the subsequent hydrogen atom transfer (HAT), is now named as Giese or Giese-type reaction, which usually employs electron-deficient alkenes as a radical trap, such as ethyl acrylate, methyl vinyl ketone, acrylonitrile, dimethyl maleate, just to name a few. Aside from HAT, the smooth addition step is extensively incorporated in the design of multi-component radical reactions.² In the retrosynthetic analysis of radical-based organic synthesis, introduced originally by Curran, alkenes are classified as radical C₂ synthons, acting as vicinal radical acceptor/radical precursor equivalents, and CO and isonitriles are radical C₁ synthons

acting as geminal radical acceptor/donor synthons.³ Multi-component coupling reactions by radicals constitute a rich area, encompassing a flexible combination of these radical C₂ and C₁ synthons. The Ryu group surveyed the examples of CO-incorporation some years ago.⁴ Vinyl sulfones are recognized as a reliable repertoire of radical C₂ synthons, exhibiting high reactivity towards nucleophilic carbon radicals. The parent case of vinyl phenyl sulfone (**1**) undergoes the regioselective addition to form a carbon radical α to the RSO₂ group (Scheme 1). On the other hand, the unique character of the organosulfonyl group capable of undergoing very fast β-scission is experienced, when radicals are located at the β-carbon, ending up with the formation of a C-C double bond.⁵ The process liberates organosulfonyl radicals, which are generally incorporated into the subsequent steps to sustain the radical chain. Such a reaction course is recognized most typically with allylic sulfones,⁶ and therefore, allylic sulfones were classified as unimolecular chain transfer (UMCT) reagents⁷ similarly to allyltributyltin⁸ and allyl bromides.⁹ While this reaction course is not an issue for the parent vinylphenylsulfone **1** due to the regioselective addition at the sterically less-hindered methylene carbon, in the case of β-substituted analogs, such as β-phenylvinyl phenyl sulfone **2**, uncontrolled regioselectivity during the addition may be observed. Russel's investigations on the regiochemistry of radical addition to alkenes effectively showed that the addition of the *t*-butyl radical onto **2** occurred with a 1/2.7 regiochemistry, favoring α-attack to give the β-alkylstyrene deprived of PhSO₂ group.¹⁰



Scheme 1 Reaction behaviors of three alkenyl phenyl sulfones **1**, **2**, and **3** (BPSE) towards radical addition.

How about 1,2-bis(phenylsulfonyl)ethene (BPSE, **3**),¹¹ bearing two phenylsulfonyl groups at vicinal 1,2-positions? Due to its symmetrical nature, BPSE leads to single addition/ β -elimination product, *i.e.* β -substituted vinylsulfones. It is also worth adding that a second addition onto the resulting vinylsulfone is usually not observed under radical conditions. Moreover, whatever the *E* or *Z* configuration of the starting BPSE, the final vinylsulfone general possesses the *E* configuration. The high reactivity of BPSE as a radical trap has been early recognized by Zard, Kim, Renaud, and Landais (*vide infra*). The oxidation potential of BPSE was calculated to be +2.41 V (vs. SCE),¹² one of the highest among vinylsulfones.¹³ This rationalizes the compatibility of BPSE in photoredox-catalyzed reactions using ordinary alkenes, in which BPSE behaves as a very robust alkene, even under photoirradiation conditions, yet serving as a reliable radical trap. While notable advancements in BPSE chemistry have been recognized particularly in multi-component radical chain reactions, recent applications include the use in photoredox-catalyzed reactions, radical-based C-H functionalization reactions, photosensitizing reactions, and stoichiometric oxidation reactions. The evolving examples of radical reactions using BPSE prompted the writing of this concise, yet documented review article on the synthetic capabilities of BPSE as a radical C2 synthon.

Whereas vinyl sulfone motifs can serve as versatile building blocks for synthetic organic transformations, recent studies have illustrated the use of vinylsulfone-based molecules as inhibitors of enzymes and chemical probes, leads, and drug candidates, represented by K777,¹⁴ working as cysteine protease inhibitor (Figure 1).^{15,16} The vinyl sulfone motif has been especially used in the design of chemotherapeutics, neuroprotective as well as radioprotective agents.¹⁷ In this regard, a review covering recent studies on the direct C-H incorporation of BPSE, and alkene-functionalization by BPSE, leading to biologically relevant targets containing the vinyl sulfone moiety may be timely. We hope that this short review will convince readers that BPSE is a useful, yet underdeveloped reagent.

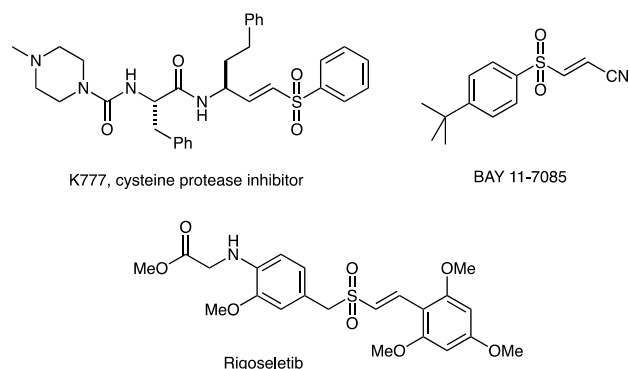
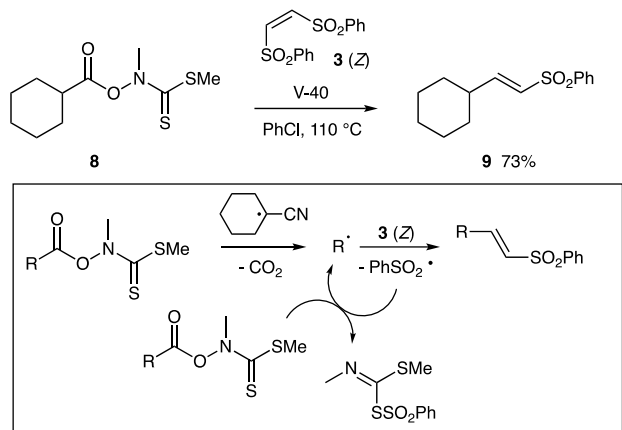


Figure 1 Vinylsulfone-based bioactive molecules.

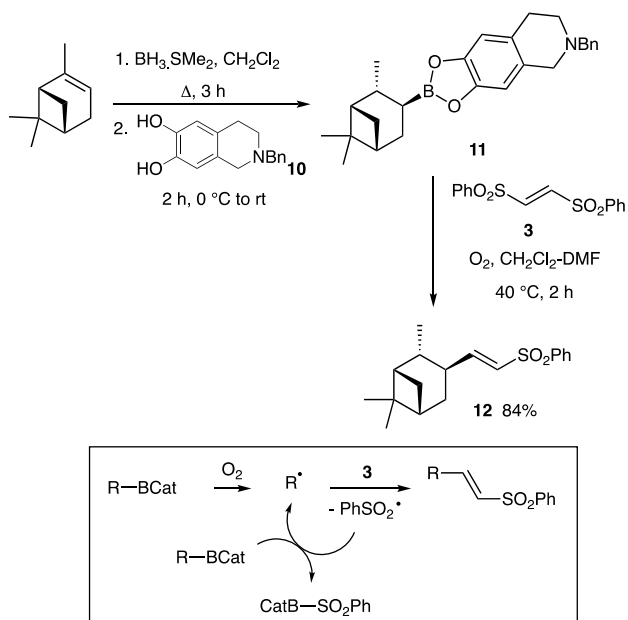
2. Use in the Radical Chain Reactions

In 2004, Kim developed a novel process involving the decarboxylation of thiohydroxamates (*i.e.* **8**, Scheme 2), which exhibited enhanced stability compared to the earlier esters pioneered by Barton.¹⁸ This advancement facilitated the decarboxylative allylation and vinylation of carboxylic acids. The reaction mechanism is initiated thermally in the presence of 1,1'-azobis(cyclohexane-1-carbonitrile) (V-40), leading to the formation of alkyl radicals subsequent to decarboxylation. These radicals then undergo addition to (*Z*)-BPSE (**3** (*Z*)), yielding (*E*)-form of vinylsulfone **9** in a high yield, as illustrated in Scheme 2. Noteworthy is the observation of double bond isomerization during the course of this transformation (*vide infra*). Importantly, the utilization of these specific conditions and thiohydroxamates mitigated the undesired trapping of alkyl radicals by the thiocarbonyl group present in esters.



Scheme 2 Decarboxylative vinylation of alkyl-thiohydroxamates.

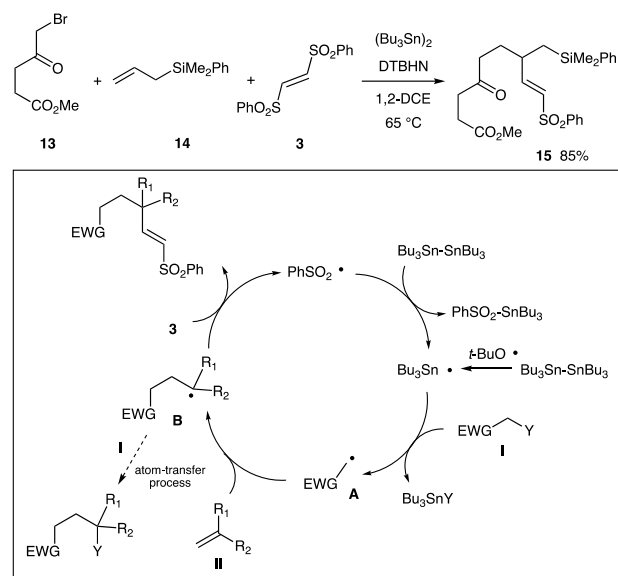
In their investigation into the reactivity of *B*-alkyl-catecholboranes, Renaud *et al.* pioneered the development of a range of new boron-based reagents, serving as precursors of alkyl radicals.¹⁹ These substrates, derived from tetrahydroisoquinolines, (*i.e.* **10**) enabled the addition products to be isolated in higher yields, as compared to those attained with simple catecholboranes (Scheme 3). The hydroboration of pinene showcased the generation of an addition product, which upon treatment with tetrahydroisoquinoline **10** yielded intermediate **11**. Subsequently, in the presence of oxygen and (*E*)-BPSE **3**, **11** afforded the pinene vinylation product **12** as a single stereoisomer with a significantly improved yield (84%) compared to the use of catecholborane (64%). The radical chain is propagated through the release of the phenylsulfonyl radical following the addition of the alkyl radical onto **3**. The PhSO₂ radical reacts at the boron center, thereby regenerating the alkyl radical, while producing CatB-SO₂Ph as a by-product.



Scheme 3 Vinylation of modified *B*-alkyl-catecholboranes.

Landais and co-workers developed a three-component process using BPSE **3** as a vinyating agent (Scheme 4).²⁰ Ditin reacted as a transfer agent and allowed the addition of electrophilic radicals onto electron-rich olefins, followed by the trapping of the resulting C-centered radical with (*Z*)- or (*E*)-BPSE. This reaction consistently proceeded with high yields and notable stereoselectivity, favoring the *E*-olefin configuration, regardless of whether (*Z*)- or (*E*)-BPSE **3** was employed. A simplified radical chain is illustrated in Scheme 4 below. The reaction is initiated

with di-*tert*-butyl hyponitrite (DTBHN), which upon heating delivers the *t*-BuO radical. The latter reacts with ditin to provide the requested tin radical, which abstracts the halogen and generates the electrophilic radical **A**. This adds to the olefin **II** to provide a nucleophilic radical, which adds efficiently onto the electron-poor double bond of (*Z*)- or (*E*)-BPSE, affording the final product. The efficiency of the process relies on the matched polarity between the three partners. Atom-transfer process is also likely operating, but the presence of excess tin reagent regenerates the radical **B**. Throughout their study, the authors demonstrated that the addition of radical **B** onto (*Z*)- or (*E*)-BPSE resulted in the product with (*E*)-configuration, showcasing over 95% diastereocontrol. This finding suggested that β -elimination occurred subsequently to rotation around the C-C bond, minimizing steric interaction between the attacking **B** fragment and the sulfonyl substituent.

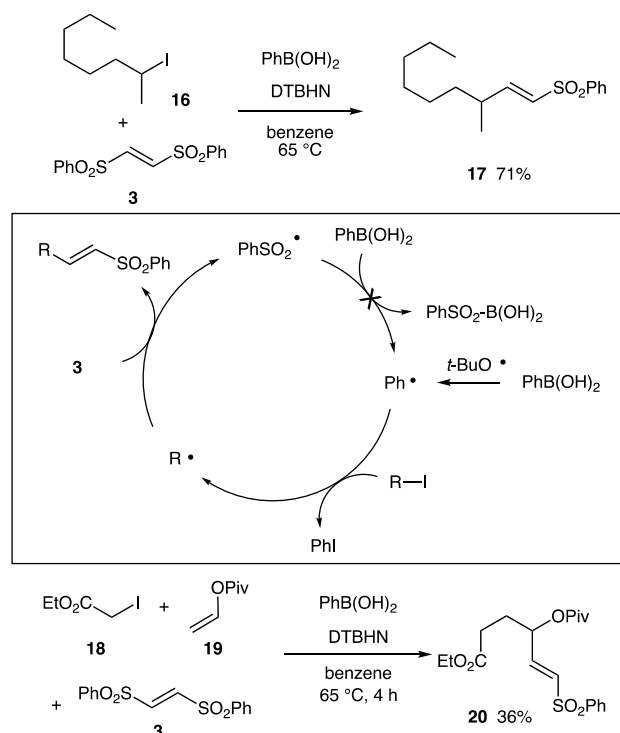


Scheme 4 Tin-mediated 3-component carbo-vinylation of alkenes.

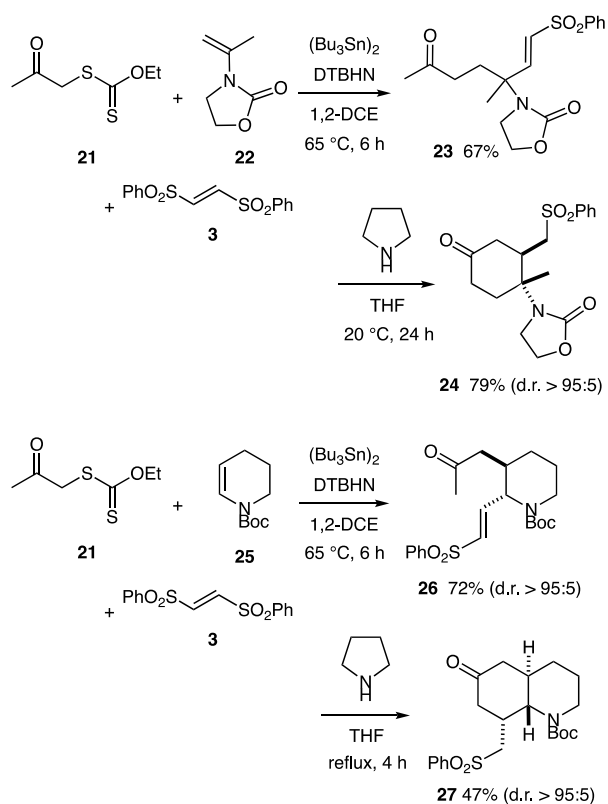
Building upon their previous research, the same authors developed an alternative approach that eliminates the need for the tin reagent, known for its perceived toxicity.²¹ Drawing inspiration from the work of Renaud and coworkers on the reactivity of organoboranes towards sulfonyl radicals,¹⁹ they employed the boronic acid PhB(OH)₂ to initiate the vinylation of alkyl halides. Addition of DTBHN onto the boronic acid delivered the phenyl radical, which was able to abstract the iodine atom from the alkyl iodide, thus generating the desired alkyl radical R• (Scheme 5). Subsequently, R• added onto **3** to yield the final olefin product, alongside the phenylsulfonyl radical. The latter however, was unable to sustain the radical chain through reaction with the arylboronic acid. This issue of chain propagation was addressed by employing an excess of the boron reagent. The methodology was extended to the 3-component process with the synthesis of **20** from iodide **18** and olefin **19**, albeit with moderate yield. The accumulation of the PhSO₂ radical in the medium, which may compete with the desired addition, by potentially reacting to the olefin, could hinder the desired outcome, albeit the addition of sulfonyl radical is known to be reversible.

Landais and his team capitalized on the residual vinylsulfone present in the three-component products derived from **21**, **3**, and **22** to explore additional cyclization pathways. For instance, in cases where the initial xanthate, such as **21**, contained a ketone functionality, an intramolecular organocatalyzed Michael addition could be performed, leading to the formation of

the six-membered ring with high level of diastereocontrol (Scheme 6).^{20b} Moreover, by utilizing a cyclic ene-carbamate such as **25** as the starting alkene, a two-step process enabled the synthesis of compound **27**,²² bearing a bicyclic structure reminiscent of the perhydroquinoline skeleton of *Lycopodium* alkaloids (Scheme 6).²³



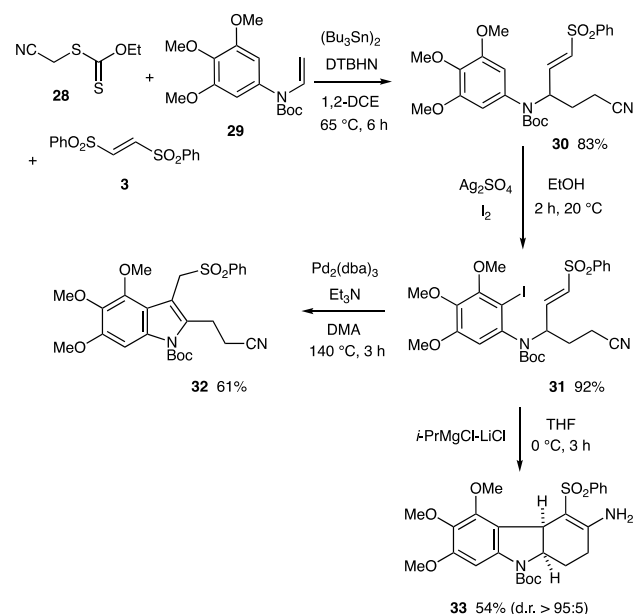
Scheme 5 Boronic acid-mediated vinylation of alkyl halides.



Scheme 6 Intramolecular Michael additions on the three-component products.

The same researchers extended their investigations to more intricate cyclization procedures. Starting with cyanoxanthate **28** and an enamine featuring an electron-rich aromatic moiety **29**, they obtained the resultant three-

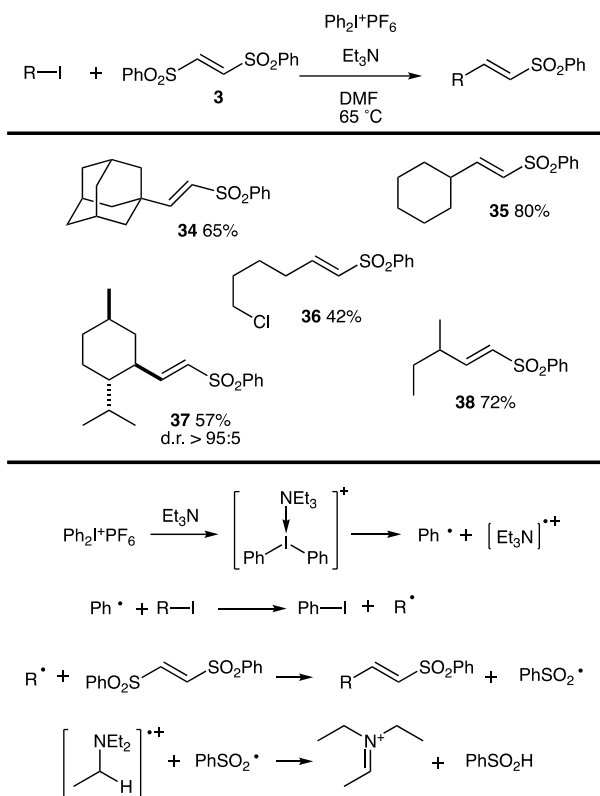
component product **30**, which was then subjected to iodination and subsequent cyclization processes. For instance, iodinated compound **31** underwent a Heck-type reaction, followed by a double bond migration within the ring, resulting in the synthesis of a highly functionalized indole **32** (Scheme 7).²⁴ Additionally, an anionic protocol was disclosed, involving the generation of a Grignard reagent leading to an intramolecular 1,4-addition and cyclization of the sulfonyl-stabilized anion onto the cyano group. This yielded compound **33**, which was formed in a stereocontrolled manner through the formation of two rings in a single step.



Scheme 7 Intramolecular Heck and anionic cyclizations on the three-component products.

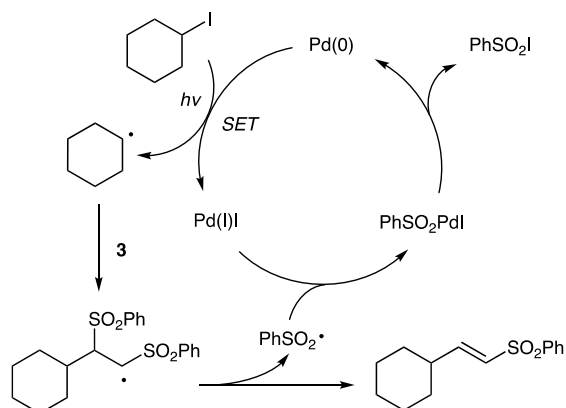
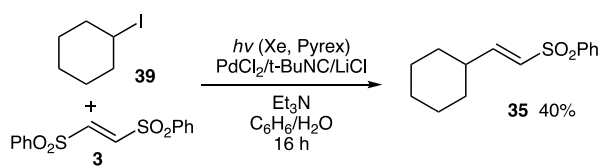
3. Use in the Reactions Utilizing Electron Transfer Process

Landais and coworkers have investigated the use of electron-donor-acceptor (EDA) complexes to create a radical initiation system.²⁵ Specifically, they focused on diaryliodonium salts, hypervalent iodine compounds, which form EDA complexes on treatment with electron-donating agents such as amines. Under heating or light irradiation conditions, electron transfer occurs between the components, leading to the generation of aryl radicals. They utilized this reaction in a sequence involving iodoalkanes and BPSE (Scheme 8). The key step is the formation of alkyl radicals by the abstraction of an iodine atom from the alkyl iodides by a phenyl radical. Finally, the desired products **34-38** are obtained through the addition of alkyl radicals onto BPSE and the subsequent β -elimination of PhSO_2 radical. In this study, the PhSO_2 radical abstracts a hydrogen atom from triethylamine radical cation, forming benzene sulfonic acid.



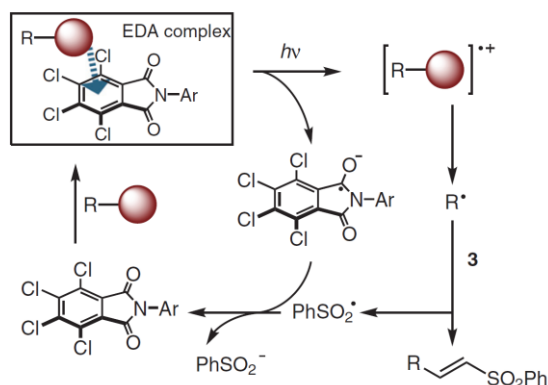
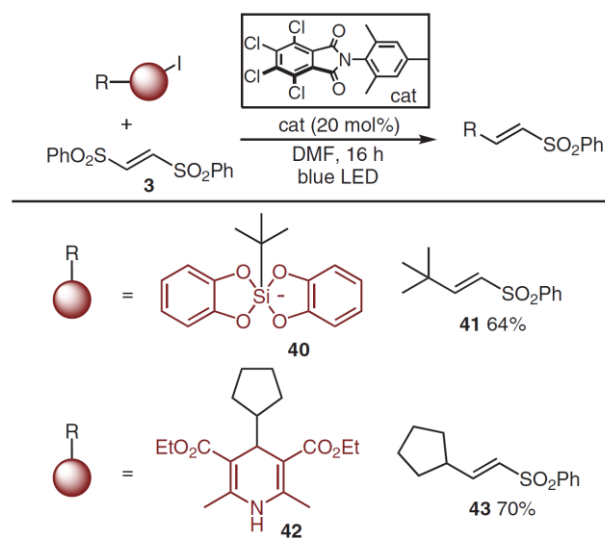
Scheme 8 Radical alkenylation of alkyl iodides using electron transfer in EDA complexes.

Radical reaction of alkyl iodides with BPSE can be performed by Pd catalysis under photoirradiation conditions.²⁶ Scheme 9 illustrates the reaction of iodocyclohexane with BPSE. The reaction mechanism involves the photoexcited Pd(0) complex undergoing a single-electron reduction with iodocyclohexane (39) leading to the formation of the radical-anion, subsequently collapsing into the cyclohexyl radical and iodide anion. Various radical-type cross-coupling and carbonylation reactions have thus been attained under photoirradiation conditions using Pd catalysis.^{27,28}



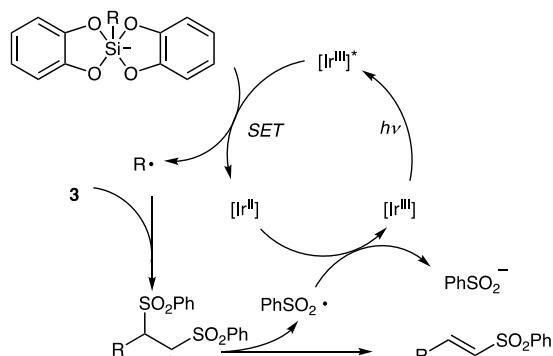
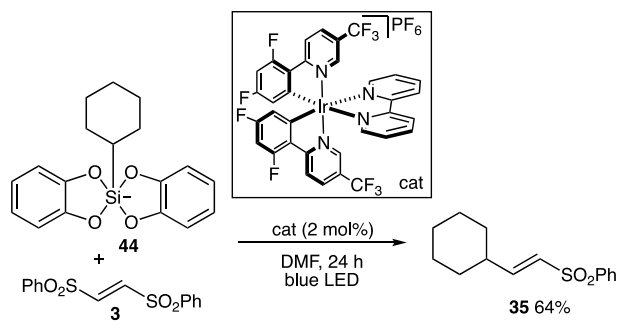
Scheme 9 Radical alkenylation of alkyl iodides using electron transfer by Pd/light system.

Melchiorre and coworkers have developed a photocatalytic method that uses electron-accepting molecules as catalytic EDA complexes, enabling electron-donating molecules, such as alkyl silicates, 4-alkyl-1,4-dihydropyridine (alkyl-DHP), and alkyl trifluoroborates, to act as radical precursors.²⁹ Radical alkenylation was accomplished when BPSE was used as a radical acceptor in the presence of an alkyl-silicate such as **40** or an alkyl-DHP such as **42** as alkyl radical sources (Scheme 10). One-electron reduction of PhSO₂ radical into PhSO₂⁻ ($E_{1/2}^{\text{red}} = +0.5\text{V vs. SCE}$) then restores the catalyst in its ground state.³⁰



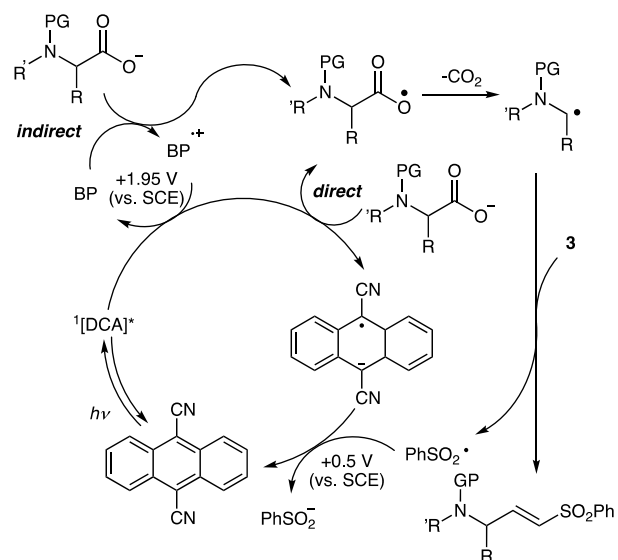
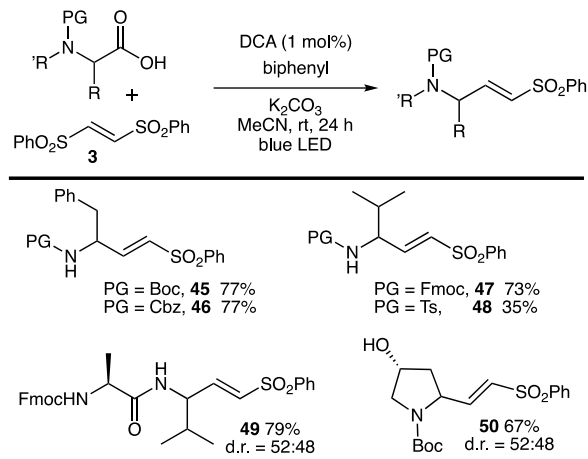
Scheme 10 Radical alkenylation of electron-donating compounds by catalytic EDA complex formation.

Ollivier, Fensterbank, and coworkers reported a photoredox-catalyzed reaction using hypervalent bis-catechol silicates as alkyl radical precursor, in conjunction with an iridium complex as a photocatalyst.³¹ Silicates **44** undergo one-electron oxidation by the photoexcited Ir complex, resulting in the generation of alkyl radicals. In this system, radical alkenylation proceeded well, when BPSE was used (Scheme 11). The photoredox catalyst system using silicates has an application to carbonylation process using CO.³²



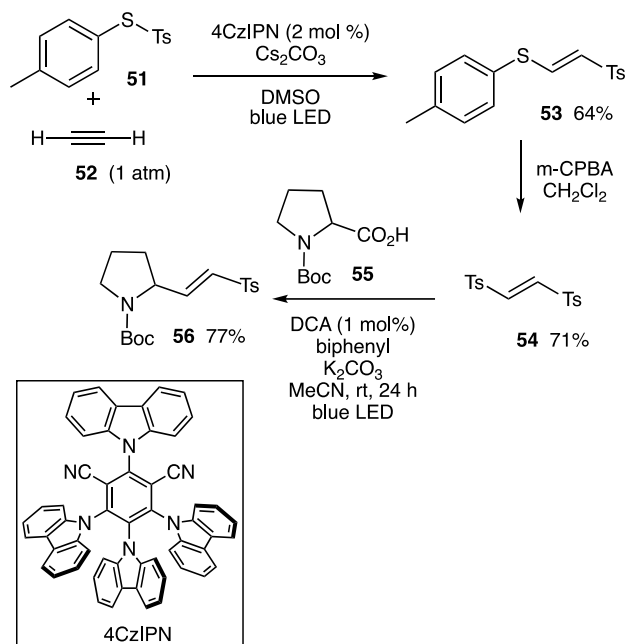
Scheme 11 Radical alkenylation of alkyl silicate using Ir-complex as photoredox catalyst.

BPSE is highly resistant to oxidation (high oxidation potential, *vide supra*), and thus behaves as an efficient radical trapping agent under oxidative reaction conditions. Opatz and coworkers successfully combined the oxidative decarboxylation of carboxylic acids with the alkenylation of the resulting alkyl radicals with BPSE, in the presence of 9,10-dicyanoanthracene (DCA) as a photoredox catalyst (Scheme 12). Although the reaction proceeds with DCA alone, the addition of biphenyl (BP) as a redox mediator enhances its efficiency.³³ When amino acids are used as substrates, the resulting aminoalkyl radicals undergo efficient reactions with BPSE, with enhanced nucleophilicity by the proximity effect of nitrogen. In contrast, primary or secondary carboxylic acids gave inferior results and tertiary or benzylic carboxylic acids were not competent precursors. The proposed reaction mechanism involves the one-electron oxidation of BP by photo-excited DCA. The resulting BP cation-radical oxidizes the carboxylate, which loses CO₂ to generate the alkyl radical. The latter then adds to BPSE, followed by β-elimination of the PhSO₂ moiety to yield the desired β-substituted vinyl sulfone. DCA is regenerated from the DCA radical-anion through a single-electron transfer to the benzenesulfonyl radical, generating the corresponding sulfinate anion thus completing the catalytic cycle.



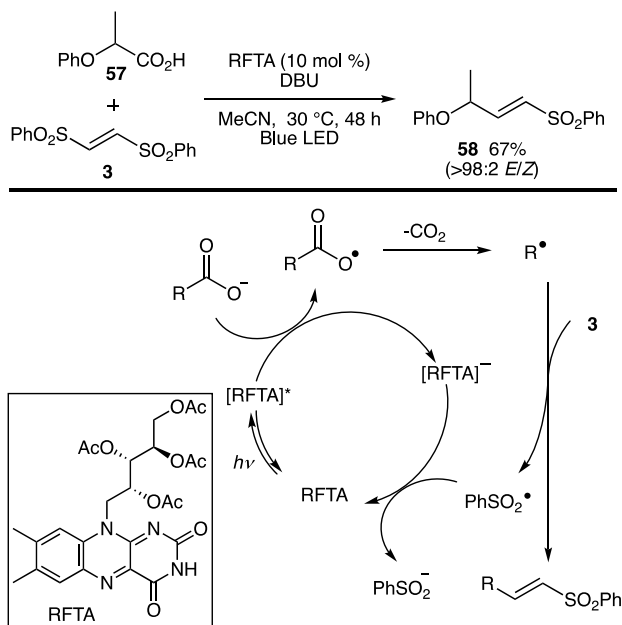
Scheme 12 Oxidative radical alkenylation with decarboxylation of amino acids catalyzed by photocatalyst.

Chen, Zhu, and coworkers have recently achieved 1,2-difunctionalization of acetylene gas through the cleavage of the SO₂-heteroatom bond (Scheme 13).³⁴ In their work, they found that thiosulfonation of acetylene proceeds by using **51** as a starting material to afford **53** and the subsequent oxidation gave (*E*)-1,2-ditosylethene (**54**). Subsequently, they reported that alkenylated compound **56** was obtained by the decarboxylative reaction of **55** with **54** using Opatz's reaction conditions.



Scheme 13 Synthesis and utilization of (E)-1,2-ditosylethene (54) by difunctionalization of acetylene gas (52).

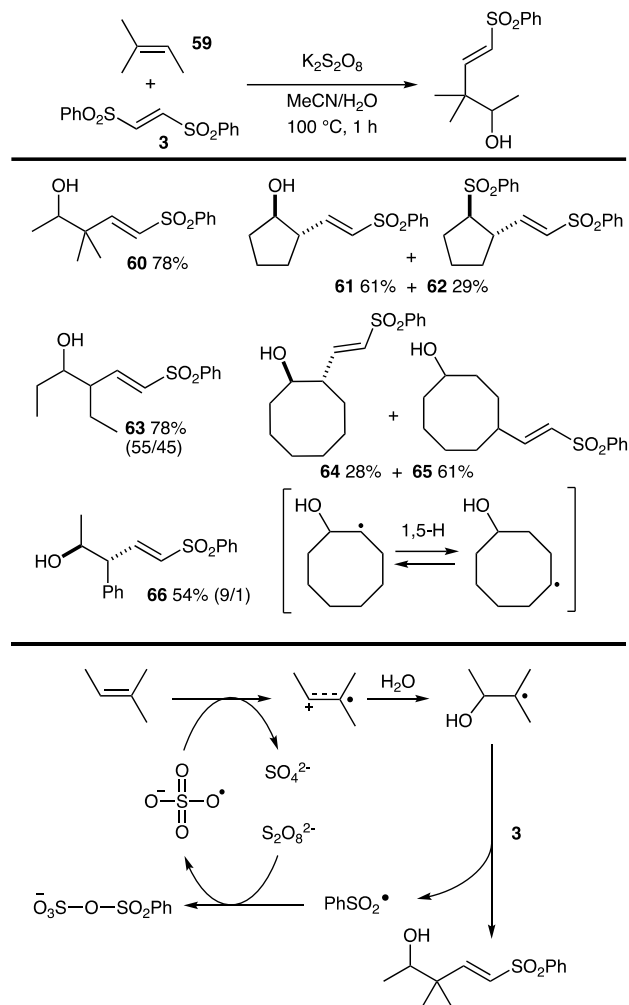
Chinchilla, Gonzalez-Gomez, and coworkers reported that riboflavin tetraacetate (RFTA), which can be derived from vitamin B₂, acts as a photocatalyst in the alkenylation of carboxylic acids using β -arylvinylnylphenylsulfone.³⁵ In the reaction of carboxylic acid 57 with BPSE, RFTA acts as a photoredox catalyst. A mechanism has been proposed in which the catalytic cycle is completed by RFTA performing the one-electron oxidation of the carboxylate then the one-electron reduction of the PhSO₂ radical generated with the product 58 (Scheme 14).



Scheme 14 Oxidative radical alkenylation with decarboxylation of carboxylic acids catalyzed by RFTA as photocatalyst.

One-electron oxidation of alkenes produces alkene radical-cations.³⁶ In the presence of water, hydroxylation takes place to give β -hydroxy alkyl radicals. Citterio and Minisci reported a reaction using benzoquinone as a radical trap and silver catalyst in the presence of peroxodisulfates as oxidant.³⁷ Ryu and coworkers accomplished oxidative hydroxyalkenylation of

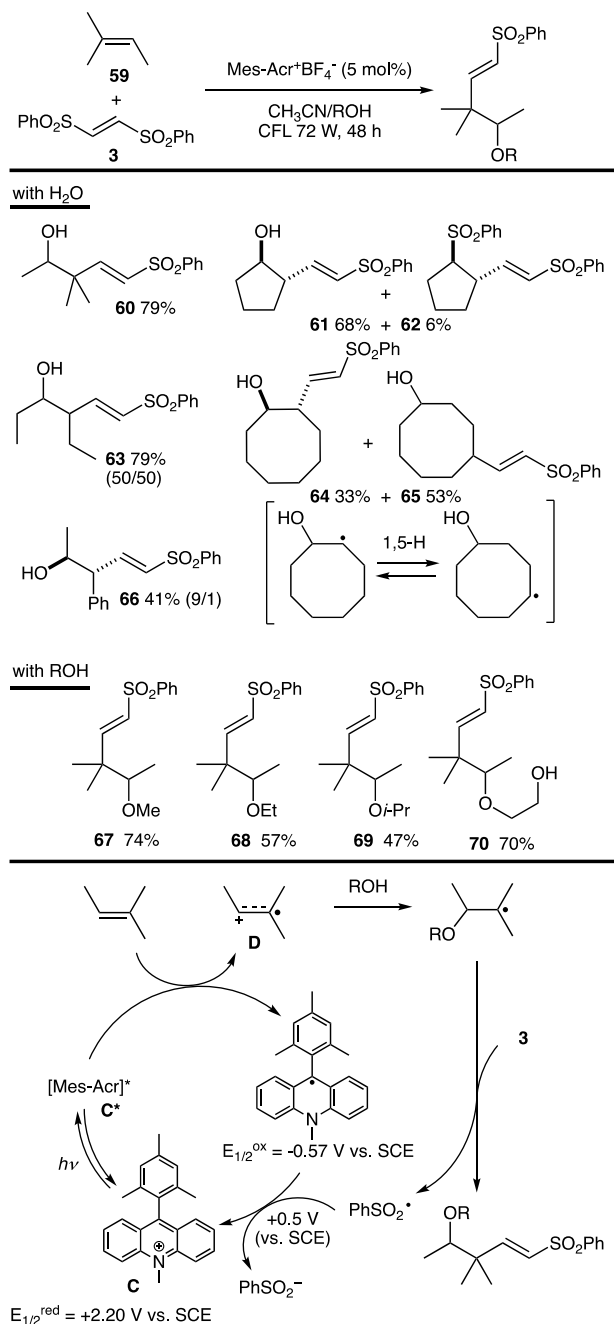
olefins using peroxodisulfate alone and BPSE in the absence of a catalyst (Scheme 15).³⁸ Cyclic olefins with 5- to 7-membered rings yield hydroxyalkenylation products in good yields. In the case of cyclooctene, 1,5-hydrogen migration followed by alkenylation with 3 led to a mixture of two hydroxyalkenylation products (64 and 65). Linear alkenes, on the other hand, yield products via more stable radical intermediates after hydroxylation. PhSO₂ radical is ultimately oxidized to form PhSO₃H. However, it often causes radical-mediated benzenesulfonyl alkenylation of alkenes as side reaction as shown in the case of cyclopentene.



Scheme 15 Oxidative hydroxyalkenylation via one-electron oxidation of alkenes.

Nicewicz and coworkers reported that Fukuzumi's acridinium salt C worked well as a photoredox catalyst to achieve anti-Markovnikov addition of HX to alkenes, in which benzenesulfonic acid or benzenethiol was used as hydrogen source for HAT to hydroxyalkyl radicals.³⁹ Ryu and coworkers devised a photocatalytic activation of alkenes based on Fukuzumi's catalyst directed toward the hydroxyalkenylation of alkenes by BPSE and water (Scheme 16).⁴⁰ This resulted in the development of a photocatalytic version of a similar stoichiometric reaction performed before by peroxodisulfates. Thus, the photoexcited acridinium catalyst C* ($E_{1/2}^{\text{red}} = +2.20$ V vs. SCE)⁴¹ promotes the one-electron oxidation of 2-methyl-2-butene (59) ($E_{1/2}^{\text{ox}} = +1.81$ V vs. SCE)⁴² to generate cation-radical D. Hydration and alkenylation using BPSE gave the product and benzenesulfonyl radical ($E_{1/2}^{\text{red}} = +0.5$ V vs. SCE), which could reoxidize the acridine radical, thus restoring the acridinium ion in its ground state ($E_{1/2}^{\text{ox}} = -0.57$ V vs. SCE), thus closing the catalytic cycle. The reaction time of the photocatalytic protocol is longer,

but the results are comparable to those achieved with peroxydisulfates. Furthermore, alkoxyalkenylation reactions also proceed by using alcohols as nucleophiles without suffering from the hydrogen abstraction in C(sp³)-H bonds that persulfate protocol often faced.



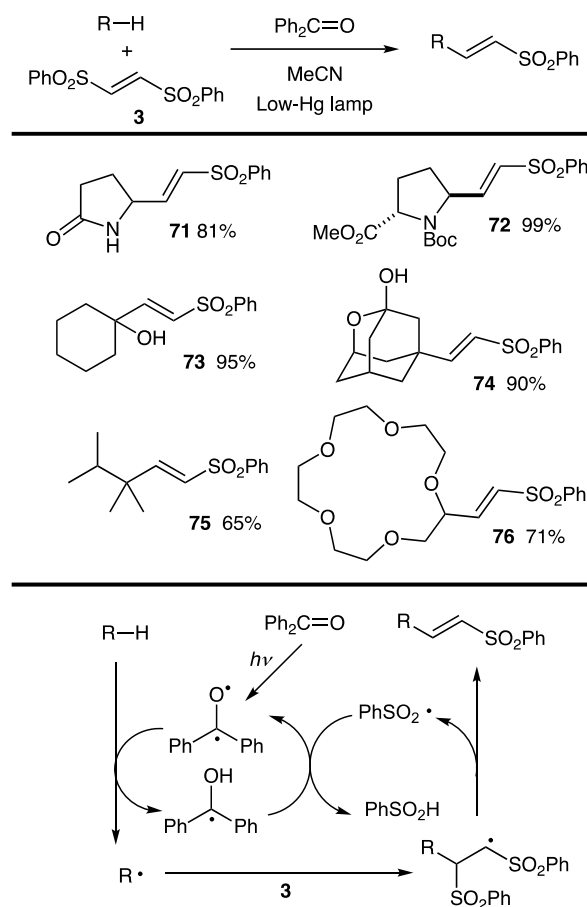
Scheme 16 Fukuzumi's acridinium salt catalyzed oxidative hydroxyalkenylation via one-electron oxidation of alkenes.

4. Use in the Radical-Based C-H Alkenylation

Alkyl radicals are generated by C(sp³)-H cleavage reactions via HAT (Hydrogen Atom Transfer) reaction, induced by heteroatom-centered radical species, such as RO•, R₂N•, and Cl•.⁴³ This chapter introduces the use of BPSE in C(sp³)-H alkenylation reactions.

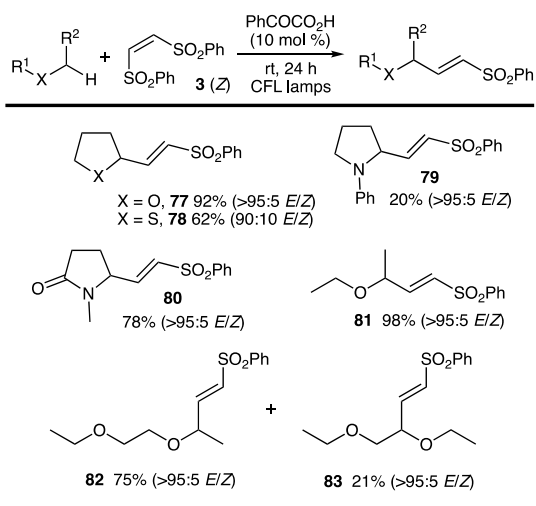
When ketones are exposed to light, the oxygen atom of the excited carbonyl group is able to abstract a hydrogen atom at the γ position (1,5-HAT), resulting in a biradical species. The overall reaction course is recognized as the Norrish type II process.⁴⁴ Inoue and coworkers extended this basic photo-reaction to

intermolecular HAT reactions. They used oxygen-centered radicals generated from photoexcited benzophenone to achieve C(sp³)-H bond cleavage, leading to cyanation, alkylation, and 4-pyridylation, among other C(sp³)-H functionalization products.⁴⁵ The electrophilic oxyl radical produced upon photoexcitation of benzophenone abstracts hydrogen atoms from electron-rich C-H bonds, resulting in the formation of new C-centered radicals. When BPSE is used as a trap, radical alkenylation reactions occur smoothly (Scheme 17).⁴⁶ PhSO₂ radicals may abstract hydrogen from hydroxydiphenylmethyl radical, allowing benzophenone to regenerate. The attempts to use a catalytic amount of benzophenone met with a limited success. However, modified benzophenone system using 4,4'-dichlorobenzophenone was reported later by the Guin group to show improved catalytic efficiency.⁴⁷



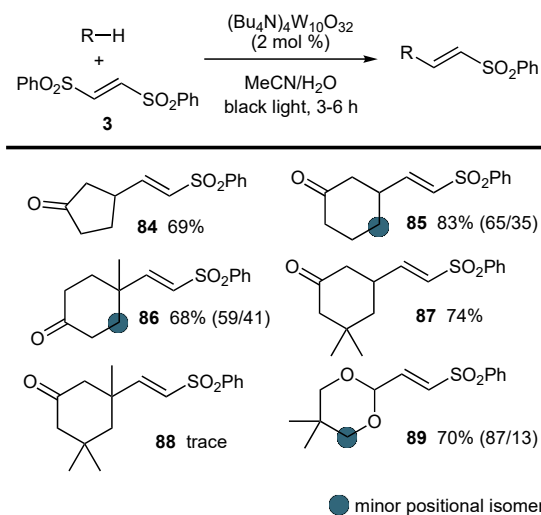
Scheme 17 Radical alkenylation using benzophenone as HAT catalyst.

Kokotos's group has reported that phenylglyoxylic acid can function as a photoinitiator capable of cleaving the C-H bond of aldehydes-CHO and the α -position of alcohols.⁴⁸ They have also reported the radical alkylation, alkenylation, alkylation, and C-N bond formation. The formation of these products is achieved via C(sp³)-H bond cleavage at the α -position of heteroatoms (N, O, and S). As illustrated in Scheme 18, vinylsulfonylation at the α -position of heterocycles and aliphatic ethers, has been accomplished using (Z)-BPSE.⁴⁹ In this reaction, the phenylglyoxylic acid is photoexcited and undergoes intersystem crossing (ISC) to the triplet state to generate ketyl or acyl radicals, which then behave as HAT agents.

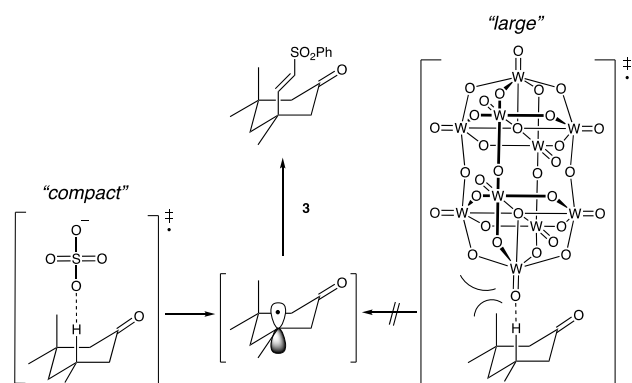


Scheme 18 Radical alkenylation using phenylglyoxylic acid as HAT catalyst.

C(sp³)-H cleavage by photo-excited decatungstate anion displayed high site-selectivity based on polar and steric effects during HAT transition states.⁵⁰ This photocatalytic HAT system ensuring site-selective C(sp³)-H bond cleavage was successfully combined with alkenylation using BPSE (Scheme 19).⁵⁰ The decatungstate anion, when photoexcited, acts as an oxygen centered radical to abstract hydrogen atoms from C(sp³)-H bonds and exhibit site-selectivity due to polar and steric effects.⁵¹ The decatungstate anion thus cleaves selectively C-H bonds at the β position of carbonyl groups, highly selective β -C-H alkenylation reactions being achieved. The reaction applied to cyclopentanone proceeds through the formation of a β -radical. Cyclohexanone, on the other hand, favors β -position reactions, while 4-methylcyclohexanone prefers reactions at the 4-position due to the stability of the radical species. Notably, 3,3-dimethylcyclohexanone exhibits selective reactivity at the 5-position to avoid steric hindrance. When using 3,3,5-trimethylcyclohexanone shown poor reactivity (Scheme 20). Additionally, in the reaction of 5,5-dimethyl-1,3-dioxane, the large decatungstate anion favors the cleavage of the C-H bond at the less-hindered 2-position in the ratio of 87 to 13 (**89**, Scheme 19).

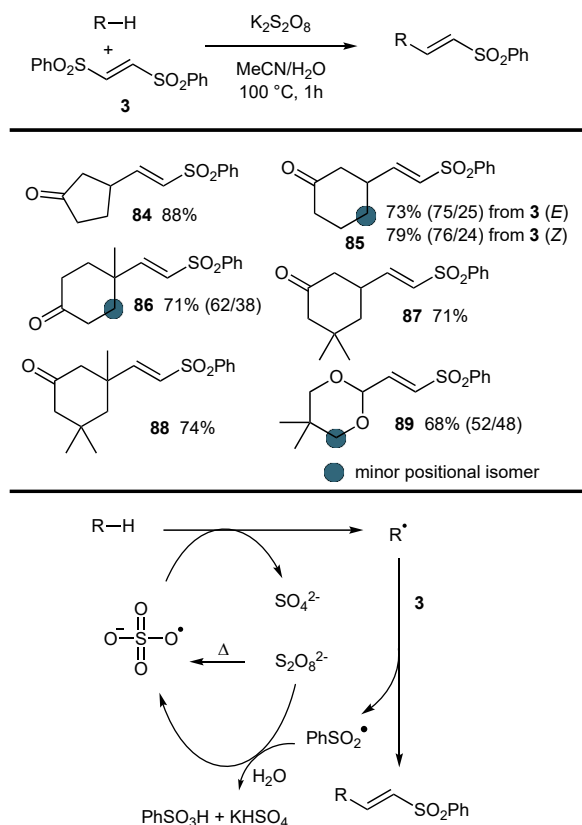


Scheme 19 Site-selective radical alkenylation using decatungstate anion as HAT catalyst.



Scheme 20 Proposed C(sp³)-H abstraction steps of 3,3,5-trimethylcyclohexanone by the large decatungstate anion and the compact sulfate radicals.

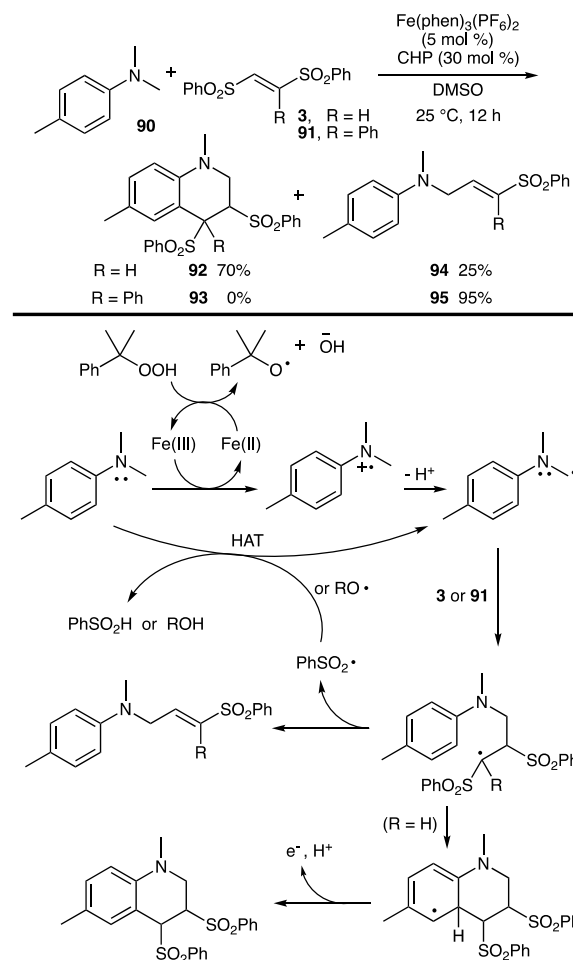
Ryu's group have also explored smaller HAT agents bringing minimal steric effects. It is interesting to note that sulfate radicals generated from persulfate exhibit position selectivity due to polar effects (Scheme 21).⁵² Similar to the decatungstate anion, sulfate radicals selectively cleave C-H bonds at the β position of carbonyl groups. The significant difference between sulfate anion-radical and decatungstate anion lies in their steric bulkiness, which leads to substantial differences in the reactivity. For instance, 3,3,5-trimethylcyclohexanone, which exhibited low reactivity with decatungstate anion due to its bulkiness, efficiently underwent alkenylation reactions with the compact sulfate radicals (Scheme 20). In the case of 5,5-dimethyl-1,3-dioxane, where alkenylation at the 4-position was favored to the 2-position in the decatungstate anion system (87/13), the use of sulfate radicals resulted in reduced steric hindrance giving a 52/48 ratio of **89** (Scheme 21).



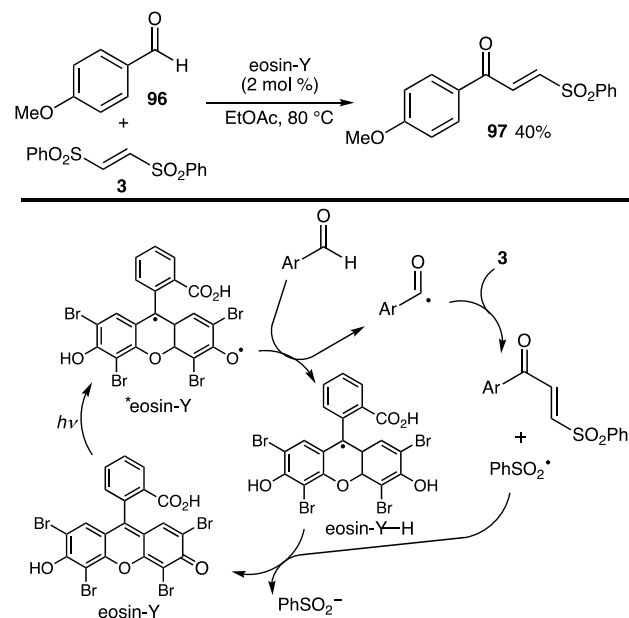
Scheme 21 Site-selective radical alkenylation using sulfate radical as HAT reagents.

Allylamine is a crucial component in the production of pharmaceuticals and agrochemicals. Kang investigated the synthesis of allylamines through α -C-H-alkenylation of *N,N*-dimethyl *p*-tolylamine by BSPE.⁵³ The reaction is based on Fenton-type reaction using cumene hydroperoxide (CHP) as an oxidizing reagent, which produces iron(III) and cumyloxy radical. The one-electron oxidation of dimethylaniline by iron (III) and the subsequent deprotonation generates an α -amino methyl radical. By using BPSE 3 as the alkenylation reagent, radical addition reaction is expected to lead to the desired allylamines. However, cyclization reaction competed, leading to the tetrahydroquinoline skeleton as the major course (Scheme 22).⁵⁴ To address this issue, Ph-substituted bisphenylsulfanyl ethylene 91 was examined to prevent cyclization. This worked well to allow for the successful synthesis of the desired allylamines in high yield.

Acyl radicals are useful intermediates in the synthesis of various carbonyl compounds. Efficient methods to generate acyl radicals often involve hydrogen abstraction from aldehydes, typically using oxidants or transition metal catalysts.⁵⁵ Zhang, Duan, Wu, and their research group proposed using neutral eosin-Y as a HAT catalyst for aldehydes hydrogen abstraction.⁵⁶ Additionally, during catalyst regeneration, phenylsulfonyl radical is reduced to give benzene sulfonic acid. This strategy allowed for the functionalization of different substrates that contain RSO_2 leaving groups, such as $\text{PhSO}_2\text{-SCH}_2\text{F}$, $\text{PhSO}_2\text{-SPh}$, $\text{Ms-C}\equiv\text{CR}^2$, and Tf-N_3 . It is worth noting that when BPSE was used, radical alkenylation reactions also proceeded to give β -phenylsulfonyl- α,β -unsaturated ketone 97 (Scheme 23).



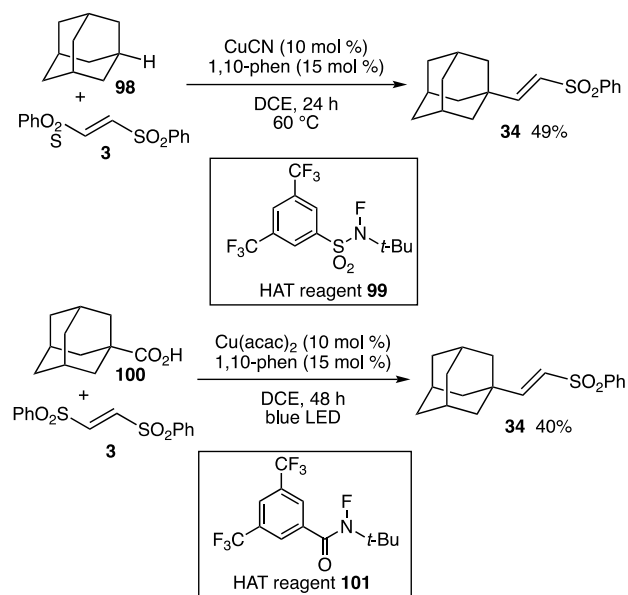
Scheme 22 Synthesis of allylamines by alkenylation via Fe-catalyzed C-H cleavage.



Scheme 23 Synthesis of enones via C-H cleavage of aldehydes by neutral eosin-Y.

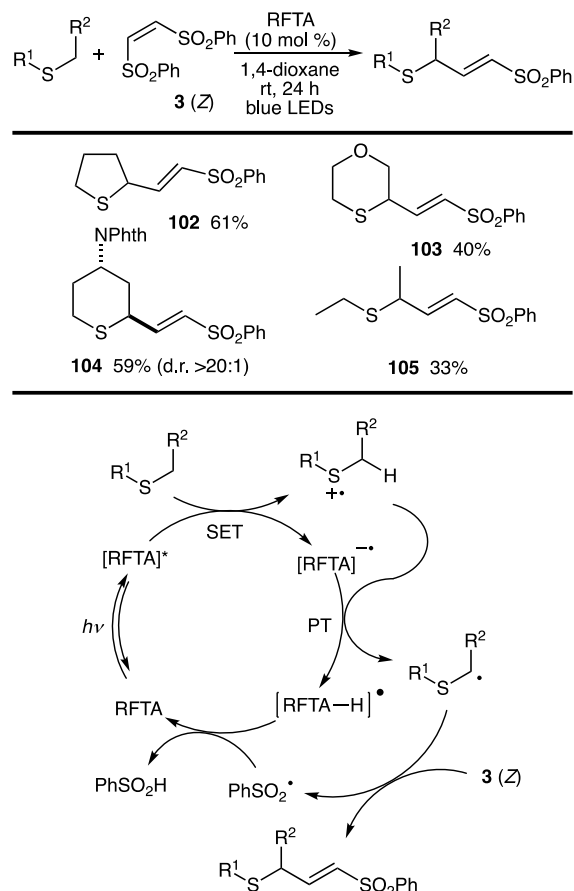
While methods that utilize N-X bonds, such as NFSI, have been explored for radical fluorination and other transformations, thus far reactions using NFSI were limited to the cleavage of active C-H bonds.⁵⁷ However, recent reports have shown that radical mediators having N-Br, N-Cl or N-xanthates, can be effective in decarboxylative functionalization reactions of carboxylic acids.⁵⁸ Hu and colleagues accomplished a

decarboxylative functionalization of carboxylic acids using N-F aromatic amides as N-centered radical sources under copper-catalyzed conditions with light irradiation.⁵⁹ Notably, N-F sulfonylamides acted as efficient HAT reagents for C(sp³)-H functionalization even in the absence of light. Although selectivity in C-H activation has not been fully discussed, reactions at heteroatom α -positions have been reported to proceed selectively. This approach allows for the use of various radical acceptors, enabling functionalization by SAR, SCF₃, F, and Cl. They reported that when using BPSE, radical alkenylation reactions can also occur (Scheme 24). For the decarboxylation of carboxylic acids, in HAT from O-H bond is proposed. The generation of the iminyl radical is proposed to occur via copper catalysis, although the rationale for this is not provided.



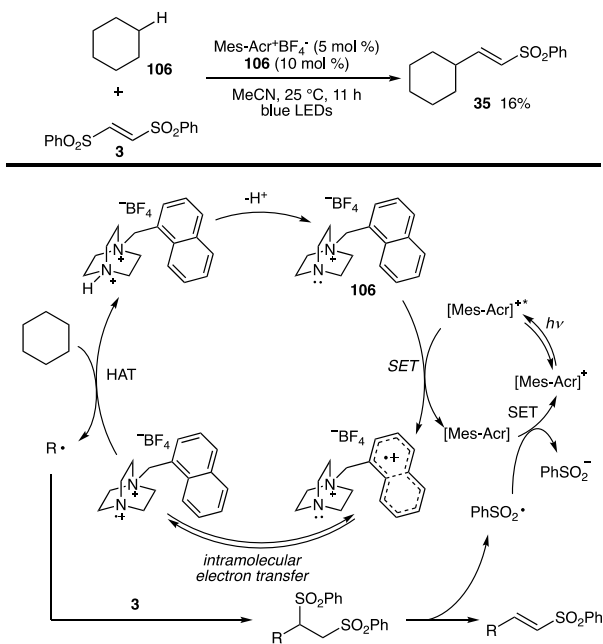
Scheme 24 Alkenylation of carboxylic acids or alkanes using N-F compounds as HAT reagents.

Procter *et al.* have reported that riboflavin (vitamin B2) can mediate C-H activation at the α -position of the sulfide by successive SET and PT, acting as a photocatalyst for Giese-type reactions.⁶⁰ They have also reported alkenylation and alkynylation by using its derivative, RFTA (riboflavin tetraacetate, *vide supra*).⁶¹ As illustrated in the Scheme 25, alkenylation proceeds with regioselectivity at the α -position of the sulfur atom of the sulfide, albeit moderately, by using (Z)-BPSE as a radical acceptor.



Scheme 25 C-H alkenylation at α -position of the sulfur atom by RFTA.

Matsumoto and Maruoka achieved C-H alkylation reactions using **106** with a 1-naphthyl group derived from DABCO as a HAT catalyst,⁶² inspired by the highly electrophilic dicationic aminium radical obtained from Selectfluor. The naphthyl group of this catalyst **106** is more easily oxidized than the DABCO skeleton, so the one-electron oxidation by acridinium salt proceeds efficiently. Intramolecular electron transfer then gives rise to aminium radicals, and then HAT proceeds. Good to excellent yields were obtained for Giese-type reactions using electron-deficient alkenes. When cyclohexane was treated with BPSE, alkenylated **107** is obtained, albeit in low yield (Scheme 26).



Scheme 26 C-H alkenylation via generation of aminyl radicals followed by intramolecular electron transfer.

5. Conclusion

BPSE, regardless of its (*E*) or (*Z*) form, exhibits reliable reactivity towards alkyl and aryl radical attack in order to function as a radical C₂ synthon in multicomponent radical reactions. With the exception of Scheme 19, where intramolecular aromatic ring attack precedes, unimolecular type β-scission of the PhSO₂ group occurs readily to give substituted vinyl sulfones as products. BPSE is a robust alkene, compatible with photo-irradiation and oxidation conditions, and acts as a reliable radical trap. We see such beautiful examples in photoredox-catalyzed reaction and photocatalytic C-H functionalization. The released PhSO₂ radical is able to propagate radical chains through the designed radical reactions, such as S_H2 reaction and radical addition. In a photoredox-catalyzed system, PhSO₂ radical can cause one-electron oxidation to restore photoredox catalysts to their ground state, as seen in the use of Fukuzumi's catalyst. Recent work by us and others has uncovered that PhSO₂ radical undergoes HAT reactions of weak C-H bonds to form a new radical such a subterranean contribution to C-H activation chemistry.^{63,64} While vinylsulfones have been recognized as important motifs in several targets of biological interest, BPSE can be used for the late-stage functionalization. Further manipulation of the vinylsulfone functionality derived by the reaction of BPSE should have many more synthetic opportunities, as illustrated in the examples of Scheme 6 and 7.

20b,24

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