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Very Important Publication

Radical C–C Bond Formation using Sulfonium Salts and Light

Áron Péter,[a] Gregory J. P. Perry,[a] and David J. Procter[a,*]

[a] Department of Chemistry, University of Manchester, Oxford Rd, Manchester, M13 9PL, U.K.
E-mail: david.j.procter@manchester.ac.uk

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Abstract: Sulfonium salts are playing an increasingly significant role in contemporary organic synthesis. In particular, the generation of radicals from sulfonium salts is a fundamental process in Nature and has been the subject of investigation for over 50 years. However, general synthetic methods that use sulfonium salts as radical precursors are rare. The advent of photoredox catalysis has triggered an upsurge of interest in the radical chemistry of sulfonium salts and this review surveys recent applications of aryl- and alkylsulfonium salts in light-mediated, radical C–C bond formation.

Keywords: C–C bond formation; cross-coupling; photochemistry; radicals; sulfonium salts

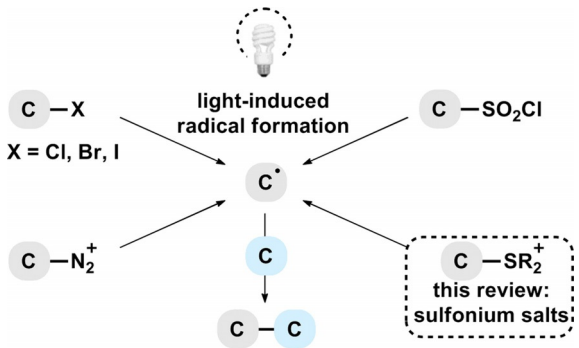
1 Introduction

Sulfur-containing motifs have long fascinated synthetic chemists due to their rich reactivity and their occurrence in functional molecules, such as drugs and materials.[1] The cleavage of C–S bonds is of fundamental importance. For example, in the refining of petroleum, C–S bond cleavage is the key to desulfurization.[2] More recently, sulfur functionalities, such as sulfides, sulfones, sulfoxides, sulfur ylides and sulfonates, have been used in methods for cross-coupling that proceed by C–S bond cleavage.[3] Organosulfur reagents are useful alternatives to traditional cross-coupling partners (e.g., aryl halides) and their application in synthesis opens up the possibility of the late-stage modification of complex sulfur-containing molecules.

The widespread use of light to drive organic chemistry is arguably the defining feature of synthesis in the 21st century to date.[4] This approach has delivered numerous new and/or improved processes involving radical intermediates.

In particular, various radical precursors have been used for C–C bond formation, including halides, diazonium salts and sulfonyl chlorides (Scheme 1).[5] The continued growth of photoredox catalysis will require the development of new methods that embrace new substrates, bearing new functional groups.

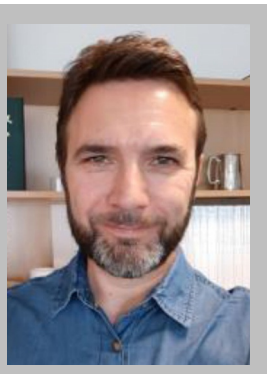
Sulfonium salts have attracted attention in recent years as versatile reagents in organic synthesis.[3] In particular, they have found application in various C–C bond-forming reactions that involve C–S bond



Scheme 1. Light-induced radical C–C bond formation.

Áron Péter received his BSc degree from the Eötvös Loránd University (Hungary) in 2018. He completed his thesis work in the Servier Research Institute focusing on the synthesis of biologically active scaffolds. He then moved to the University of Manchester to conduct his MSc studies under the guidance of Prof. David J. Procter on the use of SmI_2 in total synthesis. Following this, he received a prestigious Dean's Award and stayed in the Procter group to study for his PhD. His current research is focused on the development of new processes mediated by SmI_2.

Gregory J. P. Perry received his MChem from the University of Liverpool (U.K.) in 2012 and his PhD in 2016 from the University of Manchester (U.K.). His doctoral studies were carried out in the group of Prof. Igor Larrosa and focused on decarboxylative and C–H transformations. In 2017, he moved to Nagoya University (Japan) to work with Prof. Kenichiro Itami on the application of C–H activation in chemical biology. Since 2018, Greg has been working as a Lecturer in Organic Chemistry within the group of Prof. David J. Procter at the University of Manchester (U.K.).

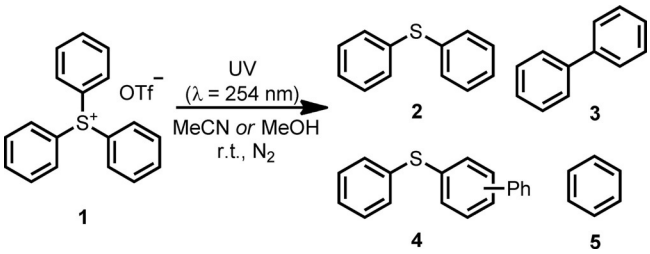


David J. Procter was born in Leyland in Lancashire, England. He obtained his BSc in chemistry from the University of Leeds in 1992 and his PhD in 1995 working with Professor Christopher Rayner on organosulfur and organoselenium chemistry. He then spent two years as a Post-doctoral Research Associate with Professor Robert Holton at Florida State University in Tallahassee, USA working on the synthesis of Taxol. In late 1997 he took up a Lectureship at the University of Glasgow in Scotland and was promoted to Senior Lecturer in 2004. In 2004, he moved to a Readership at the University of Manchester. David was promoted to Professor in 2008.

cleavage.[6] In this review, we focus on the application of sulfonium salts in light-promoted C–C bond formation (Scheme 1). Photochemistry opens up new possibilities for the use of sulfonium salts as radical precursors; a mode of reactivity that has received relatively little attention. We will also introduce methods for sulfonium salt preparation as this is the key to their applicability in synthesis. Extensive studies on the use of sulfonium salts as trifluoromethylating agents in photoredox chemistry have recently been reviewed and will not be covered here.[7]

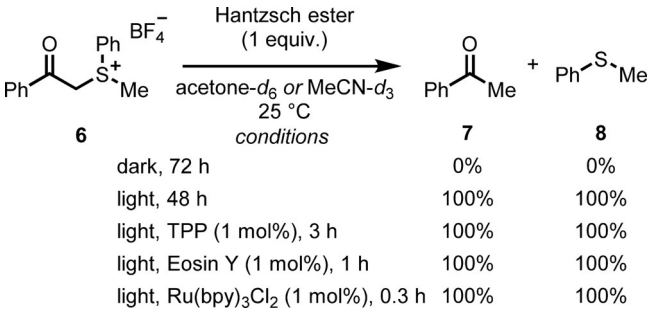
2 Early Reports on the Photochemistry of Sulfonium Salts

The generation of radical intermediates by the homolytic cleavage of C–S bonds in sulfonium salts is a fundamental process in Nature.[8] Methods that mimic this reactivity, for example, using chemistry, electrochemistry or radiolysis have been investigated for over 50 years.[9] Early reports in this area also describe the effect of light on sulfonium salts.[10] To take just one example, Hacker and colleagues observed that UV irradiation at 254 nm could trigger the rearrangement of triarylsulfonium salts (Scheme 2).[10d] A variety of products was formed in low yield, including products **3** and **4** arising from C–C bond formation. The authors suggested that these products form predominantly *via* heterolytic cleavage and formation of ionic intermediates, although they also suggested that a pathway involving homolytic cleavage and radical intermediates was possible. As shown here, the direct photolysis of sulfonium salts is generally an inefficient process.[11] Herein, we describe how photocatalysis has enabled the application of sulfonium salts in light-mediated transformations.



Scheme 2. Photolysis of triarylsulfonium salts.

In 1978, a seminal report by Kellogg and co-workers discussed the reduction of sulfonium salts **6** to give ketones **7** and sulfides **8** (Scheme 3).[12] The reaction was promoted by light and 1,4-dihydropyridines (e.g., a Hantzsch ester) were used as hydrogen atom donors. The authors suggested a mechanism involving single electron transfer (SET) reduction of the C–S bond. They also described how photocatalysts, such as *meso*-tetraphenylporphine, eosin Y and $[Ru(bpy)_3]Cl_2$, drastically accelerated the rate of the reduction from days to hours. Not only do these reports describe some of the first photoinitiated reductions of sulfonium salts, but they also constitute early examples of photoredox catalysis.[4]



6 conditions	7	8
dark, 72 h	0%	0%
light, 48 h	100%	100%
light, TPP (1 mol%), 3 h	100%	100%
light, Eosin Y (1 mol%), 1 h	100%	100%
light, $Ru(bpy)_3Cl_2$ (1 mol%), 0.3 h	100%	100%

Scheme 3. The light-mediated reduction of sulfonium salts: An early report of photoredox catalysis. ^{1}H NMR yields shown; Hantzsch ester = diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate; light = room lighting from neon fluorescent lamp; TPP = *meso*-tetraphenylporphine.

3 Sulfonium Salts in C–C Bond Formation

3.1 The Value of Arylsulfonium Salts in Light-Mediated C–C Bond Formation

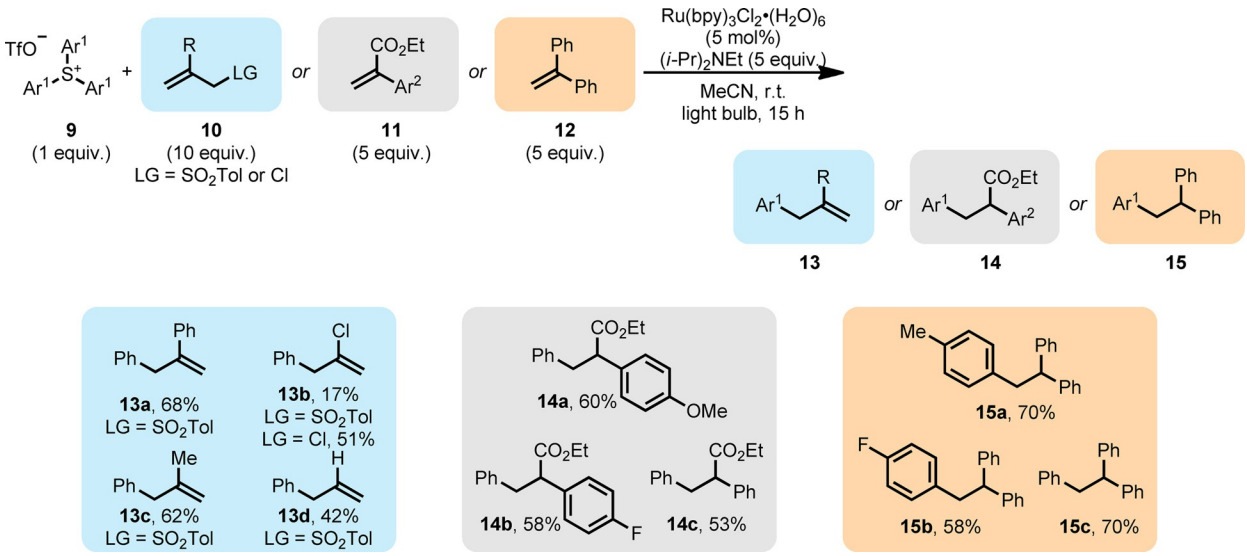
In 2013, Fensterbank, Goddard, Ollivier et al. reported visible light-mediated C–C bond formation using triarylsulfonium salts **9** and alkenes (Scheme 4).[13] A range of allyl sulfones and chlorides **10** underwent the radical addition reaction in moderate to good yields, furnishing substituted allyl arenes (**13a–d**). 2-Arylacrylates **11** and 1,1-diphenylethylene **12** were also suitable radical acceptors that provided products **14** and **15**. The electronic nature of the aryl substituents on either substrate had little effect on the reaction outcome in these cases (**14a–c**, **15a–c**). By contrast, other olefins, such as styrenes, methacrylate, acrylonitriles and *tert*-butyl vinyl ether, proved to be ineffective aryl radical traps in this process and gave products in low yield (<10%). Finally, the effect of the counter anion in the sulfonium salt **9** on the preparation of **15c** revealed that triflate (70%), tetrafluoroborate (72%), and hexafluorophosphate (65%) anions give similar results, whereas a bromide counter anion gave a lower yield (42%). To the best of our knowledge, this is the first report of a general photoredox process involving sulfonium salts.

A proposed mechanism for this transformation is provided in Scheme 5. The photoredox catalyst, $Ru(bpy)_3Cl_2$, is first excited under visible light irradiation. A standard light bulb was used in this instance, although blue LEDs are often used for performing photoredox chemistry with $Ru(bpy)_3Cl_2$ (λ_{max} = 452 nm).[4a,b] The photoexcited state of the catalyst ($E_{1/2}^{*II/I} = +0.77$ V *vs.* SCE)[4a,b] is then susceptible to single electron reduction by the amine additive. This reductive quenching process forms an Ru(I) species ($E_{1/2}^{II/I} = -1.33$ V *vs.* SCE),[4a,b] which is capable of reducing the sulfonium salt **9** ($E^{red} = -1.2$ V *vs.* MSE)[13] to give an aryl radical. Trapping of the aryl radical with the olefin (e.g., **12**) and subsequent hydrogen abstraction from the amine radical cation provides the desired product (e.g., **15**).

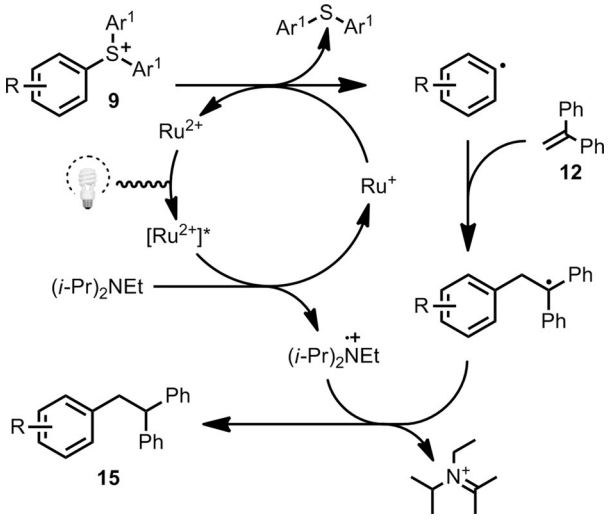
3.2 The Preparation of Benzylsulfonium Salts and their Reactivity in Light-Mediated C–C Bond Formation

Benzylsulfonium salts **17**/**18** can also participate in light-mediated C–C bond-forming reactions. The salts were prepared from the corresponding benzyl bromides **16** by a simple substitution reaction (Scheme 6).[14] To increase the stability of these salts, the bromide counter ion can be exchanged for hexafluorophosphate.[15]

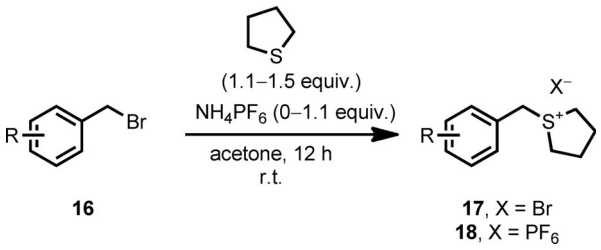
Yorimitsu and co-workers reported a visible light-mediated radical alkenylation using benzylsulfonium salts **17** as benzyl radical precursors (Scheme 7).[16] The reaction tolerates various functionalities on the phenyl ring of the sulfonium salt, including *ortho*-, *meta*-, and *para*-substitution, and electron-donating/electron-withdrawing substituents (**19a–f**). Similarly, good functional group tolerance was observed with respect to substituents on the phenyl ring of the 1,1-diarylethylenes (**19g**, **19h**). Unsymmetrical 1,1-disubstituted alkenes were also tolerated in the reaction, however, a geometric mixture of products was obtained (**19i**, **19j**). By switching the counter ion of the sulfonium salt to triflate and carrying out the reaction in co-solvent quantities of water or MeOH, the reac-



Scheme 4. Photocatalytic reduction of sulfonium salts for radical C–C bond formation.



Scheme 5. Proposed mechanism for photocatalytic, reductive, radical C–C bond formation involving arylsulfonium salts and alkenes. Ru = $Ru(bpy)_3$.



Scheme 6. Preparation of benzylsulfonium salts.

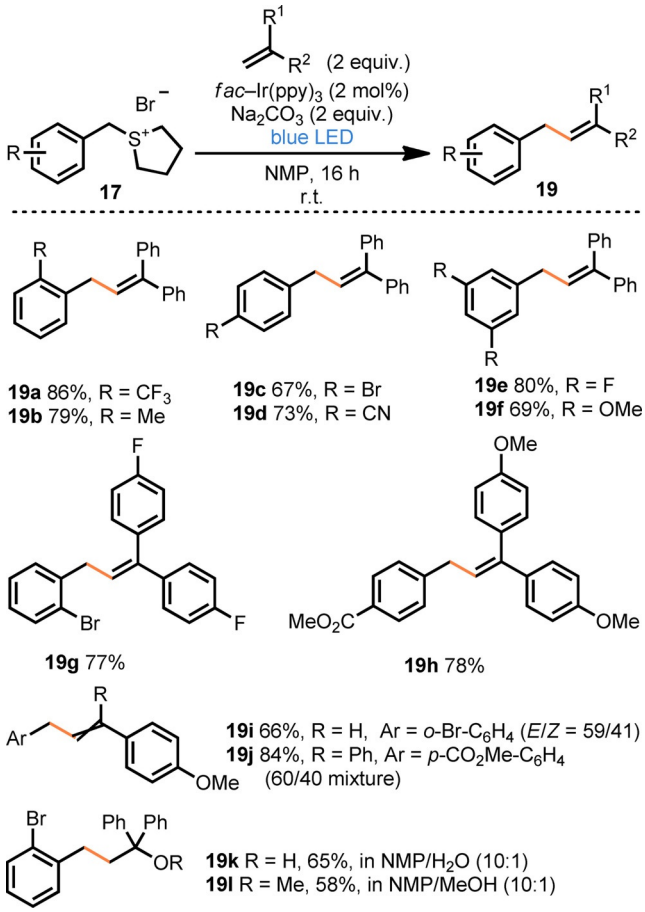
tivity was extended to the synthesis of oxygenated products (**19k**, **19l**).

The reaction was proposed to proceed by SET reduction of the benzylsulfonium **17** salt ($E^{red} = -1.48$ V *vs.* SCE)[16] by the excited state of the photoredox catalyst ($E_{1/2}^{IV/*III} = -1.73$ V *vs.* SCE, Scheme 8).[4a,b] The photoexcited state of the catalyst, *fac*-Ir(ppy)$_3$ ($\lambda_{max} =$ 375 nm),[4a,b] was accessed through irradiation with blue LEDs. This generates a benzylic radical that is trapped by the olefin (e.g., **12**). Another single electron transfer event involving the photoredox catalyst ($E_{1/2}^{IV/III} = +0.77$ V *vs.* SCE) provides the desired product **19** and closes the catalytic cycle. This mechanism is similar to that shown in Scheme 5, however, alkenyl products **19** are formed in this case as no terminal reductant [e.g., the radical cation of $(i\text{-Pr})_2$NEt] is present.

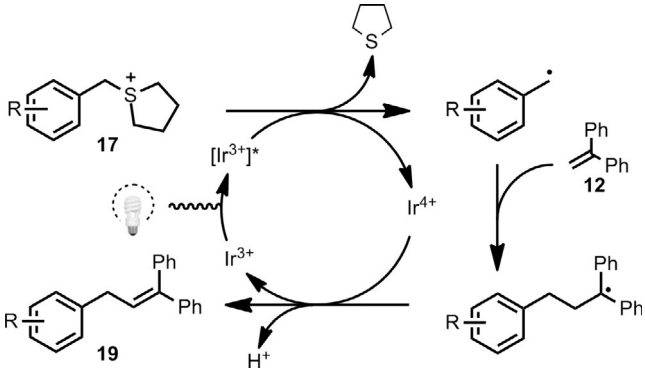
Building on this work, Novák and co-workers recently reported a metallaphotoredox coupling of benzylsulfonium salts **18** with *N*-Boc-protected prolines (Scheme 9).[15] Various electron-deficient and electron-rich benzylsulfonium salts underwent cross-coupling to provide the desired products in moderate to good yields (**20a–d**). However, substrates bearing *ortho*-substituents on the aromatic core gave lower yields, suggesting that steric hindrance plays a crucial role in the reaction efficiency (**20a**, **20b**). Heteroaromatic substrates also displayed moderate reactivity (**20e**).

3.3 The Direct Preparation of Arylsulfonium Salts for Light-Mediated C–C Bond Formation

An ideal route to arylsulfonium salts is through direct sulfenylation of C–H bonds (Scheme 10). This reactivity, often termed an interrupted Pummerer reaction, first found widespread application for the prepa-

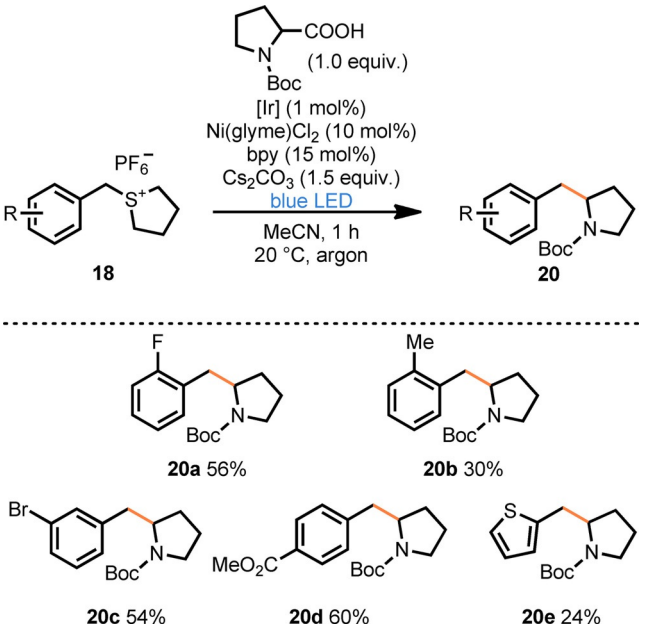


Scheme 7. Photoredox-catalysed radical alkenylation of benzylsulfonium salts.

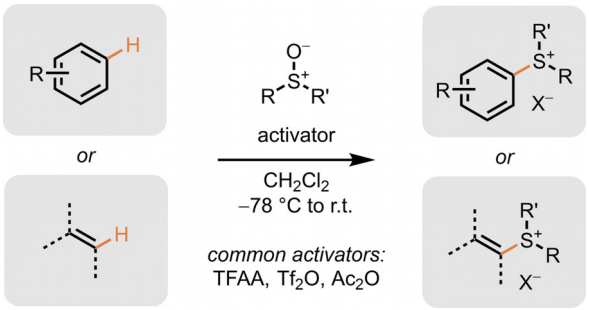


Scheme 8. Proposed mechanism for photocatalytic, reductive, radical C–C bond formation involving benzylsulfonium salts and alkenes. Ir = $Ir(ppy)_3$.

ration of trifluoromethylating agents.[17] Towards the turn of the century, Balenkova and Nenajdenko began investigating the generality of this method.[18] More recently, several groups have contributed to establishing intermolecular C–H sulfenylation using sulfoxides as a facile means for accessing sulfonium salts.[19,20] Within these reports, sulfonium salts have



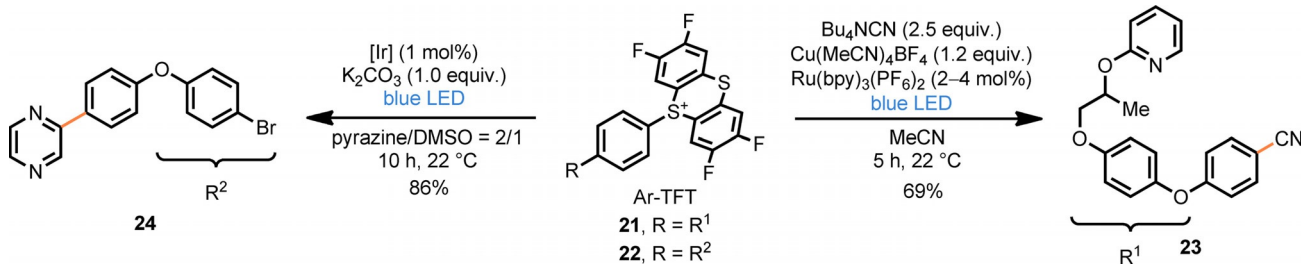
Scheme 9. Metallaphotoredox-catalysed radical alkylation of benzylsulfonium salts. [Ir] = $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$.



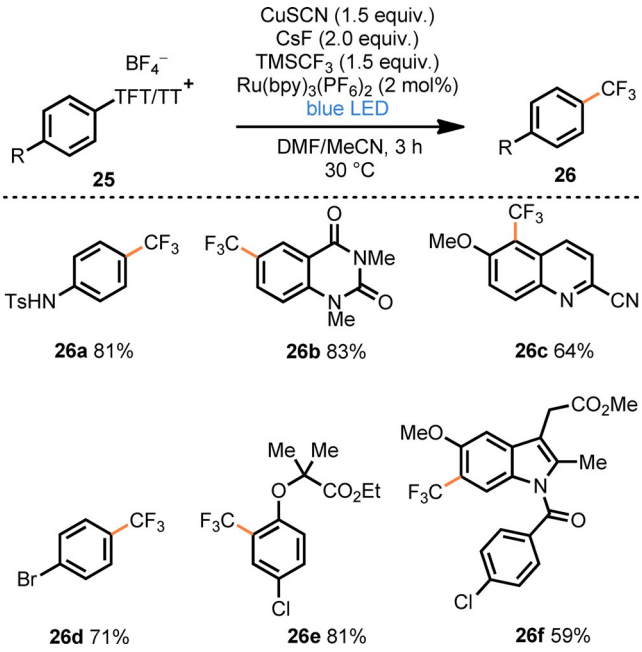
Scheme 10. The direct preparation of sulfonium salts from C–H bonds *via* an interrupted Pummerer reaction.

proved effective electrophilic partners in transition metal-catalysed C–C cross-couplings.[3,6,19,20c–f,m] In particular, formal C–H cross-couplings can occur when C–H sulfenylation and C–C bond formation are carried out in one pot.[20f]

Building on this precedent, Ritter and colleagues have developed a highly *para*-selective C–H sulfenylation of arenes.[21] The resulting tetrafluorothianthrene (TFT) sulfonium salts **21**/**22** were then engaged in photoredox- and transition metal-catalysed processes (Scheme 11).[21] For example, a derivative of the insecticide pyriproxyfen **21** underwent cyanation to give **23** and a Minisci-type C–H arylation converted **22** into **24**. Other light-mediated processes were used to introduce a range of useful functionalities, for example; Bpin, $(O)P(OPh)_2$, SCF_3, and halogens. An intermediate aryl radical is likely formed from the sulfonium salts **21**/**22** in these processes. Similarly, TFT and thianthrene (TT) salts **25** were used for site-selective



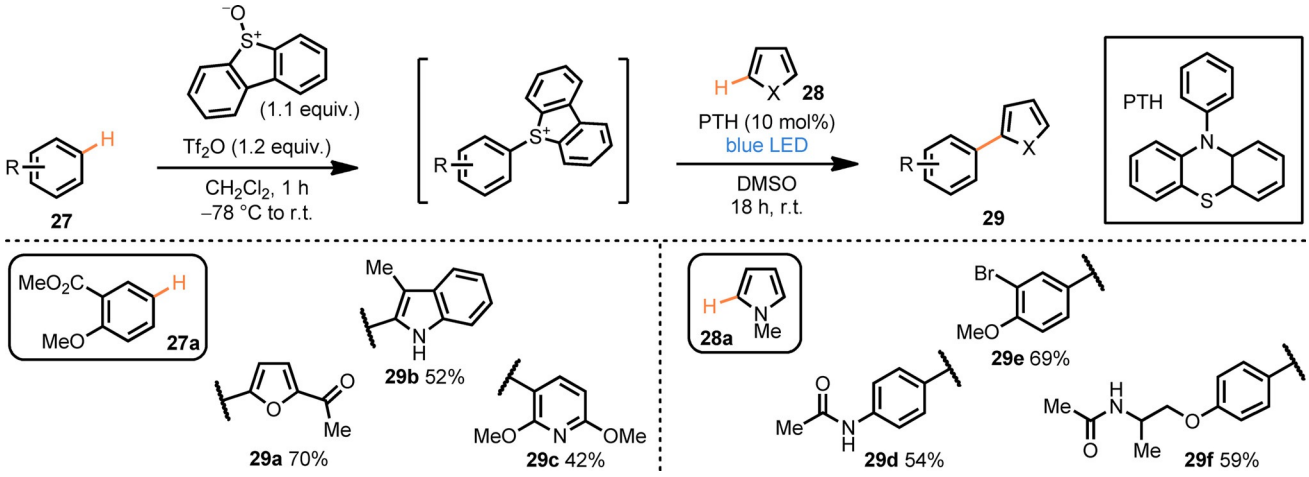
Scheme 11. Photoredox-catalysed cyanation and arylation of sulfonium salts. [Ir] = {Ir[dF(CF$_3$)ppy]$_2$(dtbpy)}PF$_6$.



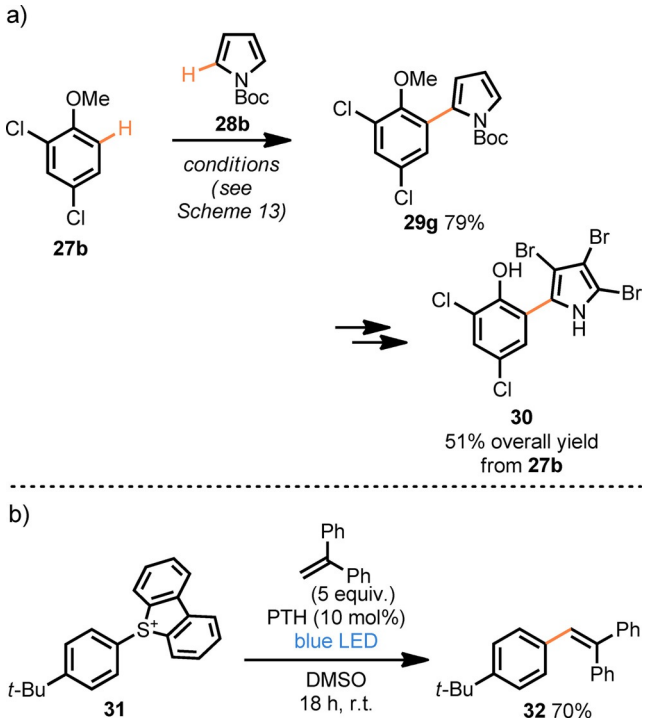
Scheme 12. Photoredox-catalysed radical trifluoromethylation of sulfonium salts.

trifluoromethylation.[22] Ritter and co-workers utilised a trifluoromethyl copper species, formed *in situ*, as the trifluoromethylating agent under the photoredox-catalysed conditions (Scheme 12). The sequence tolerates a number of functional groups; for example, aldehydes, ketones, esters, alcohols, halides and pseudohalides. Notably, the method can be used for the late-stage functionalisation of medicinally and agrochemically important compounds (**26e**, **26f**).

In 2020, Procter et al. developed a one-pot, formal C–H/C–H (hetero)biaryl coupling (Scheme 13).[23] The process uses commercially available dibenzothiophene *S*-oxide (DBTSO) to achieve selective sulfonium salt formation, *via* an interrupted Pummerer reaction, before an organic photoredox catalyst (10-phenylphenothiazine, PTH) mediates the desired radical cross-coupling. The sulfonium salts were isolable, however, the formal C–H/C–H cross-couplings were generally performed in one pot to improve overall efficiency. A range of heteroaromatics could be coupled with the sulfonium salt derived from arene **27a**, including furan (**29a**), indole (**29b**) and pyridine (**29c**). Sulfonium salts derived from phenol and aniline derivatives also provided good overall yields (**29d**), however, limitations arose when substrates with free amine and alcohol groups were used. Drug molecules were also subjected to late stage arylation, for example, in the derivatisation of the anti-arrhythmic drug mexiletine **29f**. A synthesis of the natural product pseudilin **30** was also described; the formal C–H/C–H



Scheme 13. Photoredox-catalysed arylation of arylsulfonium salts in a formal C–H/C–H cross-coupling.

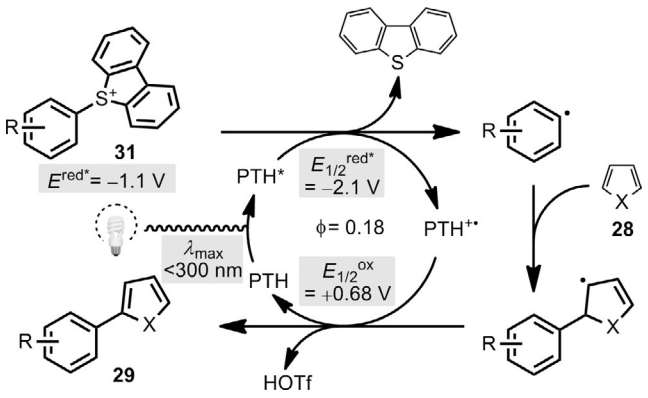


Scheme 14. Photoredox-catalysed C–C bond formation *via* arylsulfonium salts in formal C–H/C–H cross-couplings.

coupling of **27b** and **28b** gave the key intermediate biaryl **29g** (Scheme 14a).

This method was also applicable to the cross-coupling of arylsulfonium salt **31** and olefin **12** to give **32** (Scheme 14b). This result is complementary to the report of Fensterbank, Goddard and Ollivier, in which alkyl products were observed (Scheme 4), and Yorimitsu, who used benzylsulfoniums (Scheme 7).

A mechanism for the cross-coupling is provided in Scheme 15. Photoexcitation of the catalyst, PTH ($E_{1/2}^{red*} = -2.1$ V *vs.* SCE),[4c] enabled SET reduction of the sulfonium salt **31** ($E^{red} = -1.1$ V *vs.* SCE)[23] to



Scheme 15. Proposed mechanism for photocatalytic, reductive, radical C–C bond formation involving arylsulfonium salts and heteroarenes/arenes. PTH = 10-phenylphenothiazine.

generate an aryl radical. The excited state of the photoredox catalyst ($\lambda_{max} < 300$ nm)[4c] was accessed through irradiation with blue LEDs. This radical was then trapped by the arene **28** (or olefin **12**), before subsequent single electron oxidation by the radical cation of PTH ($E_{1/2}^{ox} = +0.68$ V *vs.* SCE)[4c] and deprotonation provide the desired product **29**. Stern–Volmer quenching experiments and the measurement of the quantum yield ($\Phi = 0.18$) support the proposed catalytic cycle.

4 Conclusion

While investigations into the radical chemistry of sulfonium salts reach back over several decades, it is only recently that this reactivity has found application in mainstream synthesis. Developments in the synthesis of sulfonium salts, particularly methods that allow salts to be accessed directly by C–H sulfenylation using sulfoxides, have played a key role in making highly functionalised salts available. These new methods for the efficient preparation of sulfonium salts, combined with the discovery of new reactivity, is allowing teams to reveal the synthetic potential of these reagents. The marriage of sulfonium salts and light activation is proving a particularly useful strategy for the invention of new radical C–C bond-forming reactions. As access to this underexplored functional group grows, we look forward to the discovery of new reactivity, new processes, and new applications driven by the chemistry of sulfonium salts.

Acknowledgements

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