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Iodine-based reagents in photoredox-organocatalysis

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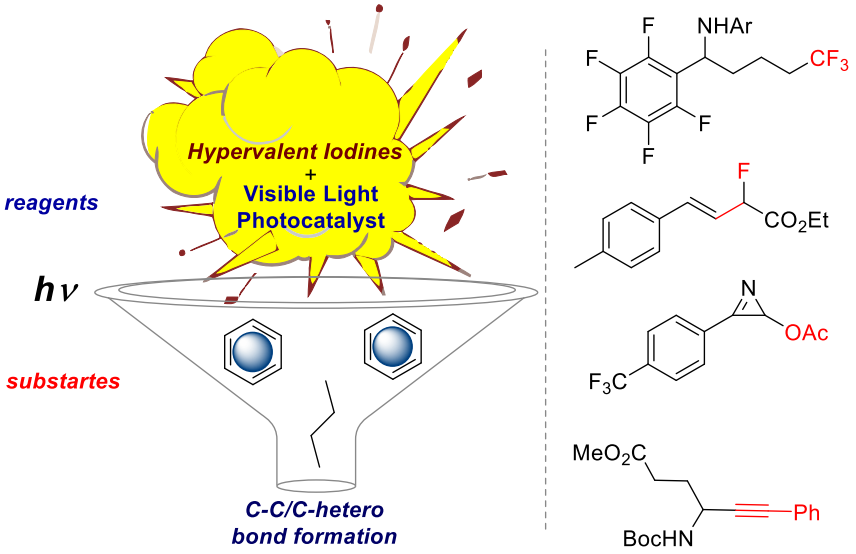
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Abstract

In recent decades, due to the rapid increase of environmental pollution and global warming, renewable energy sources for organic transformation have become popular research topics. In this aspect, photoredox catalyst under visible light irradiation and the metal-free condition has gained massive attention in organic synthesis. This review article plans to summarize the latest development and synthetic applications of hypervalent iodine reagents (HIR) combined with visible-light organo-photocatalyst. We present the HIRs in terms of the roles as group transfer reagents as well as oxidants.



Keywords: Green synthesis, Hypervalent iodine, Metal-free, Photoredox-organocatalysis, Visible light

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1. Introduction

The photochemical transformations have significantly impacted synthetic chemistry recently by the utilization of visible-light photocatalysts.[1-3] The frequently used visible-light photocatalysts are either organic dyes,[4] primarily pollutants in nature, or expensive transition-metal complexes.[5-9] Therefore the use of these photocatalysts in industrial, medicinal, and pharmaceutical applications are usually restricted. Initially, ruthenium and iridium-based complexes were used as photoredox-catalyst in organic synthesis due to their excellent absorbance in the visible region, long-lived stable excited state to act as oxidant or reductant, and single electron transfer properties.[10] Photoredox chemistry of organic chromophores is underdeveloped due to the lack of practical information on the redox potential, reaction kinetics, photophysical properties, etc. In recent times, several groups have studied some of these aspects, which have added potential value in developing organic chromophores as a sensitizer in visible light-mediated redox chemistry.[11-15]

The research area on hypervalent iodine chemistry[16-21] has been popular for a long time in synthetic organic chemistry.[22] The iodine-based reagents are environmentally friendly and also have oxidizing ability.[23-25] Among them, iodine(III) and iodine(V) reagents are commonly utilized in many useful oxidative transformations towards developing a plethora of functional molecules.[26-29] Easy accessibility, high stability, selective oxidizing ability, non-toxic nature of iodine-based reagents make them workable comfortably in the organic synthesis.[20-21] Recently, the utilization of hypervalent iodine reagents as organo-photocatalyst is gaining popularity.[30-33] Still, this research field requires substantial development, however, limited reports are available towards the use of hypervalent iodine reagents (HIRs)[22, 34-38] as photocatalyst.[39] The suitable combination of HIRs and organo-photocatalyst (OPC) using appropriate light energy and solvent can produce desired functional group transformations. The prime function of HIR in combination with OPC is to transfer any functional group to the substrate or to act as the oxidizing agent. Several reviews are covering the role of HIRs as group transfer reagents, oxidizing agents, and synthetic applications with metal-based photocatalysts.[40-41] Studer and Wang recently published a review article where they have shown the use of Iodine(III) reagents in the radical chemistry as group transfer reagents[42-43] *via* thermolysis.[44] However, this particular review highlights the merging of HIRs as group transfer and oxidizing reagent with organo-photocatalyst (OPC). There is no such review available in the literature to the best of our knowledge.

Figure 1 represents the collection of commonly used HIRs and OPCs discussed in this article. The basic criteria for an organo-photocatalyst should be its absorbance in the visible region to replace the transition metal photocatalyst. For this purpose highly conjugated organic dyes[45] like Eosin Y,[46] Methylene Blue,[47] Rhodamine B,[48] Rose Bengal,[49] Fluorescein[50] and colored compounds like acridinium salts,[51] 9,10-dicyanoanthracene,[52] 2,4,5,6-tetra(9H-carbazole-9-yl)isophthalonitrile (4CzIPN)[53] and its derivatives are being used as organo-photocatalysts. The redox properties and excited-state photochemistry of those catalysts have also been investigated and used them for organic transformations.[40]

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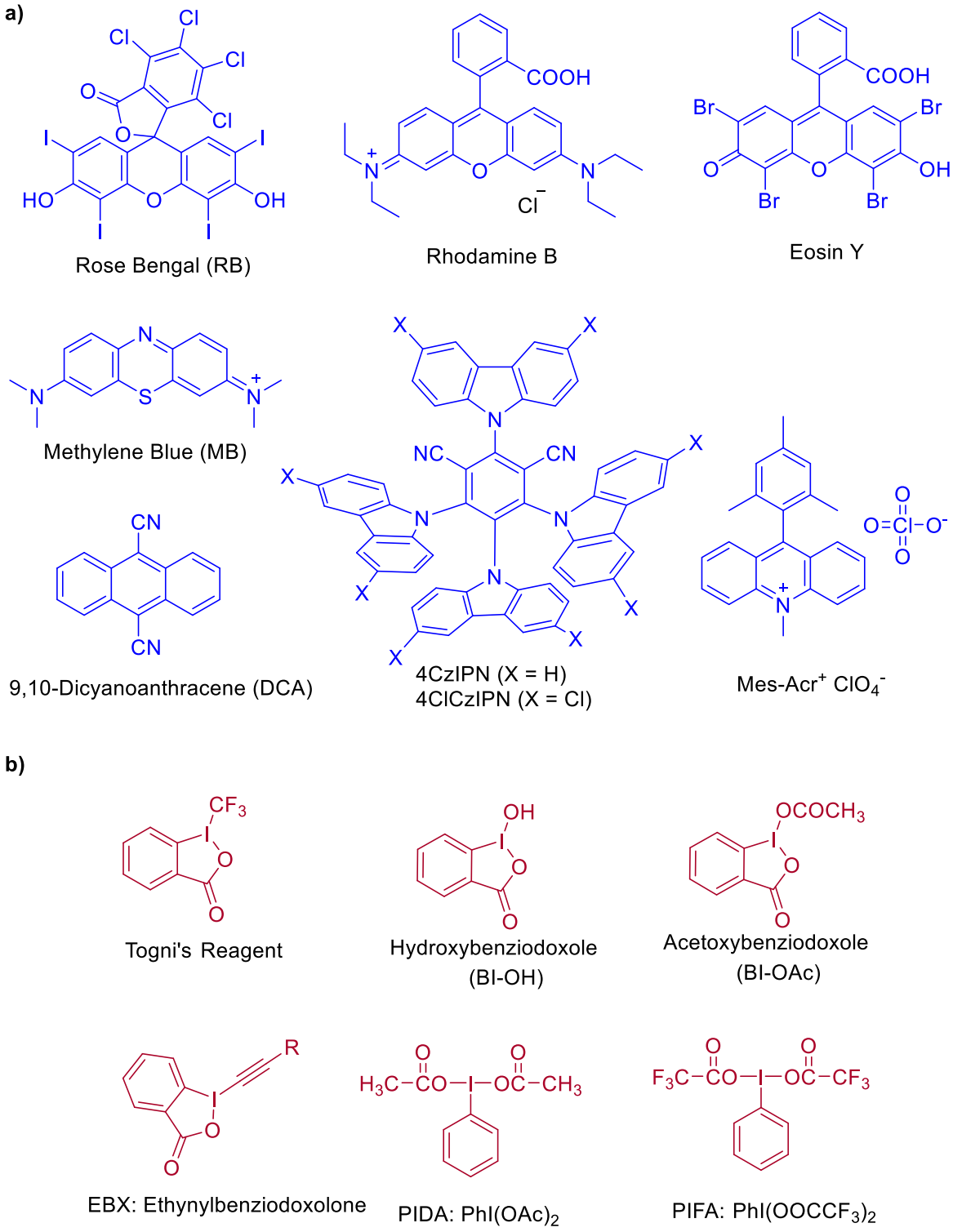


Figure 1. a) Examples of commonly used: a) organo photocatalyst (OPC) and b) hypervalent iodine reagents (HIRs).

2. Review

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The incorporation of a trifluoromethyl group in organic moiety is one of the crucial transformations in organic chemistry.[54] In 2014, Scaiano and coworkers developed a method of trifluoromethylation of electron-rich heteroaromatics (Figure 2).[55] For the first time, they used methylene blue (MB) as organo-photocatalyst for a generation of electrophilic trifluoromethyl radical from Togni's reagent[54] under white light irradiation. Using 2 mol % of MB as the photocatalyst, 1.5 equiv of Togni's reagent as CF_3 radical source, and 2.0 equiv of TMEDA as electron source they could isolate moderate yield of trifluoromethylated heteroaromatic moieties **2** from the respective electron-rich heteroaromatic molecules **1**. The reaction time was six h under the irradiation of white LED.

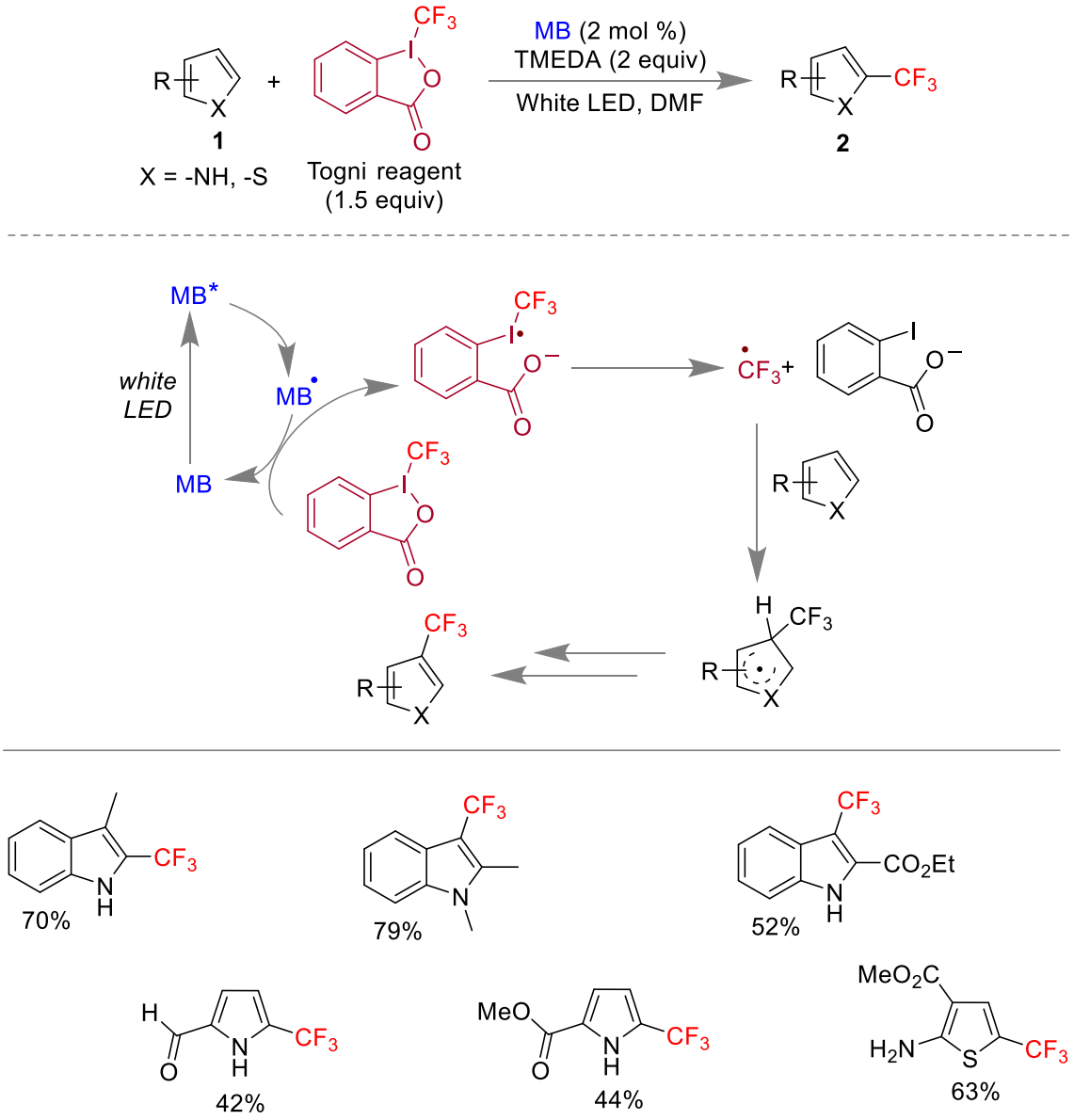


Figure 2. Trifluoromethylation of heteroarenes using MB and Togni's reagent.[55]

Scaiano and coworkers have also shown a hydrotrifluoromethylation of terminal alkynes and alkenes using a similar strategy (Figure 3).[55] This method proved to be effective in giving a moderate yield of fluorinated alkenes **4** with a good (*E/Z*) ratio in the case of hydrotrifluoromethylation of alkynes **3** under similar conditions using 2.0 equiv of base DBU (Figure 3a). Authors have not discussed the (*E/Z*)-selectivity, however, possibly

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due to the steric factors by the -CF_3 radical and the substituent present at the alkynes, the (*E*)-isomers were predominant. Similarly, a good yield of fluorinated alkane **6** was obtained from alkene **5** (Figure 3b).

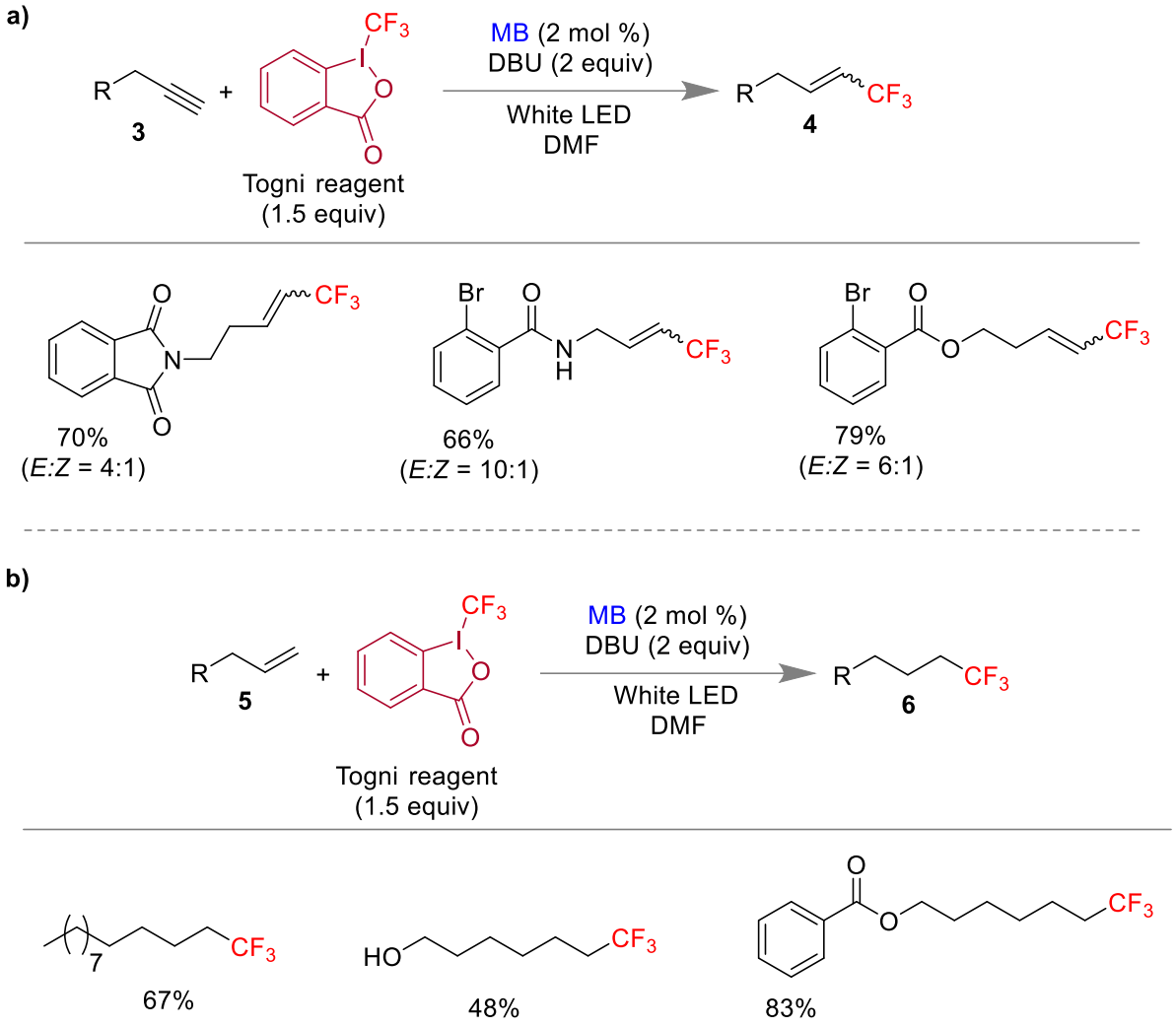


Figure 3. Trifluoromethylation using MB and Togni's reagent.[55] Reaction with a) alkynes b) alkenes.

Many allylic monofluoro and difluoro compounds are known to have biological activities.[56] Therefore, fluorination and difluorination of allylic compounds at *α*-position have high importance in synthetic chemistry.[57-58] In 2017, Xu and coworkers reported decarboxylative coupling of cinnamic acid **7** and bromodifluoroacetate or bromomonofluoroacetate to synthesize fluorinated alkenes **8** under visible light irradiation in the presence of Eosin Y as the photoredox-organocatalyst (Figure 4).[59] In this process both the reactants were coupled successfully using only 5 mol % of Eosin Y and 2.0 equiv of hypervalent iodine reagent hydroxybenziodoxole (BI-OH) and 2.0 equiv of diisopropylethylamine. Here the role of BI-OH was to activate carboxylic acid for radical decarboxylation *via* intermediate **9**. Using this method, a good amount of fluorinated products were isolated where different types of electron-donating and electron-withdrawing groups were well tolerated. Examples of difluorination and monofluorination are shown in Figures 4a and 4b, respectively.

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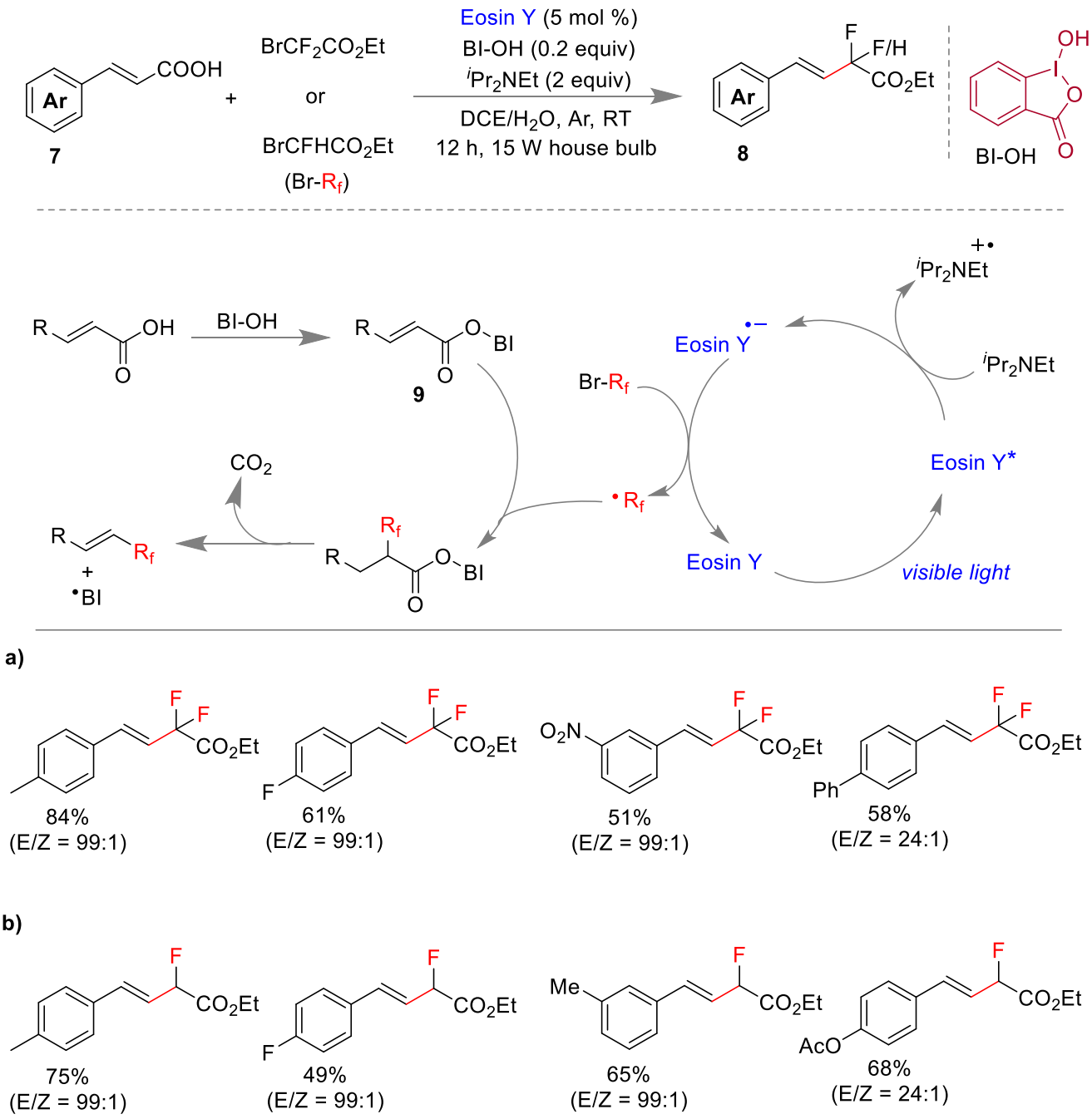


Figure 4. Decarboxylative fluorination using Eosin Y and BI-OH.[59]

Fluorinated and trifluoromethylated free alcohols and free amines are of great significance in drug discovery and biological application.[60] Recently in 2019, Xu and coworkers reported hydrotrifluoromethylation of protected alcohols and amines **10** for the formation of –CF_3 incorporated corresponding alcohols and amines **11** after *in situ* deprotection of protecting group (Figure 5).[61] In this method 2 mol % of 2,4,5,6-tetra(9H-carbazole-9-yl)isophthalonitrile (4CzIPN) as organo-photocatalyst and 1.5 equiv of Togni's reagent as CF_3 radical source were used. Within 12 h of irradiation under blue LED in dioxane and methanol, differently substituted trifluoromethylated products **11** were isolated in good yields *via* 1,5-H transfer. The yields of the reactions were found to be low, especially for amines after the 1,5-H transfer reactions. The authors have not discussed these possibilities. The radicals get extra stabilities when present next to heteroatoms like

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nitrogen.[62] Therefore 1,5-H transfer efficiency decreases for the more stable radicals of the amines than alcohols. Similarly, pyridine-containing amine led to the low yield of the corresponding products, ca. 43%.

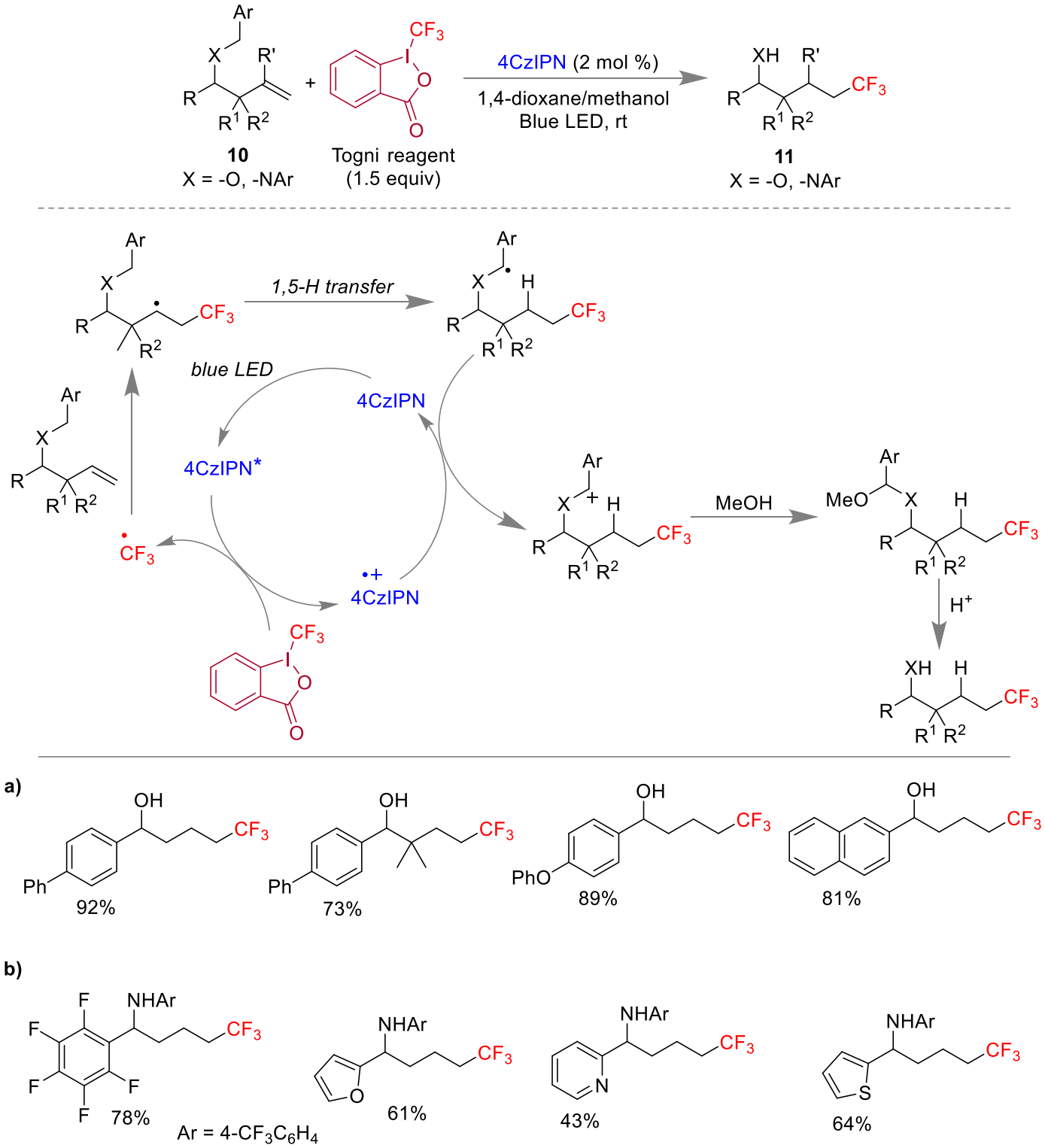


Figure 5. Photoredox-organocatalysis in the synthesis of *δ*-trifluoromethylated alcohols and Amines.[61] a) Hydrotrifluoromethylation using Togni's reagent and 4CzIPN. b) Synthesis of *α*-heteroarylated *δ*-trifluoromethylated secondary amines from the corresponding homoallylic amine derivatives.

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Alkynes are synthetically important moieties that can further be transformed into many functionalized molecules.[63-64] Therefore, the development of improved methods for the synthesis of alkynes is essential in organic chemistry.[65] For the first time, in 2016, Cheng and coworkers reported a method for decarboxylative alkynylation of carboxylic acids **12** using organo-photocatalyst (Figure 6).[52] They have used 5 mol % of DCA as organo-photocatalyst, 1.5 equiv of hypervalent iodine reagent ethenyl benziodoxolones (EBX)[66-67] as alkyne source, and 2.0 equiv of K_2CO_3 under 24 h blue light or natural sunlight irradiation to get the decarboxylative alkynylation products **13** *via* vinylic radical intermediate **14**. Here, EBX reagent acted as a group transfer reagent.

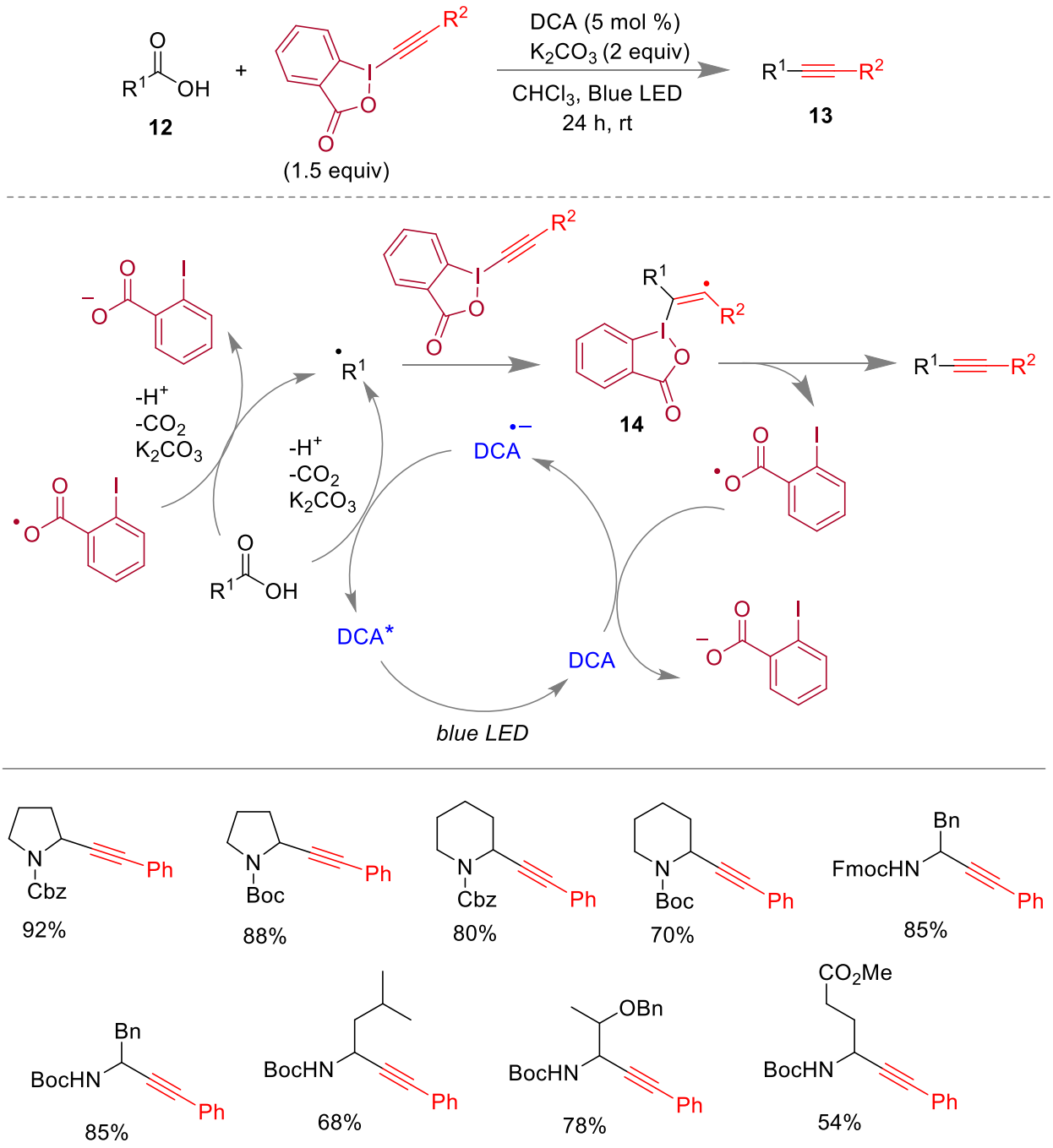


Figure 6. Decarboxylative alkynylation using DCA and EBX.[52]

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In 2019, Cheng and coworkers reported a decarboxylative alkynylation of diazonium salts using hypervalent iodine reagent and organo-photocatalyst (Figure 7).[68] Using only 1 mol % of Eosin Y as organo-photocatalyst with 1.2 equiv of acetoxybenziodoxole (BI-OAc) as an additive to promote decarboxylation in DCE solvent under a nitrogen atmosphere and green LED irradiation for 12 h they could isolate alkynes **17** in good yield from arene diazonium salt **15** and aryl propiolic acid **16**. The reaction proceeded *via* formation of aryl radical intermediate with a loss of nitrogen from diazonium salt by photoexcited Eosin Y and consequent formation of vinyl radical intermediate **19** from **18** by BI-OAc to promote loss of CO_2.

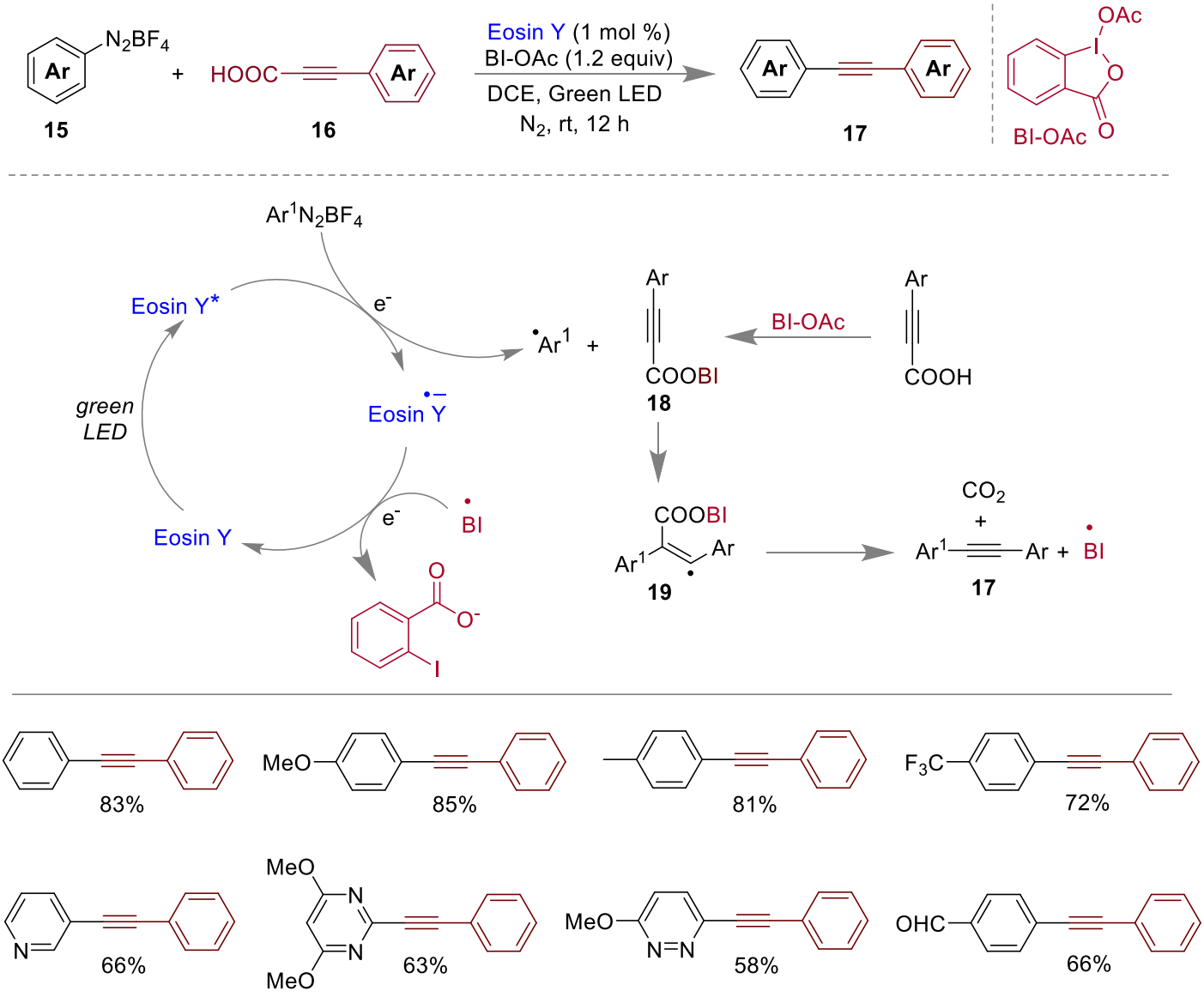


Figure 7. Decarboxylative alkynylation of arene diazonium salt using Eosin Y and BI-OAc.[68]

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Recently, 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN) and similar halogen-substituted organic compounds have emerged as valued organo-photocatalyst for various organic bond formation reactions under visible light irradiation. In 2018, Waser and coworkers developed a highly sophisticated method for the radical cascade fragmentation of cyclic ketoximes for alkynylation reactions (Figure 8).[69] For this transformation 3 mol % of 4ClCzIPN as the catalyst, 2.0 equiv of hypervalent iodine reagent ethynyl benziodoxolones (EBX) as alkyne source, 1.1 equiv of K_2CO_3 as a base were used in dichloroethane solvent under blue light irradiation to synthesize the alkynylnitrile compounds **21** from highly substituted cyclic oxime ethers **20**.

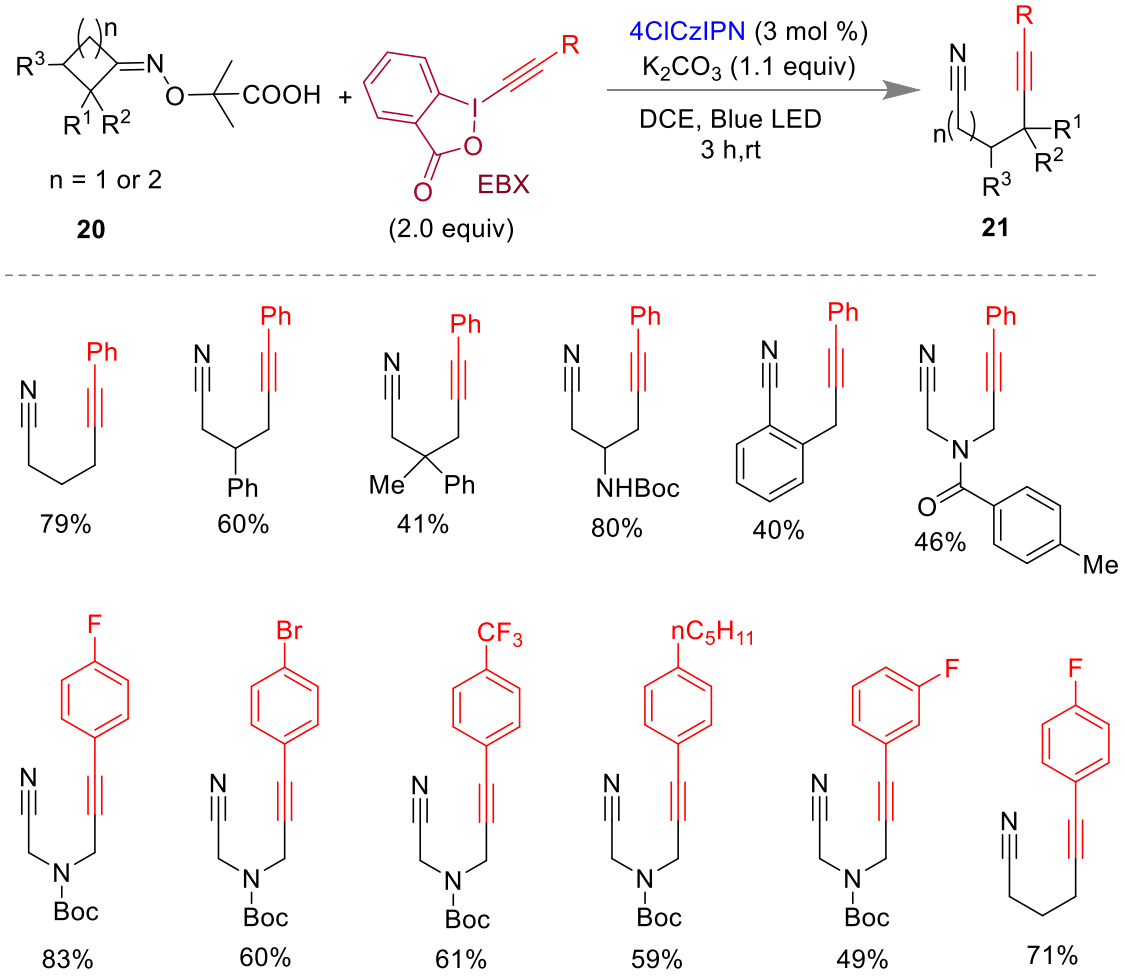


Figure 8. Alkynylation of ketoxime using 4ClCzIPN and EBX.[69]

In 2018, Frenette and coworkers developed a method for decarboxylative alkylation of heteroarenes under metal-free conditions (Figure 9).[70] For the first time they have used 1 mol % of 9-mesityl-10-methylacridinium perchlorate (Mes-Acr$^+$ClO$_4^-$)[51] as a catalyst along with 2.0 equiv of PhI(OOCCF$_3$)$_2$ or PIFA under blue LED light irradiation to get alkylated heteroarenes **24** from differently substituted carboxylic acid **23** and heteroarenes **22**. Plausibly the reaction proceeded *via* the formation of alkyl radical intermediate from phenyl iodine dicarboxylate derivative **25**.

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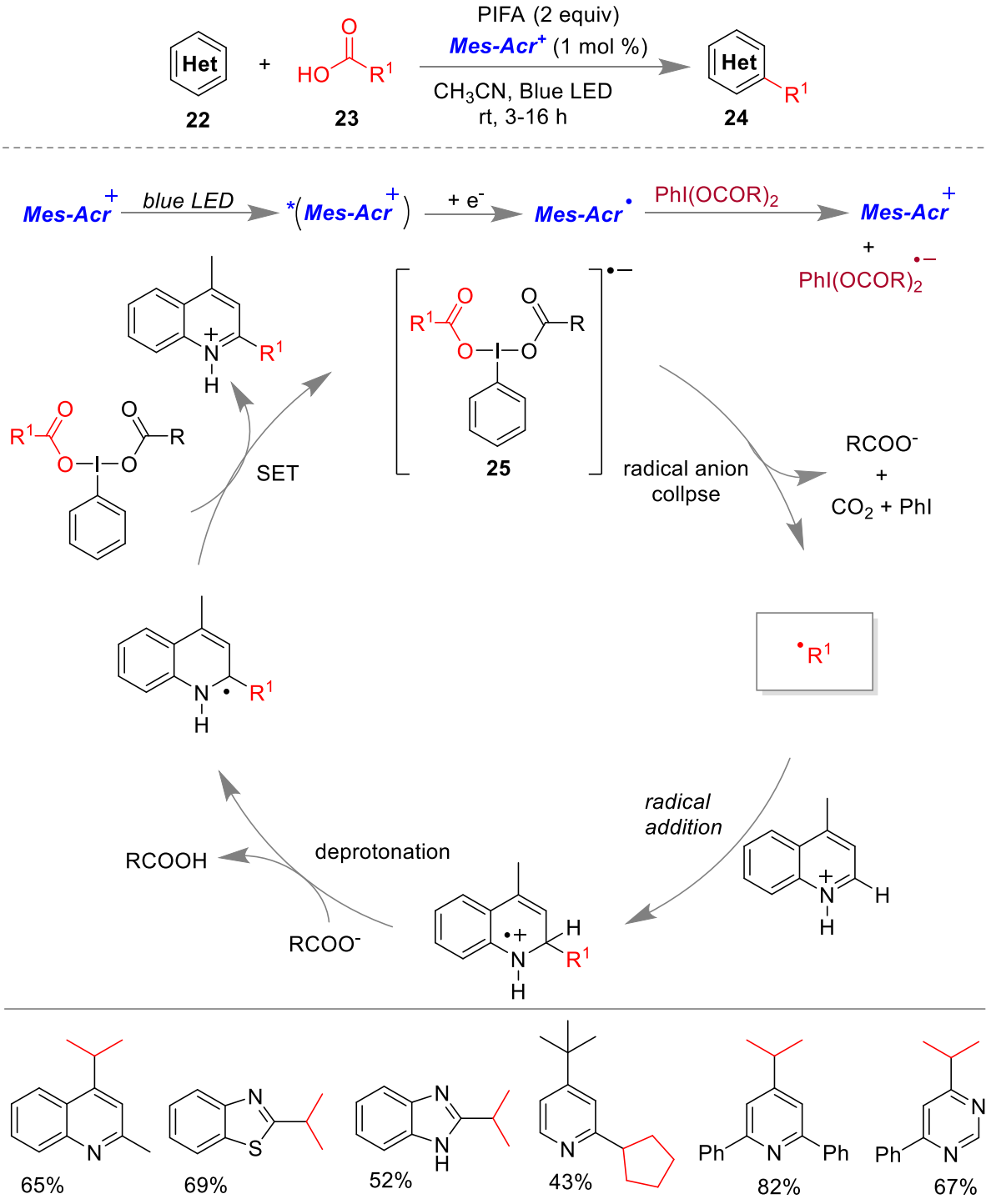


Figure 9. Decarboxylative alkylation of heteroarenes using PIFA and Mes-Acr^{+}.[70]

The functionalization of C(sp^3)-H bonds of azirine molecules[71] are challenging due to high ring strain and facile ring-opening reactions.[72] Majee and coworkers developed a method for acyloxylation of 2H-azirine molecules using PhI(OAc)$_2$ or PIDA as acyl source under visible light irradiation using organo-photocatalyst (Figure 10).[73] In this study, they concluded that 2 mol % of Rose Bengal (RB) as photocatalyst was good enough for the C(sp^3)-H acyloxylation of 3-aryl-2H-azirines **26** using 2 equiv of PIDA under blue LED irradiation. Aryl rings containing electron-donating groups at -ortho, -meta, or -para positions provided a good yield of the corresponding –OAc incorporated products. A radical-mediated pathway was proposed for the reaction *via* SET from the excited photocatalyst.

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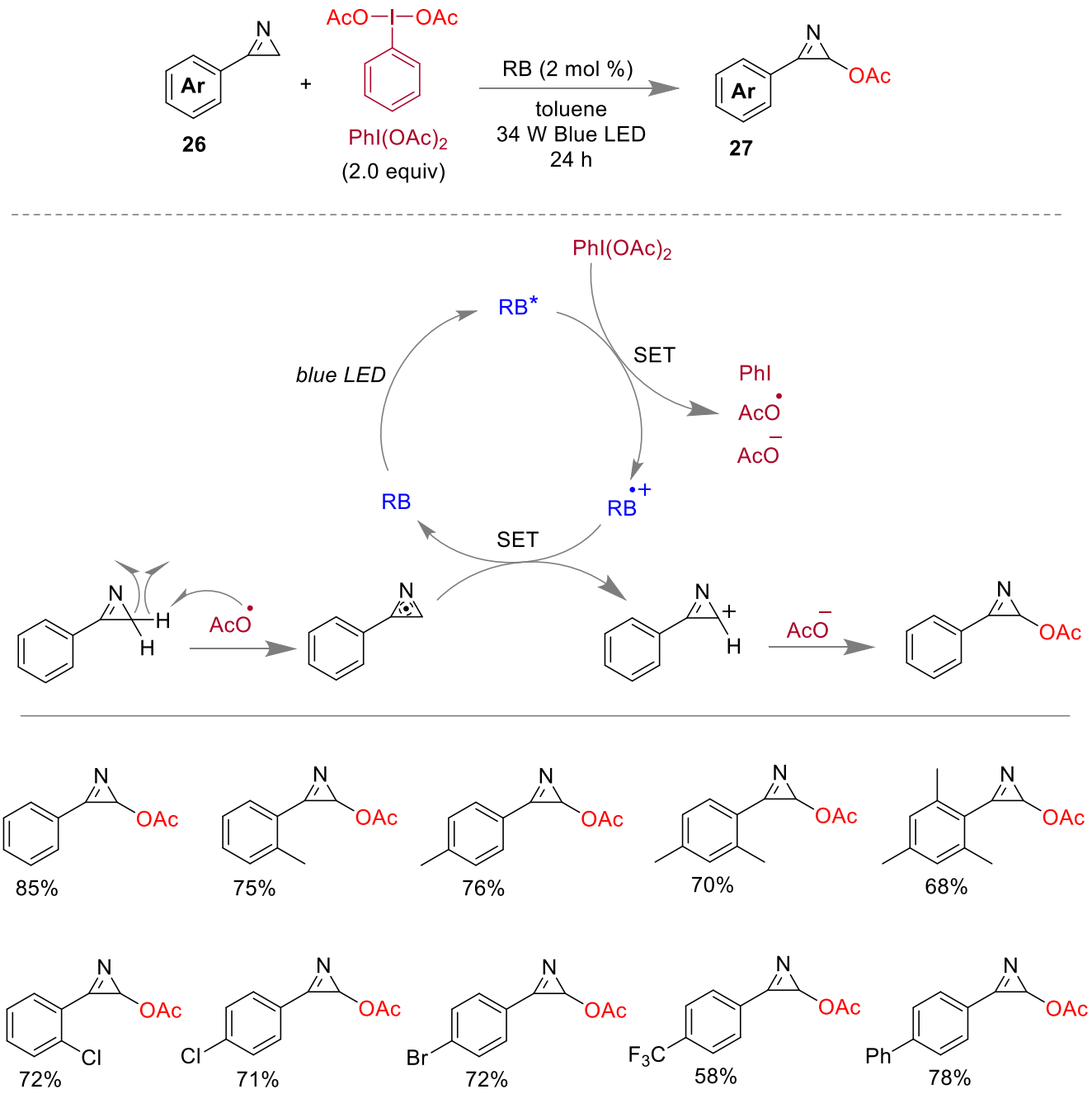


Figure 10. Functionalization of azirines using PIDA and Rose Bengal.[73]

Phenyl iodine diacetate (PIDA) or diacetoxyiodobenzene is one of the important hypervalent iodine reagents used as oxidizing reagent as well as a radical generator for various organic transformations.[20] In 2009, Yadav and coworkers reported the activation of PIDA under visible light irradiation using Eosin Y as organo-photocatalyst. With this activation reaction, they were successful in converting aryl boronic acids **28** to the corresponding phenols **29**. For this conversion, only 0.5 equiv of PIDA was required in presence of 1 mol % of Eosin Y in acetonitrile solvent under N_2 atmosphere and visible light irradiation (Figure 11).[74] In this report, a plausible mechanism is proposed, which is shown in Figure 11.

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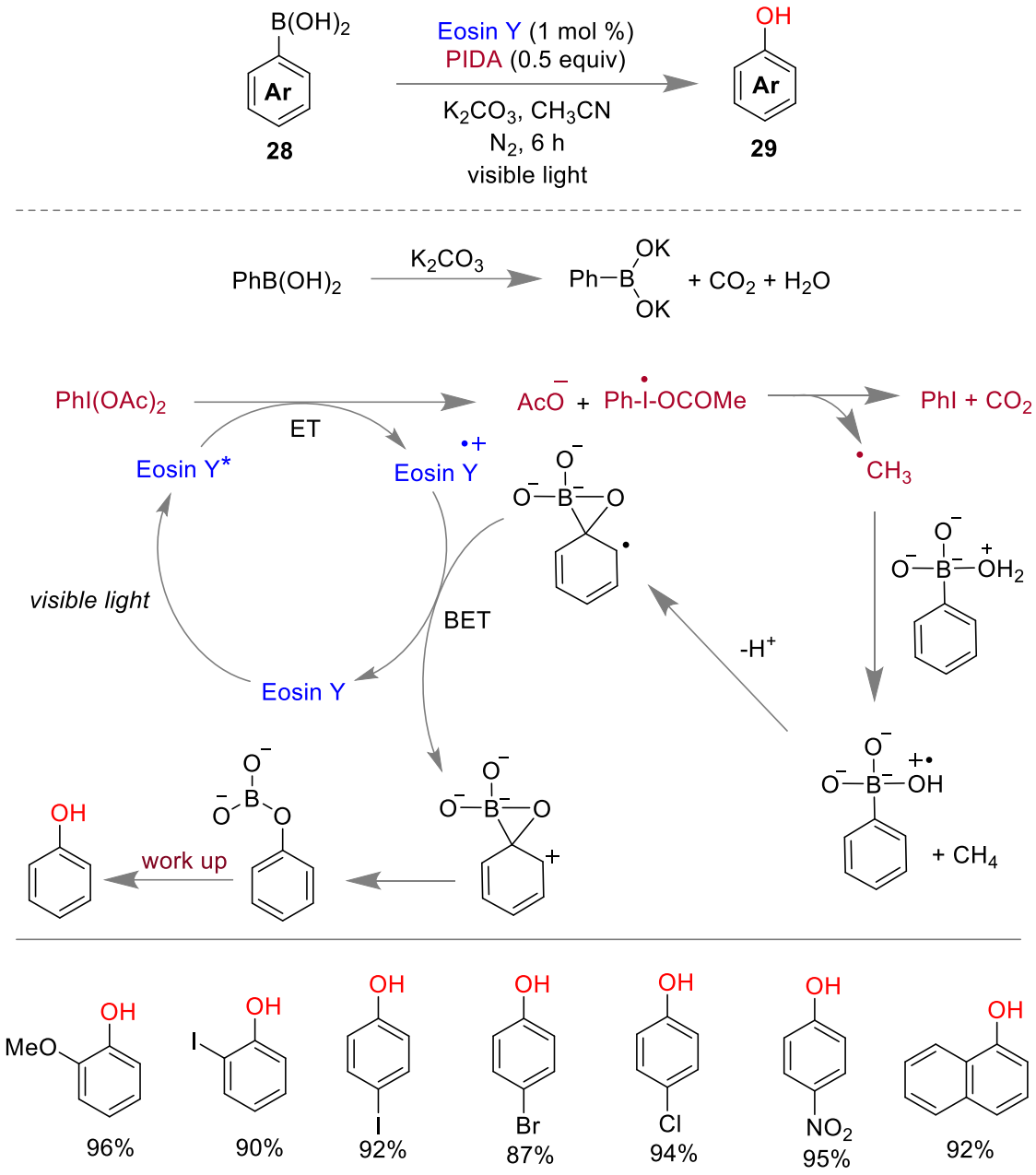


Figure 11. Synthesis of phenol using Eosin Y and PIDA.[74]

Recently, the application of hypervalent iodine reagent with organo-photocatalyst in rearrangement reactions for the construction of highly functionalized molecules *via* dual catalysis has become popular.[75] The first visible light-induced Smiles rearrangement[76] was reported by Chen and coworkers in 2019 for the synthesis of hydroxybenzophenone derivatives from aryl ketoacids *via* radical rearrangement (Figure 12).[77] For this transformation the combination of 2 mol % of 9-mesityl-10-methylacridinium perchlorate (Acr-Mes$^+$ClO$_4^-$) as organo-photocatalyst and 20 mol % of acetoxybenziodoxole (BI-OAc) were used under 4 h of irradiation with blue light to isolate good to excellent yield of hydroxybenzophenone derivatives **31** from ortho ketoacid substituted biaryl ethers **30**. Here the role of BI-OAc possibly activated carboxylic acid for decarboxylation reaction *via* intermediate **32** to generate acyl radical intermediate which upon *ipso*-substitution resulted in **33** and followed by rearrangement yielded the desired product.

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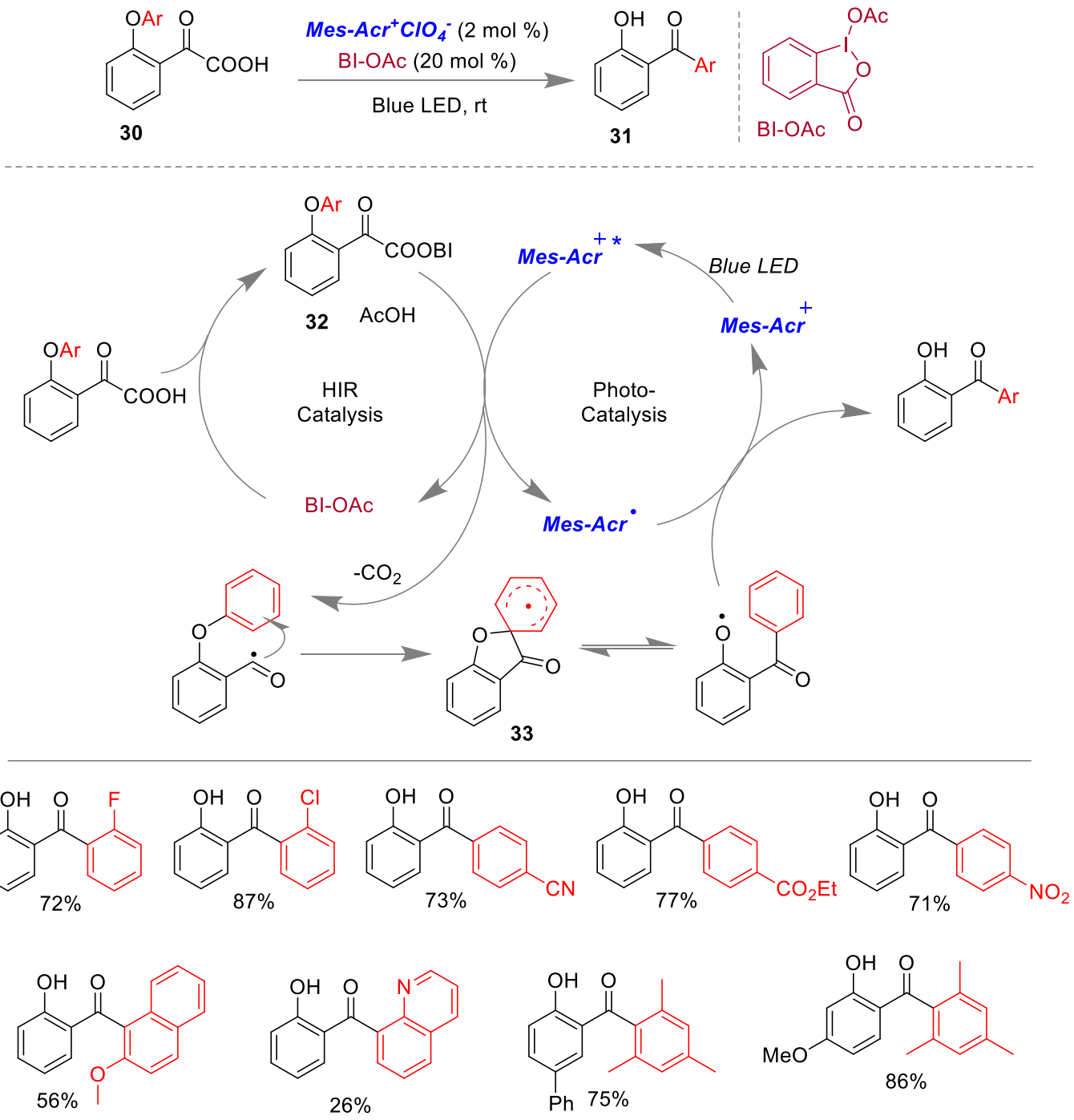


Figure 12. Photo-catalytic Smiles rearrangement using Mes-Acr$^+$ClO$_4^-$ and BI-OAc.[77]

Selective synthesis of sulfoxide molecules is well known in organic chemistry.[78] In 2018, Cai and coworkers developed a method *via* 1,2-aryl group migration reaction for the synthesis of highly substituted *α*-aryl-*γ*-methylsulfinyl ketones (Figure 13).[79] In this work they have used the synergic effect of organo-photocatalyst with hypervalent iodine reagent to activate C(sp^3)-H bond of dimethylsulfoxide (DMSO) under visible light irradiation. Using 2 mol % photocatalyst 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN),[53] 2.0 equiv of hypervalent iodine reagent PIDA as oxidant and 2.0 equiv of trimethoxybenzene as an additive in DMSO solvent up to 12 h irradiation under blue LED they could isolate the sulfoxide incorporated rearranged products **35** from *α*,*α*-diaryl allylic alcohol derivatives **34**. Mechanistically it was shown that the sulfinyl radical

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acted as the key intermediate for the formation of radical **36**, which upon 1,2-aryl migration and subsequent oxidation led to the final products.

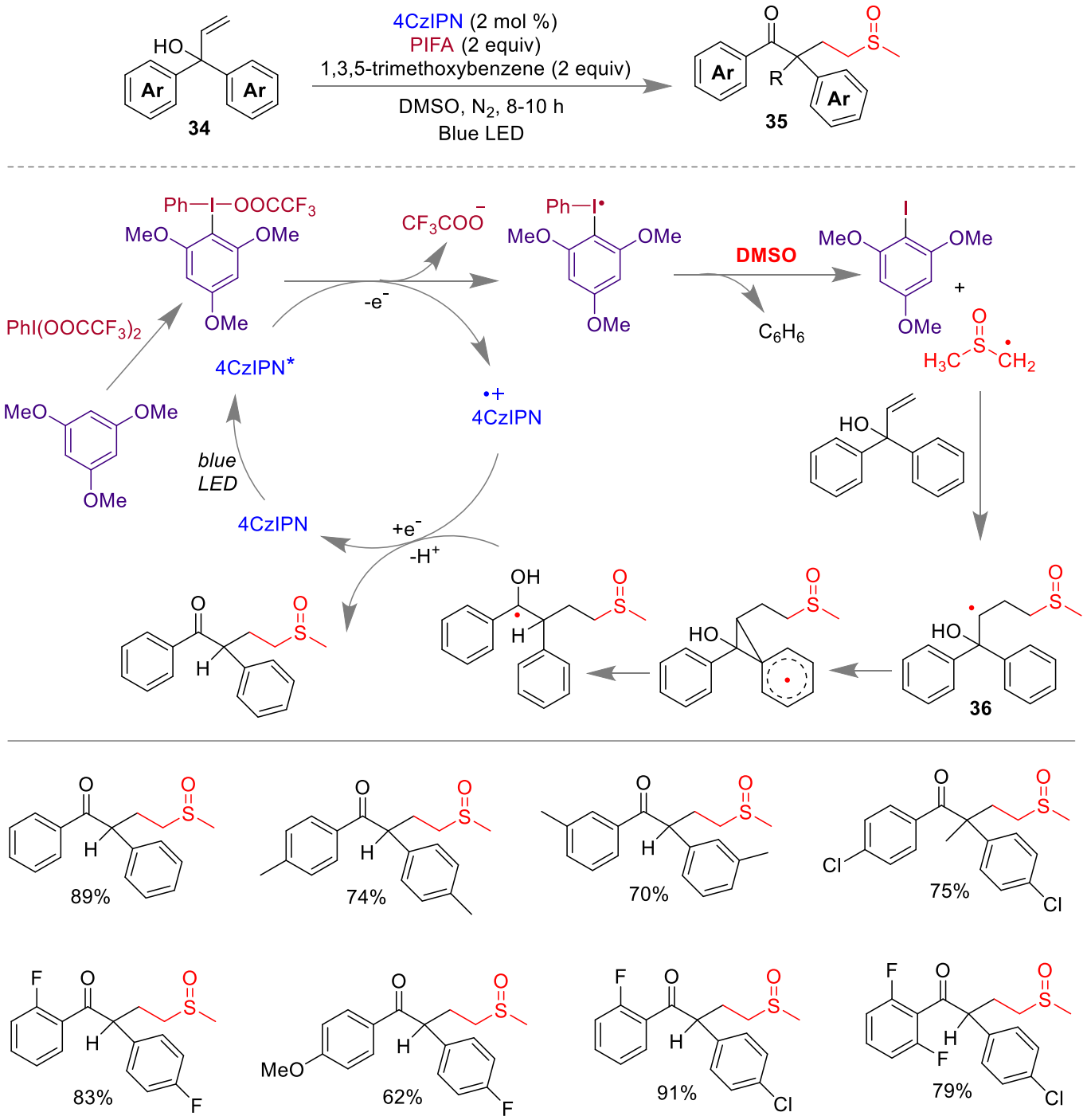


Figure 13. Synthesis of *α*-aryl-*γ*-methylsulfinyl ketones using 4CzIPN and PIFA.[79]

In 2017, Duan's group reported a decarboxylative C-C bond formation followed by ring expansion of vinylcyclobutanol system for the synthesis of substituted cyclopentane rings having quaternary carbon (Figure 14).[80] In this work they have investigated the efficacy of dual catalysis of organo-photocatalyst and hypervalent iodine reagent under visible light irradiation. Using 5 mol % of Rhodamine B (RB) as photocatalyst and 2.0 equiv of BI-OH as hypervalent iodine reagent under visible light at room temperature condition, they have synthesized cyclopentyl derivatives **39** from cyclobutanols **38** and *α*-keto acids **37** as acyl source followed by ring expansion with good yield.

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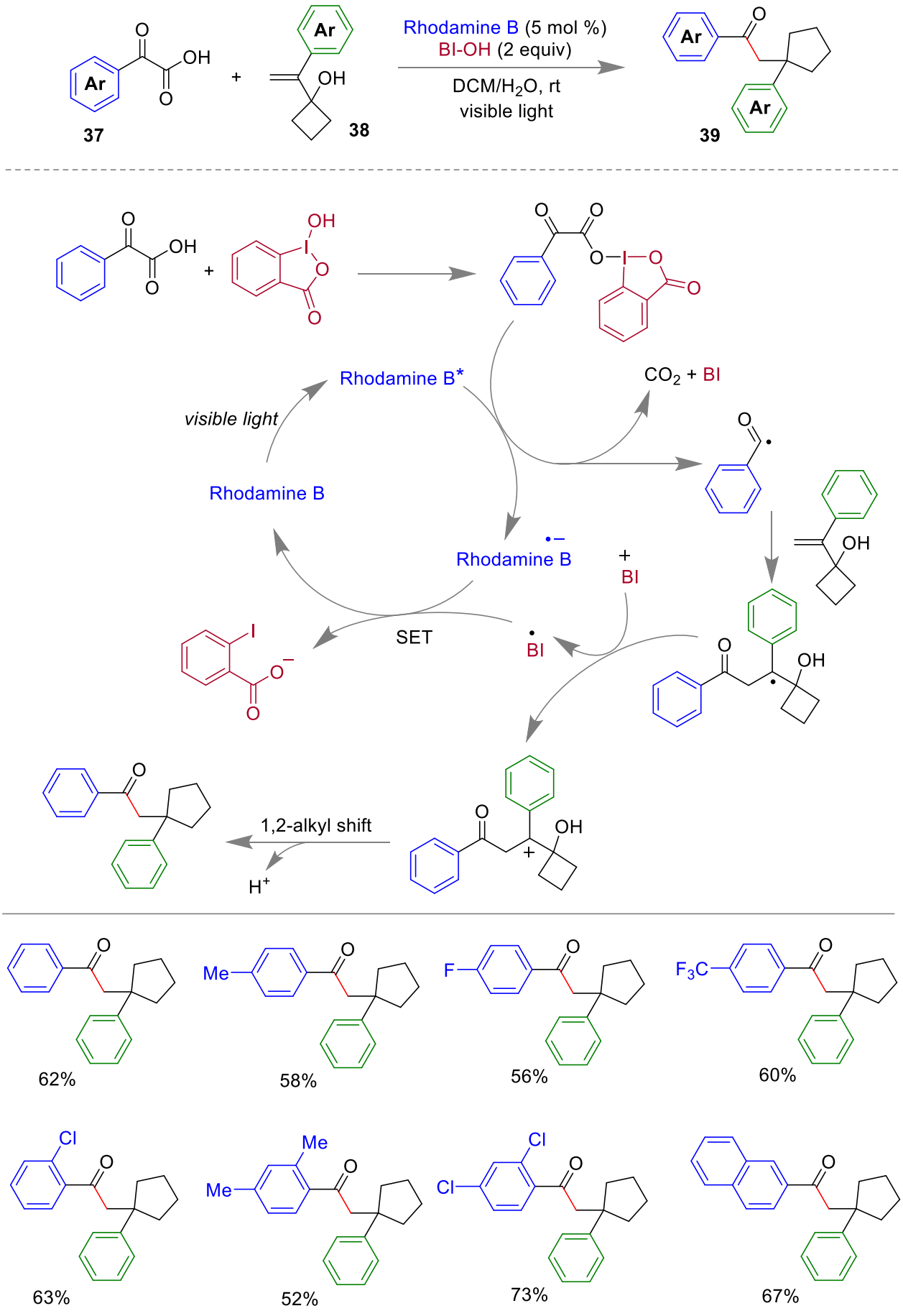


Figure 14. Ring expansion of cyclobutane system using Rhodamine B and BI-OH.[80]

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3. Conclusions

In conclusion, herein we have collected the literature which can prescribe many efficient pathways towards making desirable functional molecules using photoredox organocatalysis in combinations with hypervalent iodine reagents. We present the HIRs in terms of the roles as group transfer reagents as well as oxidants. To the best of our knowledge, this review based on metal-free photocatalysts will be a unique addition to hypervalent iodine chemistry. We hope that this research field will make an important contribution in chemistry by bridging different areas like organic synthesis and visible light photolysis. We anticipate that this review article will benefit the synthetic community in large so that many chemical transformations can be achieved successfully under ambient conditions.

Acknowledgements

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