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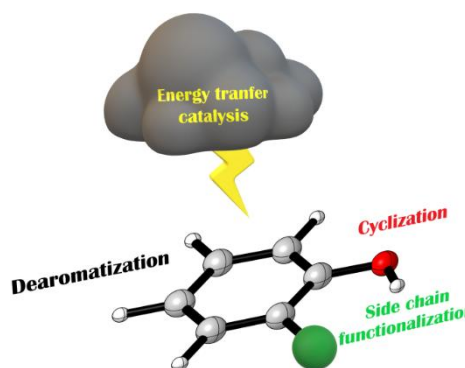
Visible-Light Driven Transformations of Phenols via Energy Transfer Catalysis

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Abstract In the past decade, the field of visible-light mediated photocatalysis has been particularly thriving by offering innovative synthetic tools for the construction of functionalized architectures from simple and readily available substrates. One strategy that has been of interest is energy transfer catalysis which a powerful way of activating a substrate or an intermediate by using the combination of light and a relevant photosensitizer. This review deals with recent advances in energy transfer catalysis applied to phenols which are ubiquitous in chemistry both as starting materials and as high-added value products. Processes involving energy transfer from the excited photosensitizer to ground state oxygen and to phenol-containing substrates will be described.

- 1 Introduction
- 2 Intermolecular reactions
- 3 Intramolecular processes
- 4 Conclusions and outlook

Key words Photochemistry, Phenol, Dearomatization, Cycloaddition, Singlet Oxygen.

1. Introduction

The concept of harnessing visible light to trigger chemical transformations is a powerful tool in organic chemistry.¹ Nevertheless, most of organic compounds do not possess the relevant absorption features for a direct photoexcitation strategy under visible light.² Within this context, visible-light mediated photocatalysis has significantly contributed to the advent of photochemistry by enabling the excitation – and further transformation – of an organic molecule through electron or energy transfer processes. While enormous achievements have been made in photo-initiated electron transfer catalytic processes (photoredox catalysis),³ the field of energy transfer catalysis (EnT) has comparatively received less attention. Energy transfer catalysis involves the combination of a photosensitizer (PS), a substrate (S) and light.⁴ This photochemical process is based on the deactivation of an

excited-light absorbing sensitizer (PS*) by transferring its energy to a substrate S leading to the formation

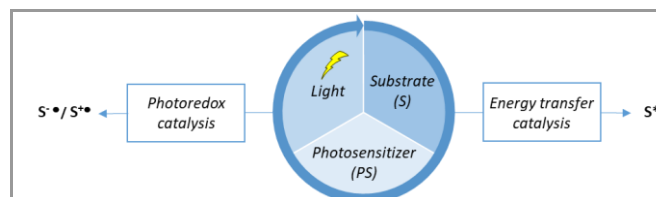


Figure 1 Energy transfer and photoredox catalysis.

of the excited substrate S* (Figure 1). Unlike photoredox catalysis, no single-electron transfer occurs between the excited photocatalyst and the substrate or any intermediates from the reaction mixture.

Breakthroughs in energy transfer catalysis have been driven by the design of new photosensitizers and the implementation of innovative synthetic transformations with applications in a range of contexts.⁵ By careful examination of the reaction conditions, visible-light induced energy transfer catalysis has been harnessed in a series of transformations such as [2+2] photocycloadditions, alkene photoisomerizations, sensitization of metal complexes, oxidative processes through the formation of singlet oxygen, or the activation of azide and diazo compounds to form heterocyclic compounds.⁴ Amongst the substrates tested, phenol derivatives were deemed worthy of investigation because of their unique chemical behavior. Besides classical reactivities such as electrophilic aromatic substitutions⁶ and C-O bond forming reactions,⁷ considerable attention has been given in recent years to dearomatization processes⁸ and direct C-H functionalizations of the aromatic ring.⁹ In addition, recent advances regarding valorization of biomass to produce phenols have made these compounds attractive platforms in organic chemistry.¹⁰ The manifold reactivity of phenols with the synthetic appeal of energy transfer catalysis offers a powerful strategy to reach novel

molecular architectures (Figure 2). This is the subject of this review which does not intend to be comprehensive but rather to point out the synthetic potential and future challenges of this methodology.

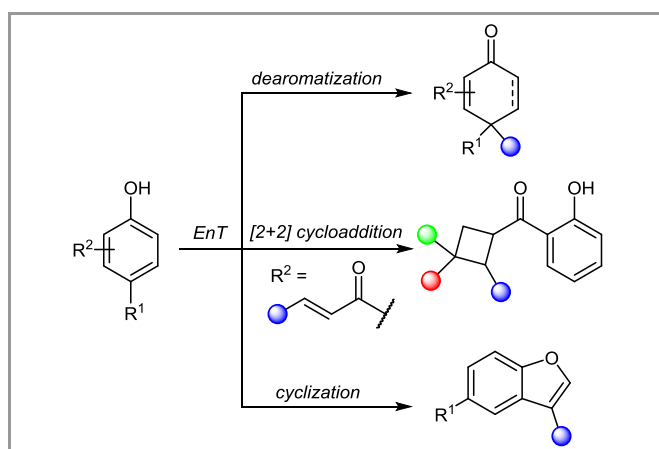


Figure 2 Phenol transformation via energy transfer catalysis.

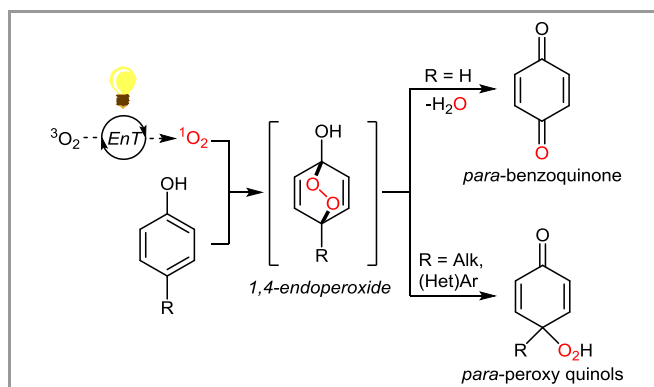
2. Intermolecular processes

In intermolecular transformations, the reaction can be initiated by energy transfer from the excited triplet photosensitizer to the phenol-containing substrate or the reactant such as ground state triplet oxygen ($^3\text{O}_2$) leading to the formation of the highly electrophilic species singlet oxygen ($^1\text{O}_2$). The two strategies will be discussed in the following examples.

2.1 Reaction with singlet oxygen

For many decades now, it has been demonstrated that singlet oxygen ($^1\text{O}_2$) is a powerful reactant toward electron-rich substrates.¹¹ An energy of 94 kJ.mol⁻¹ is required to form the highly electrophilic singlet oxygen from ground state oxygen. Many photosensitizers (tetraphenylporphyrin, rose bengal, methylene blue to cite only a few) possess a triplet energy (E_T) equal or greater than 94 kJ.mol⁻¹ required to efficiently sensitize triplet oxygen into its singlet state. In synthetic chemistry, electron-rich phenols are prone to react with singlet oxygen and this research field has received considerable attention from a mechanistic and synthetic point of view.

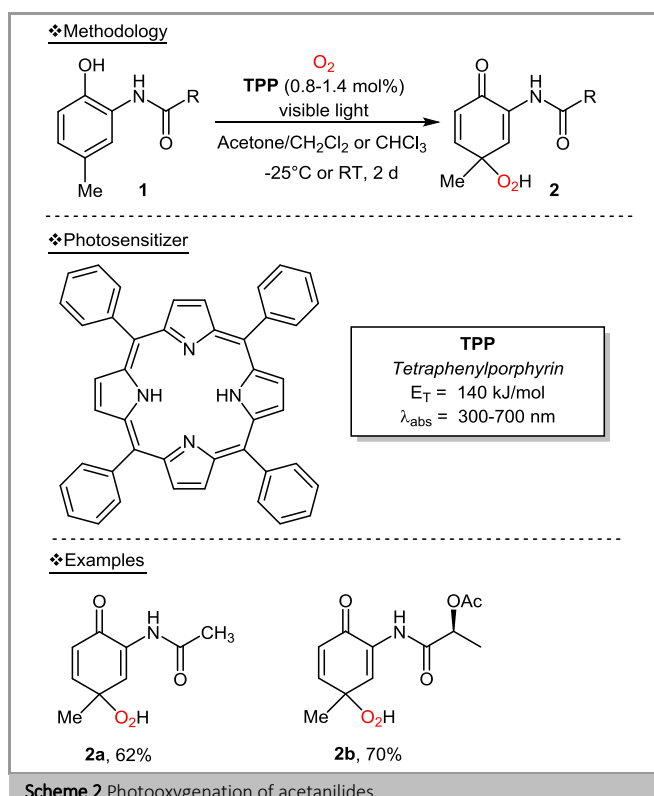
In 2019, Długogorski and co-workers reported a mechanistic and kinetic study on the photooxygenation of phenol (Scheme 1, R = H).¹² Based on DFT calculations and Electron Paramagnetic Resonance (EPR), their results provided evidence for the 1,4-endoperoxide intermediate, obtained after a [4+2] cycloaddition, yielding *para*-benzoquinone as the only detected product after ring opening. Indeed, the 1,4-cycloaddition of $^1\text{O}_2$ at the *ipso* and *para* positions requires a 17–22 kJ.mol⁻¹ lower energy barrier than the corresponding addition at the *ortho* and *meta* carbons.



Scheme 1 Singlet-oxygen mediated oxidation of phenols.

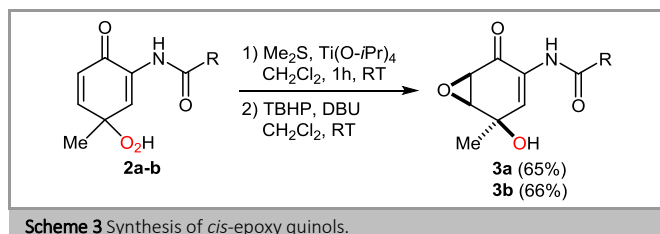
When singlet oxygen reacts with *para*-substituted phenols, the *in-situ* opening of the corresponding 1,4-endoperoxides results in the formation of *para*-peroxy quinols, that could then be reduced smoothly with triphenylphosphine or dimethylsulfide to give the corresponding alcohols.¹³ The photooxidative dearomatization of *para*-substituted phenols with $^1\text{O}_2$ led to highly oxygenated frameworks and was subsequently applied as a key reaction in numerous multistep reactions as these structures can be found in many natural products. In this short review, we will focus our attention to the recent advances in $^1\text{O}_2$ -mediated dearomatizations of *para*-substituted phenols.

As a first example, Kilic and co-workers prepared the hydroperoxides **2** after photooxygenation of the acetanilides **1** towards their syntheses of epoxy quinol antibiotics (Scheme 2).¹⁴ This reaction was realized with tetraphenylporphyrin (TPP)¹⁵ as photosensitizer and no control on stereoselectivity was observed for this oxidation starting from a chiral substrate **1b**.

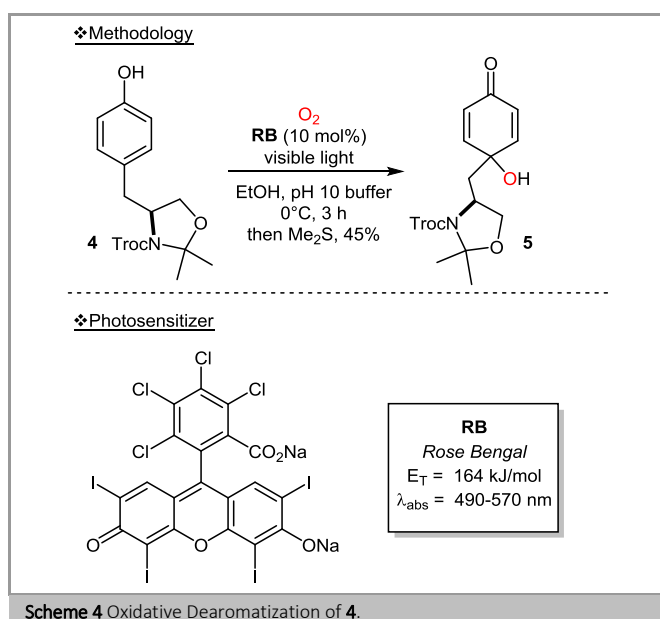


Scheme 2 Photooxygenation of acetanilides.

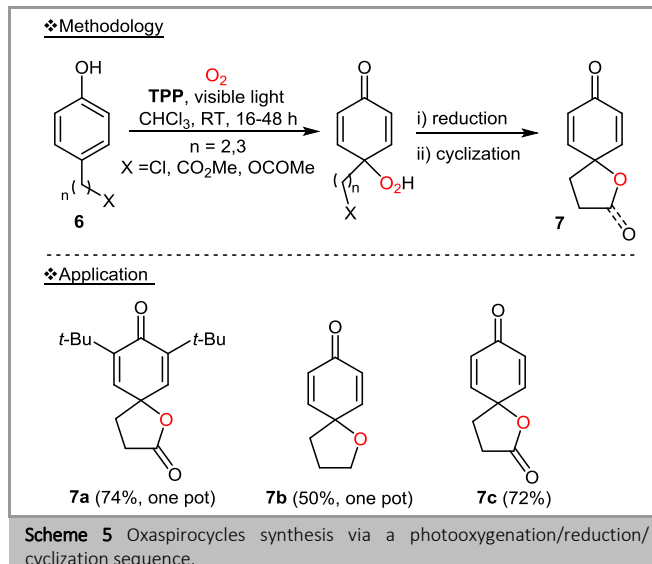
The hydroperoxides **2** were then reduced to the corresponding alcohols which underwent a Weitz-Scheffer epoxidation with *tert*-butylhydroperoxide (TBHP) leading to the *cis*-epoxy quinols **3**, important building blocks in Manumycin natural products (Scheme 3).



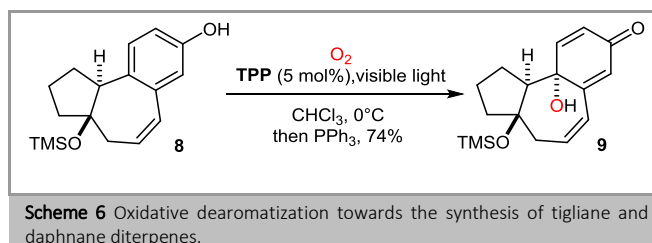
Oxidative dearomatization was also used by Hoye and co-workers in their synthesis of the polar pharmacophoric subunit of (+)-scyphostatin.¹⁶ The singlet oxygen mediated oxidation of **4** with rose bengal¹⁷ as photosensitizer under basic conditions followed by reduction with Me₂S was found as an efficient and atom economic alternative to a classical phenyliodine diacetate oxidation (Scheme 4).



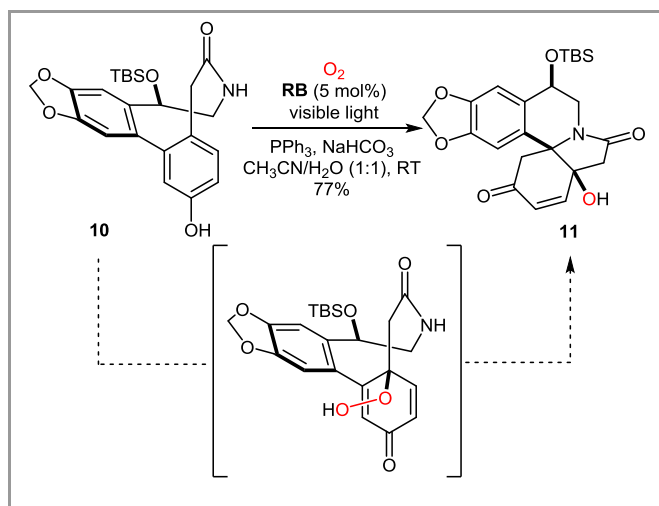
Following these results, Klusmann and co-workers described in 2013 a sequence of peroxide formation, reduction and intramolecular cyclization of **6** to give access to oxaspirocycles **7** (Scheme 5).¹⁸ This sequence could be executed stepwise or more conveniently in a one-pot fashion, without isolation of the hydroperoxide intermediates. Here again, the key oxidative dearomatization is an atom-economic alternative to hypervalent iodine reactants. Although the scope is limited to 3 examples of oxaspirocyclic compounds **7**, it demonstrated the potential of photosensitized dearomatization of phenols to obtain more complex structures.



Singlet oxygen chemistry has been harnessed in total synthesis of natural and biologically relevant products.¹⁹ For instance, an elegant diastereoselective visible-light induced oxidative dearomatization was observed by the group of Li during their synthesis of the tricyclic framework contained in tiglianes and daphnanes (Scheme 6).²⁰ Using TPP as photosensitizer in chloroform under a strong visible light, irradiation followed by reduction of the corresponding *para*-peroxy quinol led to the alcohol **9** as a single diastereoisomer with a high yield (74%). The relative configuration was established by X-ray diffraction analysis, and it was assumed that this stereoselectivity was due to the trimethylsilyl ether moiety and its steric hindrance on one face of the phenol, leading singlet oxygen to react on the other face.

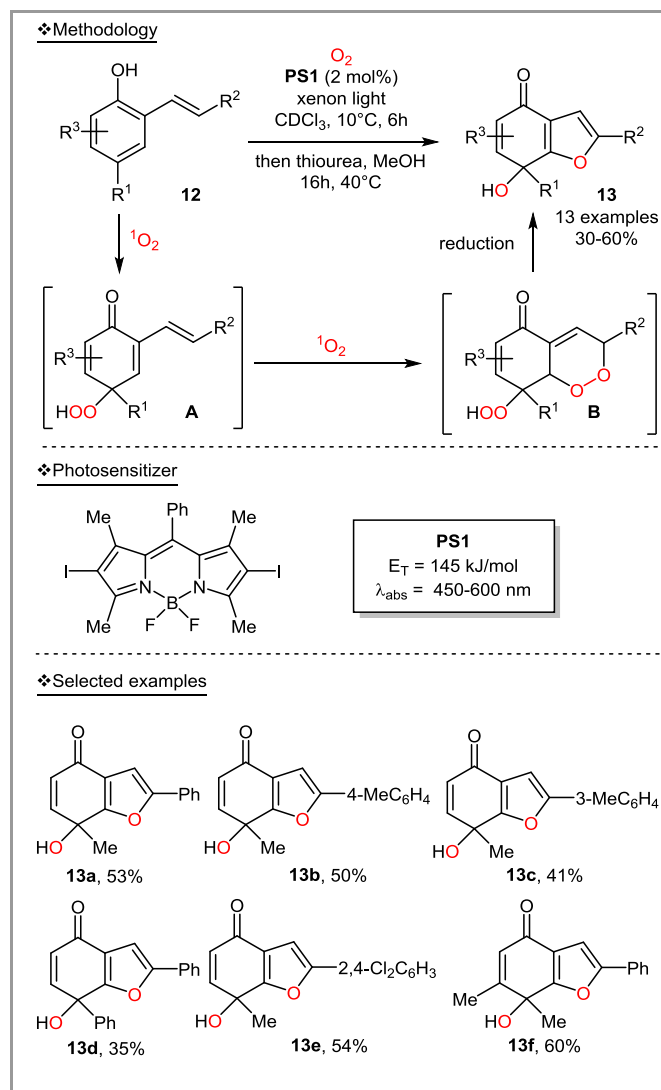


Another diastereoselective oxidative transformation was conducted as a key step in the synthesis of Erythrina alkaloids by the group of Kitamura and Fukuyama (Scheme 7).²¹ Here again, the steric hindrance around the phenol has a strong influence on the stereoselective ¹O₂ addition. An X-ray analysis confirmed that the silyloxy group is pointing toward the phenol moiety. This configuration and the atropisomeric stereochemistry are guiding singlet oxygen to react specifically on one face of **10** to give selectively a peroxide that will lead to a spontaneous reaction with the amide nitrogen yielding efficiently (77%) **11** as a single diastereomer.



Scheme 7 Multibond-forming process.

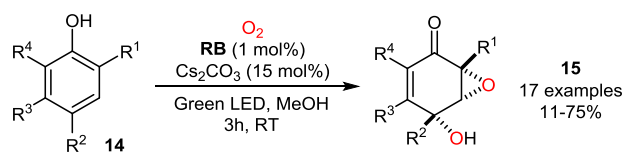
Inspired by these results, we reported in 2018 a one-pot Bodipy-catalyzed domino photooxygenation.²² A photosensitized singlet-oxygen mediated phenol dearomatization, followed by a [4+2] cycloaddition gave a variety of six-membered ring fused furans **13** under mild conditions (Scheme 8). The best results were obtained by using the readily available Bodipy **PS1** as a photosensitizer.²³ Starting from 2-alkenylphenols **12**, we envisioned that a first singlet oxygen molecule would react as previously described with the more electron-rich phenol, giving the corresponding hydroperoxide **A**. A second singlet oxygen molecule could then react with these intermediates in a classical [4+2] cycloaddition that would ultimately render the fused furans **13** after reduction. Mechanistic studies were carried out to outline the importance of singlet oxygen in the reaction outcome.



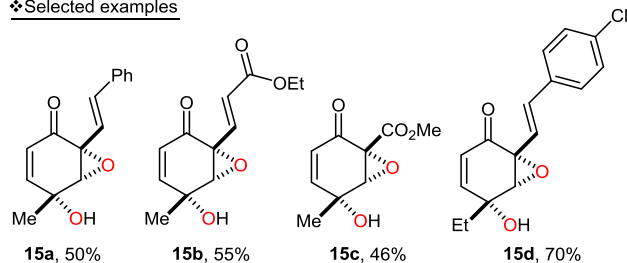
Scheme 8 Catalyzed domino photooxygenation.

The importance of functionalized epoxyquinol frameworks in natural products served to challenge synthetic organic chemists.²⁴ Previous reports have shown that phenols were interesting substrates to get access to epoxyquinols through a $^1\text{O}_2$ -mediated dearomatization/reduction/epoxidation sequence (Scheme 3). Nevertheless, the reduction/oxidation tactic lowers the synthetic appeal of this strategy. In order to harness the full potential of singlet oxygen by transferring both oxygen atoms, we reported a one-pot synthesis of *cis*-epoxyquinols **15** starting from phenols **14** (Scheme 9).²⁵ The key point for the success of the reaction lies in the use of basic conditions. After optimization studies and mechanistic insights, we demonstrated that using rose bengal as photosensitizer and cesium carbonate as base led

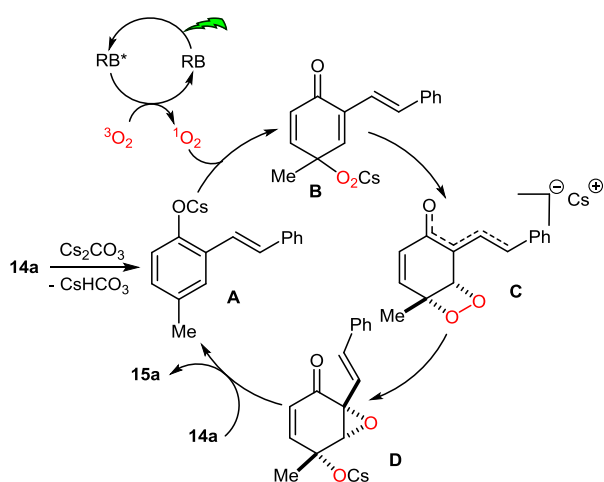
❖Methodology



❖Selected examples



❖Proposed mechanism



Scheme 9 Epoxyquinol synthesis via photooxygenation under basic conditions.

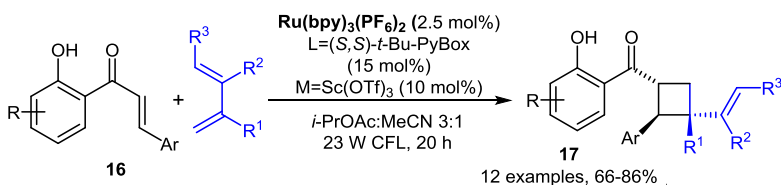
to a large scope of functionalized epoxyquinols. Cesium carbonate plays a pivotal role by increasing the kinetic of the photooxygenation step while triggering the epoxidation reaction.

2.2 [2+2] cycloadditions

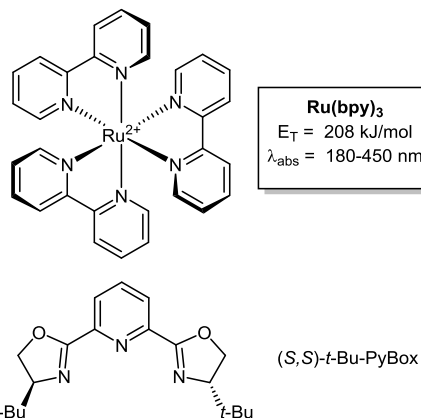
A second class of reactions initiated by energy transfer is [2+2] cycloaddition reactions. Contrary to photoredox strategies, visible light photocatalyzed [2+2] cycloadditions by energy transfer are not limited by electrochemical potentials. This was demonstrated by the breakthrough work of Yoon and co-workers who developed a two-catalyst strategy for enantioselective cycloadditions of phenol derivatives **16**.²⁶ Indeed, scandium (III) salts in presence of a chiral ligand formed a chiral Lewis acid acting as a catalyst for inducing enantioselectivities (Scheme 10).²⁷ A large diversity of asymmetric [2+2] cycloadditions was conducted on diversely substituted phenol derivatives **16** and dienes.

After mechanistic and computational investigations, they demonstrated that complexation of **16a** with Sc(III) salts results in a dramatic decrease in the energy of the triplet state, from $E_T(\text{exp})=54$ kcal/mol to 32 kcal/mol. No reaction occurred in the absence of any Lewis acid as well as in absence of light. The formation of the chiral complex **A** involving the Sc(III) salt, the chiral PyBox ligand and the two oxygens of the 2'-hydroxy-

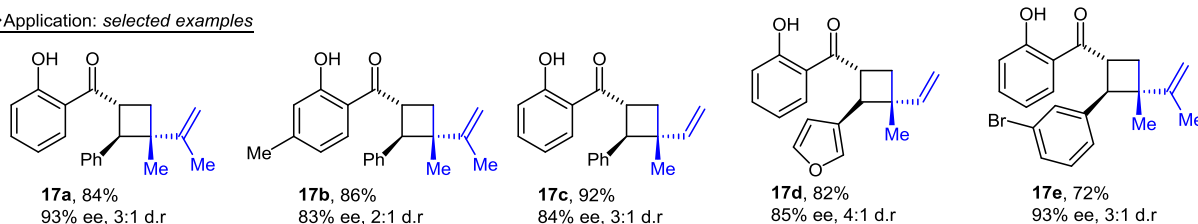
❖Methodology



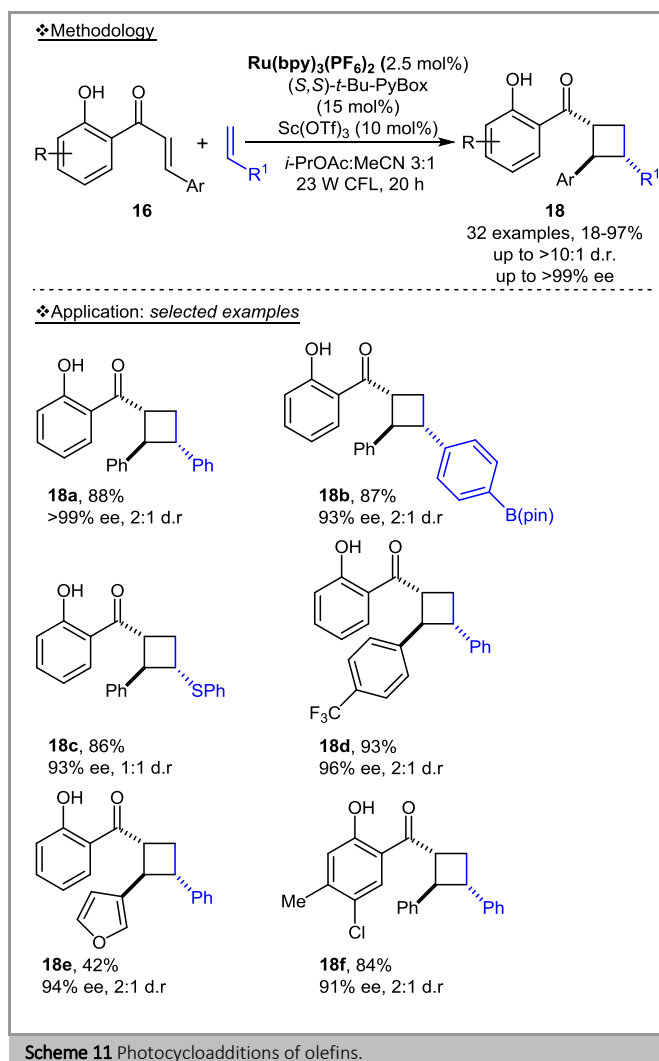
❖Catalytic system



❖Application: selected examples

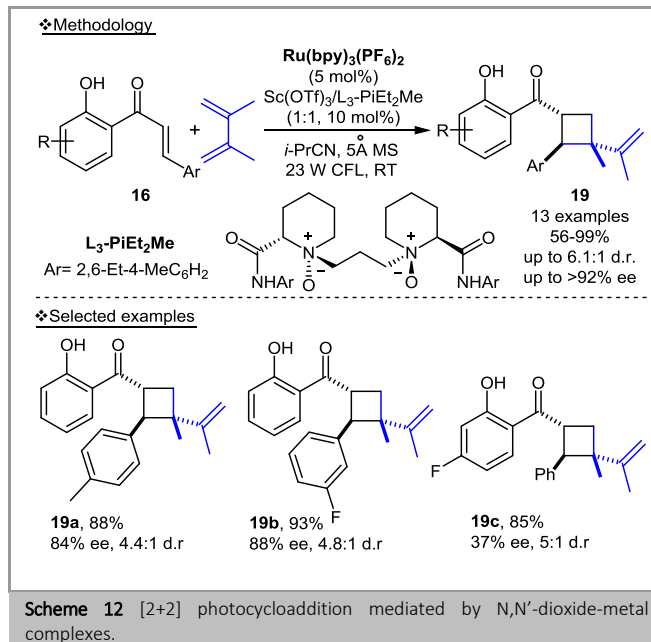


Scheme 10 Enantioselective [2+2] cycloadditions through Lewis acid-catalyzed triplet energy transfer.



chalcone **16** is probably the key intermediate, leading the [2+2] cycloaddition to proceed in an enantioselective way. Very recently, Chen, Shen and co-workers carried out a detailed computational study on the mechanism of this transformation.²⁸ Among many other data, they explained the origin of chirality in this reaction by energy changes in the triplet state depending of the attacked side of the coordinated chalcone.

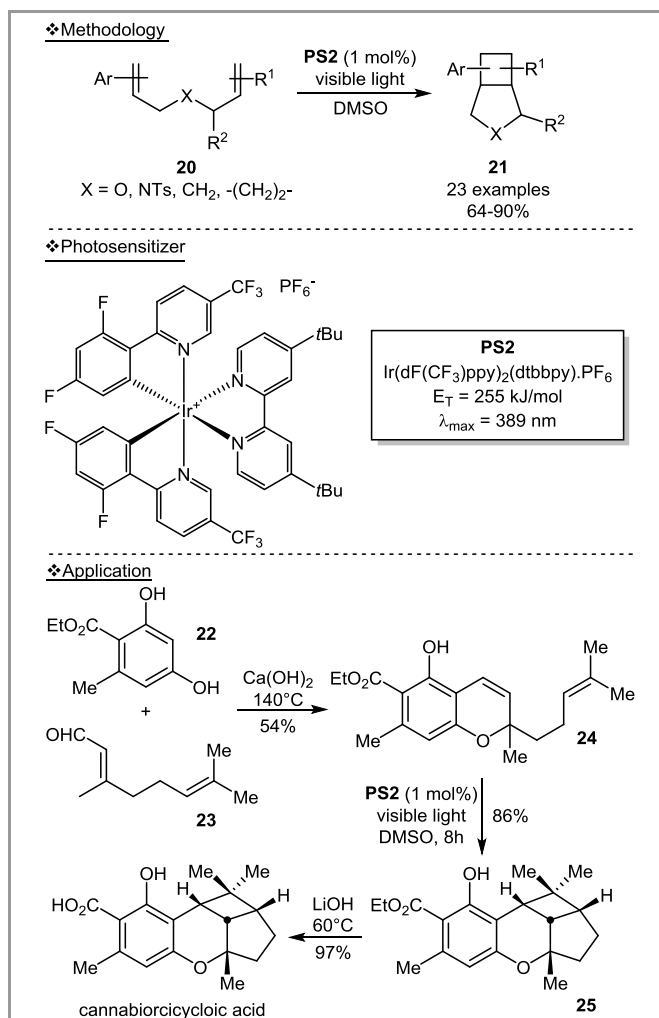
In a further study, the group of Yoon extended the scope of the reaction to various styrenes and diene systems, obtaining high enantiomeric excesses and giving a direct access to diarylcyclobutane natural products (Scheme 11).²⁹ Following Yoon's pioneering works, Feng, Liu and co-workers also reported an enantioselective [2+2] cycloaddition involving 2'-hydroxychalcones **16** (Scheme 12).³⁰



Reaction conditions are quite similar but tetradentate *N,N'*-dioxide platforms were used to form a chiral cluster with Sc(III). Results are comparable to those obtained by Yoon in term of yields and enantiomeric excesses, but are generally better in term of diastereoselectivities, with ratios up to 6.1:1.

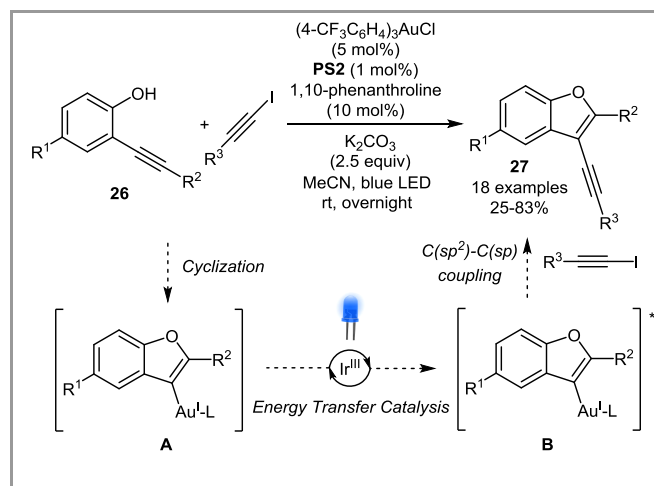
3. Intramolecular transformations

Although limited, intramolecular visible light photocatalyzed transformations of phenols by energy transfer have already been reported. As highlighted in the previous section, alkenes are prone to undergo [2+2] cycloadditions by energy transfer catalysis. In 2012, the group of Yoon explored the [2+2] photocycloaddition of alkenes **20** performed in the presence of 1 mol% of **PS2** under visible light (Scheme 13, top).³¹ This transformation was applied to the expedient synthesis of racemic cannabiorcyclolic acid which is a natural product belonging to the family of cannabinoids (Scheme 13, down). Condensation of the phenol **22** and citral **23** gave rise to the cycloadduct precursor **24** in 54% yield. The photocycloaddition was performed in the presence of 1 mol% of **PS2** in DMSO under visible light. After 8 h of irradiation, the desired cyclobutane-containing compound **25** was isolated in 86% yield and subsequent hydrolysis of the ester function gave rise to the natural product in 97% yield.



Scheme 13 Synthesis of cannabiorcycloic acid using a [2+2] photocycloaddition as the key step.

In previous examples, the energy transfer took place between the reactants and the excited photosensitizers. The concept of energy transfer catalysis has been also applied to transition metal complexes providing a wealth of untapped synthetic potential in organometallic chemistry.³² This strategy has been harnessed by Mouriès-Mansuy, Ollivier, Fensterbank and co-workers for the Au(I)-catalyzed formation of alkynylbenzofuran derivatives **27** (Scheme 14).³³ The combination of electrophilic gold catalysis and photosensitization by means of **PS2** allowed the formation of the decorated benzofurans **27** starting from phenols **26** and alkynyl iodide partners. The optimized reaction conditions were applied to a series of substrates and moderate-to-excellent yields of the desired alkynylbenzofurans were obtained. While a wide substrate scope was observed, no reaction occurred with an iodoalkyne bearing a 4-nitro aryl group and the protodeauration cyclization product was formed.



Scheme 14 Merging electrophilic gold catalysis and photosensitization to prepare alkynylbenzofurans.

Detailed mechanistic investigations were carried out to shed light on the formation of **27** by performing control experiments, photophysical analyses and modelling studies. The reaction sequence would start by the 5-endo-dig gold-catalyzed O-cyclization of **26** to afford the vinylgold(I) species **A**. A Dexter-type energy transfer between this intermediate and the long-lived triplet state ³[Ir-F] would occur to afford the excited state of the vinylgold(I) species **B**, a key intermediate for triggering the oxidative addition. Gold(I) complexes are rather reluctant to oxidative addition and therefore, specific reactions conditions are generally required to provide the corresponding gold(III) intermediates. Given that triplet sensitization can promote oxidative addition under convenient conditions, this strategy should offer new synthetic opportunities in the near future.

4. Conclusions and outlook

This review has brought to light recent advances in visible-light mediated transformation of phenols by energy transfer catalysis. The unique properties of phenols enabled their transformation into synthetically interesting directions. The hydroxyl group directly attached to the aromatic ring makes phenols electron rich compounds and this property was harnessed in dearomatization reactions by means of singlet oxygen. The hydroxyl group was also involved in O-cyclization reactions and in chelate complexes as key intermediates to deliver [2+2] photocyclized adducts with excellent selectivities. As energy transfer is not limited by the redox properties of the substrates, energy transfer catalysis has a bright future in organic synthesis and therefore in phenol chemistry. For instance, the design of new catalytic systems is expected to tackle the challenge of asymmetric photooxygenation of aromatic compounds such as phenols. This review aimed at collecting examples of visible-light driven transformations of phenols *via* energy transfer catalysis and in the near future, we hope that new examples will show off the synthetic potential of this strategy.

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Biosketches



Vincent Coeffard (left) was born in Nantes (France) in 1981. He studied chemistry at Université de Nantes and he completed his Ph.D studies in 2007 in the group of Prof. Jean-Paul Quintard. He then moved to University College Dublin (Ireland) to work as a postdoctoral research fellow for two years in asymmetric catalysis under the guidance of Prof. Pat Guiry. He then spent ten months in Spain for a second postdoctoral experience in the group of Prof. Antonio M. Echavarren to investigate gold chemistry. In 2010, he was appointed CNRS researcher in the group of Prof. Christine Greck at Université de Versailles Saint-Quentin-en-Yvelines (France) to work on the design of organocatalysts and implementation of catalytic technologies to access enantioenriched organic architectures. In 2016, he moved to Université de Nantes where his current research interests include asymmetric organocatalysis and photochemistry.

Pierrick Nun (middle) was born in Brest (France) in 1982. After undergraduate studies at Université de Nantes (France), he completed his Ph.D. in 2009 under the supervision of Dr. Frédéric Lamaty at Université de Montpellier (France), working on mechanical activation and solvent-free synthesis. He then joined the group of Prof. Steven P. Nolan at the University of St. Andrews (Scotland) as a post-doctoral researcher. Following a second post-doctoral fellowship with Prof. Annie-Claude Gaumont at the Ecole Nationale Supérieure d'Ingenieurs of Caen (France), he was appointed Assistant Professor at Université de Nantes and he is currently working on singlet oxygen applications in organic synthesis and medicine.

Jérôme Fischer (right) was born in 1994 in Mulhouse (France). After finishing his high school diploma, he studied chemistry at the Ecole Nationale Supérieure de Chimie of Mulhouse and joined the group of Dr. Vincent Coeffard for his Ph.D. thesis in 2017. His research focuses on the design of new photosensitizers for applications in selective photooxidative processes.