

Phenols as Novel Photocatalytic Platforms for Organic Synthesis

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This article is dedicated to our longtime friend Professor *Robert Deschenaux* on the occasion of his retirement

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In recent years, organic chemists have devoted a great deal of effort towards the implementation of novel green photocatalytic synthetic protocols. To this end, the development of new effective, non-toxic, inexpensive photocatalysts, which are capable of driving value-added chemical transformations, is highly desirable. Interestingly, phenols fulfill all these requirements due to their outstanding physicochemical features, therefore emerging as promising metal-free photocatalytic platforms for organic synthesis. This Perspective aims at highlighting the most recent applications of phenols in organic photocatalysis. More specifically, phenolate anions, formed upon deprotonation of phenols, are photo-active organic intermediates that may absorb light within the visible region. Thus, when in the excited states, these anions may be used as reductants to generate reactive open shell species from suitable precursors under mild operative conditions. Alternatively, phenolate anions and suitable radical precursors can form electron donor-acceptor (EDA) complexes. Specifically, the photochemical activity of these molecular aggregates can be used to initiate organic radical reactions. Lastly, forward-looking opportunities within this research field have been discussed.

Keywords: anions, photocatalysis, radicals, redox chemistry, synthetic methods.

1. Introduction

Phenols are important organic molecules that play crucial roles in many different research fields, including synthetic, industrial and natural product chemistry.^[1] As a matter of fact, a wide number of natural products contain at least a phenol moiety, such as vitamins, amino acids, hormones, neurotransmitters.^[2–4] Moreover, phenol derivatives are largely employed as synthetic building blocks for the production of a variety of bioactive drugs on an industrial scale.^[5] The importance of phenols is also due to the fact that these aromatic compounds can straightforwardly be produced from renewable, readily available, and inexpensive biomasses, for instance lignin.^[6] In recent years, phenols have also emerged as a novel class of metal-free photocatalysts (PCs) capable of driving the synthesis of relevant products (P) under visible-light

irradiation (*Scheme 1,a*).^[7] In particular, phenol derivatives have proved their photocatalytic potential for various C–C and C–X (X=heteroatom) bond forming reactions, thus arising as economic and greener options than the most used Ru- and Ir-based photocatalytic systems.^[7–10] Importantly, the reliance on noble metal-based catalysts has been constantly declined over the years because of cost, availability and toxicity.^[10] Eventually, less expensive, abundant and less harmful classes of metal-free photocatalysts are making their way as valuable alternatives for achieving greener chemical productions.^[11,12]

In this regard, the conjugate bases of phenols, namely phenolate anions, are both electron rich aromatic intermediates and active organic chromophores.^[13] Recently, organic chemists have demonstrated that phenolate anions can be used to

directly generate reactive open shell intermediates from suitable substrates either 1) by reaching an electronically excited state upon light absorption or 2) by forming a photoactive electron donor–acceptor (EDA) complex (Scheme 1,b). In fact, it is well established that phenolates in the excited state (ArO^{-*}) become strong reductants able to undergo single electron transfer (SET) processes with electron-poor precursors (namely R-X), eventually generating reactive intermediates that may take part in radical transformations.^[7,13–18] In particular, the reduction potential of an excited-state phenolate can be easily estimated on the basis of electrochemical and spectroscopic measurements by using the *Rehm–Weller* theory.^[19] Indeed, it is possible to estimate this reduction potential (namely $E_{\text{ArO}^{-*}/\text{ArO}^{-}}^0$) by subtracting E_{00} , which is the energetic content of the phenolate after one-photon excitation process (also called excitation energy), to the value of the oxidation potential of the phenolate anion in the ground-state, namely $E_{\text{ArO}^{-}/\text{ArO}^{-}}^0$ (Eqn. 1). Therefore, $E_{\text{ArO}^{-*}/\text{ArO}^{-}}^0$ should be smaller than $E_{\text{ArO}^{-}/\text{ArO}^{-}}^0$ implying that the excited-state of a

phenolate is a better electron donor than its ground-state.^[20] In particular, the excitation energy (namely E_{00}) may be estimated spectroscopically from the position of the long wavelength tail of the absorption spectrum of the phenolate anion or, alternatively, from the position of the short wavelength tail of its emission spectrum.^[20] Instead, the value of $E_{\text{ArO}^{-*}/\text{ArO}^{-}}^0$ may be evaluated by electrochemical measurements. Then, the free-energy change associated to an electron transfer (ΔG_{et}^0) between an excited phenolate anion and a ground-state radical precursor (R-X) may be estimated by using Eqn. 2.^[21] In particular, $E_{\text{R-X}/\text{R-X}^{-}}^0$ is the reduction potential of the substrate in the ground-state, while C is a coulombic factor dependent on the solvent. If the value of ΔG_{et}^0 is < 0 , the SET process is spontaneous. On the other hand, if the value of ΔG_{et}^0 is > 0 , the electron transfer event is not spontaneous.

$$E_{\text{ArO}^{-*}/\text{ArO}^{-}}^0 = E_{\text{ArO}^{-}/\text{ArO}^{-}}^0 - E_{00} \quad (1)$$

$$\Delta G_{\text{et}}^0 = E_{\text{ArO}^{-*}/\text{ArO}^{-}}^0 - E_{\text{R-X}/\text{R-X}^{-}}^0 + C \quad (2)$$



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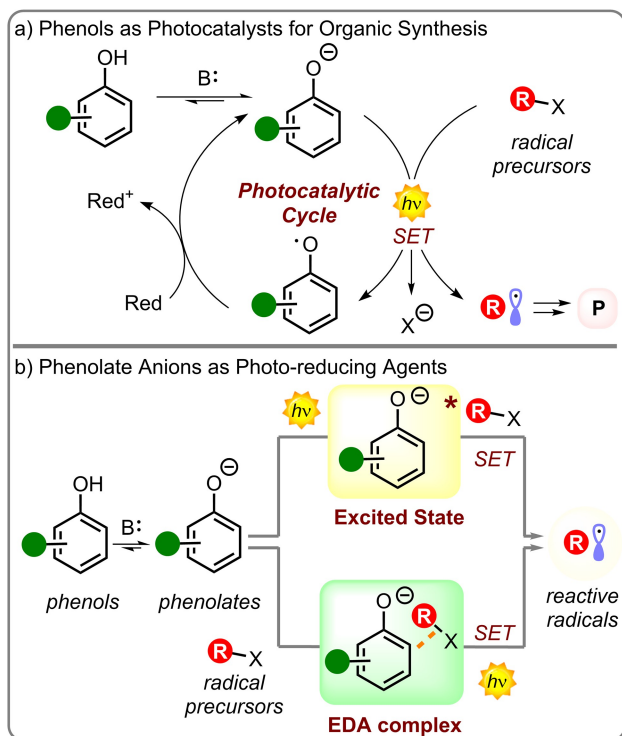


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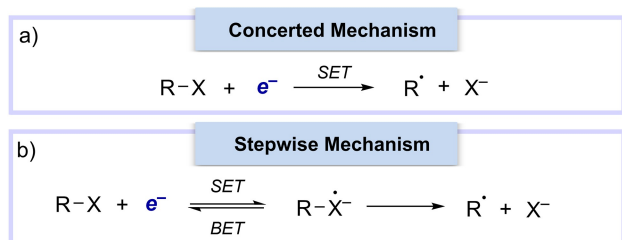
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of innovative carbon-based functional materials, for applications in materials science, nanomedicine and catalysis.



Scheme 1. a) Exploitation of phenols as photocatalysts for synthetic applications. b) Use of phenolate anions for the photochemical formation of reactive radicals from suitable radical precursors. B: base; SET: single electron transfer; X: leaving group (e.g., halogen atom); Red: sacrificial reducing agent; P: reaction product.

Due to the SET process the radical precursor may undergo fragmentation to afford a neutral open shell species (R^\bullet) along with an anionic leaving group (X^-).^[22] Mechanistically, two different dissociative pathways are possible (Scheme 2): a) the concerted mechanism, where the $R-X$ bond cleavage and the SET event take place at the same time; b) the stepwise mechanism, which involves the formation of a radical-anion intermediate. This radical-anion intermediate may undergo either back-electron transfer (BET), returning the starting species, or may undergo



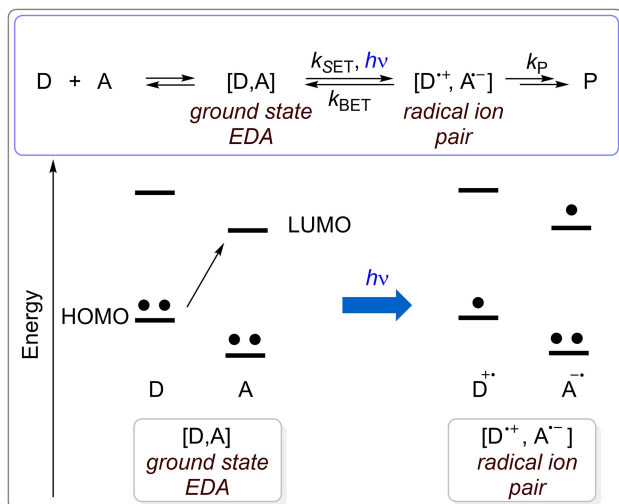
Scheme 2. Stepwise vs. concerted dissociative mechanisms.

fragmentation to give a neutral radical along with an anionic leaving group.^[23]

Both thermodynamic and kinetic factors govern the competition between these two mechanisms.^[22] The transition from a stepwise to a concerted mechanism is expected to arise the more the ion-radical is unstable, since its cleavage becomes faster and faster. Additional insights into the interaction between $ArO^{\bullet-}$ and $R-X$ may be achieved by investigating the features of the phenolate anion in the excited state.^[24]

In fact, the study of this aspect is fundamental to understand and predict how these electron-rich aromatic intermediates may interact with other chemical species and which chemical processes they can be able to trigger. Generally, an excited-state phenolate anion may decay back to the ground state through a radiative pathway, thus emitting light.^[7] Therefore, the feasibility of a SET process, between an excited-state phenolate anion and a given radical precursor ($R-X$), may be investigated by performing Stern–Volmer quenching studies, that basically are luminescence quenching analysis.^[24] In particular, if the presence of $R-X$ decreases the emission intensity of the excited phenolate, a SET event between these chemical species might occur. Phenolates are also excellent electron-rich candidates to generate photo-active EDA complexes with $R-X$.^[25–29] In fact, these intermediates bear negatively charged oxygen atoms, that may act as powerful electron releasing groups by means of mesomeric effect. This effect increases the electronic density on both the *ortho* and *para* positions of the aromatic ring. This scenario is corroborated by the aromatic resonance parameter of the negatively charged oxygen atom which is reported to be -0.6 .^[30]

In general, an EDA complex is a ground-state molecular association formed through non-covalent interactions between an electron-rich donor (D; such as a phenolate anion) and an electron-poor acceptor (A; for instance $R-X$).^[31] An EDA complex is typically characterized by the formation of a new absorption band that typically reaches the visible region of the spectrum. Thus, when the EDA complexes are irradiated with a proper source of photons, a SET from the highest occupied molecular orbital (HOMO) of the electron donor to the lowest unoccupied molecular orbital (LUMO) of the acceptor can occur, hence generating radicals or radical ions (Scheme 3).^[25,32] The radical ion pair, formed after the first photo-induced electron transfer, may either return to the initial state through a rapid back electron transfer (BET) process or undergo subsequent transformations. The BETs are generally faster with respect to all other processes that



Scheme 3. Photochemical activity of electron donor acceptor (EDA) complexes.

could happen after the SET ($k_{\text{BET}} > k_{\text{P}}$). This fact has greatly limited the synthetic utility of EDA complexes in organic synthesis.^[32] To avoid the occurrence of BET, a suitable leaving group (X, for instance halogen atoms) needs to be included in the radical precursors. In this manner, reactive intermediates (e.g., radical species) may be generated in solution through the irreversible fragmentation of the substrates. Then, these open shell species may be employed to initiate valuable organic transformations.^[25] From a mechanistic point of view, the formation of an EDA complex may be studied by UV-Vis and nuclear magnetic resonance (NMR) spectroscopy, density-functional theory (DFT) calculation and X-ray single-crystal analysis.^[26,33,34]

In recent years, these complementary scenarios have paved the way for the development of a wide range of relevant photocatalytic organic transformations. In this Perspective, we summarize the most recent and relevant advances in the application of phenols as photocatalysts, also providing forward-looking opportunities and possible future directions of this intriguing research field. It is important to emphasize that, within this Perspective, phenols are referred as photocatalysts (PCs), while phenolate anions, which are formed upon basic treatment of PCs, are indicated as the photo-active catalytic intermediates. Accordingly, the choice of the base (organic or inorganic), and therefore that of the resulting counter cation, can drastically influence the solubility of the phenolate anion and thus its photocatalytic activity.

2. Structure-Property Relationships of Phenols and Phenolate Anions

Phenols are a class of organic aromatic molecules in which one or more hydroxy groups are directly bound to an aromatic ring. Due to the electron donating nature of the OH group this class of molecules is generally electron rich and presents a marked tendency towards oxidation to quinones, especially in derivatives presenting more hydroxy groups on the same ring. The conjugation with the aromatic system of the OH group also results in decreased $\text{p}K_{\text{a}}$ values compared with corresponding alcohols (9.9 in H_2O for parent phenol compared to 17 for cyclohexanol),^[35] making the formation of phenolate anions easily achievable without strong bases. The formation of phenolate anions is also associated to a bathochromic shift in the absorption profile compared to the phenol precursor.^[7] In general, the properties of phenol systems can be tailored by introducing functional groups on the aromatic ring, resulting in modification of the $\text{p}K_{\text{a}}$ and of the optical properties (Scheme 4). The presence of electron withdrawing groups (NO_2 , CN, etc.) especially in *para* position on the aromatic ring has been linked to decreased $\text{p}K_{\text{a}}$ and to the formation of aromatic push-pull systems.^[38] This last aspect is particularly important when the phenolate anion is generated. In fact, phenolate anions are more electron rich compared to phenols since the presence of the charge results in an increase in the electro donating ability of the oxygen. Consequently, the presence of conjugated electron withdrawing groups in phenolates results in marked bathochromic shifts compared to non-functionalized phenolate or to derivatives presenting *ortho* and *para* electro donating groups. (Scheme 4).^[7] Along with the introduction of functional groups on the phenol scaffold also moving to π -extended phenol systems can be effective in tuning the properties of phenols and phenolate anions

	$\text{p}K_{\text{a}}$	$\lambda_{\text{abs}}(\text{OH})$	$\lambda_{\text{abs}}(\text{O}^-)$
<i>p</i> -H	9.94	268 nm	285 nm
<i>p</i> - NO_2	7.1	317 nm	405 nm
9-anthrol	7.9	407 nm	445 nm
1-pyrenol	8.9	375 nm	400 nm

Scheme 4. $\text{p}K_{\text{a}}$ and absorption values for functionalized and π -extended phenolic derivatives.^[36,37]

(Scheme 4). In fact, this approach can result in increased extinction coefficients and in a redshifted absorption caused by the extended π -system.^[36,39,40]

This is particularly interesting if the excited state is considered. In fact, molecules in the excited state become more reducing and more oxidant compared to the ground state counterparts, and from this point of view, π -extended derivatives could enable a rich visible light triggered photocatalysis. Despite this potential interest, π -extended phenolic systems are still only marginally considered in the literature for their photocatalytic properties, leaving great margin for their exploitation in this field.

3. Applications of Phenols in Photocatalysis

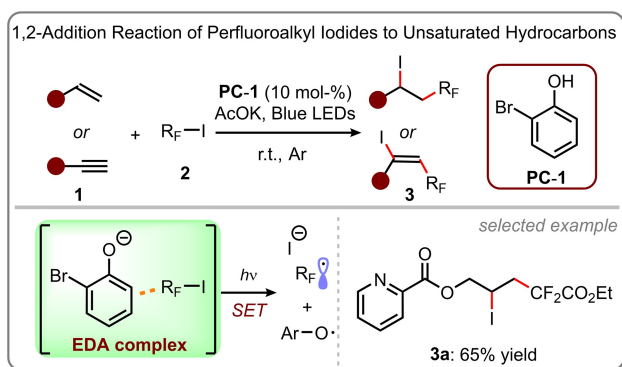
The first examples describing the use of phenols as photocatalysts to drive organic reactions were reported between the 1980s and 1990s.^[41–43] In particular, the *Soumillion* group found that simple naphtholate anions may trigger the photochemical dechlorination of aryl chlorides under UV-light irradiation ($\lambda = 350$ nm). However, it is worth mentioning that these transformations were performed under harsh reaction conditions employing high energetic sources of photons. In more recent time, *Zhao* and co-workers employed *o*-bromophenol **PC-1** as photocatalytic system to promote atom transfer radical addition (ATRA) reactions between unsaturated hydrocarbons **1** – namely olefins and alkyne derivatives – and perfluoroalkyl iodides **2** to give products **3** (Scheme 5).^[28] Specifically, the authors used potassium acetate as base to deprotonate **PC-1**. The resulting bromophenolate was capable of forming photo-active EDA complexes with **2**, as proven by UV-Vis absorption studies. These molecular aggregates can photochemi-

cally initiate the radical reactions driving the synthesis of the fluorinated adducts **3** with high chemical yields.

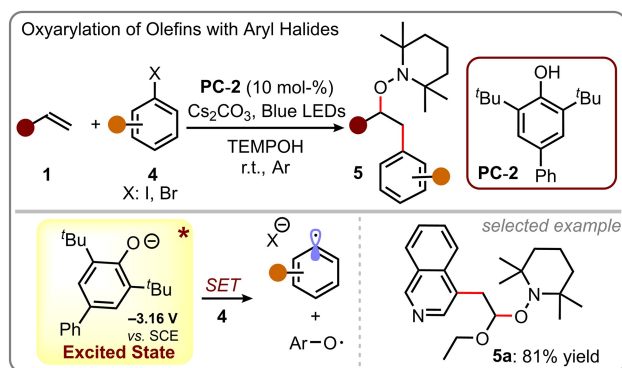
In 2020, *Xia* and co-workers described a new photocatalytic protocol for the direct oxyarylation of olefins **1** using a phenol derivative as catalyst (Scheme 6).^[16] Specifically, by following an optimization study, the authors demonstrated that **PC-2**, in combination with Cs_2CO_3 , displayed the highest photocatalytic effectiveness for the model transformation.

From a mechanistic point of view, the excited phenolate anion, formed upon deprotonation of **PC-2**, directly reduced the aryl halides **4** forming the corresponding open shell species. These reactive intermediates then react with the terminal olefins **1** starting the radical transformations, hence leading to the production of **5**. Recently, *Guan, Shang* and collaborators reported the use of a novel *o*-phosphinophenol derivative, namely **PC-3**, as photocatalytic system to initiate direct cross-coupling reactions of aryl halides **4** (Scheme 7).^[44]

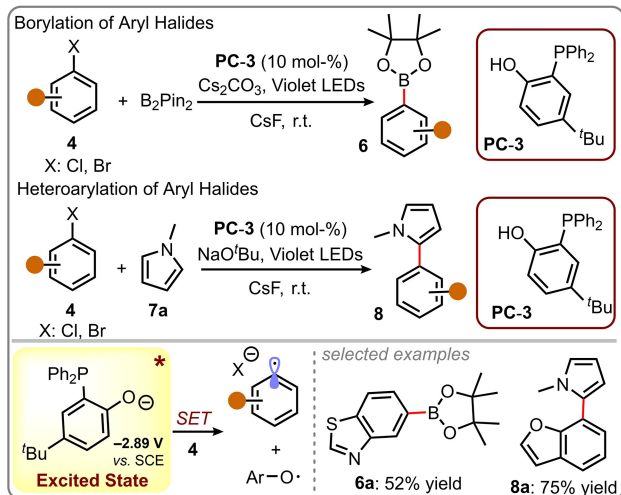
In particular, **PC-3** may be easily deprotonated in the presence of a suitable base producing the related phenolate anion in solution. This aromatic intermediate can directly reach an electronically excited state, after light absorption, becoming a competent reducing agent. Thus, this excited catalytic intermediate may reduce **4** to provide reactive aryl radicals. Lastly, these reactive chemical species can effectively trap either bis(pinacolato)diboron (B_2Pin) or *N*-methylpyrrole **7a** yielding products **6** and **8**, respectively. The same research group, in 2022, demonstrated that **PC-3** can also be employed to drive defluoroalkylation reactions between trifluoroacetamides **9** with terminal olefins **1** (Scheme 8).^[45]



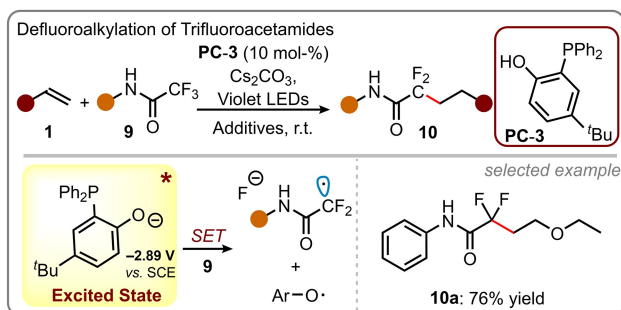
Scheme 5. Photocatalytic reactions between perfluoroalkyl iodides **2** and unsaturated compounds **1**.



Scheme 6. Photocatalytic oxyarylation of olefins **1** with aryl halide **4** and TEMPOH. TEMPOH: 2,2,6,6-tetramethylpiperidin-1-ol.



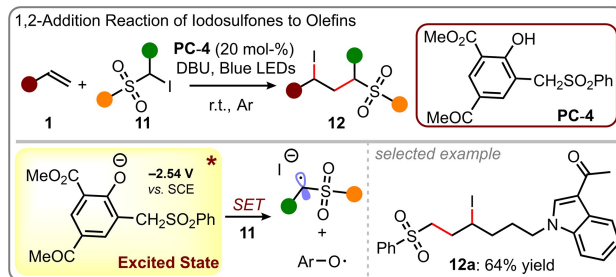
Scheme 7. Photocatalytic borylation and heteroarylation of aryl halide **4**.



Scheme 8. Photocatalytic defluoroalkylation reactions between trifluoroacetamides **9** and olefins **1**.

Mechanistically, when in the excited state, the redox potential of the corresponding phenolate of **PC-3** is sufficiently high to reduce compounds **9** affording reactive carbon-centered radicals. These electrophilic radicals can then react with **1** leading to the formation of the desired compounds **10**. In the same year, our research group developed a new phenol-based photocatalytic system, namely **PC-4** (Scheme 9).^[17]

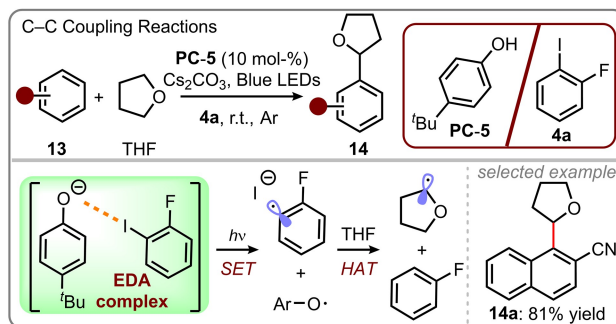
It was demonstrated that **PC-4** can be deprotonated upon addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to form the related phenolate anion. This electron rich intermediate may absorb blue light to reach an electronically excited state that is capable of producing electrophilic radicals from **11**. Therefore, these reactive chemical species may trigger radical chain mechanisms to produce the final products **12**. Importantly, **PC-4** was easily recovered and reused up to five times without any significant drop in yield. Akiyama and co-workers showed that phenol **PC-5**, in



Scheme 9. Photocatalytic ATRA reactions between iodosulfones **11** and terminal olefins **1**. DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene.

combination with an aryl iodide **4a** as a co-catalyst, may drive the direct C–H functionalization of a wide variety of aromatics compounds **13** with tetrahydrofuran (Scheme 10).^[29]

In particular, the authors demonstrated that the related phenolate anion of **PC-5** can form an EDA complex with **4a**. Interestingly, this complex is held together by a halogen bond interaction between the oxygen atom of the phenolate anion and the aryl iodide. Then, the absorption of a blue photon can induce a SET event from the phenolate to **4a** leading to the formation of the corresponding aryl radical. This intermediate is capable to produce reactive open shell species from tetrahydrofuran through a hydrogen atom transfer (HAT) process. Eventually, this alkyl radical reacts with an aromatic compound **13** through a classical homolytic aromatic substitution pathway yielding **14**. An additional class of phenol-based photocatalytic systems which can be used for synthetic applications is represented by the tricyclic aromatic ketone 9-anthrone and its derivatives (e.g., **PC-6** and **PC-7**).^[13] In solution, these cyclic compounds are generally present in a tautomeric equilibrium,



Scheme 10. Photocatalytic C–C coupling reactions between arenes **13** and THF. HAT: hydrogen atom transfer; THF: tetrahydrofuran.

where the keto-enol ratio relies on the hydrogen bonding ability of the solvent. Moreover, under basic conditions, anthrone derivatives can be easily deprotonated. The resulting anionic intermediate may present a delocalized charge between the oxygen and the C-atom in position 10.^[39,46,47] Recently, König and collaborators described the use of the 10-bromo-9-anthrone **PC-6** to photocatalyze C–H arylation reactions between aryl chlorides **4** and arene derivatives **13** under blue light irradiation (Scheme 11).^[48]

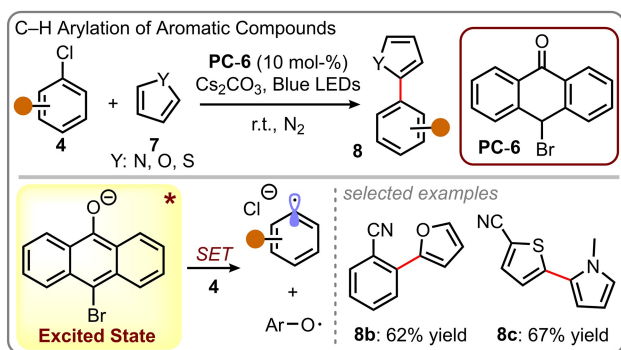
From a mechanistic point of view, the authors employed cesium carbonate to deprotonate **PC-6**. The resulting anthrolate derivative is an active chromophore that can effectively absorb blue light. In the excited state the anthrolate is able to reduce aryl chlorides **4** to afford the corresponding aryl radicals. These reactive open shell species are then trapped by **7**, ultimately forming products **8**. Recently, the same research group showed that tetramethoxyanthrone **PC-7** can efficiently drive C–H carboxylation reactions of styrene derivatives **1** and heteroaromatics **7** with CO₂ under visible light irradiation (Scheme 12).^[49]

Interestingly, the corresponding carboxylic acids **15** and **16** were isolated in very high yields. The authors carried out mechanistic studies that indicated that the

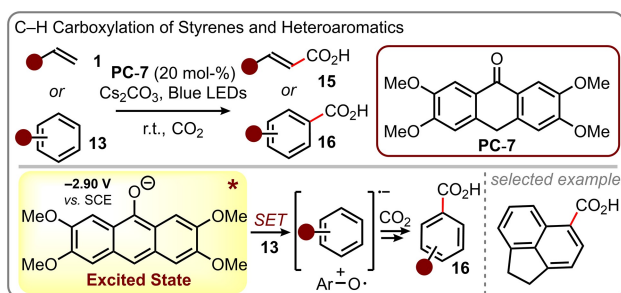
observed reactivity is initiated by the light-excited tetramethoxyanthrolate which can reduce the aromatic compound **13**. Then, CO₂ can attack the so-formed radical anion providing the desired carboxylic acid **16**.

4. Conclusions and Future Perspectives

In recent times, the increasingly high attention in the direction of green and sustainable chemical processes prompted the development of novel metal-free photocatalysts. Phenols have emerged as excellent candidates, thanks to their outstanding physicochemical properties. Thus, phenol derivatives have been exploited as effective photocatalytic platforms to drive a number of organic reactions. Although promising findings have been obtained so far, a number of unsolved challenges remain to be addressed. Indeed, phenols are generally used in relatively high photocatalytic loading (up to 20 mol-%). Moreover, these homogeneous catalysts are typically constrained by inability to be recycled and instability under certain reaction conditions. In fact, phenolate anions often turn out to be highly unstable when in presence of open shell species. Indeed, these anions can effectively react with radicals through homolytic aromatic substitution (HAS) pathways or undergo side reactions such as radical polymerization. Thus, a careful design of the chemical structure of the **PC** is essential to overcome this limitation. Therefore, there is a need for development of novel and increasingly active phenols derivatives. This would allow to reduce the photocatalytic loading and improve the productivity of the whole processes. For instance, the development of π -extended phenol systems could generate photocatalysts with improved visible light absorption enabling a fine tuning of the redox potentials by introducing more parameters that can be controlled, such as the extension of the conjugation and the edge shape. Moreover, the presence of an extended π -surface could enable the insertion of more functional groups. Control over the aromaticity patterns in extended systems can also help to enhance resistance towards oxidation to quinones, resulting in more stable and recyclable derivatives. In addition, potentially recyclable phenol-containing materials could be investigated as novel heterogenous photocatalysts. In particular, lignin and its derivatives appear as excellent candidates for this application. To conclude, we expect that those investigations on these research topics will



Scheme 11. Photocatalytic C–H arylation of heteroarenes **7** with aryl chloride **4**.



Scheme 12. Photocatalytic C–H arylation of heteroarenes **7** with aryl chloride **4**.

contribute to determine the future directions in organic synthesis for both academia and industry.

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author Contribution Statement

G. F., J. D. and M. P. conceived and wrote the manuscript.

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