

Excited-State 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ*) Initiated Organic Synthetic Transformations under Visible-Light Irradiation

Palani Natarajan^{*[a]} and Burkhard König^{*[b]}*Dedicated to Prof. Shunichi Fukuzumi on the occasion of his 70th birthday.*

The one-electron oxidizing capacity of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) improves significantly by visible-light excitation. The excited-state DDQ (DDQ*) even converts benzene, fluoroarenes, heteroarenes, benzyls, and olefins into their corresponding radical cations as well as chloride and other anions into their radicals. These reactive intermediates have

been utilized for the generation of C–C and C–X (N, O, or Cl) bonds in the synthesis of valuable organic compounds and natural products. This mini review provides an overview of such DDQ*-initiated organic transformations with their scope and limitations and discusses the proposed reactions mechanisms.

1. Introduction

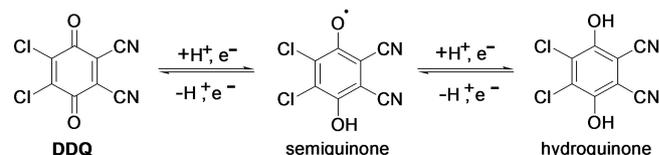
Visible-light-mediated photoredox catalysis^[1] has developed into a widely used method in synthetic organic chemistry over the previous decade because of its unique reactivity patterns, mild reaction conditions, and tolerance to functional groups. Simple application of the method enables numerous previously unachievable transformations through single-electron transfer process.^[2] Over time, a series of new C–C and C–X (N, O, F, P, S, Cl, or Br) bond forming reactions from native C–H and other bonds have been developed via visible-light photocatalysis.^[3] For the most part, Ru- and Ir-based coordination complexes were used as catalysts due to their relatively long excited state life times and suitable redox potentials.^[4] Parallel to transition-metal complexes, efforts have been made to create metal-free visible-light photoredox catalysis using organic dyes include cyanoarenes,^[5] xanthenes,^[6] and acridiniums^[7] for synthetic transformations.^[8] Comprehensive reviews on many organic and metal-based photoredox catalysis are available.^[9–10] In 2017, Qin and coworkers^[9] provided a summary of organocatalysis in inert C–H bond functionalization including one article reporting the oxygenation of benzene with DDQ as photocatalyst under

visible-light irradiation. Likewise, in 2019, Fukuzumi and co-workers^[10c] published a mini review on the oxygenation of organic compounds using H₂O as an oxygen source and O₂ as the oxidant, which includes visible-light-excited DDQ-assisted oxygenation of benzene to phenol. However, organic transformations-initiated by visible-light-excited DDQ have not been comprehensively reviewed so far; this short review aims to provide such a summary.

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, Scheme 1) is a versatile reagent in organic synthesis^[11] and exhibits three available oxidation states: the oxidized quinone, one-electron-reduced semiquinone, and two-electron-reduced hydroquinone (Scheme 1).^[12] DDQ is commercially available, easy to handle, possesses a good solvent solubility, often generates the corresponding reduced compound such as 2,3-dichloro-5,6-dicyano-1,4-hydroquinone (DDQH₂) as a non-toxic byproduct in the course of its reactions.^[11] DDQ can be readily recovered from DDQH₂ by treating with nitrates or metal oxides.^[13] The oxidation potential of ground state DDQ is 0.51 V vs SCE^[14] and the compound is widely used for aromatization in organic synthesis.^[11] Nevertheless, the one-electron oxidizing capacity of DDQ improves significantly by visible-light excitation from 0.51 V vs SCE to 3.18 V vs SCE^[15] by excitation to its triplet (³DDQ*) or 3.8 V vs SCE^[16] by singlet-excitation (¹DDQ*). The excited-state DDQ even converts benzene, fluoroarenes, heteroarenes, benzyls and olefins to their corresponding radical cations (*vide infra*) as well as chloride and other anions into

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Scheme 1. The chemical structure of DDQ with its readily accessible oxidation states.

their radicals. These reactive intermediates have been utilized for the generation of new C–C and C–X (N, O, or Cl) bonds in the synthesis of organic compounds and natural products. We summarize in this focused mini-review DDQ*-initiated organic transformations and their proposed reactions mechanisms.

1.1. Why DDQ photoredox catalysis?

Recent literature reviews on photoredox catalysis covered predominantly the synthetic applications of non-quinone chromophores.^[3–10] Despite the fact that quinones, in particular DDQ, has been long known for its ability to participate in photoinduced electron transfer processes,^[17] its catalytic use as applied to organic synthesis is somewhat less familiar. One might inquire what DDQ as a photoredox catalyst has to offer compared to non-quinone catalysts? The potent reactivity afforded by DDQ allows access to unique reactions activating a broad range of substrates that are unreactive under typical synthesis reaction conditions.^[15] For example, fluoroarenes being unamenable to classical S_NAr methods, but the high oxidation potential of photo-excited DDQ (DDQ*) enables functionalization of electron-poor fluoroarenes and other hydrocarbons at ambient conditions (*vide infra*). Moreover, DDQ is readily recycled from DDQH₂ using *tert*-butyl nitrite (TBN) or MnO₂ as a re-oxidant.^[13]

1.2. What makes DDQ special as a photocatalyst?

Normally, electron addition to quinones is a thermodynamically favorable process (exothermic reactions often fall into the inverted Marcus region) leading to stable charge separation at intermediate steps of photosynthesis or cellular respiration.^[18] All quinines show photoinduced electron transfer reactivity, but the unsubstituted parent benzoquinone is only a moderate oxidant and poor reductant in its lowest triplet state T₁.^[19] In contrast, photo-excited DDQ (i.e., ³DDQ*) is a very strong oxidant ($E_{red} = 3.18$ V vs SCE)^[15] and can oxidize even benzene and fluoroarenes by electron transfer.^[9–10] In cases, when easier

oxidizable products compared to the substrates are formed (e.g. phenol or aniline derivatives from benzene), no further functionalization of the products occurs due to a fast back electron transfer between DDQ* and the respective radical cations.

1.3. Photophysical characteristics of DDQ and DDQ*

An excited state is usually characterized by three important properties such as energy (E), lifetime (τ) and quantum yield (ϕ).^[20] DDQ, in general, absorb photons of a wavelength of approximately 400 nm and is excited into the S₁/S_n states (Figure 1).^[21] Fast photophysical processes ensure that the DDQ fluorescence quantum yield from the S₁-state to S₀-state is virtually zero at ambient conditions, while the lowest n- π^* triplet T₁-state responsible for the photochemical behavior is significantly populated (close to 100% or $\phi_{ISC} = 1.0$) by intersystem crossing.^[22] The triplet-triplet (T₁→T_n) absorption spectrum of DDQ (³DDQ*) was observed at 630 nm in deaerated MeCN by nanosecond laser flash photolysis ($\lambda_{ex} = 430$ nm).^[23] Moreover, the T₁→S₀ transition is spin forbidden, T₁ states tend to be the longest-lived. The lifetime of the triplet excited state of DDQ (³DDQ*) has been reported from the decay of T→T absorption band and it was 2.4 ms.^[23] In addition, the formation of the DDQ-semiquinone anion radical (DDQ*⁻) by reduction of DDQ has been confirmed by its characteristic absorption at $\lambda_{max} = 590$ nm in UV-Vis measurements^[24] as well as by ESR with a resonance signal at $g = 2.0047$.^[25]

1.4. A general reaction mechanism for DDQ*-initiated organic transformations under visible-light

DDQ acts as an effective catalyst for the synthesis of a series of organic compounds and natural products under visible-light irradiation. A general reaction mechanism for these transformations is shown in Figure 2. Upon visible-light irradiation, DDQ is excited to its singlet excited state (¹DDQ*) that rapidly decays into a triplet state (³DDQ*). The lifetime of ¹DDQ* is



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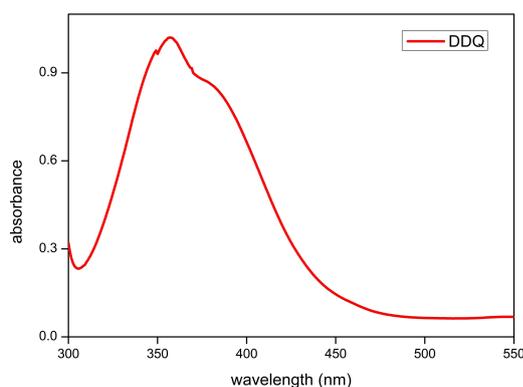


Figure 1. UV-Vis absorption spectra of DDQ in dry acetonitrile.

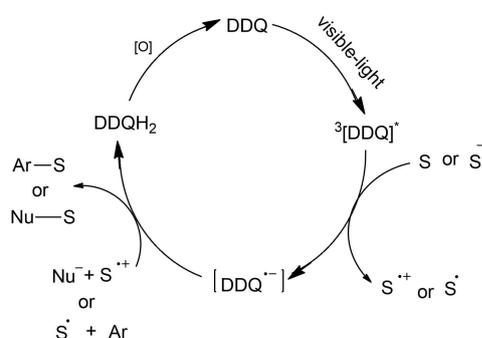


Figure 2. A general mechanism for DDQ-photocatalyzed organic transformations under visible-light irradiation.

short and in the order of a few picoseconds. The $^3\text{DDQ}^*$ -assisted one electron oxidation of a neutral molecule (S) or an anion (S^-) provides $\text{S}^{\bullet+}$ or S^\bullet and a DDQ-semiquinone anion radical ($\text{DDQ}^{\bullet-}$, Figure 2). A reaction between radicals (S^\bullet) and arenes/olefins (Ar) or cation-radicals ($\text{S}^{\bullet+}$) and nucleophiles (Nu) affords the desired product after hydrogen atom transfer to $\text{DDQ}^{\bullet-}$. During the process, DDQ acts as a two-electron acceptor and is reduced to DDQH_2 , which is reoxidized to DDQ by a suitable oxidant to close the catalytic cycle.

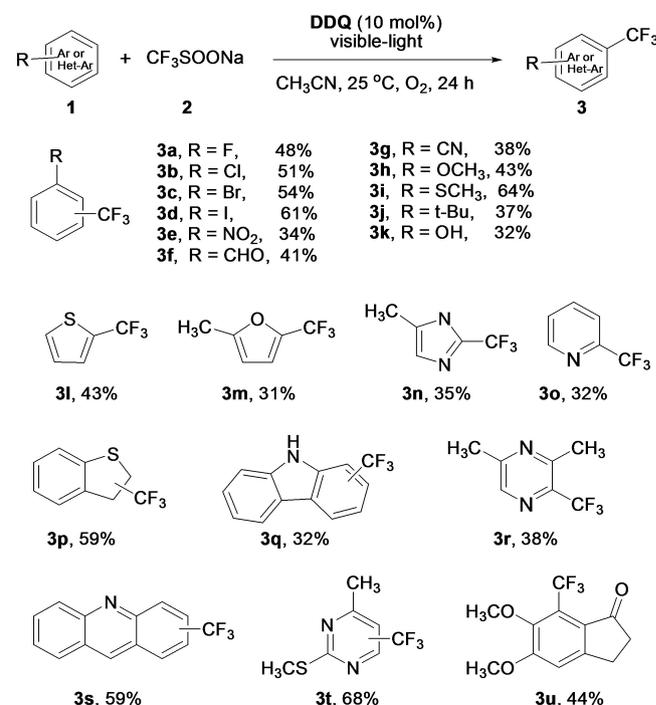
In some reports, DDQH_2 is regenerated by a terminal oxidant in a separate reoxidation process.^[13] Other examples employ DDQ in a (super)stoichiometric amount instead of a catalytic quantity (vide infra). Both situations differ from the strict definition of a photocatalysts or sensitizer. Nevertheless, the reversible formation of DDQH_2 under irradiation corresponds to a photoredox catalysis and a chemical or electrochemical reoxidation would be feasible even if not described in the reported example.^[1–10]

2. DDQ-initiated C–C bond formation under visible-light irradiation

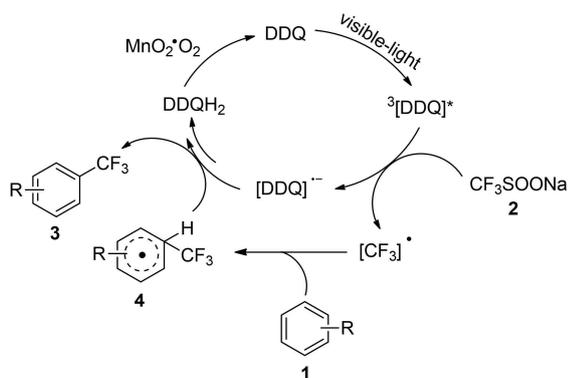
DDQ acts as an effective catalyst for C–C bond formation reactions under visible-light irradiation. In 2017, Chang and

coworkers^[26] described a DDQ-photocatalyzed direct trifluoromethylation of (hetero)arenes (**1**) using $\text{CF}_3\text{SO}_2\text{Na}$ (**2**) as the CF_3 -radical source under visible-light irradiation (Scheme 2). In this method, different benzoquinone derivatives including benzoquinone, methyl-*p*-benzoquinone, 2,6-dimethyl-*p*-benzoquinone, duroquinone, 2,6-dichloro-*p*-benzoquinone, tetrafluoro-*p*-benzoquinone, tetrachloro-*p*-benzoquinone, tetra-bromo-*p*-benzoquinone, and DDQ were tested. DDQ gave the desired product in moderate to good yields (Scheme 2). The high redox potential after excitation is essential to promote the generation of the CF_3 -radical leading to trifluoromethylated products. A wide variety of (hetero)arenes (**3a–3u**, Scheme 2) with electron-withdrawing or electron-donating substituents gave the expected product in moderate to good yields. Moreover, they utilized the protocol for the synthesis of an oral antidiabetic sulfonylurea agent precursor (**3t**) and an Alzheimer drug (aricept) precursor (**3u**), in yields of 68% and 44%, respectively.^[26]

A possible mechanism for the trifluoromethylation of arenes with DDQ under visible-light irradiation is shown in Scheme 3.^[26] Upon visible-light irradiation, DDQ is excited to its triplet state, i.e., $^3\text{DDQ}^*$. The $^3\text{DDQ}^*$ -assisted one electron oxidation of CF_3SO_2^- gave CF_3 -radicals and a DDQ-semiquinone anion radical ($\text{DDQ}^{\bullet-}$, Scheme 1). A reaction between CF_3 -radicals and (hetero)arenes (**1**) gave intermediate **4** that subsequently afforded the desired trifluoromethylarenes after hydrogen atom transfer to $\text{DDQ}^{\bullet-}$. During the process, DDQ is reduced to DDQH_2 and was reoxidized by using a $\text{MnO}_2 \cdot \text{O}_2$ -fixed bed to DDQ.^[26]

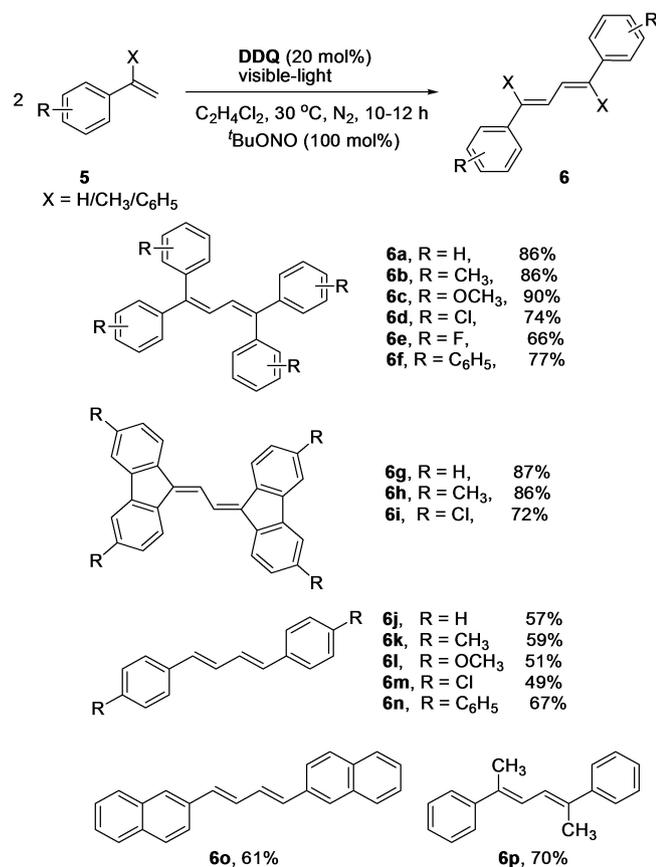


Scheme 2. The substrate scope for DDQ-photocatalyzed trifluoromethylation of (hetero)arenes under visible-light irradiation.



Scheme 3. A proposed mechanism for DDQ-photocatalyzed trifluoromethylation of arenes under visible-light irradiation.

In 2018, we reported a DDQ-photocatalyzed approach for the oxidative homo-coupling of a variety of olefins (5) to the corresponding symmetrical buta-1,3-dienes (6) under blue LED irradiation (Scheme 4).^[27] The control experiments without either light or DDQ did not give any conversion to the product. Benzoquinone, anthraquinone and *p*-chloranil were studied as alternative catalysts in place of DDQ, but none of them gave



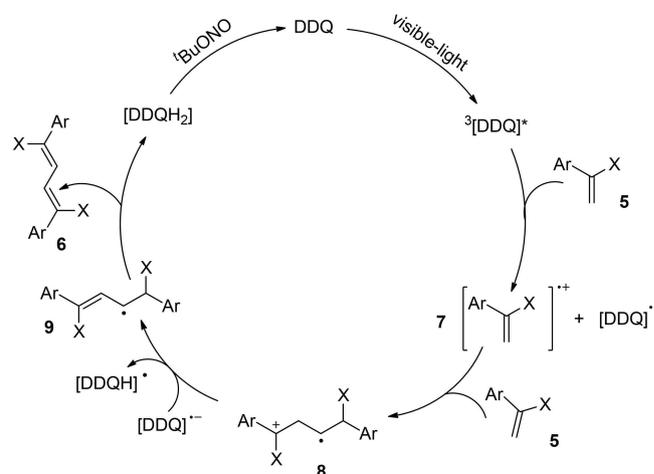
Scheme 4. The substrate scope for DDQ-photocatalyzed homo-coupling of substituted olefins to symmetrical buta-1,3-dienes under visible-light irradiation.

better results than DDQ. The failure of other quinone photocatalysts has been ascribed to their lower oxidation potential in both the ground and in the excited states compared to DDQ. Changing the light source from blue to green light under otherwise similar conditions (Scheme 4) decreased the product yield. The substrate scope comprises terminal olefins containing either an electron-donating group (such as methyl, methoxy or phenyl) or an electron-withdrawing group (including fluoride or chloride), which were selectively transformed into their corresponding buta-1,3-dienes in good yield (Scheme 4). Nevertheless, oxidative dimerization was not observed for 1-phenylpropene (C₆H₅-CH=CH-CH₃), 2-vinylpyridine (C₅H₄N-CH=CH₂), and allylbenzene (C₆H₅-CH₂-CH=CH₂) due to their poor stability under the employed reaction conditions.^[27]

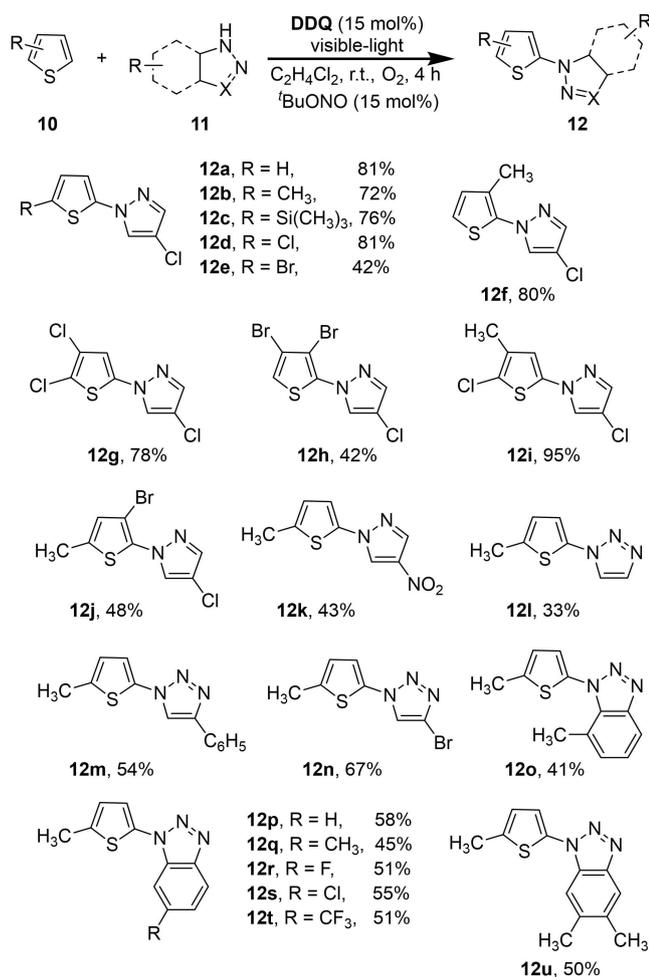
A plausible mechanism for the DDQ-photocatalyzed formation of buta-1,3-dienes (6) from olefins (5) under visible-light irradiation is shown in Scheme 5.^[27] Upon irradiation by visible-light, DDQ is excited into its triplet state (i.e., ³DDQ*), which oxidizes suitable olefinic-double bonds to the corresponding radical cations (7). Radical-addition reaction of radical cation intermediate 7 to another olefin yields a new radical-cation intermediate 8, which is then transformed into radical intermediate 9 by proton abstraction by [DDQ]^{•-}. Radical 9 loses another hydrogen atom yielding the expected buta-1,3-dienes product (6) and DDQH₂. In this reaction, DDQ was regenerated from DDQH₂ by oxidation using *tert*-butyl nitrite and molecular oxygen.^[27]

3. DDQ-initiated C–N bond formation under visible-light irradiation

In 2017, Song and coworkers^[28] reported a DDQ-photocatalyzed methodology for the direct C₂-H amination of thiophene (10) by azoles (11) under visible-light irradiation (Scheme 6). This protocol has been found applicable to a series of thiophenes



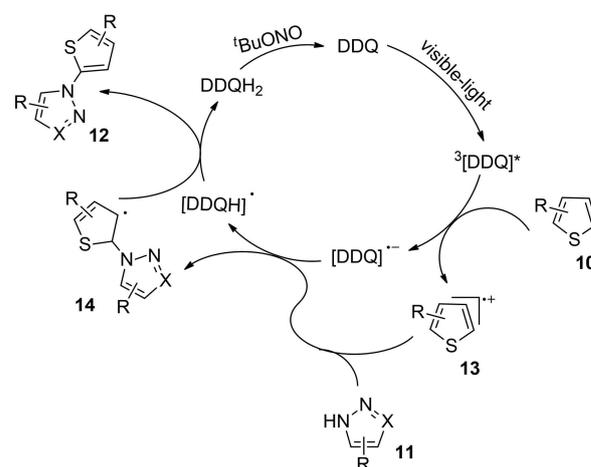
Scheme 5. A plausible mechanism for the DDQ-catalyzed formation of buta-1,3-dienes from olefins under visible-light irradiation.



Scheme 6. The substrate scope for DDQ-photocatalyzed direct C₂-H amination of thiophene under visible-light irradiation.

containing either an electron-donating group (such as alkyl, trimethylsilyl or dioxolan) or an electron-withdrawing group (including chloride or bromide). They were selectively transformed into their corresponding amination products (12) in good yield. Moreover, various nitrogen sources like pyrazole, triazole, benzotriazole and their derivatives have shown to be tolerated and afforded the expected product in moderate to good yields (Scheme 6). The authors found no desired product formed without light or DDQ. However, they detected only a small quantity of product in the absence of *tert*-butyl nitrite as the photocatalyst is not recycled.

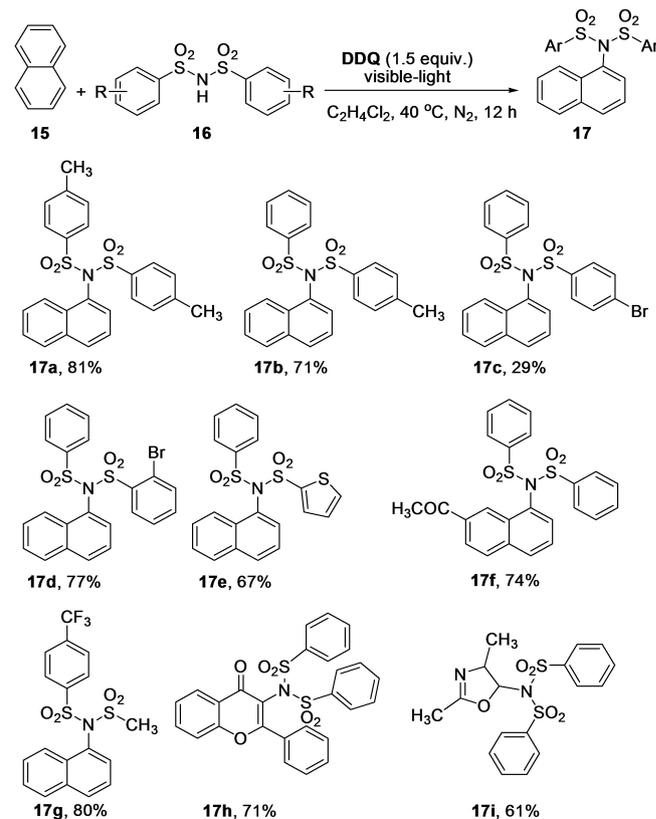
The mechanism for DDQ-photocatalyzed direct C₂-H amination of thiophene by an azole under visible-light irradiation is depicted in Scheme 7.^[28] Upon irradiation by visible-light, DDQ has been excited into its triplet state (i.e., ³DDQ*). The ³DDQ*-assisted one-electron oxidation of thiophenes (10) afforded the corresponding radical cation intermediate (13). A reaction between intermediate 13 and a nucleophilic amine gave a new intermediate (14), which afforded the desired product (12) after the loss of an electron and a proton (Scheme 7). During these processes, DDQ is reduced to DDQH₂ and was oxidized by the



Scheme 7. A plausible mechanism for the DDQ-photocatalyzed direct C₂-H amination of thiophene under visible-light irradiation.

reaction with *tert*-butyl nitrite and molecular oxygen via intermediate NO₂ to regenerate DDQ.^[28]

In 2017, Sakakibara and coworkers^[29] reported a DDQ-assisted method for the direct C-H amination of naphthalenes (15) by sulfonimides (16) under visible-light irradiation (Scheme 8). DDQ has been found essential for this trans-



Scheme 8. The substrate scope for DDQ-assisted C-H amination of naphthalenes by sulfonimides under visible-light irradiation.

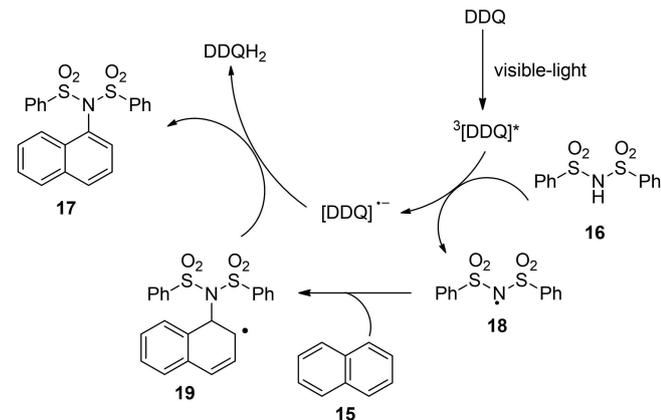
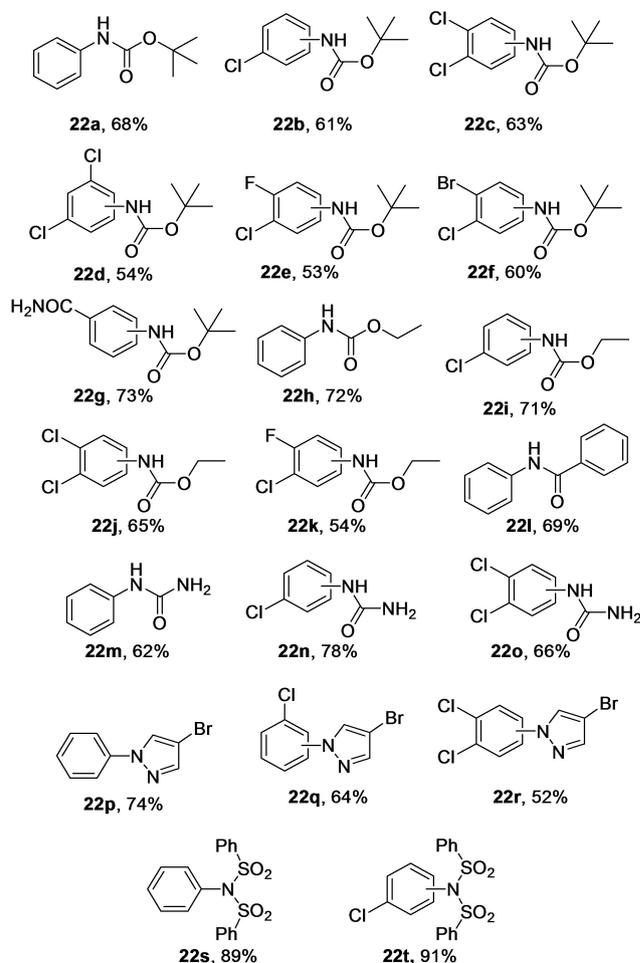
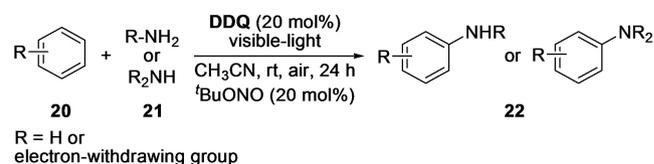
formation to proceed, because other quinone-based oxidants, such as *p*-benzoquinone, duroquinone, 1,4-naphthoquinone, anthraquinone, *p*-chloranil, *o*-chloranil, and 2,5-dichlorobenzoquinone were ineffective for the reaction. Likewise, control experiments without either a light source or DDQ did not give any conversion to the product. For the substrate scope, naphthalene (**15**), 2-acetylnaphthalene, 2,4-dimethyloxazole and flavone were effectively imidated in moderate to good yields (Scheme 8). In addition, the reaction tolerates diaryl-sulfonimides with alkyl, bromo, and trifluoromethyl substituents giving the corresponding coupling products in significant yields (Scheme 8).

Scheme 9 shows a possible mechanism for DDQ-assisted direct C–H amination of naphthalenes (**15**) by sulfonimides (**16**) under visible-light irradiation.^[29] Upon irradiation by visible-light, DDQ is excited into its triplet state (i.e., ³DDQ*). The ³DDQ*-assisted one-electron oxidation of diaryl-sulfonimides (**16**) afforded the corresponding imidyl radical intermediate (**18**). A reaction between the imidyl radical (**18**) and naphthalene gave a new radical intermediate (**19**), which afforded the desired product after loss of an electron and a proton (Scheme 9). During these processes, DDQ was reduced to DDQH₂.

In 2017, we described a protocol for DDQ-photocatalyzed direct C–H amination of both electron-deficient arenes (Scheme 10) and electron-rich arenes (Scheme 11) with a series of amines under visible-light irradiation at ambient conditions.^[30] The reaction outcome can be well predicted for different substrates. Electron neutral and electron-deficient arenes like benzene, chlorobenzene, dichlorobenzene, etc., do not form a charge-transfer complex with DDQ and react with all amine nucleophiles such as Boc-amine, amides, pyrazole, triazole, sulfonamide or urea that do not spontaneously react with DDQ in the ground-state (Scheme 10). Nevertheless, electron-rich arenes such as naphthalene, phenanthrene, anisole, xylenes, 2-methylfuran, etc., which form a charge-transfer complex with DDQ react only with more nucleophilic amines, such as pyrazole and triazoles, but not with amides (Scheme 11). Amines that are more nucleophilic than pyrazoles

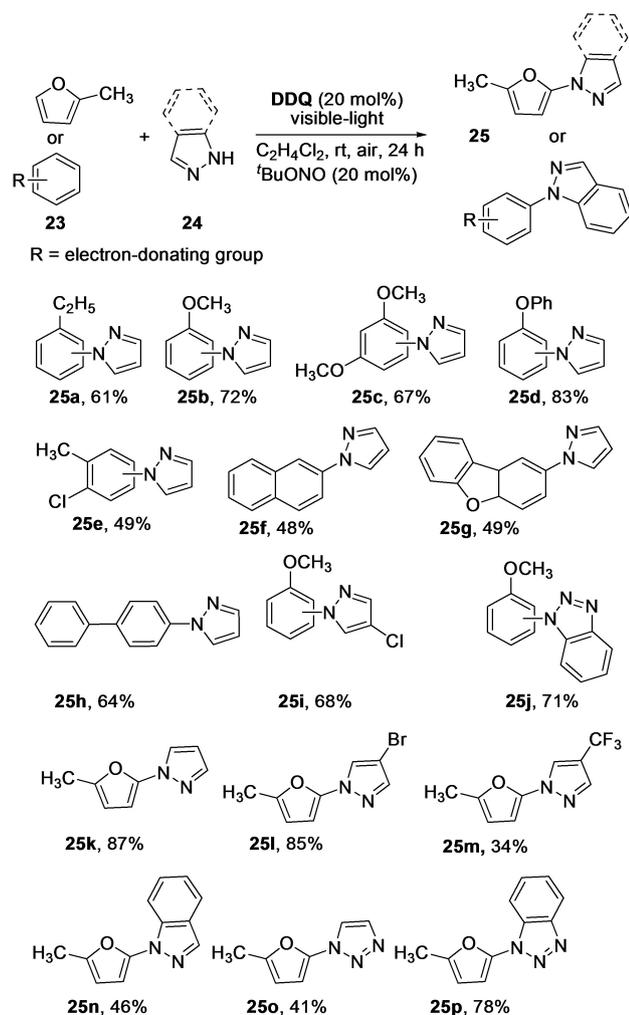
and triazoles (e.g. imidazole and indole) react spontaneously with DDQ in its ground-state. The different reactivity of electron-deficient and electron-rich arenes towards amines is explained by the different electrophilicity of the aromatic radical cations. Accordingly, the radical cation generated from benzene or chlorobenzene reacted with all amine nucleophiles, while the radical cation of anisole was less reactive and afforded products only with better nucleophiles.^[30]

Scheme 12 shows two possible mechanistic pathways for DDQ-photocatalyzed direct C–H amination of arenes under visible-light irradiation.^[30] The first mechanistic proposal (mechanism I in Scheme 12) is based on ³DDQ*-assisted one-electron oxidation of arenes. Upon irradiation by visible-light, DDQ is excited into its triplet state (i.e., ³DDQ*). Afterwards, ³DDQ* converts all arenes (**20**) to their corresponding radical cations (**26**). A nucleophilic reaction between the arene radical cation



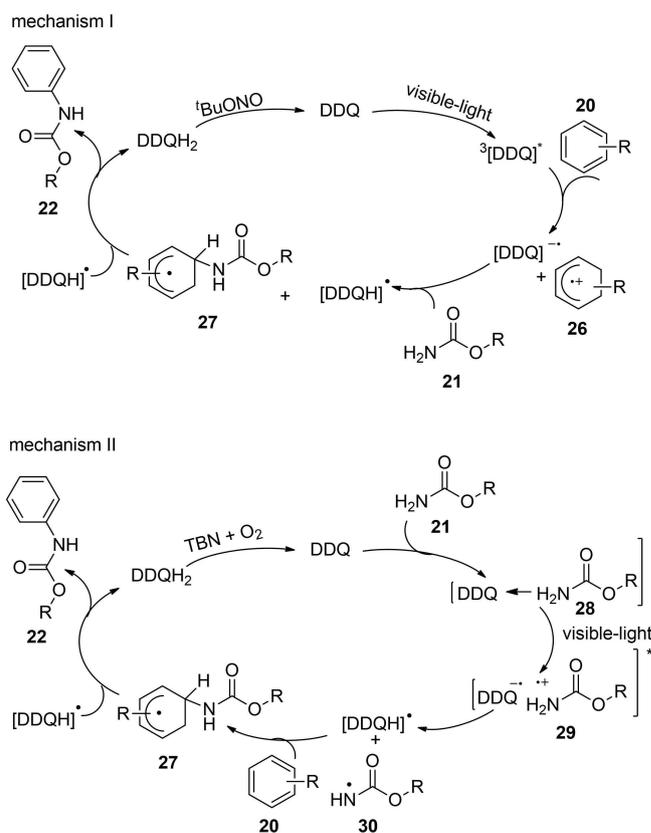
Scheme 9. A plausible mechanism for DDQ-assisted direct C–H amination of naphthalenes by sulfonimides under visible-light irradiation.

Scheme 10. The substrate scope for DDQ-photocatalyzed direct C–H amination of electron-deficient arenes under visible-light irradiation.



Scheme 11. The substrate scope for DDQ-photocatalyzed direct C–H amination of electron-rich arenes under visible-light irradiation.

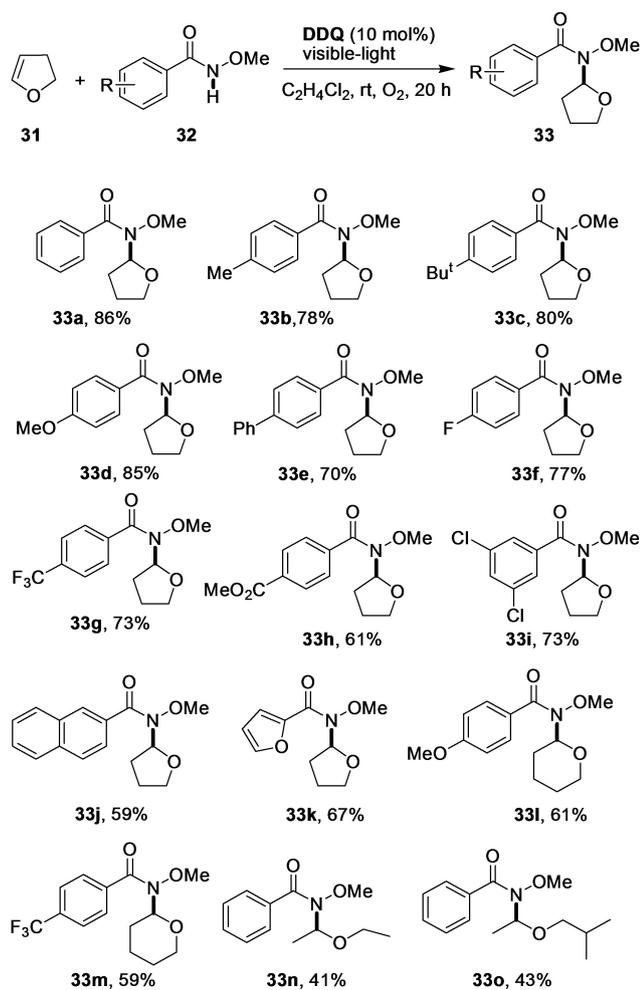
(26) and amines (21) followed by oxidation of the resulting species (27) yielded the desired product (22, Scheme 12). The second mechanistic proposal (mechanism II in Scheme 12) is based on the formation of a charge-transfer complex between amines and DDQ in the ground state. Excitation by visible-light, [DDQ-amine] charge-transfer complex (28) initiated hydrogen atom transfer occurs generating an amine radical (30) and a [DDQH] radical. The amine radical reacts with an arene (20) to a radical intermediate (27), which affords the desired product after loss of an electron and a proton (Scheme 12). In both mechanistic proposals, DDQ is reduced to DDQH₂ and reoxidized by reaction with *tert*-butyl nitrite and molecular oxygen. Experimental observations favor mechanism I as the DDQ charge-transfer band spans from 450 nm to almost 600 nm, but green light excitation afforded significantly less product and electron-deficient arenes with very high oxidation potentials (e.g. ethyl benzoate, benzonitrile) were beyond the substrate scope.^[30] However, a detailed time resolved spectroscopic study will be necessary to fully elucidate the mechanism of the reaction.



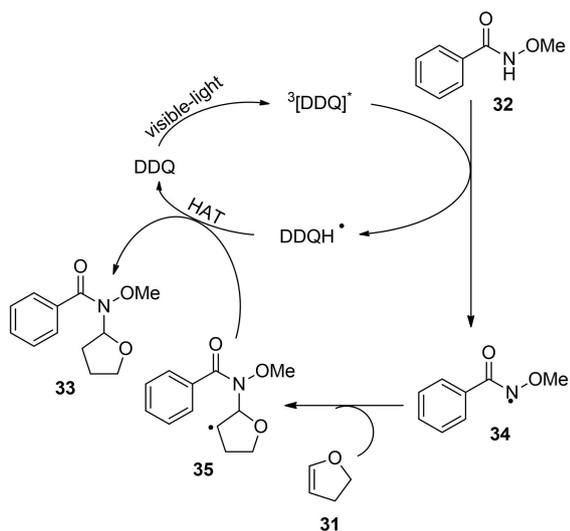
Scheme 12. Two mechanistic hypotheses for the DDQ-photocatalyzed direct C–H amination of arenes under visible-light irradiation.

In 2018, Zhang and coworkers^[31] reported a DDQ-photocatalyzed method for the addition of amides to C=C bonds of enol ethers (31) under visible-light irradiation (Scheme 13). Different vinyl ethers such as ethyl vinyl ether, propyl vinyl ether, ethyl propenyl ether, *n*-butyl vinyl ether or *iso*-butyl vinyl ether, as well as cyclic vinyl ethers like 3,4-dihydro-2H-pyran are selectively transformed into their corresponding amide-functionalized products in moderate to good yields. *N*-methoxyamides as amine coupling partners with electron-donating and weakly electron-withdrawing substituents (methyl, ethyl, *tert*-butyl, methoxy, ethoxy, phenyl, fluoro, chloro, and bromo) at the *para*-positions of the phenyl rings underwent the transformation smoothly and afforded the desired products in good yield (Scheme 13). In contrast, *N*-methoxyamides with a strong electron-withdrawing group like CF₃O, CF₃, CN and COOCH₃ at the *para*-position of the aromatic ring gave only a moderate yield of the desired product. In control experiments, the authors found no expected product without light or DDQ. DDQ is essential for the reaction; other photocatalysts including [Ru(phen)₃]²⁺, [Ru(bpy)₃]²⁺, eosin Y and rose bengal failed to catalyze the reaction under the irradiation of visible-light.^[31]

Scheme 14 shows a plausible mechanism for the addition of amides (32) to C=C bonds of enol ethers (31) under visible-light irradiation.^[31] DDQ*-assisted oxidation of *N*-methoxybenzamide (32) through a single electron transfer process affords the *N*-centered radical intermediate 34 and a [DDQH]⁺ radical. An



Scheme 13. The substrates scope for DDQ-photocatalyzed addition of amides to the C=C bond of enol ethers under visible-light irradiation.

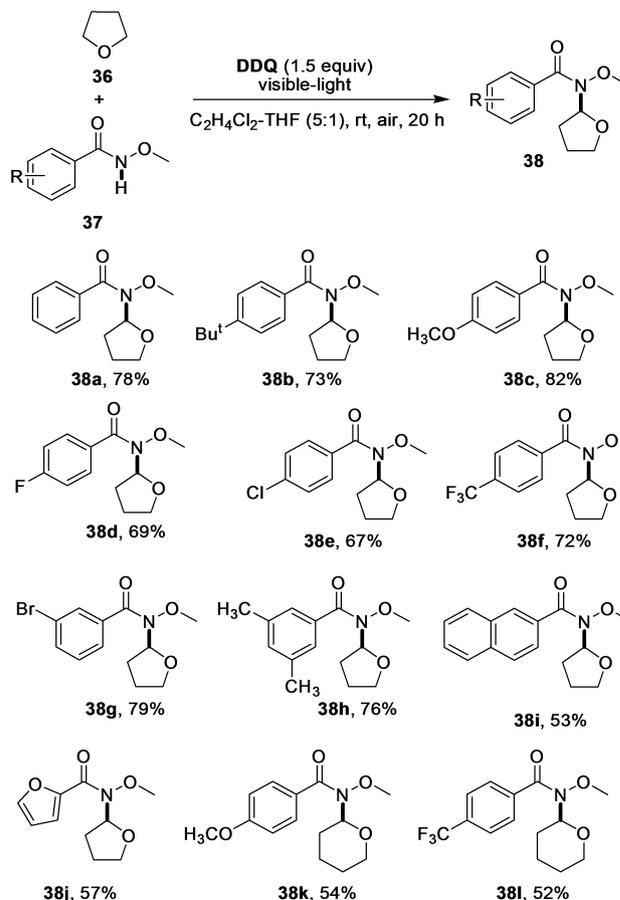


Scheme 14. A plausible mechanism for the DDQ-photocatalyzed addition of amides to the C=C bond of enol ethers under visible-light irradiation.

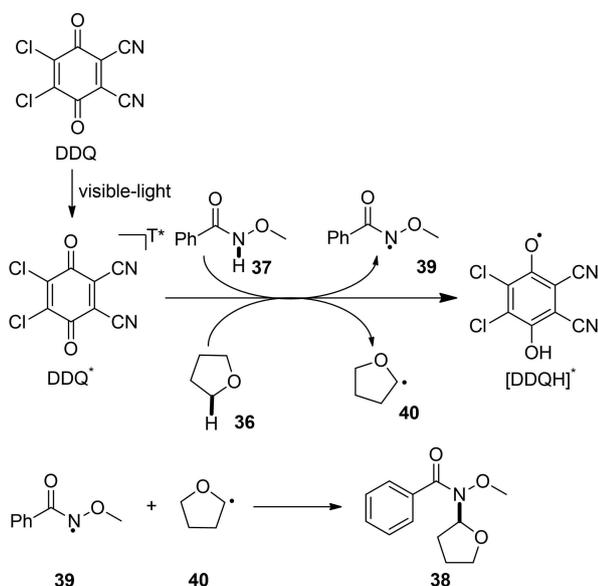
addition reaction between amide radical **34** and the α -carbon of the olefinic bond in enol ethers (**31**) provides a new carbon-centered radical intermediate **35**. Subsequently, radical **35** abstracts the hydrogen atom from the [DDQH] \cdot semiquinone radical and gave the desired product. This process regenerated DDQ (Scheme 14).

A year later, Zhang and coworkers^[32] reported a DDQ-assisted strategy for the direct C–H amination of ethers (**36**) by N-alkoxyamides (**37**) under visible-light irradiation (Scheme 15). This protocol requires DDQ and visible-light for product formation. A variety of N-methoxyamides (**37**) bearing electron-donating groups (methyl, *tert*-butyl and methoxy) and electron-withdrawing groups (trifluoromethyl, fluoro, chloro, and bromo) on the aryl ring smoothly reacted with ethers (tetrahydrofuran and tetrahydropyran) and afforded the desired products in good yield. However, under the optimized reaction conditions, acyclic alkyl (thio)ethers, such as diethyl ether and tetrahydrothiophene gave not the desired products. Thus, a series of N-methoxyamides were cross-coupled with tetrahydrofuran or tetrahydropyran using DDQ and visible-light (Scheme 15).

A possible mechanism for the DDQ-assisted C–H amination of ethers is shown in Scheme 16.^[32] Upon visible-light irradiation, DDQ is excited to its triplet state. $^3\text{DDQ}^*$ has been found capable to oxidize both N-methoxyamides (**37**) and ethers (**36**)



Scheme 15. The substrates scopes for DDQ-assisted direct C–H amination of ethers under visible-light irradiation.

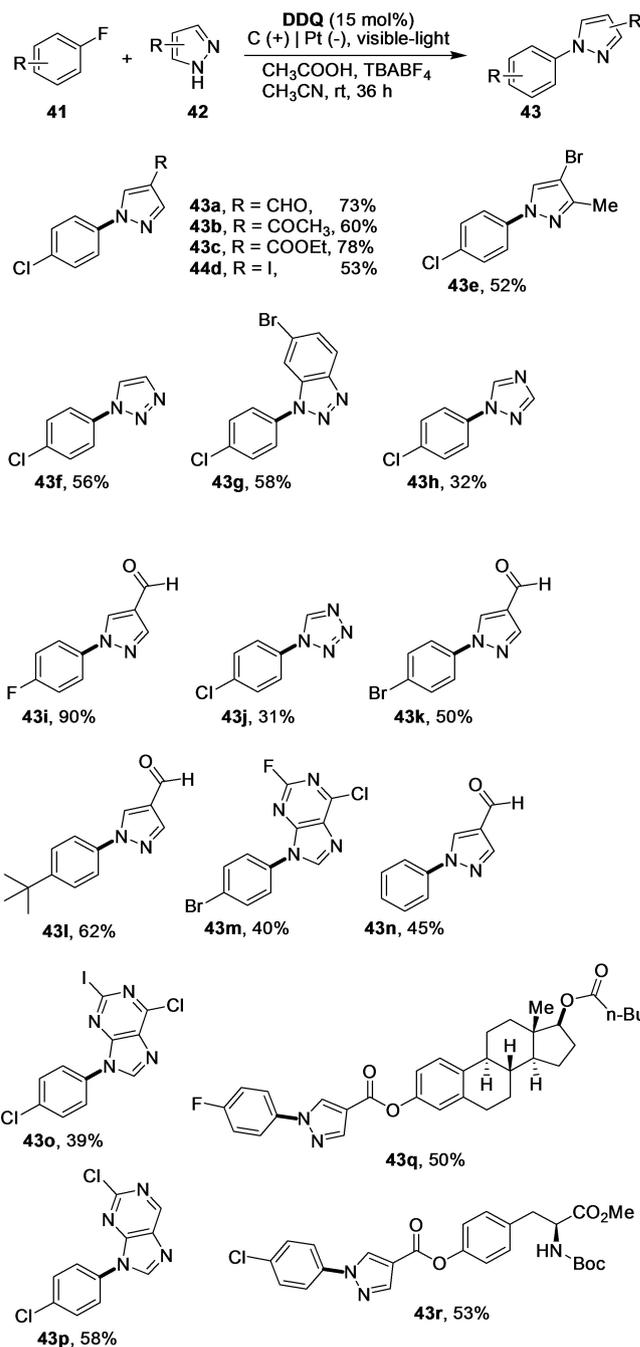


Scheme 16. A plausible mechanism for the DDQ-assisted direct C–H amination of enol ethers under visible-light irradiation.

via a single electron transfer process. Accordingly, $^3\text{DDQ}^*$ reacted with N-methoxyamides and ethers and afforded the aminyl radical intermediates **39** and ether radical intermediates **40**, respectively. Radical-radical combination is proposed to yield the reaction products **38** (Scheme 16).

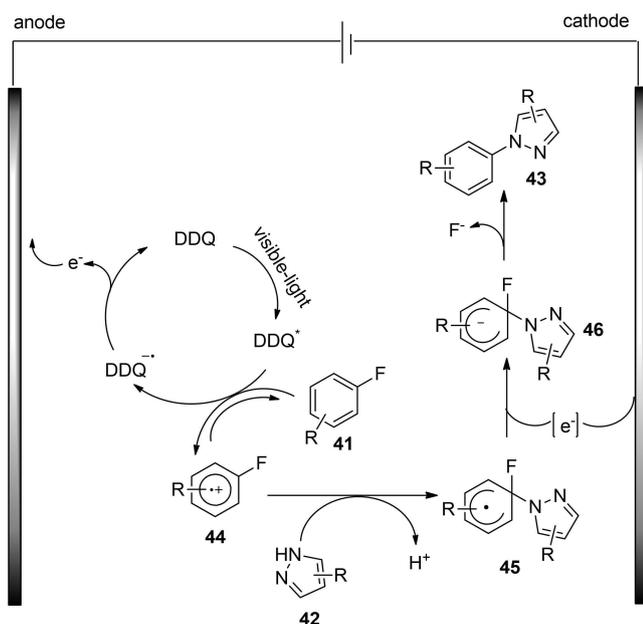
In 2020, Huang and coworkers^[33] published an electro-photo-chemical approach for the C–F amination of fluoroarenes (**41**) by azoles (**42**) using DDQ as a catalyst under visible-light irradiation (Scheme 17). The protocol uses an excess of the fluoroarene substrates and a stoichiometric amount of the heteroarene nucleophiles as limiting reagent. A series of fluoroarenes with chloro, bromo and cyano substituents on the phenyl ring were selectively transformed into their corresponding amination products (**43 a–43 r**) in moderate to good yields. Likewise, azole coupling partners, pyrazole, triazole, imidazole, purine and their derivatives react smoothly and afford the desired products in moderate yield. The authors mention that ester moieties of products that are typically labile under strongly basic conditions of a classic $\text{S}_{\text{N}}\text{Ar}$ reaction are tolerated (**43 q–43 r**) by this methodology.^[33] DDQ is recycled electro-chemically (Scheme 18).

The mechanism for DDQ photoelectro-catalyzed direct C–F amination of fluoroarenes is depicted in Scheme 18.^[33] Irradiation by visible-light excites DDQ into its triplet state. The $^3\text{DDQ}^*$ -assisted one-electron oxidation of the fluoroarene (**41**) affords the corresponding radical cation intermediate (**44**). A reaction between **44** and a nucleophilic azole (**42**) gives a new carbon-centered radical intermediate (**45**). The intermediate **45** is reduced electrochemically yielding anion **46** responsible for formation of product (**43**) after loss of the fluoride anion. DDQ, which was reduced to $\text{DDQ}^{\cdot-}$, was reoxidized electrochemically to close the catalytic cycle (Scheme 18).^[33]

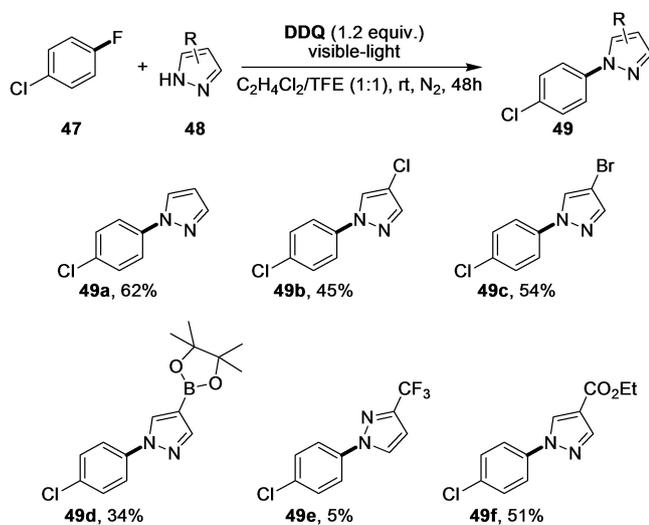


Scheme 17. The substrate scope for DDQ photoelectro-catalyzed direct C–F amination of fluoroarenes by azoles.

In 2020, Sheridan and coworkers^[34] also reported a protocol using DDQ for the C–F amination of fluoroarenes (**47**) with pyrazoles (**48**) under visible-light irradiation (Scheme 19). In this method, the authors used either trifluoroethanol (TFE) or 1:1 mixture of dichloroethane (DCE) and trifluoroethanol (TFE) as reaction medium due to its ability to stabilize the radical cation intermediate of the substrate. Moreover, to avoid the direct reaction of pyrazole with DDQ, the authors added azole slowly over the course of reaction. Using these conditions, a series of



Scheme 18. A plausible mechanism for the DDQ-photocatalyzed direct C–F amination of fluoroarenes by azoles via electrophotochemical approach.



Scheme 19. The substrates scope for DDQ-assisted direct C–F amination of chlorofluoroarenes by pyrazoles under visible-light irradiation.

chlorofluoroarenes and a small set of functionalized pyrazoles reacted well and were selectively transformed into their corresponding amination products (**49a–49f**) in low yield.^[34] A reaction mechanism was not proposed. However, it is likely that the ³DDQ^{•+}-assisted one-electron oxidation of fluoroarene to the corresponding radical cation intermediate followed by nucleophilic pyrazole attack and rearrangement gave the reaction products.

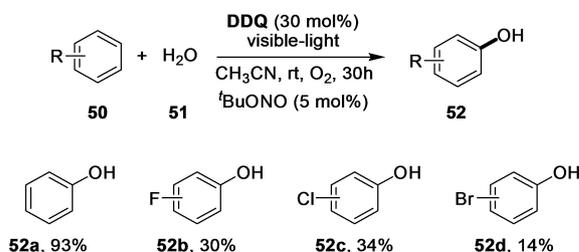
4. DDQ-initiated C–O bond formation under visible-light irradiation

Phenol is an important commodity chemical in industry.^[35] Among the various methods for its synthesis^[36] one ideal manufacturing process is to oxidize benzene under mild conditions.

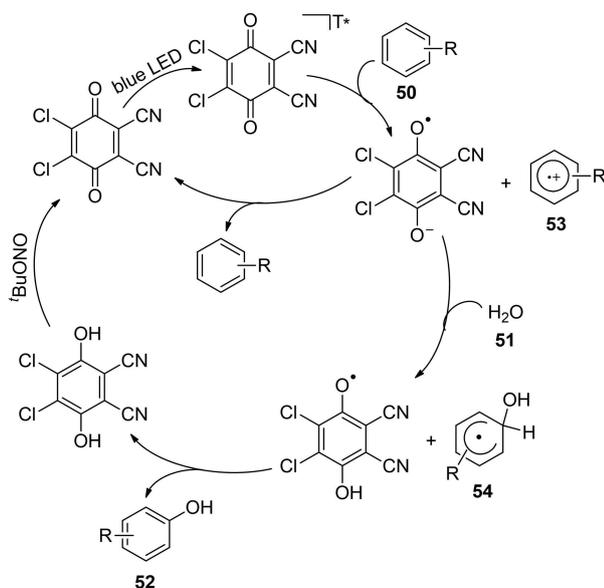
In 2013, Ohkubo and coworkers^[37] described a methodology employing DDQ as catalyst for the oxidation of benzene (**50**) to phenol (**52**) under visible-light irradiation (Scheme 20). The success of this reaction relies on the strong oxidation ability of the triplet-state DDQ, ³DDQ^{•+} [$E_{\text{red}} = 3.18 \text{ V vs SCE}$], which is capable to oxidize benzene ($E_{\text{ox}} = 2.32 \text{ V vs SCE}$) at ambient conditions. The quantum yield (Φ) for formation of phenol from benzene under optimized conditions was estimated as high as 0.45. In addition, when benzene was replaced by halogenated benzenes such as fluorobenzene, chlorobenzene, and bromobenzene, the photooxygenation effectively occurred under similar reaction conditions and afforded the corresponding phenols (**52b–52d**, Scheme 20) in moderate yield. In all cases, selective mono C–H hydroxylation of the arenes without over-oxidation of the hydroxyarene product is observed due to the fast back electron transfer between the hydroxyarene radical cation and [DDQ]^{•–} (Scheme 21).^[37]

A proposed mechanism for DDQ-photocatalyzed direct C–H hydroxylation of arenes under visible-light irradiation is shown in Scheme 21.^[37] Irradiation by visible-light excites DDQ into its triplet state, ³DDQ^{•+}, which converts arenes (**50**) to their corresponding radical cations (**53**) by one electron oxidation. A nucleophilic addition reaction between the arene radical cation (**53**) and water (**51**) followed by oxidation of the resulting OH-adduct radical (**54**) yields the desired product (**52**). During these processes, DDQ is reduced to DDQH₂, which is reoxidized by reaction with *tert*-butyl nitrite and oxygen to close the catalytic cycle (Scheme 21).

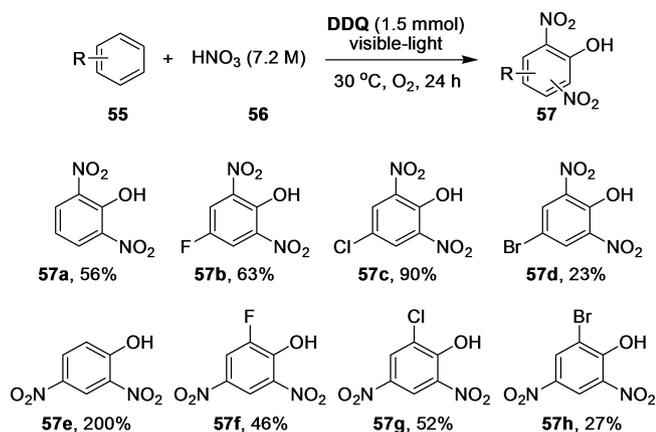
In 2018, Hofmann and coworkers^[38] reported a DDQ-assisted methodology for one-pot selective nitrohydroxylation (Scheme 22) and hydroxylation (Scheme 23) of benzene and halobenzenes employing nitric acid and water/nitrogen oxides, respectively, under visible-light irradiation. In this protocol, the authors coupled the photocatalytic hydroxylation of arenes (Scheme 20) to the use of HNO₃ for an additional NO₂-functionalization. They observed that reactions of arenes (**55**),



Scheme 20. The substrates scope for DDQ-photocatalyzed direct C–H hydroxylation of arenes under visible-light irradiation.



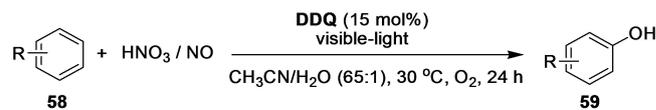
Scheme 21. A plausible mechanism for the DDQ-photocatalyzed direct C–H hydroxylation of arenes by water under visible-light irradiation.



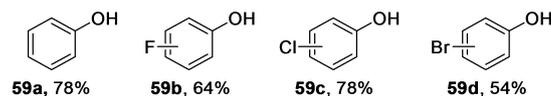
Scheme 22. DDQ-assisted dinitrohydroxylation of arenes under visible-light irradiation.

an excess quantity of HNO₃ (7.2 M, 20 mL) and a stoichiometric quantity of DDQ under visible-light irradiation gave in a one-pot synthesis dinitrophenols in moderate to good yields (Scheme 22). In contrast, the reaction of arenes (**58**), water, a stoichiometric quantity of NO or HNO₃ and a catalytic amount of DDQ (15 mol%) under visible-light irradiation afforded pure phenols (Scheme 23), without contamination by nitro compounds. In the latter reaction conditions, NO or HNO₃ reoxidize DDQH₂ to DDQ by NO₂ (Scheme 23).^[38] A control experiment without either a light source or DDQ did not give any conversion to the product.

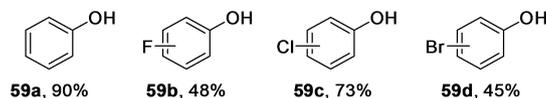
The proposed reaction mechanism (Scheme 24) for these transformations (Schemes 22 and 23) is very similar to the one described in Scheme 21.^[38] The triplet state of ³DDQ* converts arenes (**58**) into their corresponding radical cations (**60**) by a



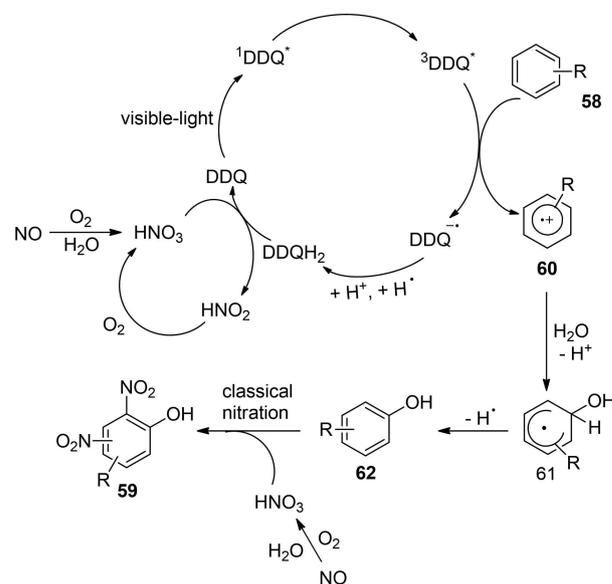
NO used to reoxidize DDQH₂ to DDQ



HNO₃ used to reoxidize DDQH₂ to DDQ



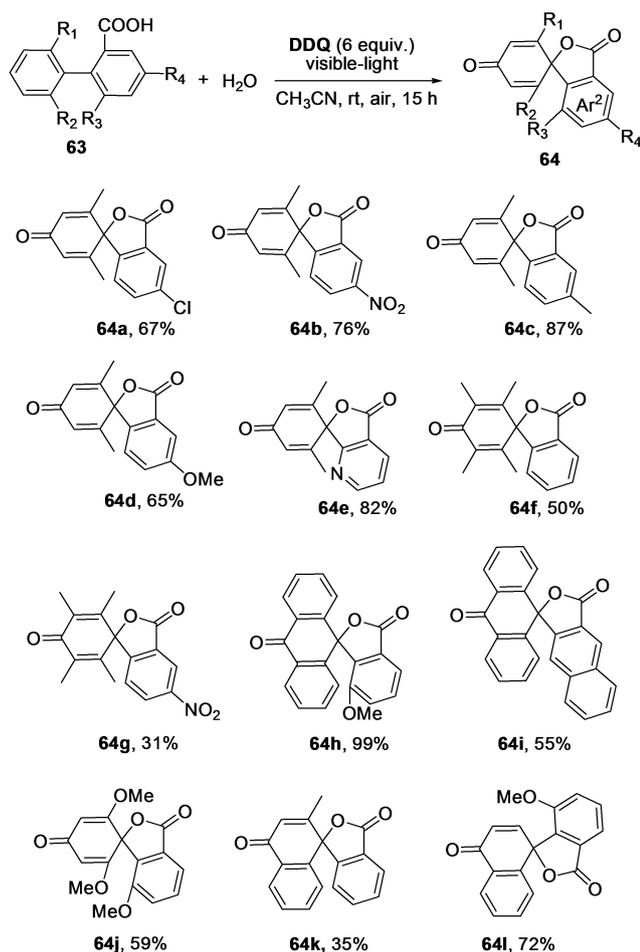
Scheme 23. DDQ-photocatalyzed hydroxylation of arenes under visible-light irradiation.



Scheme 24. A plausible mechanism for DDQ-assisted direct one-pot synthesis of dinitrophenols from arenes under visible-light irradiation.

single electron transfer process. A nucleophilic addition of the arene radical cation (**60**) by water and subsequent rearomatization combined with electron and proton transfer steps, gave hydroxyarenes (**62**) and DDQH₂. The dinitrophenols were obtained from the mixture of hydroxyarenes (**62**) and HNO₃ by a classical electrophilic aromatic nitration reaction (Scheme 24).^[39]

In 2019, Li and coworkers^[40] described a DDQ-assisted protocol for the synthesis of spiro lactones (**64**) through dearomatization of nonphenolic biaryls (**63**) under visible-light irradiation (Scheme 25). This protocol was applied to a range of different 1-biaryl-2-carboxylic acids and 1,1'-biaryl-2-carboxylic acids containing either an electron-donating group (such as alkyl or methoxy) or an electron-withdrawing group (include chlorine or nitro), and gave the corresponding *spiro*-products in

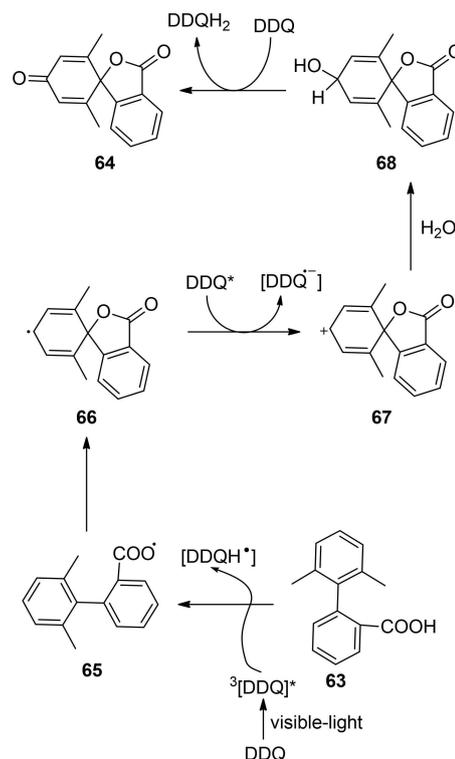


Scheme 25. The substrates scope for DDQ-assisted synthesis of spirolactones from 1-biaryl-2-carboxylic acids and 1,1'-biaryl-2-carboxylic acids under visible-light irradiation.

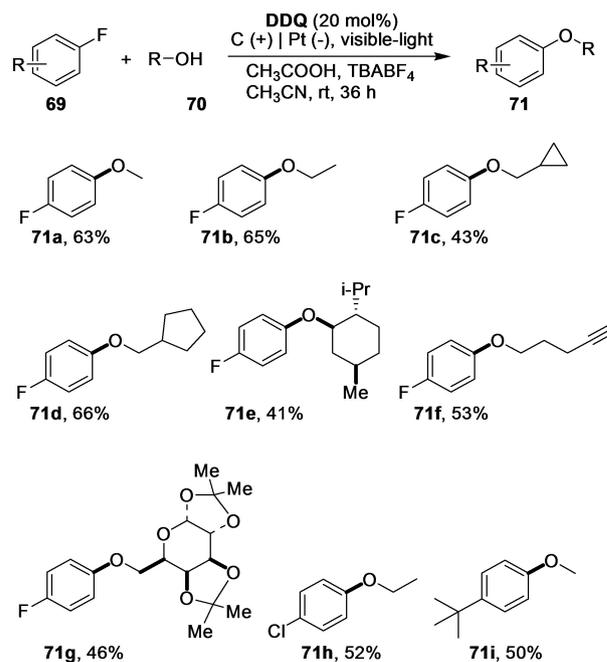
moderate to good yields (Scheme 25). In all cases, the dearomatization has been induced by electrophilic attack of the carboxyl radical **65** (Scheme 26) on the nearest arene unit. Interestingly, the authors also developed a complementary methodology in which 9-mesityl-10-phenylacridinium was used as a photooxidant to generate the spirolactones from 1-biaryl-2-carboxylic acids and 1,1'-biaryl-2-carboxylic acids (**63**) under aerobic conditions.^[40]

Scheme 26 shows the proposed mechanism for DDQ-assisted synthesis of spirolactones under visible-light irradiation.^[40] The triplet state ³DDQ* mediates the oxidation of the carboxylates (**63**) through a single electron transfer process affording a carboxyl radical intermediate **65**. The carboxyl radical intermediate **65** gave the new intermediate **66** by intramolecular cyclization and dearomatization. Subsequently, intermediate **66** underwent a one-electron oxidation and gave cation **67**, which provides the desired spirolactones (**64**) after nucleophilic attack of water and an oxidation reaction (Scheme 26).

In 2020, Huang and coworkers^[33] published an electro-photochemical approach for the C–F oxygenation of fluoroar-



Scheme 26. A plausible mechanism for the DDQ-photocatalyzed synthesis of spirolactones under visible-light irradiation.



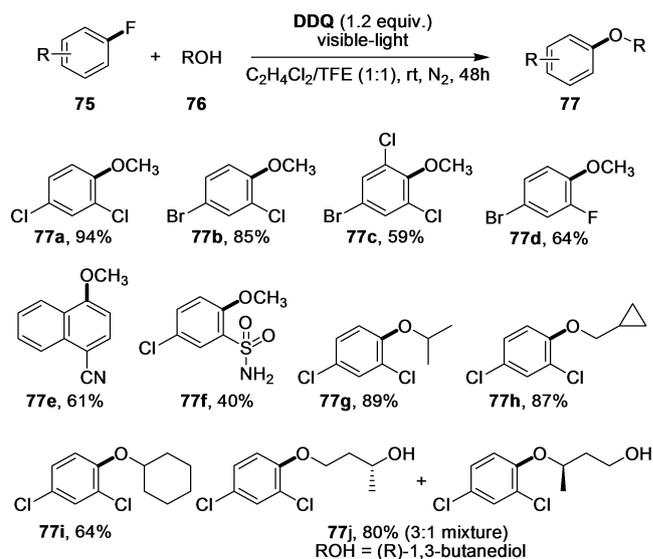
Scheme 27. The substrates scope for DDQ-photocatalyzed direct C–F oxygenation of fluoroarenes by alcohols via electrophotochemical approach.

enes (**69**) by alcohols (**70**) using DDQ as a catalyst under visible-light irradiation (Scheme 27). This protocol was performed having an excess of fluoroarene substrates and a stoichiometric

amount of alcohol nucleophiles as limiting reagent. This method was applied to 1,4-difluorobenzene, 1-chloro-4-fluorobenzene and 1-*tert*-butyl-4-fluorobenzene (**71 a–71 i**) and selectively transformed the compounds into their corresponding aryl alkyl ethers in moderate to good yields. Likewise, for alcohol coupling partners, methanol, ethanol, cyclopropylmethanol, cyclopentylmethanol, 4-pentyn-1-ol and so on react smoothly and afforded the desired products in good yield (Scheme 27). The authors mentioned that even a protected sugar (**71 g**) could be engaged as a coupling partner despite concerns of oxidative destruction of the acetal moiety. In this method, DDQ has been recycled electrochemically.^[33]

The mechanism for DDQ-photocatalyzed direct C–F oxygenation of fluoroarenes (**69**) is depicted in Scheme 28.^[33] Upon irradiation by visible-light, DDQ is excited into its triplet state (³DDQ*), which induces the one-electron oxidation of the fluoroarene (**69**) affording the corresponding radical cation intermediate (**72**). A reaction between radical cation **72** and the alcohols (**70**) gives a new carbon-centered radical intermediate (**73**). The intermediate radical **73** undergoes a one-electron reduction electrochemically and yields the anion **74** responsible for the formation of product (**71**) after extrusion of the fluoride anion. During these processes, DDQ is reduced to [DDQ]^{•–} and was oxidized electrochemically to recycle DDQ (Scheme 28).

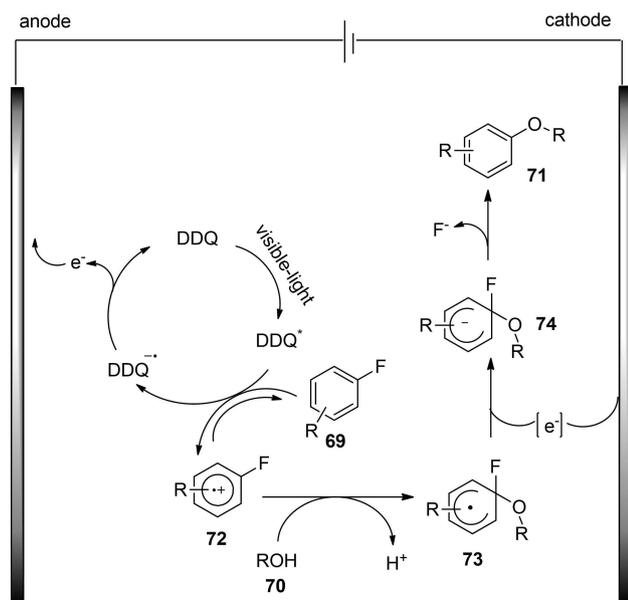
In 2020, Sheridan and coworkers^[34] also reported a protocol utilizing DDQ for the C–F oxygenation of fluoroarenes (**75**) with alcohols (**76**) under visible-light irradiation (Scheme 29). In this method, the authors used a 1:1 mixture of DCE and trifluoroethanol as a reaction medium due to its ability to stabilize the radical cation intermediate of the substrate. A series of halogenated fluoroarenes and a set of alcohols (menthol, ethanol, cyclohexanol and isopropanol) reacted well and were selectively transformed into their corresponding aryl alkyl ethers



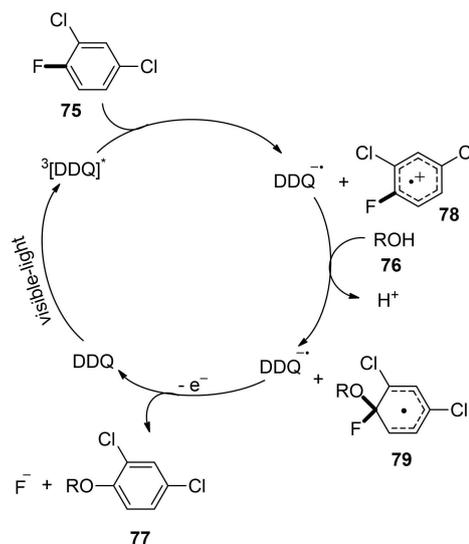
Scheme 29. The substrate scope for DDQ-assisted direct C–F oxygenation of halofluoroarenes by alcohols under visible-light irradiation.

(**77**) in moderate to good yields (Scheme 29). However, alcohols with larger steric hindrance, i.e., *tert*-butanol as a substrate did not give any product.

The mechanism for DDQ-assisted direct C–F oxygenation of halofluoroarenes (**75**) is depicted in Scheme 30.^[34] Irradiation by visible-light excites DDQ into its triplet state. The ³DDQ*-assisted one-electron oxidation of a halofluoroarene (**75**) affords the corresponding radical cation intermediate (**78**). A reaction between radical cation **78** and a nucleophilic alcohol (**76**) gives the corresponding cyclohexadienyl radical intermediate (**79**). The radical intermediate **79** undergoes a one-electron reduction



Scheme 28. A plausible mechanism for the DDQ-photocatalyzed direct C–F oxygenation of fluoroarenes by alcohols via electrophotochemical approach.



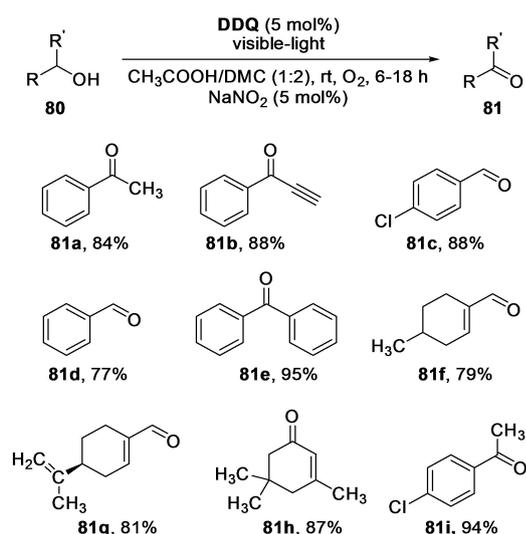
Scheme 30. A plausible mechanism for the DDQ-assisted direct C–F oxygenation of halofluoroarenes by alcohols under visible-light irradiation.

by DDQ radical anion (DDQ^{•-}) followed by fluoride anion loss affording the desired product **77** and DDQ (Scheme 30).

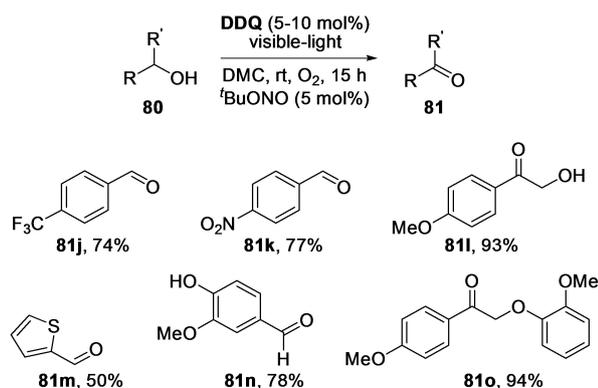
5. DDQ-initiated oxidation under visible-light irradiation

In 2014, Walsh and coworkers^[41] described a DDQ-photo-catalyzed protocol for the oxidation of benzylic alcohols and allylic alcohols under visible-light irradiation (Schemes 31 and 32). This methodology has been applied to a series of benzylic alcohols (**81a–81e** and **81i**) and a few allylic alcohols (**81f–81h**) containing electron-withdrawing (CF₃, NO₂ and Cl) and electron-donating (alkyls and aryl) groups (Scheme 31). All types of alcohols (**80**) were effectively transformed into the corresponding carbonyl compounds (**81**) in moderate to good yields.

Moreover, the present method was explored for the oxidation of β-O-4 lignin models (**81l**, **81n** and **81o**) and found



Scheme 31. The substrates scope for DDQ-photocatalyzed oxidation of benzylic alcohols and allylic alcohols under visible-light irradiation.

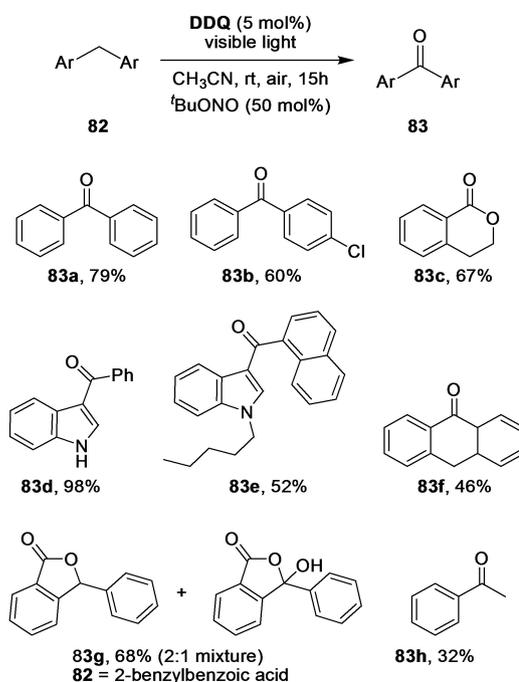


Scheme 32. The substrates scope for DDQ-photocatalyzed oxidation of benzylic alcohols and allylic alcohols under visible-light irradiation.

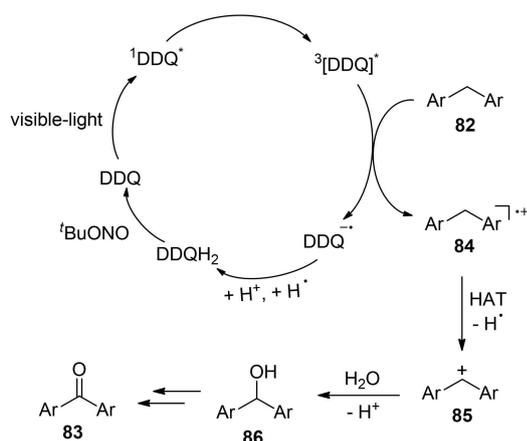
capable of selectively oxidizing the secondary benzylic alcohol unit in good yield (Scheme 32). Oxidation of 4-nitrobenzyl alcohol and 4-(trifluoromethyl)benzyl alcohol were reported unsuccessful by conventional synthetic methods,^[42] but the authors obtained product yields of 74% (**81j**) and 77% (**81k**), respectively, with this protocol. No desired product formed without light or DDQ. In this protocol, sodium nitrite (Scheme 31) or *tert*-butyl nitrite (Scheme 32) were used for the reoxidation of DDQH₂ to DDQ.^[41]

In 2016, Rusch and coworkers^[43] described a DDQ-photo-catalyzed method for aerobic benzylic C–H oxygenations of diarylmethanes and arylalkylmethanes under visible-light irradiation (Scheme 33). Again, no product in control experiments without either a light source or DDQ is observed. The protocol was used with ethylbenzene (**83h**) and a few diarylmethanes (**82**) containing electron-withdrawing (chloro and carboxyl) and electron-donating (methoxy) groups and afforded the corresponding ketones (**83**) in low to moderate yields. Curiously, 9,10-dihydroanthracene and 2-benzylbenzoic acids, respectively, undergo aromatization (anthracene formed) and intramolecular lactonization (**83g**, phthalides generated) under the optimized conditions (Scheme 33).^[43] Moreover, ethylbenzene gave significant amounts of 1-phenylethanol in addition to the desired acetophenone.

A proposed mechanism for DDQ-photocatalyzed aerobic benzylic C–H oxygenation of diarylmethanes and arylalkylmethanes is shown in Scheme 34.^[43] Visible-light excitation converts DDQ into its triplet state that oxidizes benzylic groups (**82**) to the corresponding radical cation (**84**) by one electron oxidation. Subsequently, **84** undergoes hydrogen-atom transfer



Scheme 33. The substrates scope for DDQ-photocatalyzed aerobic benzylic C–H oxygenations of diarylmethanes and arylalkylmethanes under visible-light irradiation.

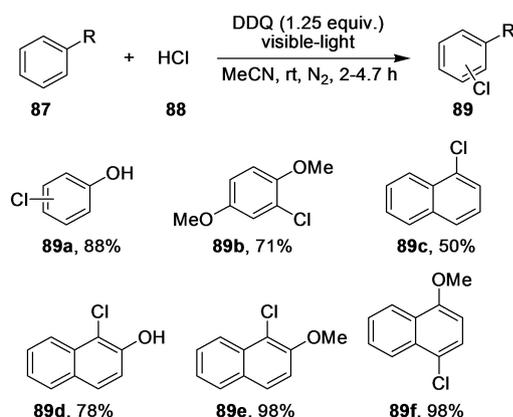


Scheme 34. A plausible mechanism for the DDQ-photocatalyzed aerobic benzylic C–H oxygenation of diarylmethanes and arylalkylmethanes under visible-light irradiation.

(HAT) with $\text{DDQ}^{\bullet-}$ and affords the benzylic cation intermediate (**85**), which provided the desired ketone as product after nucleophilic attack by water and oxidation reaction (Scheme 34). During these processes, DDQ is reduced to DDQH_2 . Reaction with *tert*-butyl nitrite and molecular oxygen regenerates DDQ.

6. DDQ-initiated chlorination under visible-light irradiation

In 2016, Ohkubo and coworkers^[44] reported the DDQ-assisted direct C–H chlorination of arenes (**87**) by hydrogen chloride (**88**) under visible-light irradiation (Scheme 35). Only electron-rich substrates, such as phenol, anisole, 1,4-dimethoxybenzene, naphthalene, 2-naphthol, 2-methoxynaphthalene and 1-methoxynaphthalene afford the corresponding mono-chlorinated products in moderate to good yields (Scheme 35). Chlorination



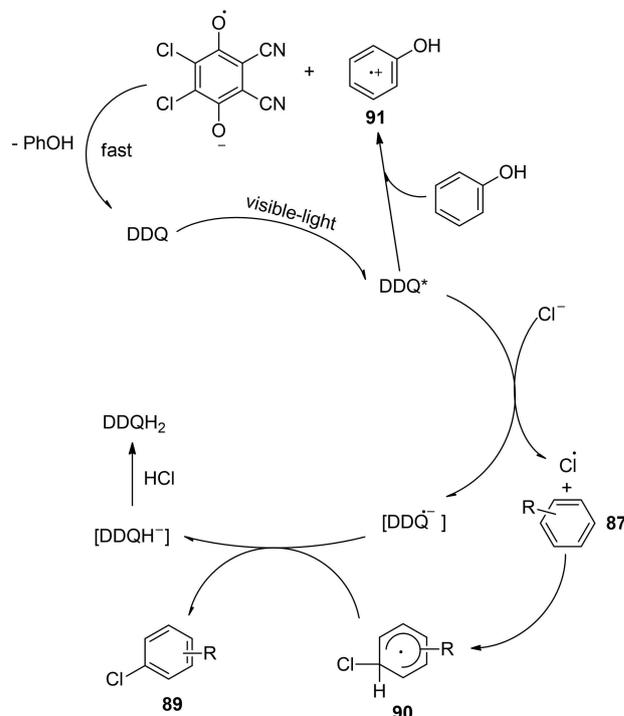
Scheme 35. The substrates scope for DDQ-assisted direct C–H chlorination of arenes by hydrogen chloride under visible-light irradiation.

of biphenyl was not achieved. The authors propose that the chlorination occurs via electron transfer from Cl^- to $^3\text{DDQ}^*$ and not via an electron transfer from the arene to $^3\text{DDQ}^*$ (Scheme 36). The reaction quantum yield (Φ) gradually increases with increasing concentration of phenol and exhibits a sigmoidal curve at low HCl concentration (0–20 mM). The Φ value reached a maximum value of 4.1% at high HCl concentration (120 mM). In other words, when the reaction was carried out at low concentrations of HCl or high concentrations of phenol, electron transfer from phenol to $^3\text{DDQ}^*$ occurred dominantly without quenching of $^3\text{DDQ}^*$ by Cl^- . In such a case, no chlorinated product was produced due to the fast back electron transfer from $\text{DDQ}^{\bullet-}$ to phenol^{•+}.^[44]

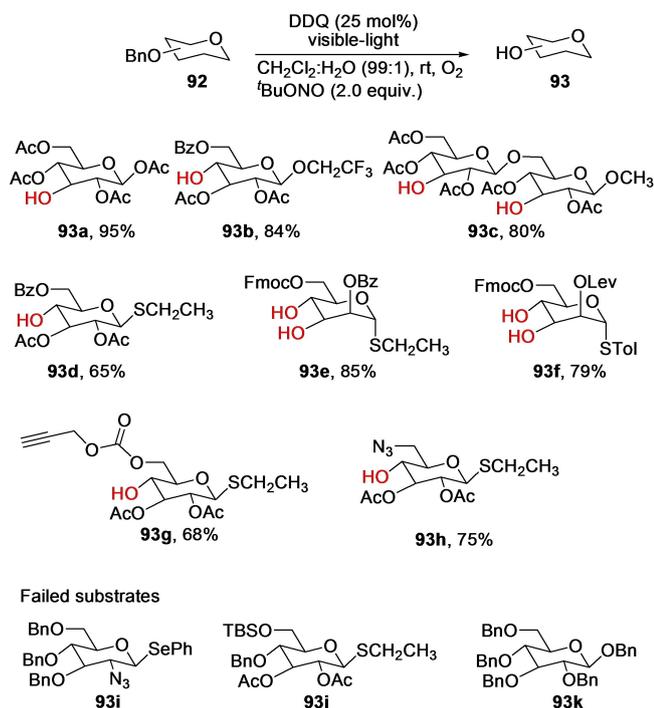
A proposed mechanism for DDQ-assisted direct C–H chlorination of arenes (**87**) by hydrogen chloride (**88**) under visible-light irradiation is shown in Scheme 36.^[44] A reaction between $^3\text{DDQ}^*$ and the chloride anion affords a chlorine radical (Cl^\bullet) and a $[\text{DDQH}^\bullet]$ radical. The chlorine radical reacts with the arene (**87**) to give a chlorine-adduct radical intermediate (**90**), which affords desired product (**89**) after hydrogen atom transfer from the $[\text{DDQH}^\bullet]$ radical. In these processes, DDQ is reduced to DDQH_2 (Scheme 36).

7. DDQ-initiated oxidative cleavage of benzyl ethers under visible-light irradiation

A DDQ-assisted protocol for the oxidative debenzoylation of benzyl ethers (**92**) under visible-light irradiation (Scheme 37)



Scheme 36. A plausible mechanism for the DDQ-assisted direct C–H chlorination of arenes by hydrogen chloride under visible-light irradiation.



Scheme 37. Substrate scope for the DDQ-assisted oxidative debenzoylation of benzyl ethers under visible-light irradiation.

was reported by Cavedon and coworkers^[45] in 2020. This protocol is applicable to a variety of substrates containing acetyl, benzoyl and isopropylidene protecting groups and smoothly deprotected them in less than 4 h in good yield. The authors mention that thioethers (93d–93h), azides (93h) and several common protecting groups (that do not survive in a hydrogenolysis or Birch reduction) such as fluorenylmethoxy, carbonyl, levulinic ester, allyl carbonate, and propargyl carbonate, and benzylidene were tolerated by the photo-oxidative benzyl ether cleavage (Scheme 37). Nevertheless, phenylselenenyl (93i) and *tert*-butyldimethylsilyl (93j) groups are not stable under the conditions applied. Likewise, full deprotection of perbenzylated glucose (93l) was not feasible and a complex mixture of partially protected derivatives formed. The choice of the irradiation source is crucial for reaching high selectivities of benzyl ether cleavage. Green light irradiation was reported to be superior over blue light in suppressing the formation of side products during reactions. The control studies confirmed that light and DDQ are necessary for the reaction. The authors also tested a continuous flow approach for the debenzoylation of C(3)-benzyl-glucofuranose, which reduced the reaction time significantly to three minutes.^[45]

8. Conclusions and outlook

The synthetic protocols discussed in this mini-review illustrate that the increased oxidation potential of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) upon visible-light irradiation

can be used in organic synthesis. The increased oxidation power of the excited-state DDQ was used to prepare trifluoromethylated arenes, buta-1,3-dienes, amine-functionalized arenes and alkylys, hydroxylated arenes, spiro-lactones, amide-functionalized ethers and other molecules. A utilization of DDQ under visible-light may replace conventional and metal-assisted cross-dehydrogenative coupling reactions by a more sustainable and facile route. DDQ and DDQH₂ are biocompatible. They are commercially available, handled without any special precautions and can be stored for longer periods at ambient conditions.

Despite some progress in the field, there is room for further development. Most of the reactions known for C–H bond functionalization involve the use of aromatic compounds as starting material and only two examples used benzylic compounds and olefins. The use of aliphatic compounds as starting substrates in the DDQ-mediated synthesis of organic compounds waits to be studied. In addition, asymmetric reactions, improved reaction selectivity and larger scale application are future challenges in DDQ catalysis.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Cross coupling · DDQ · Dehydrogenative coupling · Photooxidation · Quinones

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