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Entry

Cycloadditions and Cyclization Reactions via Post-Synthetic Modification and/or One-Pot Methodologies for the Stabilization of Imine-Based Covalent Organic Frameworks

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Definition: Interest in covalent organic frameworks as high-value materials has grown steadily since their development in the 2000s. However, the great advantage that allows us to obtain these crystalline materials—the reversibility of the bonds that form the network—supposes a drawback in terms of thermal and chemical stability. Among the different strategies employed for the stabilization of imine-based Covalent Organic Frameworks (COFs), cycloaddition and other related cyclization reactions are especially significant to obtain highly stable networks with extended π-delocalization and new functionalities, expanding even further the potential application of these materials. Therefore, this entry gathered the most recent research strategies for obtaining stable COFs by means of cyclization reactions, including the Povarov reaction and intramolecular oxidative cyclization reactions as well as some other recent innovative approaches.

Keywords: covalent organic frameworks; post-synthetic modification; one-pot synthesis; stabilization; imine-based-COFs; cycloaddition reaction; Povarov reaction; aza-Diels–Alder; oxidative cyclization

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1. Introduction

Since the first reported synthesis of covalent organic frameworks (COFs) in 2005 by Yaghi and collaborators [1], these porous and crystalline materials have gained attention, importance, and applicability in different scientific and technological areas such as catalysis [2] (including photo- [3,4] and electrocatalysis [5–7]), CO_2 capturing [8], electronics [9], medicine [10,11], and food security [12], among others [13–15]. The great relevance acquired by these materials is mainly due to the possibility of tuning different chemical or physical properties such as porosity, functionalities, and stability according to the specific needs, with imine-based COFs being of special interest [16,17]. In this regard, stability is often one of the limiting factors for the applicability of COFs because the characteristic reversibility of the bonds formed in the polymerization reactions makes these materials more prone to chemical or thermal degradation. Therefore, the development of new COFs nowadays involves a thorough design toward stabilization to prevent degradation processes as much as possible.

The prevention of the degradation of imine-based COFs has been addressed by employing different strategies, such as the design and construction of materials with specific interlayer interactions that help maintain the integrity of the network. Other efforts have focused on preventing hydrolysis of the imine group, either by blocking it from nucleophiles or by creating intramolecular hydrogen bonding or hydrophobic environments around the imine group [18]. However, the blocking of the -C=N- bond that seems to be gaining attention during the last few years is its irreversible transformation into another functional group. The conversion of the reversible imine linkages into irreversible moieties has also been used to simultaneously incorporate new functionalities into the network.

Thus, this strategy has allowed the conversion of the imine linkages into amines using different methods such as the Leuckart–Wallach reduction [19], the thiol-ene click reaction [20], or the Strecker reaction [21]. Other efforts have been focused on embedding the imine linkages into new heterocyclic rings, amplifying the π-electron delocalization of the lattices and, in many cases, adding new functionalities. These blocking bond steps initially were performed by the post-synthetic modification (PSM) of the COFs. However, one-pot (OP) syntheses, in which COF and its transformation are carried out in a cascade process, are gaining importance due to the savings in efforts and recurses that it entails.

The great interest generated by obtaining ultra-stable crystalline networks from different imine-based COFs by the formation of different cycles is evidenced by the growing number of publications focused on their synthesis and the evaluation of their structural, chemical, and electronic properties for later applications. This entry gathered the synthetic strategies, both by PSM and OP, for the transformation of reversible links of imine-based COFs into stabilized heterocyclic moieties by using cycloaddition or cyclization reactions. Particular attention will be paid to the most recent publications to reflect the state of the art in this field.

2. Cycloadditions and Cyclization Reactions for the Stabilization of Imine-Based Covalent Organic Frameworks

2.1. Formal [4 + 2] Cycloadditions: The Povarov Reaction

Cycloaddition reactions play a fundamental role in synthetic organic chemistry and their implementation for the development of a novel COFs field was only a matter of time. In this regard, the cycloaddition reaction used most frequently is the copper-catalyzed 1,3-dipolar azide-alkyne cycloaddition (CuAAC) reaction. The great versatility and good tolerance of this reaction to several functional groups have allowed the introduction of a variety of functionalities within the pores of COFs [22]. This click reaction takes place without changing the connectivity within the crystalline lattices and is therefore not effective in the search for improved electronic mobility or chemical stability. On the other hand, further cycloadditions have enabled the modification of the structural architecture of COFs, one example being the impressive conversion of 2D COFs into three-dimensional crystalline networks that have been achieved by reversible [2 + 2] or [4 + 4] photoinduced cycloaddition reactions [23,24]. These solid-state transformations are favored by the structural characteristics of the vinylene and anthracene-based COFs used for the study, in which interlayer distance and eclipsed stacking are suitable for the achieved structural modifications. However, cycloreversion to the original structure also occurs when the three-dimensional COFs are subjected to high temperatures. Nevertheless, the cycloaddition reaction that has aroused the most interest is the Povarov reaction, a formal [4 + 2] cycloaddition between an imine and an alkene or alkyne moiety to irreversibly obtain the corresponding quinoline derivative [25].

The first example of this type of aza-Diels–Alder reaction (aza-DA) with an imine-based COF was reported by Yaghi and co-workers in 2018 [26]. In this seminal contribution, the imine-based **TPB-DMTP-COF** was reacted with different para-substituted ethinylbenzene derivatives in the presence of boron trifluoride as Lewis acid and chloranil as an oxidant in toluene at 110 °C to yield a series of different quinoline-containing COFs (Figure 1a). The formation of quinoline rings inside the COF network, although occurring with moderate conversions (27–35%), resulted in an extraordinary improvement in the chemical stability of the materials. The exploitation of all the possibilities offered by this [4 + 2] cycloaddition has become a topic of great interest that has also expanded to other related fields such as MOFs research [27].

Povarov's reaction not only made it possible to obtain materials resistant to acidic, basic, or redox agents but also allowed the introduction of new functionalities into **TPB-DMTP-COF** that paved the way for the subsequent post-synthetic modification of the COF. As a result, a series of different quinoline-based materials **QB-COF** (Figure 1a) have been designed, synthesized according to Yaghi's conditions, and evaluated for different purposes, such as the capture and sensing of pesticides [28,29], *cis*-diol molecules [30], radioiodine [31], fluoride anion [32], and methylmercury [33], and their use as electrocatalysts for oxygen evolution [34,35] or for the fabrication of batteries [35,36]. This approach has been also used to convert other imine-based COFs into the corresponding quinoline-based derivatives. Thus, Chen et al. used this strategy with a triazine-based COF for its application in lithium–sulfur batteries [37]. It is especially remarkable that aza-DA reactions carried out in imine-based COFs endowed them with propargyl moieties (Figure 1b). In this type of system, the cycloaddition reaction takes place intramolecularly to yield chromenoquinoline-functionalized COFs (**CQ-COF**, Figure 1b) with high chemical stability and with cyclization degrees of up to 90% [38].

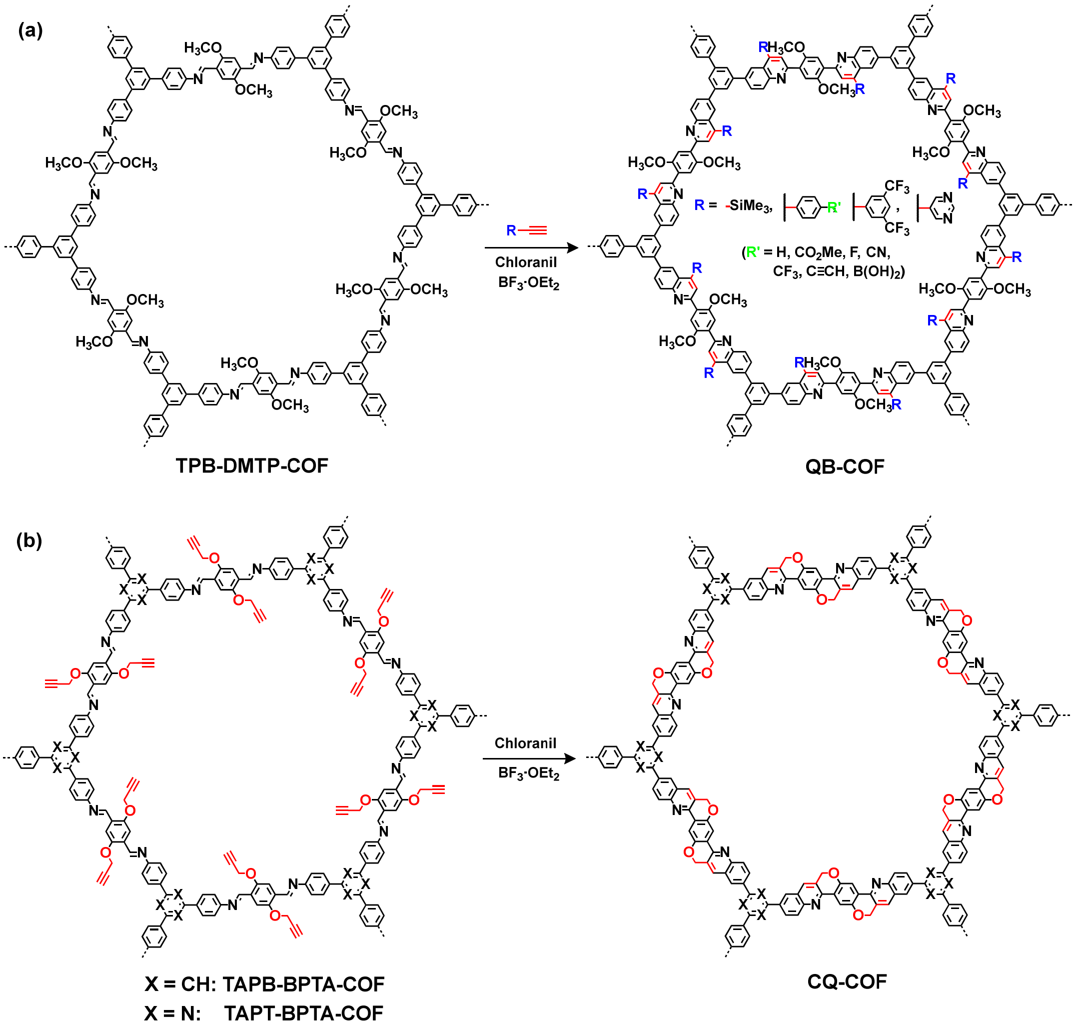

Figure 1. (**a**) PSM of imine-based **TPB-DMTP-COF** into quinoline-based COFs (**QB-COF**) via the Povarov reaction with alkyne derivatives [26,28–36]. (**b**) Intramolecular Povarov reactions of **TAPB-** and **TAPT-BPTA-COF** [38].

As has been mentioned, the Povarov reaction allows the introduction of new functional groups in the COF while reversible imine groups become irreversible. The interest generated in this PSM approach is such that substrates other than alkynes have been explored to obtain new advanced materials. To begin with, the use of alkenes as building blocks has made it possible to obtain quinolines in different degrees of oxidation depending on the reaction conditions. Thus, tetrahydroquinoline-containing COFs can be obtained when the Fe (III)-catalyzed aza-DA reaction is accomplished in the absence of oxidants [39], while quinoline-based **QB-COFs** containing phenyl rings as substituents are obtained when the reaction is performed with styrene in presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and $BF_3{\cdot}OEt_2$ [21].

The Povarov reaction with alkenes as reagents has not only been successful when applied on COFs resulting from the condensation of 1,3,5-tris(4-aminophenyl)benzene (**TAPB**) or 4,4′,4″-(1,3,5-triazine-2,4,6-triyl)trianiline (**TAPT**) with a terephthalaldehyde derivative but has also been applied effectively on other networks, including the 3D-COF **PYTRI-COF-1** shown in Figure 2a. Under the same oxidative conditions, the treatment of **PYTRI-COF-1** with styrene resulted in **PYTRI-COF-2**, more stable and with a higher π-conjugated system, which showed high lithium-ion storage capacity when tested for battery application (Figure 2a) [40]. Another interesting example was published by Guan et al., creating porous hydrophilic **COF-Qs** materials by reacting the aryl imine-based **COF-LZU1** with various enamides in the presence of iron trichloride as a catalyst for further evaluation in oil–water separation (Figure 2b) [41]. The latter example is particularly noteworthy because, despite the formation of pyridoquinoline residues, requiring a reconfiguration of the imine bonds, the resulting materials retained their crystalline structure.

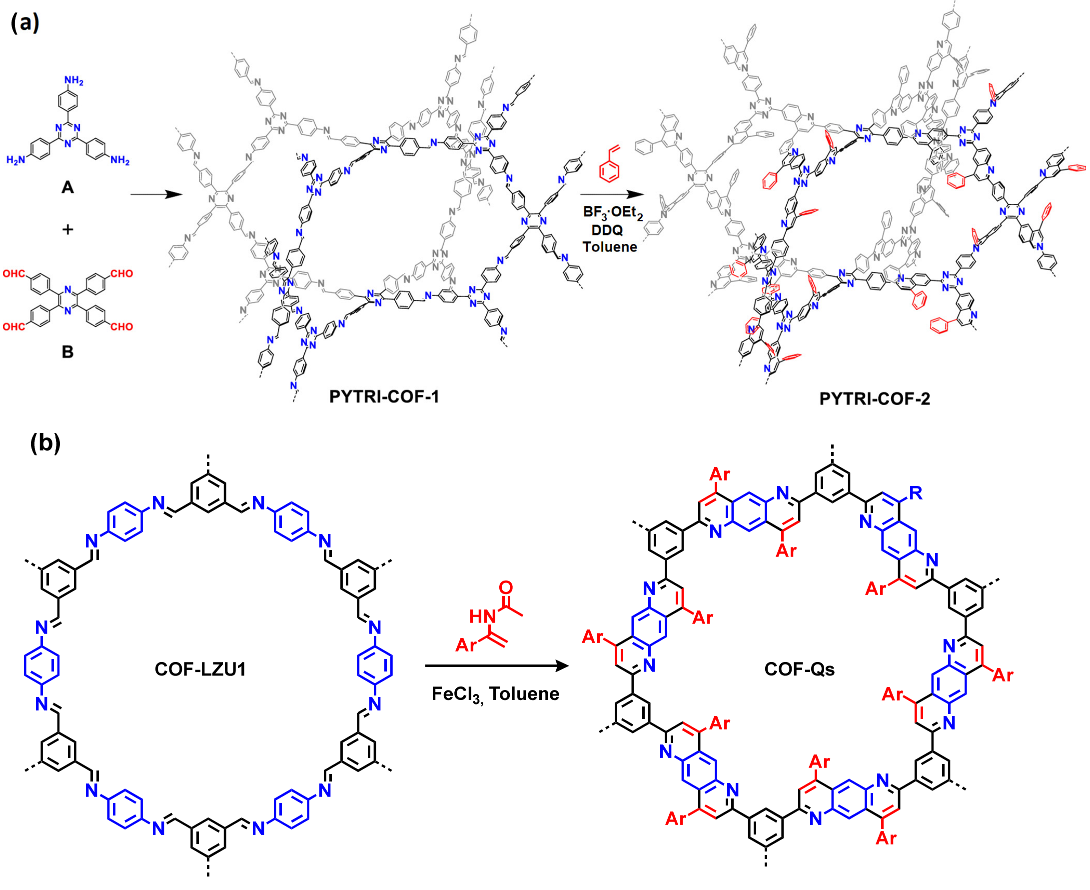

Figure 2. (**a**) Synthesis and PSM of **PYTRI-COF-1**. Adapted with permission from *ACS Appl. Mater. Interfaces* **2023**, *15*, 830–837 (Ref. [40]). Copyright 2023 American Chemical Society. (**b**) Fe(III)-catalyzed Povarov reaction with diverse enamines. Adapted with permission from *Chemical Engineering Journal* **2022**, *448*, 137,687 (Ref. [41]), published by Elsevier.

As mentioned in the introduction, a growing trend in this field of research is to obtain robust and ultrastable 2D crystalline materials by multicomponent one-pot (OP) reactions, in which the COF and its subsequent modification are carried out in a single synthetic step. Despite the arduous and demanding work involved in optimizing this type of operation, the use of OP methodologies helps to reduce reaction times, simplifies the elaboration and purification processes, and leaves the way free to synthesize certain materials that are not possible to obtain by PSM [42]. Quinoline-based COFs have already been constructed employing OP strategies, the first example having been reported in 2020 by Dong and coworkers, where different crystalline materials were obtained in a one-pot procedure by the three-component Povarov reaction between **TAPB**, a terephthalaldehyde derivative, and styrene or dihydropyran as reagents (Figure 3a) [21]. The reaction conditions are particularly remarkable because the cyclized COFs are formed in the same reaction times as the corresponding imine-based materials using the same solvents but adding the corresponding alkene, Lewis acid, and oxidant. Thus, the formation of the crystal lattice is advanced before the [4 + 2] cycloaddition process blocks the reversibility of the Schiff base. Since this first report, other examples of OP approaches for obtaining **QB-COF** derivatives, using other reagents or reaction conditions, have been reported (Figure 3a) [43,44]. These three-component OP Povarov reactions have not only been used for obtaining **QB-COF**-type structures but have also been employed for the synthesis of porphyrin- and quinoline-containing and fully conjugated networks, which have been tested as photoactive materials for various purposes such as CO_2 activation and C-C scission, with promising results [45,46]. Such is the interest generated by these one-pot COF methodologies that the synthesis of different chromenoquinoline-functionalized COFs in a single step by promoting an intramolecular cascade sequence promoted by the addition of scandium triflate to the reaction mixture containing a mixture of the corresponding *O*-*p*-tolylpropargyl salicyaldehyde and a multitopic aniline has already been described (Figure 3b). As discussed above in the OP synthesis of **QB-COF**, intramolecular cyclization and subsequent oxidation take place after the formation of imine-based COFs (Figure 3b) [47]. All these COFs obtained by OP showed excellent crystallinity, stability, and porosity parameters, as did the corresponding analogous compounds synthesized by PSM, so it is expected that the number of published protocols for obtaining different 2D crystalline materials will increase in a short period of time.

2.2. Other Reactions for the Synthesis of Quinoline-Based COFs

As shown in the previous section, the Povarov and related aza-DA reactions are of special interest among different researchers because they allow the attainment of ultra-stable COFs based on quinolines with different functionalities and applications. However, the limitations encountered in the introduction of different functionalities have encouraged research on obtaining such materials, with other catalyzed or metal-free procedures that allow access to other stable quinoline-based networks from Schiff-based crystalline materials having been published.

In addition to the fact that metal catalysis has yielded an immeasurable number of molecules, its application in COFs has also been successful as a PSM strategy. Apart from CuAAC, other metal-mediated reactions have been applied for PSM and, in addition, have been effective for the stabilization of COFs through the formation of heterocyclic rings on crystal lattices. Particularly noteworthy is the rhodium-catalyzed [4 + 2] annulation of imine-bridged COFs with vinylene carbonate, published by Xiang et al. [48,49]. Contrary to the Povarov reactions detailed in Section 2.1, this Rh-catalyzed oxidant-free dehydrogenative procedure allows one, thanks to the use of ethylene carbonate as a reagent, to obtain, by PSM, unsubstituted quinoline-linked COFs such as **NQ-COFA1**, as shown in Figure 4, which has shown promising results as a photocatalyst [48]. Similar to the Povarov and oxidative cyclizations, the synthesis of the same quinoline-based unsubstituted COF has also been achieved in a one-step cascade process by adding the necessary reagents for PSM and magnesium sulfate to the monomer mixture, proving that the presence of this salt proved crucial for the correct course of imine formation and subsequent Rh-catalyzed annulation (Figure 4) [49]. In this case, it is also particularly striking that the crystallinity of **NQ-COFA1** obtained by OP is higher than that obtained by PSM.

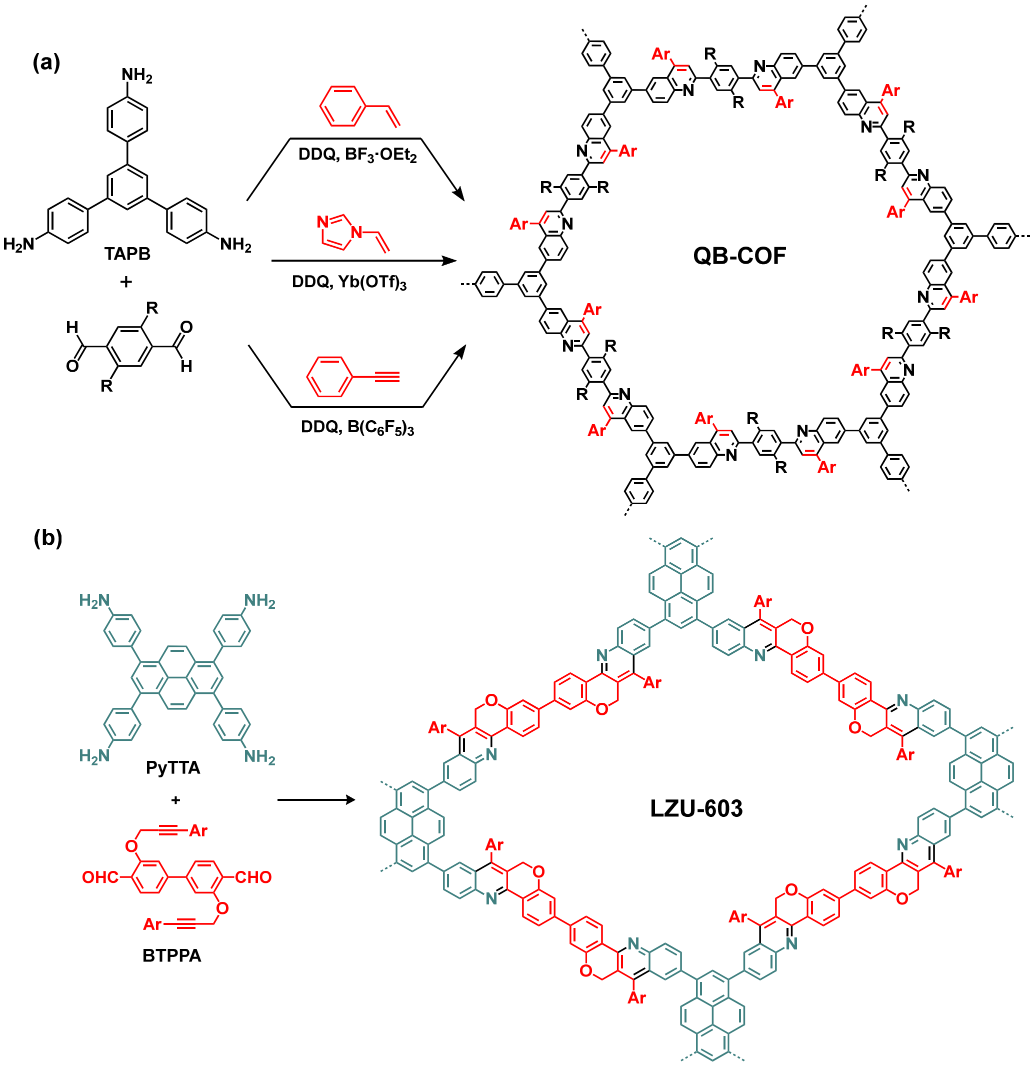

Figure 3. Examples of the OP synthesis of quinoline-based COFs. (**a**) OP multicomponent reactions for obtaining **QB-COF**. (**b**) OP cascade reaction for obtaining an example of chromenoquinoline-functionalized COF **LZU-603** [47].

Other cyclization reactions carried out on imine-based COFs are metal-free and have resulted in stabilized quinoline networks with architectures or substituents that could not be obtained by aza-DA reactions. One case is that reported by Cai et al., where 4-carboxyl-quinoline-linked COFs were obtained by both PSM and OP procedures via the Doebner reaction [50]. Although only two materials have been described and evaluated for use in nanofiltration, the authors claim the universal applicability of the reaction of imine-based networks with pyruvic acid.

Finally, oxidative cyclizations have proven, as will be seen in the next section, to be a powerful tool for the stabilization of imine-bound COFs. A special case was published by Zhao and co-workers, applying the Pictet–Spengler reaction on **B-COF-1** and **T-COF-1** (Figure 5) [51]. In both materials, the carbon atoms of the imine groups reacted with the β-carbon of the thiophene rings, giving rise to the fully π-conjugated thieno [3,2-*c*]pyridine-linked COFs **B-COF-2** and **T-COF-2** (Figure 5). As expected, the blocking of the imine bond led to an improvement in the chemical stability of the new materials and, in the specific case of **T-COF-2**, efficient photoenzymatic catalytic activity was observed thanks to its electronic structure.

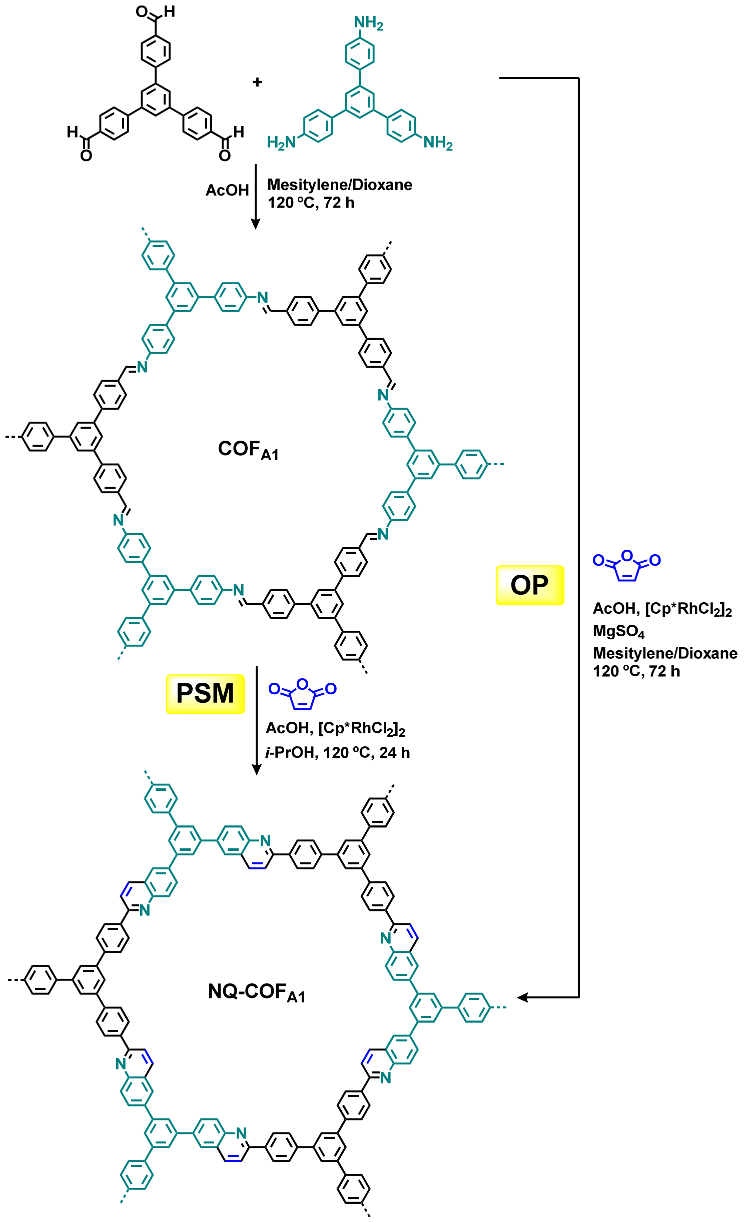

Figure 4. Rhodium-catalyzed production of quinoline-based COFs by PSM and OP methodologies.

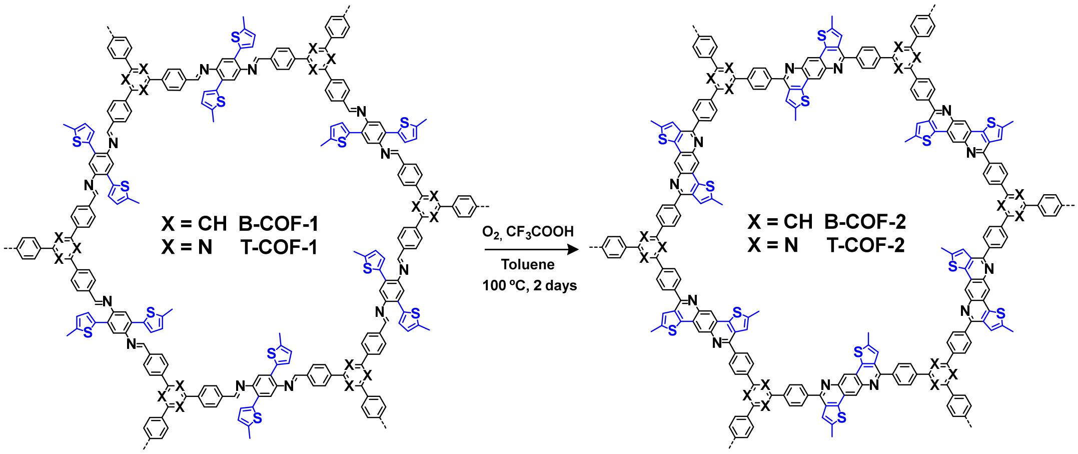

Figure 5. Pictet–Spengler oxidative cyclization of **B-COF-1** and **T-COF-1** [51].

2.3. Intramolecular Oxidative Cyclization Reactions

The formation of quinoline rings by Povarov and the other reactions shown are not the only ones that have allowed the modification of the pristine network of imine-based COFs. Prior to them, intramolecular oxidative cyclizations began to be explored as a powerful tool to stabilize this class of covalent organic structures by converting reversible imine bonds into irreversible ones. Although these reactions are not useful for the introduction of new functionalities within COF networks, the extension of π-electron delocalization allows their application as photoactive materials, with some of the following networks being studied as photocatalysts or enhancers of different processes.

The intramolecular oxidative cyclization of imine-based COFs is possible when a nucleophilic group is anchored at the ortho position of the imine, thus obtaining different COFs based on benzofused heterocyclic systems. However, in practice, obtaining this type of material has been a challenge because intramolecular cyclization is prone to take place before the crystal lattice is formed, transforming the reversible imine bonds into irreversible ones and obtaining amorphous polymers [52]. For this reason, obtaining benzoxazole and benzothiazole networks from imine-based COFs was first tackled by starting with materials lacking the nucleophile moiety, introducing the reactive functionality in a subsequent step, such as linker exchanges [53] or by the introduction of a sulfur atom in the COF structure [54,55], and finally causing oxidative cyclization. It is worth mentioning the post-synthetic oxidative cyclization reported by Baek et al., in which **I-COF** (Figure 6), a poor stable crystalline material containing the deprotected nucleophile in the appropriate position relative to the imine group for the intramolecular cyclization, was synthesized, isolated, characterized, and subsequently transformed post-synthetically into the respective stable benzoxazole derivative **BO-COF** by DDQ treatment (Figure 6) [56].

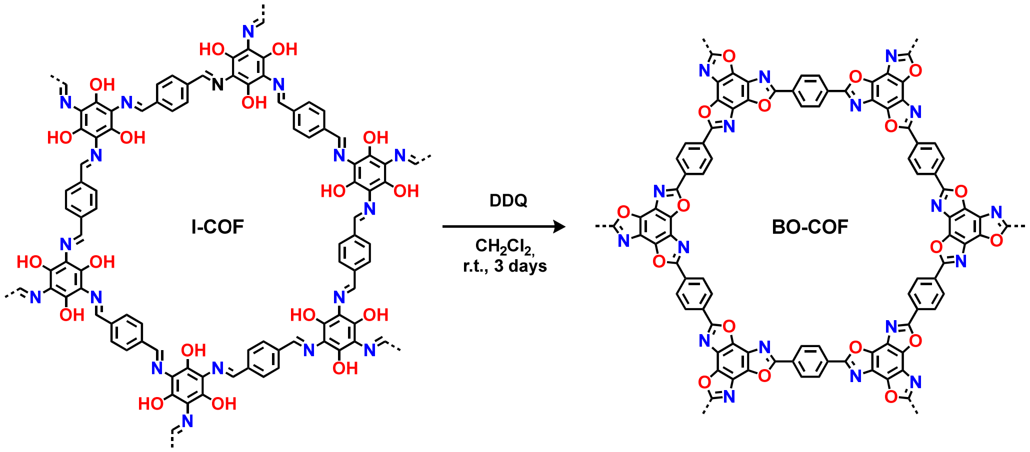

Figure 6. PSM oxidative cyclization of **I-COF** for the synthesis of **BO-COF.** Adapted with permission from *J. Am. Chem. Soc.* **2019**, *141*, 22, 11786–11790 (Ref. [56]). Copyright 2019 American Chemical Society.

The synthesis of analogous materials containing indazole and benzimidazolylidene moieties has also been explored by employing the Cadogan reaction, an efficient method for the synthesis of various indole and aza-indole derivatives [57]. The indazole-based COF termed **TPB-indazole-COF** was prepared from the *o*-nitroaryl imine **TPB-imine-COF** in a cascade process involving (1) the reduction of the nitro group in the presence of tributylphosphine and (2) subsequent cyclization (Figure 7a) [58]. Contrary to other PSM COF cyclizations, full conversion of the product was achieved in a few hours and with a PXRD pattern similar to that of the starting material. The same **TPB-indazole-COF** was profitably obtained in a one-pot procedure from the corresponding monomers under practically the same reaction conditions under which PSM was accomplished, with only a slight decrease in crystallinity being observed relative to the stepwise material prepared. An example of the potential advantages of OP methodologies over PSM is revealed in the same article published by Yang et al. [58], where the Cadogan reaction failed when attempting to prepare benzimidazolylidene containing **BIY-COF** from **Ketoenamine-NO_2-COF**, but succeeded when the reaction between 2,4,6-trimethoxybenzene-1,3,5-tricarbaldehyde and 3,3′-dinitrobenzidine was carried out in the presence of tributylphosphine (Figure 7b).

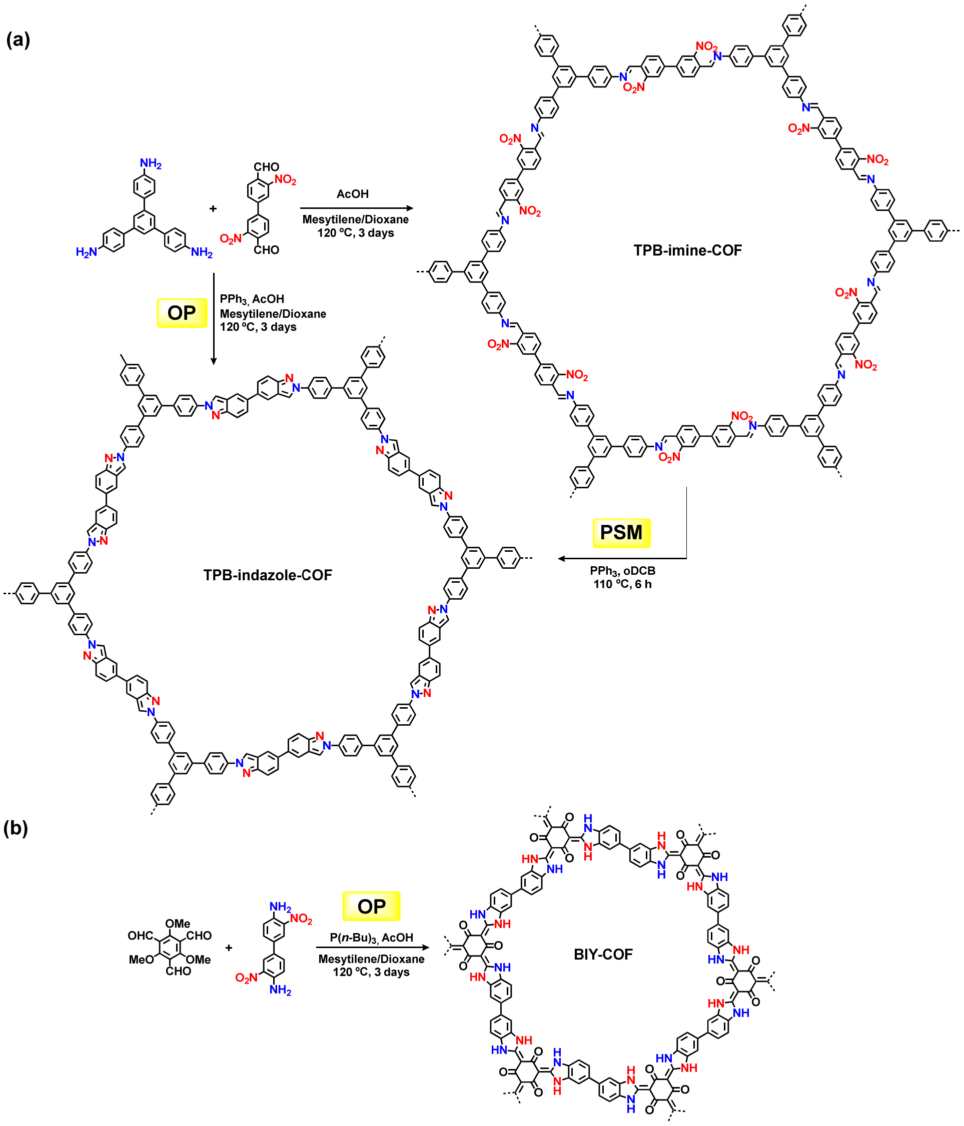

Figure 7. (**a**) Transformation of **TPB-imine-COF** into **TPB-indazole-COF** by the Cadogan reaction via PSM and OP. (**b**) Synthesis of **BIY-COF** by OP.

The synthesis of **TPB-indazole-COF** and benzimidazolylidene **BIY-COF** are not the first examples of the synthesis and oxidative cyclization of COFs in a single step. As previously mentioned, obtaining indazole, benzothiazole, and benzoxazole derivatives involves arduous optimization work to avoid the formation of irreversible bonds before the material is crystalline. The OP synthesis of three benzoxazole-linked COFs was successfully described by Wang through cascade reactions involving imine-formation, cyclization, and oxidative dehydrogenation [59]. This procedure has further been employed to obtain other benzoxazole-based materials both for photocatalysis [60] and other applications such as photoenhanced uranium recovery [61,62] and solar desalination [62]. Cascade one-pot processes for the acquisition of different photoactive benzothiazole-linked COFs have also been successfully optimized, being a process that implies firstly the formation of the imine-linked COF followed by the addition of thiol functionality, cyclization, and an ulterior oxidative process [63,64].

3. Conclusions and Prospects

Currently, research on covalent organic frameworks continues to be of great interest and the activity of creating new networks is of fundamental importance for obtaining new high-value materials. As reported, the stabilization of networks by converting reversible bonds into irreversible ones by cyclization is an effective strategy that allows for the modification of chemical and electronic properties, further maximizing the potential application of these materials. Early examples of the stabilization of imine-based COFs consisted of oxidative cyclizations leading to benzoxazole, benzothiazole, and indazole derivatives and whose extended π-delocalization has enabled their use as photoactive materials. However, the synthetic strategy that appears to be a prolific focus of research at present is Povarov, related aza-Diels–Alder reactions, and the remaining annulations that produce quinoline-based COFs, either via PSM or OP approaches. These methods not only give rise to ultra-stable networks with a conjugated electronic structure but also allow the introduction of different functional groups, which enhances the potential applications of this type of material. Undoubtedly, a considerable number of new articles using any of these transformations will be published in the near future.

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Abbreviations

AcOH: acetic acid; aza-DA: aza-Diels–Alder; COF: covalent organic framework; CuAAC: copper-catalyzed 1,3-dipolar azide-alkyne cycloaddition; DDQ: 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; MOF: metal–organic framework; oDCB: *o*-dichlorobenzene; OP: one pot; PSM: post-synthetic modification.

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