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Review

Organoselenium Catalyzed Reaction: Sustainable Chemistry from Laboratory to Industry

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Abstract: Selenium catalysis has emerged as a powerful and sustainable approach for diverse organic transformations, including oxidations, halogenations, and C–H functionalizations. This review highlights its advantages—mild reaction conditions, high selectivity, and compatibility with green oxidants—while emphasizing industrial application potential through heterogeneous and recyclable catalytic systems. Beyond direct catalytic roles, selenium also enhances catalyst performances in energy and environmental applications. By reducing reliance on toxic metals and enabling atom-efficient processes, selenium catalysis aligns with sustainable engineering principles, offering eco-friendly solutions for chemical synthesis. Finally, prospects for scalable industrial implementation are discussed.

Keywords: selenium; catalysis; fine chemical; green chemistry; oxidation

1. Introduction

Selenium is an important trace element for human beings [1–4]. It has been shown to have good chemical and bio-activities and has been widely utilized in both organic synthesis, medicinal chemistry, and materials science [5–16]. Over the past century, significant research has focused on the synthesis of organoselenium compounds [17–31]. In recent years, their catalytic activities have attracted growing interest [32–39]. Organoselenium catalysts present several compelling advantages compared to traditional transition metal catalysts. Firstly, since selenium is an essential trace element that can be metabolized by organisms, these catalysts eliminate the need for the stringent safety measures typically required when handling toxic transition metals. It should be noticed that people's understanding of the toxicity of selenium has begun to change, and the tolerance for selenium residues in products has gradually been relaxed. The most typical example is that the latest standard for selenium-enriched agriculture product (T/HNFX001-2017) has removed the upper limit of selenium content. Secondly, organoselenium-catalyzed reactions often proceed through simple and clean procedures, with water frequently being the sole byproduct, making them environmentally favorable. Moreover, these catalysts demonstrate remarkable stability and robustness, exhibiting resistance to common poisoning effects that plague metal-based systems. Another practical benefit lies in their recyclability, as many organoselenium catalysts can be readily recovered and reused without significant loss of activity. From an economic perspective, selenium's relative abundance renders it substantially more cost-effective than precious noble metals like palladium or platinum. Perhaps most intriguingly, the unique reactivity profile of organoselenium compounds may unlock novel synthetic pathways, offering fresh opportunities for methodological development in organic synthesis.

Selenium is a chalcogen element, but its properties are significantly different from those of sulfur. The atomic radius of selenium is larger than that of sulfur, which makes its bound valence electrons looser. Therefore, selenium is more easily oxidized than sulfur. However, the larger hybrid orbitals and longer bond length of the selenium-oxygen double bond result in weaker π bonds, making it more easily reducible. Thus, organoselenium compounds may act as an "oxygen carrier" to catalyze the oxidation reactions. Currently, organoselenium catalysts have been effectively employed for epoxidations, dihydroxylations, halo-hydroxylations, halo-lactonizations and halo-amidations of alkenes. They have also been shown effective in Baeyer-Villiger reactions, the oxidations and halogenations of aromatic, allylic or α-C-H bonds of carbonyls. Oxidation of hydroxide, amidogen and sulfides are also known. Recent progress showed that organoselenium catalysis might have much more comprehensive application scope with great industrial potential in green synthesis. The engineering of selenium-based catalytic technologies is just unfolding, with polymer-supported organoselenium catalysts emerging as a noteworthy development. The inherent advantages of polymeric supports—including versatile processability into various forms such as granules, films, textiles, and porous plates, coupled with their robust stability that prevents leaching of active sites—make them exceptionally suitable for diverse reactor configurations including fixed-bed, fluidized-bed, and microreactor systems. Through deliberate polymer molecular design, researchers can precisely modulate material properties such as thermal stability and solvent resistance, thereby significantly enhancing their industrial viability. Remarkably, these polymer-supported catalysts demonstrate unique catalytic behaviors that differ fundamentally from their small-molecule analogues [33]. A striking example is the polymeric matrix's ability to stabilize reactive Se(VI) and Se(II) species by preventing their disproportionation to the less active Se(IV) state [33]. This stabilization effect substantially boosts catalytic activity, particularly in molecular oxygen activation processes, enabling the practical use of ambient air as an oxidant—a development that dramatically reduces costs while improving safety profiles for industrial applications. Furthermore, alternative supporting materials such as inorganic matrices offer additional pathways for cost-effective catalyst preparation, collectively advancing the prospects for industrial implementation of selenium catalysis.

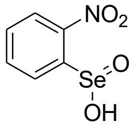
Despite a steady stream of review articles documenting advances in selenium catalysis over the past decade [32–39], the literature remains dominated by narrowly focused mini-reviews that largely overlook the critical discussion of industrial applications. This conspicuous gap underscores the pressing need for a comprehensive review that systematically examines both fundamental developments and technological translation of selenium catalysis. This paper aims to address this need by thoroughly analyzing selenium catalyst technologies and their industrial potential, offering researchers and industrial practitioners a much-needed perspective on this evolving field. The discussion encompasses not only the scientific fundamentals but also the practical considerations that bridge laboratory-scale innovations to industrial-scale applications.

2. Reactions of Alkenes

The organoselenium-catalyzed reactions of alkenes involve epoxidation reactions, dihydroxylation reactions, electrophilic addition reactions and oxidative cracking reactions. They can be employed to synthesize difuctional compounds or carbonyls.

2.1. Expoxidation Reactions

The pioneering work of Sharpless and colleagues in the 1970s marked a significant milestone in organoselenium chemistry with their report on the stoichiometric selenium-mediated epoxidation of alkenes [40–42]. While this early system required stoichiometric amounts of organoselenium reagents, it fundamentally established the potential of selenium-based transformations in organic synthesis. A major advancement came when Reich and coworkers demonstrated the first truly catalytic application of organoselenium compounds, successfully employing nitroaromatic selenium catalysts **1** and **2** (Figure 1) in olefin oxidation reactions using hydrogen peroxide as the terminal oxidant [43]. Addressing the critical issue of selenium leaching, Taylor subsequently developed polymer-immobilized organoselenium catalyst **3** (Figure 1), representing an important step toward practical applications by enabling catalyst recovery and minimizing metal contamination in products [44]. These foundational studies collectively established the framework for modern selenium catalysis research.



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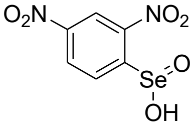

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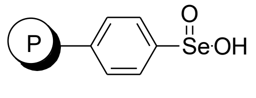

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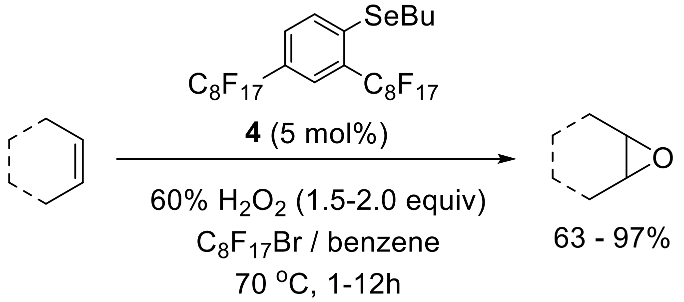
Figure 1. Organoselenium catalysts **1**, **2** and **3**.

Immobilizing the catalyst on an insoluble polymer not only prevented selenium contamination of the reaction products but also enabled efficient catalyst recycling. In 1999, Knochel et al. reported the organoselenium-catalyzed epoxidation of alkenes in perfluorinated solvents, which allowed for catalyst recovery through liquid-liquid extraction (Scheme 1) [45]. The reaction proceeded homogeneously at 70 °C, while cooling to 25 °C induced phase separation between the organic and fluorous layers, permitting straightforward isolation of the catalyst from the fluorous phase. Notably, the catalyst can be reused up to ten times without significant loss of activity. Although this method demonstrated broad substrate compatibility, cyclododecene and octahydronaphthalene unexpectedly yielded only *trans*-diols instead of the desired epoxides.



Scheme 1. Organoselenium-catalyzed epoxidation of alkenes in perfluorinated solvents.

The preceding studies demonstrated that organoselenium catalysts bearing electron-withdrawing groups exhibited superior performance in epoxidation reactions. In 2001, Sheldon et al. conducted a systematic investigation of catalyst substituent effects for the epoxidation of cyclohexene [46]. Through comprehensive screening of various catalyst precursors (Figure 2), bis[3,5-bis(trifluoromethyl)phenyl] diselenide (**5**) emerged as the most effective pre-catalyst. In the reaction, diselenides were initially oxidized to corresponding selenious acids, which are the actual catalysts for the reaction. Under optimized reaction conditions, this catalyst system achieved near-quantitative conversion of cyclohexene to its corresponding epoxide.

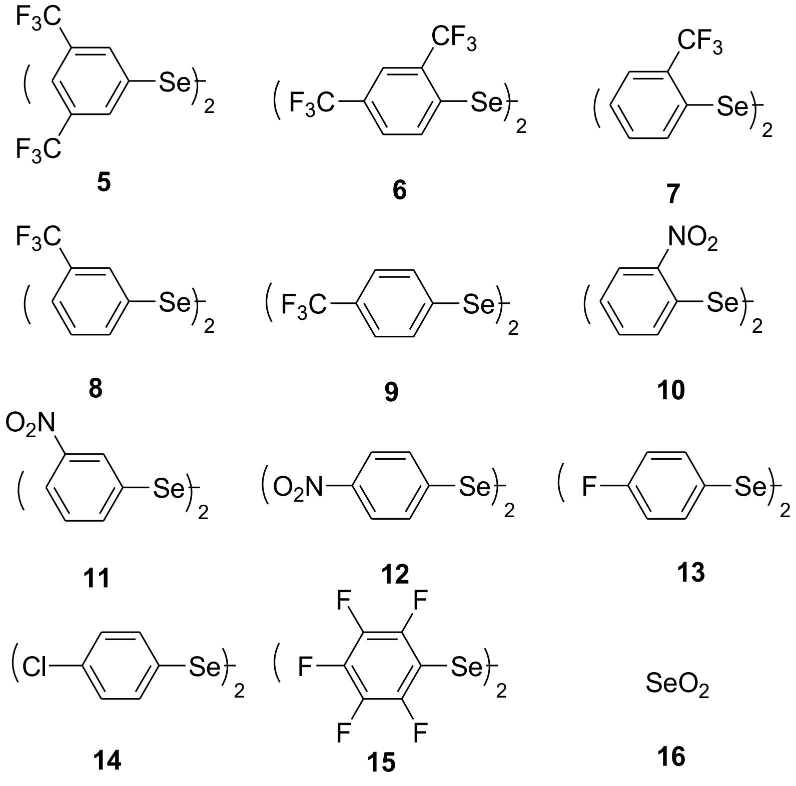
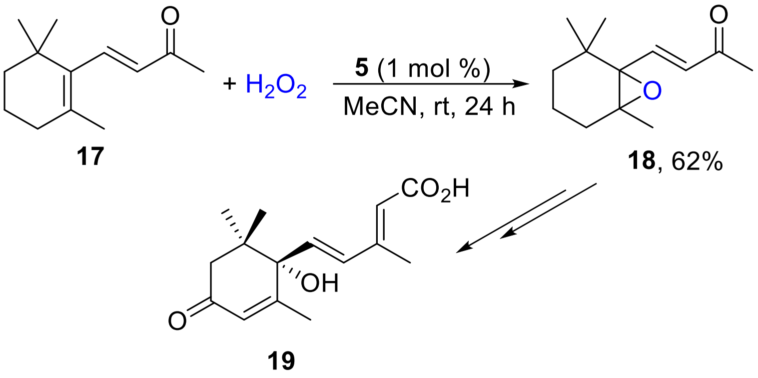


Figure 2. Organoselenium catalyst precursors **5**–**16**.

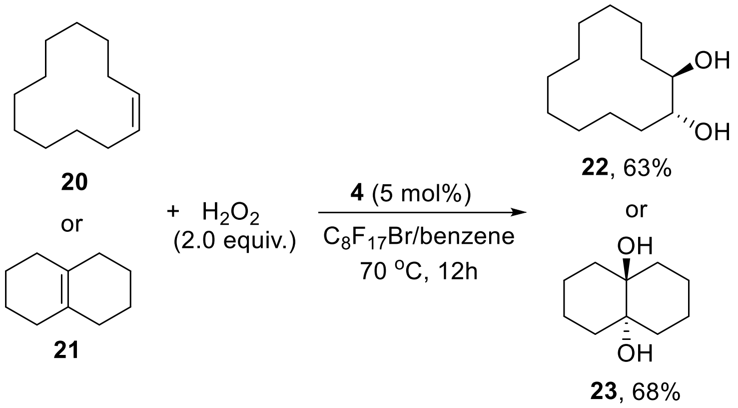
Epoxides are widely prevalent in pharmaceutical intermediates and natural products. For instance, an epoxide intermediate was employed in the total synthesis of the plant hormone abscisic acid. This intermediate can be synthesized through organoselenium-catalyzed epoxidation of *β*-ionone [47]. In this reaction, the electron-deficient diselenide **5** was again identified as an effective catalyst precursor for the epoxidation. Under optimized conditions with 1 mol% of diselenide **5**, *β*-ionone (**17**) underwent efficient oxidation with hydrogen peroxide to afford epoxide **18**. This key epoxide intermediate can be further transformed to complete the synthesis of abscisic acid (**19**) (Scheme 2). In some cases, the epoxidation reaction of C=C may trigger the subsequent rearrangements. For example, in the organoselenium-catalyzed reaction of methylenecyclopropanes, the ring enlargement reactions occur leading to the production of cyclobutanone as the major product[48].



Scheme 2. Organoselenium-catalyzed epoxidation of β-ionone.

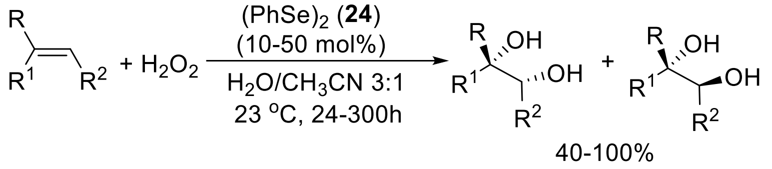
2.2. Dihydroxylation Reactions

In 1999, Knochel et al. reported the organoselenium-catalyzed dihydroxylation of alkenes (Scheme 3) [45]. Catalyzed by organoselenide (**4**), both (Z)-cyclododecene (**20**) and 1,2,3,4,5,6,7,8-octahydronaphthalene (**21**) could be oxidized by hydrogen peroxide to afford 1,2-diols **22** and **23**, respectively. The diols are the hydration product of epoxides, which are generated by the first-step reaction during the process. Notably, the resulting diols exclusively adopted the *trans*-configuration, which can be rationalized by the reaction mechanism involving initial epoxide formation followed by the attack of water from the backside during hydrolysis. However, since the primary objective of this study focused on epoxide synthesis with diols being merely byproducts, these particular transformations were not subjected to systematic investigation despite their mechanistic significance.



Scheme 3. Oxidation of cyclododecene or octahydronaphthalene.

1,2-Diols are valuable industrial intermediates, and developing efficient synthetic methods to access these compounds remains an active research area. In 2008, Santi et al. reported a diphenyl diselenide (**24**)-catalyzed reaction between alkenes and hydrogen peroxide to synthesize 1,2-diols (Scheme 4) [49]. Using acetonitrile as a solvent (chosen for its ability to dissolve both organic and aqueous phases), the reaction proceeded under mild conditions, affording 1,2-diols in moderate to excellent yields. However, the reaction speed was notably slow, sometimes requiring up to 300 h for completion. To improve the reaction rate, the authors increased the catalyst loading to as much as 50 mol%.



Scheme 4. Diphenyl diselenide catalyzed dihydroxylation of alkenes.

Building on their previous work, the Santi group explored the enantioselective dihydroxylation of alkenes using chiral organoselenium catalysts. They designed three optically active pre-catalysts (**25**–**27,** Figure 3) and evaluated their performance in asymmetric dihydroxylation reactions [50,51].

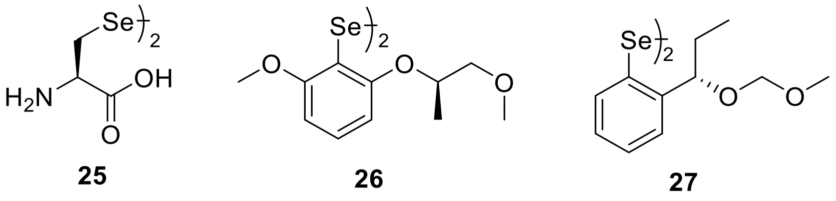
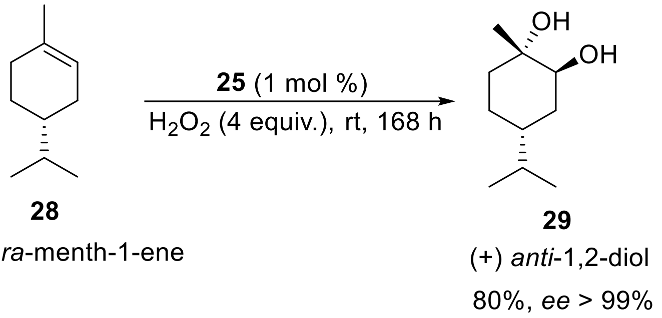


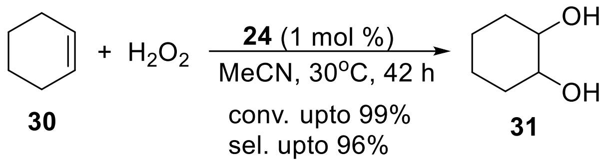
Figure 3. Optically pure catalyst precursors **25**, **26** and **27**.

Notably, when employing **25** as the catalyst, the dihydroxylation of (+)-*para*-menth-1-ene (**28**) proceeded with excellent enantioselectivity, achieving up to 99% ee (Scheme 5). This result demonstrated the potential of organoselenium catalysts in stereocontrolled synthesis. However, the system exhibited limited substrate generality. For instance, when applied to styrene—a common benchmark substrate in asymmetric dihydroxylation—the reaction failed to induce significant enantioselectivity, yielding a racemic mixture [51,52]. This inconsistency suggests that the catalytic efficiency and stereocontrol of the selenium-based system may be highly dependent on the alkene's structural features, such as steric hindrance or electronic properties. Further mechanistic studies could help elucidate the factors governing selectivity and expand the substrate scope.



Scheme 5. Asymmetric dihydroxylation of (+)-para-menth-**1**-ene (**28**).

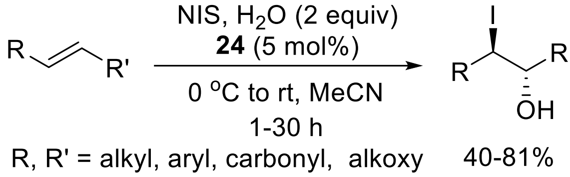
Cyclohexene (**30**), a readily available industrial feedstock, is commonly produced via the selective hydrogenation of benzene [53]. The dihydroxylation of **30** to form *trans*-cyclohexane-1,2-diol (**31**) is a strategically important transformation, as **31** serves as a key intermediate in the synthesis of high-value fine chemicals. Notably, **31** can be further converted into adiponitrile via ammonia-mediated oxidation, an attractive route for adiponitrile production that bypasses traditional petroleum-derived precursors [54]. The dihydroxylation reaction of **30** can be efficiently catalyzed by organoselenium compounds under mild and environmentally benign conditions (Scheme 6) [55]. Notably, using just 1 mol% of diphenyl diselenide (**24**) as the catalyst precursor, the reaction of **30** with hydrogen peroxide in acetonitrile proceeded cleanly, affording **31** in excellent yield (99% cyclohexene conversion, 96% diol selectivity). In the process, water in aqueous H_2O_2 (30%) facilitates the ring-open reaction of the intermediate epoxide to produce **31**. However, the reaction suffered from sluggish kinetics, requiring **42** h for completion. Subsequent studies revealed that employing the electron-deficient catalyst precursor **5** significantly accelerated the process, reducing the reaction time to just 5 h while maintaining high efficiency [56].



Scheme 6. Organoselenium-catalyzed synthesis of cyclohexane-1,2-diol.

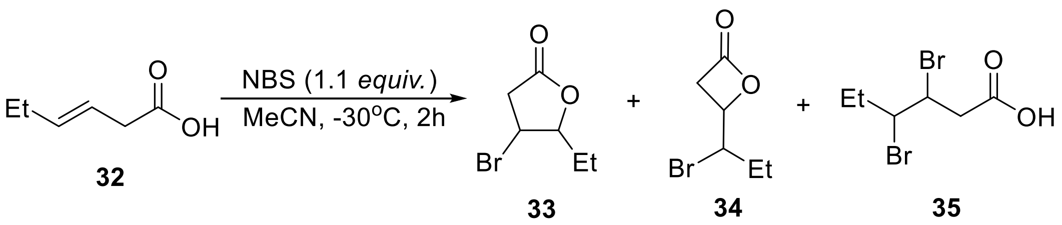
2.3. Electrophilic Addition Reactions

The simultaneous introduction of two distinct functional groups is a powerful strategy in organic synthesis, enabling efficient and selective transformations to synthesize functionalized compounds. In the field of organoselenium catalysis, a notable example was reported by Seoane et al. in 2006, who developed a diphenyl diselenide (**24**)-catalyzed iodo-hydroxylation of olefins (Scheme 7) [57]. While the reaction proceeds even in the absence of the catalyst, the addition of diphenyl diselenide significantly enhances its efficiency—reducing reaction time while improving product yield. Importantly, the stereoselectivity of the transformation remains unaffected by the catalyst, suggesting that diphenyl diselenide primarily accelerates the reaction without altering the mechanistic pathway. This method offers a practical approach to vicinal iodo-alcohol synthesis, which are valuable intermediates in medicinal and materials chemistry. Further studies could explore the scope of this catalytic system, including its applicability to more complex substrates and potential asymmetric variants.



Scheme 7. Organoselenium-catalyzed iodine-hydroxylations of alkenes.

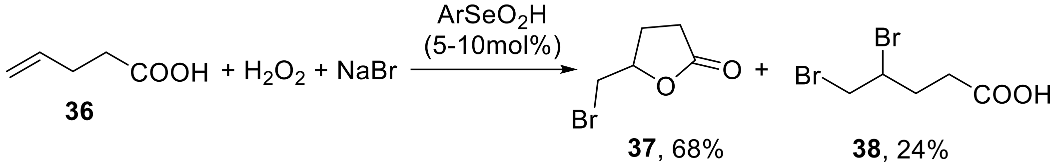
The incorporation of organoselenium catalysts in halo-lactonization reactions has proven particularly valuable for improving both reactivity and selectivity. A representative example is the bromo-lactonization of (*E*)-hex-3-enoic acid **32** (Scheme 8) [58]. When conducted with 5 mol% of diphenyl diselenide (**24**) as catalyst, the reaction demonstrates remarkable regioselectivity, favoring 5-*endo* cyclization over the alternative 4-*exo* pathway by an impressive 17:1 ratio of **33** vs. **34**, but a small amount of chain product **35** was also generated. This catalytic enhancement is mechanistically significant, as uncatalyzed versions of such transformations typically show lower selectivity between competing cyclization modes. The selenium catalyst likely facilitates halonium ion formation while simultaneously directing the nucleophilic attack of the carboxylate to the more substituted carbon, thereby promoting endo-cyclization.



	33	34	35
no catalyst	2	1	0
with 5 mol % of $(PhSe)_2$	17	1	2

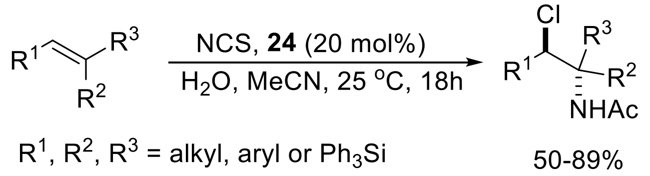
Scheme 8. Diphenyl diselenide catalyzed cyclization of (E)-hex-3-enoic acid.

A highly atom-economical bromocyclization strategy has been developed using organoselenium catalysts in combination with sodium bromide and hydrogen peroxide. This catalytic system enables the in situ generation of reactive bromonium (Br^+) species via the oxidation of sodium bromide, offering distinct advantages over conventional *N*-bromosuccinimide (NBS) methods from the atom economy perspective [59–60]. The process generates only environmentally benign byproducts (sodium hydroxide and water), representing a greener alternative to traditional bromination reagents. For example, arylseleninic acid-catalyzed the bromo-cyclization of pent-4-enoic acid (**36**) led to the intramolecular cyclization adduct **37** in 68% yield, with the generation of by-product **38** in 24% yield (Scheme 9) [60]. Similarly, the reaction could also be well-catalyzed by organoselenoxides [61]. Moreover, by which xerogel-sequestered selenoxide catalysts, the reaction could be performed under aqueous conditions [62].



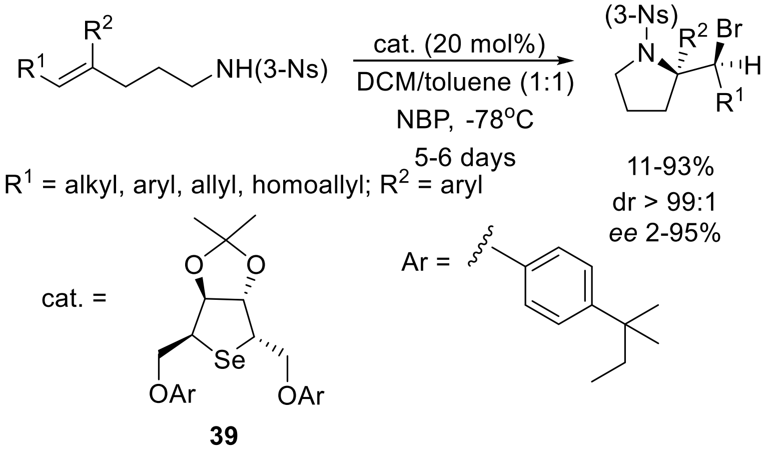
Scheme 9. Organoselenium-catalyzed cyclization.

Traditional approaches to halo-amidation reactions have predominantly relied on Lewis acid catalysts, some of which often require harsh reaction conditions and demonstrate limited compatibility with acid-sensitive functional groups. A significant breakthrough was achieved by Yeung and coworkers through their development of a diphenyl diselenide (**24**)-catalyzed halo-amidation protocol (Scheme 10) [63]. The catalytic system operates under exceptionally mild conditions (25 °C), making it compatible with a broad spectrum of functional groups and structurally diverse substrates. Moreover, water was employed as partial solvent, leading to a relatively safe and green conditions for large-scale preparation considerations. Catalyzed by chalcogen, similar transformations could be applied on the terminal difluoro-substituted alkenes, affording the convenient access to related functionalized fluorin-containing organic compounds [64]. Besides, organoselneium-catalyzed electrophilic addition reactions could be employed to introduce sulphur [65–68]. It can be applied intramolecularly to synthesize a series of caboncycles **67** or heterocycles [69–71].

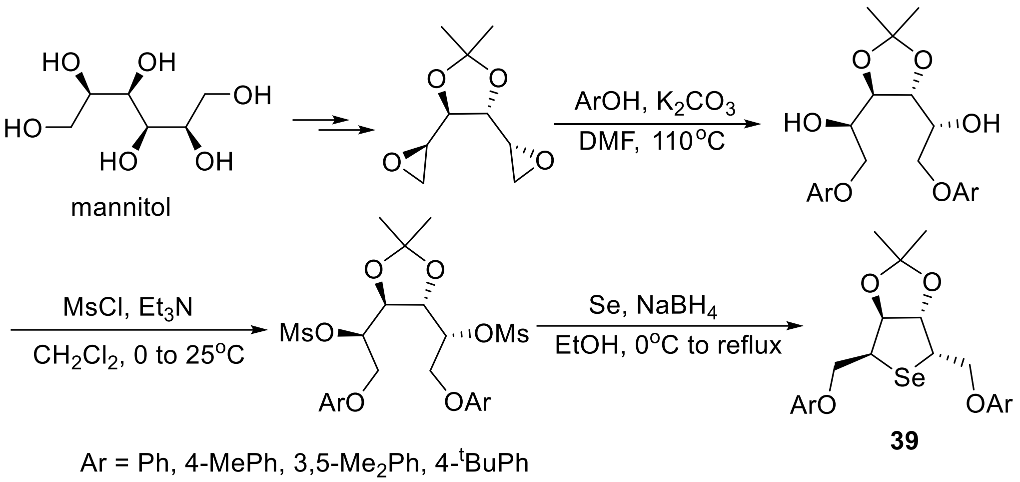


Scheme 10. Organoselenium-catalyzed halo-amidations.

Building upon the success of intermolecular variants, intramolecular halo-amidations have also been effectively catalyzed by organoselenium compounds, enabling the efficient construction of valuable *N*-containing heterocycles. This approach demonstrates particular advantages in asymmetric synthesis when employing chiral organoselenium catalysts, with reported enantiomeric excesses reaching up to 95% ee (Scheme 11) [72]. The chiral organoselenium catalyst **39** could be synthesized from the inexpensive, readily available chiral starting material, mannitol (Scheme 12).

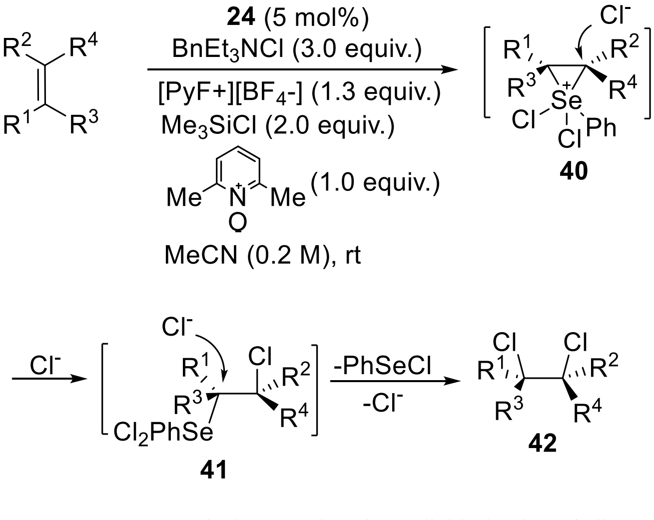


Scheme 11. Organoselenium catalyzed asymmetric halo-amidations.



Scheme 12. Synthesis of chiral organoselenium catalyst from mannitol.

In the halogenation of alkenes, the introduction of a selenium (Se) catalyst can significantly alter the stereochemical outcome of the reaction, even reversing the inherent selectivity observed under standard conditions. For instance, although the syn-dichlorination of alkenes is often disfavored in conventional halogenation processes, the use of diphenyl diselenide (**24**) as a catalyst enables this otherwise challenging transformation [73]. This remarkable reversal in stereoselectivity is attributed to a double inversion of configuration mediated by key selenium-containing intermediates. Initially, the alkene reacts with an electrophilic Se^+ species to form intermediate **40**, which subsequently undergoes nucleophilic attack by chloride to generate the Se and Cl adduct **41**. The formation of this adduct, followed by its stereospecific decomposition, ultimately leads to the syn-dichlorinated product **42** (Scheme 13). This catalytic pathway provides access to thermodynamically less stable syn-adducts and highlights the unique ability of selenium to modulate reaction selectivity through reversible intermediate formation.



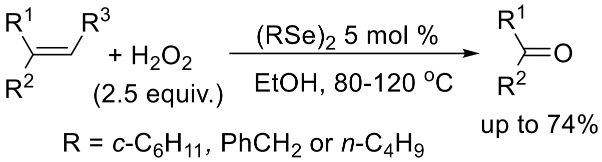
Scheme 13. Organoselenium-catalyzed syn-dichlorination of alkenes.

2.4. Oxidative Cracking Reactions

Oxidative cracking reactions involve the selective cleavage of carbon-carbon double bonds in alkenes, leading to the formation of corresponding carbonyl compounds. Although these reactions inherently disrupt the alkene structure, they hold significant synthetic and industrial value due to their broad applications. They serve as a versatile strategy for the preparation of aldehydes, ketones, and other carbonyl derivatives, which are essential intermediates in fine chemical synthesis, pharmaceuticals, and materials science. Additionally, oxidative cracking plays a crucial role in the degradation of unsaturated macromolecules, enabling the controlled breakdown of polymers and complex organic frameworks in environment protection.

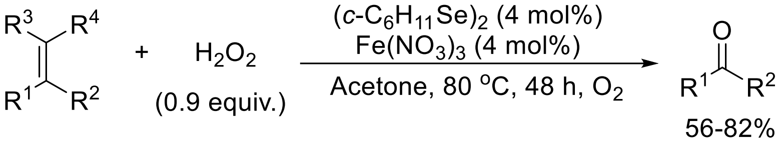
Besides, this transformation is a key step in several industrially important processes. A notable example is the cyclohexene ammonia oxidation to produce adiponitrile, in which the oxidative cleavage of cyclohexene to adipaldehyde is the first key unit reaction [74]. Given its relevance in both laboratory-scale synthesis and large-scale industrial applications, oxidative cracking represents a promising area of research [75]. Further exploration of catalytic systems, mechanistic insights, and sustainable oxidants could enhance the efficiency and environmental compatibility of this transformation, making it an attractive tool for modern organic and industrial chemistry [76–82].

In 2017, we reported an organoselenium-catalyzed oxidative cracking reaction of alkenes, offering a greener alternative to traditional methods for synthesizing carbonyl compounds (Scheme 14) [83]. Using diaryl diselenides as the catalyst precursor and hydrogen peroxide as the oxidant could effectively cleave alkenes at 80–120 °C in ethanol, producing carbonyls in moderate to good yields. The method avoids toxic transition metal catalysts and harsh reagents, aligning with sustainable chemistry goals. The catalysts are recyclable, while the substrate scope is broad, encompassing gem-disubstituted, trisubstituted, and even strained cyclic alkenes. However, the reaction faces limitations with tetrasubstituted alkenes and exhibits over-oxidation side products in some cases. This work expands the utility of organoselenium catalysis and provides a practical, eco-friendly tool for oxidative alkene cleavage, although further optimization may be needed to enhance yields and selectivity for certain substrates.



Scheme 14. Organoselenium-catalyzed oxidative cracking reaction of alkenes.

Recently, it was reported that introducing iron salt as co-catalyst could markedly enhance the reaction efficiency (Scheme 15) [84]. Compared to the previous work, the new Se/Fe system enables the use of molecular oxygen (O_2) as a partial oxidant, reducing the required amount of H_2O_2 from 250 mol% to just 90 mol%. This modification lowers costs and minimizes hazardous peroxide residues, making the process safer for large-scale applications. The hybrid mechanism, combining ionic and radical pathways, is supported by control experiments and XPS analysis, highlighting the synergistic role of Se and Fe in activating O_2. This work demonstrates broader substrate compatibility and improved yields under milder temperatures (80 °C). The inclusion of Fe also addresses limitations in tetrasubstituted alkene reactivity, though steric hindrance remains a challenge. Overall, this dual-catalyst system represents a greener, more practical approach to oxidative alkene cleavage, with notable industrial potential.



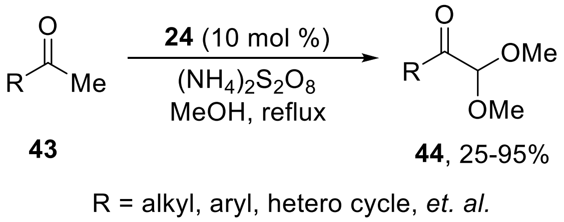
Scheme 15. Oxidative cracking reaction of alkenes catalyzed by Se/Fe system.

3. Reactions of Carbonyl Compounds and Their Derivatives

Carbonyl compounds have multiple reaction sites: the α-H, the C-C(carbonyl) and the carbonyl and its derivatives. The reactions of carbonyls are catalyzed by selenium to change the functional group. The reactions involve both redox and non-redox reactions.

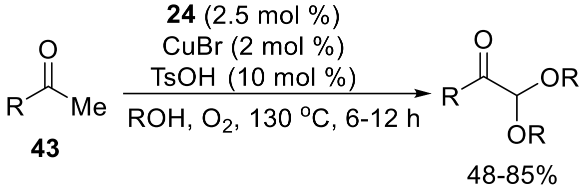
3.1. Oxidation of the α-H of Ketones

In 1990, Tiecco and colleagues reported an advancement in organic synthesis by developing the organoselenium-catalyzed method for the conversion of methyl ketones (**43**) to α-keto acetals (**44**, Scheme 16) [85]. This transformation employed diphenyl diselenide (**24**) as the catalyst and ammonium peroxydisulfate [$(NH_4)_2S_2O_8$] as the oxidant. The reaction demonstrated remarkable versatility, accommodating a broad range of methyl ketone substrates with various functional groups and steric demands. Particularly noteworthy was the method's excellent functional group tolerance and high yields, which enabled the preparation of diverse α-keto acetals. The researchers systematically investigated the reaction scope, providing a comprehensive platform for the synthesis of these useful compounds. This method contributes to the field of selenium-mediated oxidations and expands the toolbox for carbonyl compound functionalization.



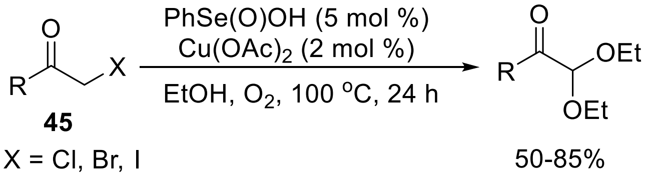
Scheme 16. Organoselenium catalyzed oxidation of ketone α-H.

Recently, we reported a synergistic Se/Cu-catalyzed method for the direct synthesis of *α*-keto acetals from methyl ketones using molecular oxygen as the oxidant and alcohols as both solvent and alkoxylation reagents (Scheme 17) [86]. This work addressed key limitations of prior methods, such as the use of toxic oxidants like ammonium peroxydisulfate or harsh conditions, by leveraging the cooperative catalysis of diphenyl diselenide (**24**) and CuBr under acidic conditions. The reaction exhibited broad substrate scope, accommodating electron-rich and electron-deficient aryl methyl ketones, heterocycles, and even bis-ketones, yielding *α*-keto acetals in good to excellent yields (48–85%). Notably, the system utilized O_2 as a clean oxidant, enhancing its industrial appeal, and demonstrated scalability (100 mmol) with catalyst recyclability over five cycles without significant yield loss. Mechanistic studies revealed that CuBr facilitated the oxidation of selenium intermediates, enabling critical selenoxide syn-elimination and regeneration of the active catalyst. Control experiments, including radical trapping with TEMPO and isolation of key intermediates like (*E*)-1,4-diphenylbut-2-ene-1,4-dione and phenylselenyl ketone, supported a pathway involving enol formation, radical addition, and Pummerer-type rearrangement. The method's practicality was further highlighted by its compatibility with linear alcohols (e.g., MeOH, *n*-octanol), though sterically hindered alcohols (e.g., *tert*-BuOH) proved ineffective. This study underscored the potential of organoselenium catalysis in sustainable C–H functionalization, offering a robust, eco-friendly alternative to traditional oxidative approaches while expanding the toolbox for synthesizing valuable *α*-keto acetals.



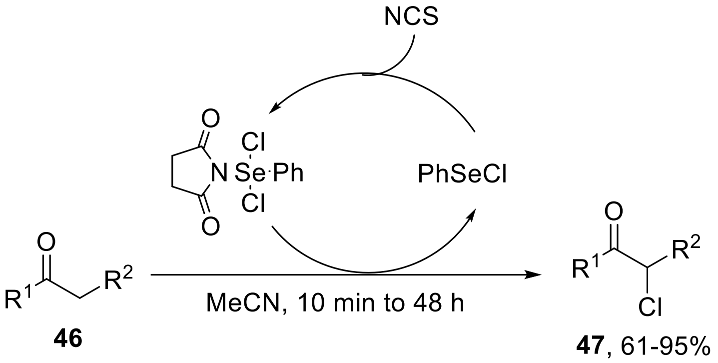
Scheme 17. Synergistic Se/Cu-catalyzed synthesis of *α*-keto acetals from methyl ketones.

In 2021, we reported an improved method using *α*-halomethylene ketones (**45**) as substrates (Scheme 18) [87]. This system eliminated the need for acidic additives (e.g., TsOH) by leveraging HBr generated in situ from the substrates, enabling milder conditions (100 °C vs. 130 °C) and air as the oxidant. The PhSe(O)OH/Cu(OAc)$_2$ catalytic system achieved higher yields (up to 85%) for diverse substrates, including electron-rich and -deficient aryl ketones, and demonstrated scalability (kilogram scale) with catalyst recyclability. Mechanistic studies highlighted the synergistic role of Cu in oxidizing Se intermediates via O_2 activation. This work addressed industrial safety and cost concerns by replacing H_2O_2 with O_2/air while simplifying the reaction setup, advancing the green synthesis of *α*-keto acetals.



Scheme 18. Se/Cu-catalyzed oxidation/alkoxylation of *α*-halomethylene ketones.

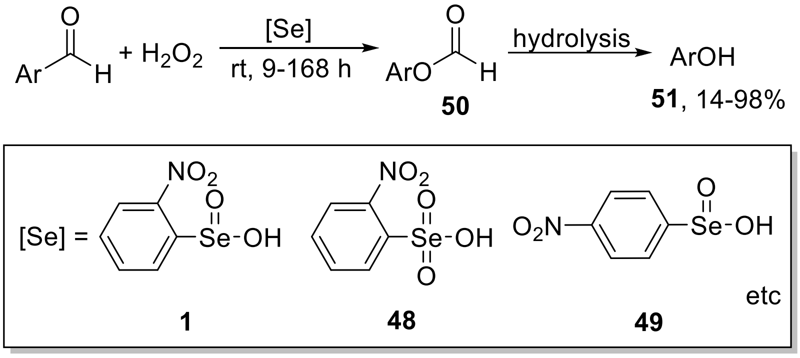
Wang and Tunge demonstrated the first example of selenocatalytic *α*-halogenation of ketones using *N*-halosuccinimides (Scheme 19) [88]. The authors showed that phenylselenides (5 mol %) could activate NCS/NBS by forming electrophilic Se(IV)-halide intermediates, which facilitated selective *α*-chlorination/bromination of *β*-ketoesters, cyclic ketones, and *α*,*β*-unsaturated ketones under mild conditions. Key mechanistic studies ruled out enolate selenylation pathways, instead supporting a direct "chloronium" transfer to enols via Se-mediated NCS activation. Notably, the reaction exhibited unique solvent-dependent regioselectivity—methanol trapped monochlorinated cyclohexanone as a hemiacetal (72% yield), while acetonitrile favored vinyl halide formation from mesityl oxide. This work established selenium's ability to modulate halogen electrophilicity in catalytic cycles, diverging from traditional enolate-based approaches. The method's compatibility with olefins and functional groups highlighted its synthetic utility, laying the groundwork for later developments in electrophilic halogenation catalysis. The authors' mechanistic insights into Se(IV) intermediates remain influential in contemporary selenium catalysis design.



Scheme 19. Organoselenium- Catalyzed α-Halogenation of Ketones.

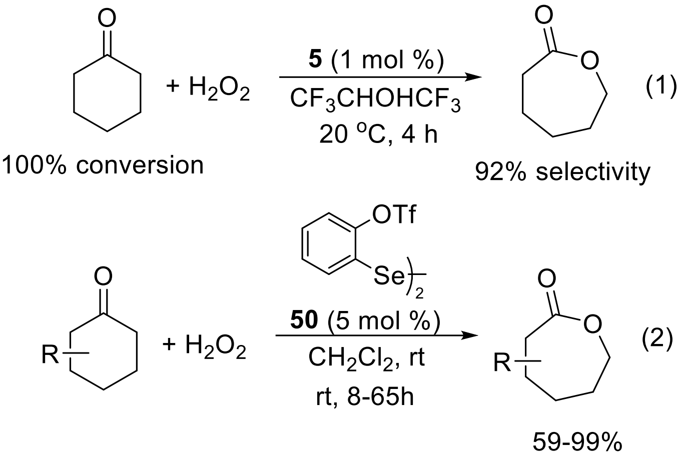
3.2. Baeyer-Villiger Reactions

The Baeyer-Villiger reaction represents a well-established and industrially significant transformation, and in a notable advancement reported in 1989, Syper and colleagues developed an organoselenium-catalyzed variant capable of converting aromatic aldehydes to phenols (Scheme 20) [89–91]. Through a systematic evaluation of fourteen organoselenium catalysts, the researchers identified 2-nitrobenzeneseleninic acid (**1**) as the most effective, delivering an excellent phenol yield of 96% within 30 h [91]. The study revealed crucial structure-activity relationships, demonstrating that seleninic acids exhibit superior catalytic activity compared to their more oxidized selenonic acid counterparts-evidenced by the diminished performance of 2-nitrobenzeneselenonic acid (**48**), which afforded only a 52% yield and required an extended reaction time of 51 h. Furthermore, the position of the nitro substituent on the catalyst scaffold played a pivotal role, as relocating it from the ortho to the para position (**49**) drastically reduced both efficiency and reaction rate, yielding merely 46% phenol after 163 h. These findings underscore the profound influence of electronic and steric factors on catalytic performance, providing key insights for the rational design of optimized organoselenium catalysts for Baeyer-Villiger oxidations.



Scheme 20. Organoselenium-catalyzed Baeyer-Villiger reactions of aromatic aldehydes.

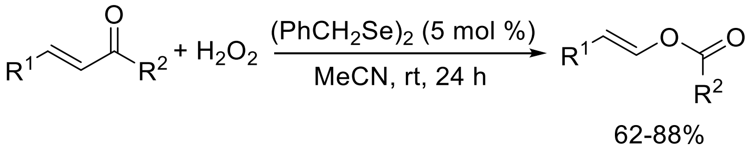
The Baeyer-Villiger oxidation of cyclohexanone to ε-caprolactone holds particular industrial significance due to its crucial role in nylon production, serving as a key monomer for polycaprolactone and various polyamide polymers. Sheldon and co-workers made a significant breakthrough in 2001 by developing an efficient organoselenium-catalyzed system for this transformation using environmentally benign hydrogen peroxide as the terminal oxidant (Scheme 21, Equation (1)) [92]. It was found that cyclohexanone was efficiently converted to ε-caprolactone with excellent efficiency under mild reaction conditions. Through an extensive catalyst screening process, bis[3,5-bis(trifluoromethyl)phenyl] diselenide (**5**) emerged as the optimal catalyst when employed in hexafluoroisopropanol as solvent, achieving an impressive 92% yield of the desired lactone product. The remarkable catalytic performance was attributed to the strong electron-withdrawing effect of the trifluoromethyl groups, which enhanced both the stability and oxidative activity of the selenium catalyst. Further development in heterophasic catalysis made organoselenium catalyst recyclable [93]. Moreover, using the aryl-trifluoromethanesulfonate diselenide **50** (Scheme 21, Equation (2)), the Baeyer-Villiger reaction of ketones could be carried out in moderate to excellent yields without fluorous solvent [94].



Scheme 21. Baeyer-Villiger reaction of cyclohexanones.

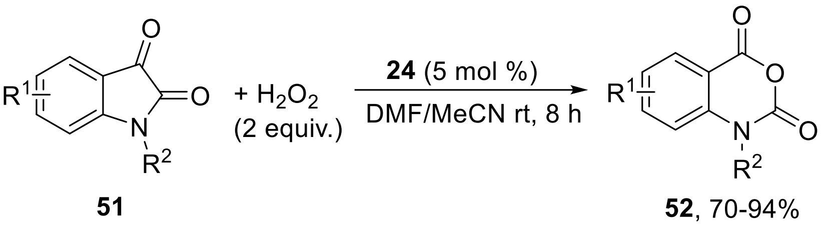
The Baeyer-Villiger oxidation of substituted cyclic ketones presents an intriguing opportunity for asymmetric synthesis, as the reaction can generate new chiral centers during lactone formation. Pioneering work by Uemura and colleagues demonstrated the feasibility of enantioselective organoselenium catalysis in this transformation, achieving modest but promising enantiocontrol (up to 19% ee) using chiral diselenide catalysts [95]. This early success, while yielding relatively low enantioselectivity, established an important proof-of-concept for asymmetric induction in selenium-catalyzed Baeyer-Villiger reactions. Beyond traditional diselenide catalysts, subsequent studies revealed that aryl alkyl selenoxides could also serve as effective pre-catalysts for these oxidations [96], expanding the toolbox of available selenium-based catalytic systems. These findings opened new avenues for developing more sophisticated chiral organoselenium catalysts that could potentially deliver higher levels of stereocontrol in this valuable transformation. The ability to perform enantioselective Baeyer-Villiger oxidations using organoselenium catalysts represents an important step toward more sustainable asymmetric synthesis methods, complementing existing metal-catalyzed approaches while avoiding the use of transition metals.

In 2015, Zhang et al. represented an advancement in organoselenium-catalyzed Baeyer-Villiger oxidations, demonstrating a practical and environmentally benign approach for converting *α,β*-unsaturated ketones to (*E*)-vinyl esters using H_2O_2 as the oxidant (Scheme 22) [97]. The authors systematically evaluated various organoselenium catalysts, identifying dibenzyl diselenide as the optimal pre-catalyst due to its high efficiency (92% yield) and compatibility with diverse substrates, including aryl-, alkyl-, and dienyl-substituted ketones. Notably, the method exhibits excellent functional group tolerance and chemoselectivity, favoring C(vinyl)-C(carbonyl) bond cleavage over competing pathways. The recyclability of the catalyst, though with gradual yield reduction over cycles, adds to the sustainability of the process. A proposed mechanism involving seleninoperoxide acid intermediates rationalizes the observed reactivity. Compared to prior methods relying on toxic metals or oxone, this protocol stands out for its mild conditions, water as the sole byproduct, and avoidance of heavy metals.



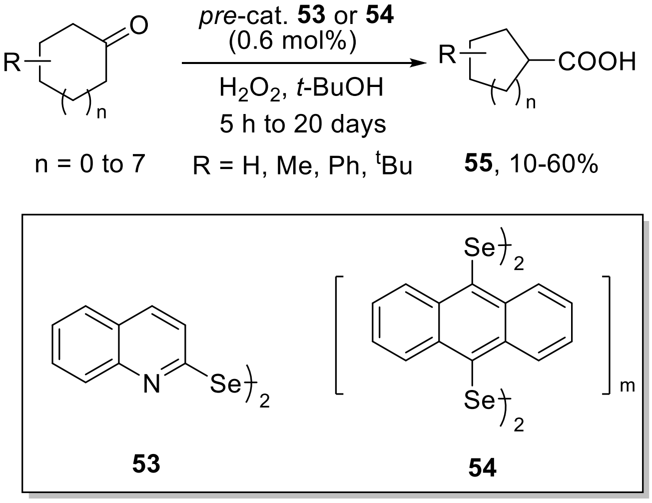
Scheme 22. Baeyer-Villiger reaction of *α,β*-unsaturated ketones.

Organoselenium-catalyzed Baeyer-Villiger reaction can be employed to synthesize useful heterocycles. In 2015, we found an efficient and sustainable approach for the oxidation of isatins (**51**) to isatoic anhydrides (**52**) using diphenyl diselenide (**24**) as a catalyst and H_2O_2 as the green oxidant under mild and neutral conditions (Scheme 23) [98]. The method stands out for its high functional group tolerance, scalability (up to 50 mmol), and excellent yields (up to 94%). A key advantage is the recyclability of both the catalyst and solvent, with the catalytic system maintaining efficiency over seven cycles. Compared to traditional methods requiring harsh oxidants or acidic conditions, this protocol offers a cleaner, waste-free alternative with water as the sole byproduct.



Scheme 23. Oxidation of isatin to isatoic anhydrides.

Organoselenium catalysts exhibit remarkable control over reaction selectivity, particularly in oxidative transformations. Intriguingly, the oxidation of cyclic ketones can yield divergent products depending on the catalyst structure-while typical Baeyer-Villiger oxidation occurs with most organoselenium catalysts, the use of catalysts **53** or **54** induced an unexpected ring contraction pathway instead, affording the unexpected product 55 (Scheme 24) [99]. This alternative pathway generates carboxylic acids bearing smaller rings, effectively bypassing the conventional lactone formation. Although current yields remain moderate, this discovery establishes a novel strategy for constructing carbocyclic carboxylic acid systems from readily available cyclic ketones. The observed switch in reaction pathway highlights the nuanced influence of catalyst design on oxidative transformations, where subtle modifications in the organoselenium structure can redirect substrate reactivity toward fundamentally different products. This finding not only expands the synthetic toolbox for ring contraction methodologies but also underscores the importance of catalyst selection in controlling oxidative reaction manifolds.



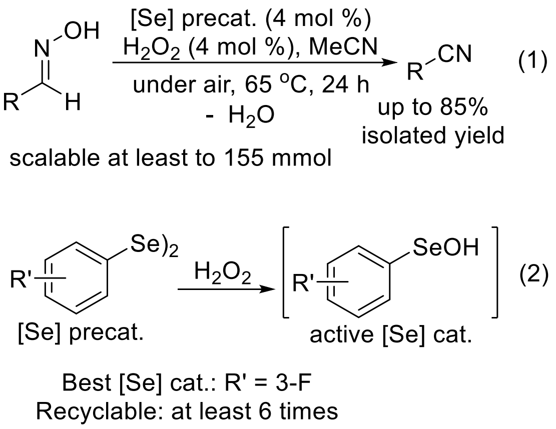
Scheme 24. Organoselenium- catalyzed ring contraction.

Moreover, organoselenium catalysis has demonstrated utility in environmental applications through Baeyer-Villiger oxidation reactions. A notable example is the work by Zhang et al., who developed an organoselenium-catalyzed system for the oxidative degradation of benzoin to benzoic acid—a transformation relevant to pollutant remediation [100]. This method leverages the unique redox properties of selenium catalysts to facilitate selective C–C bond cleavage under mild conditions, offering advantages over traditional peroxide- or metal-mediated processes. By avoiding stoichiometric oxidants and transition metals, the approach aligns with green chemistry principles while expanding the synthetic toolbox for environmental remediation strategies. This application underscores the dual role of organoselenium compounds in both organic synthesis and sustainable chemical degradation processes.

3.3. Reaction of Oximes

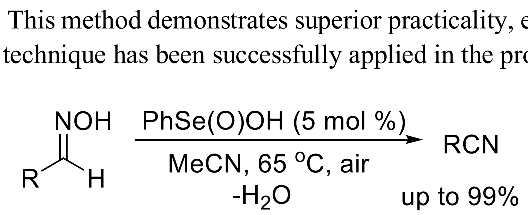
Oximes represent an important class of carbonyl derivatives that can be readily prepared through the condensation of ketones or aldehydes with hydroxylamine. In laboratory, this transformation is particularly convenient to execute using hydroxylamine hydrochloride ($NH_2OH\cdot HCl$) as the hydroxylamine source, owing to its commercial availability, low cost, and excellent handling properties. The reaction proceeds smoothly under mild conditions, often requiring only a basic aqueous or alcoholic medium to generate the reactive hydroxylamine species in situ. This straightforward protocol has made oxime synthesis one of the most accessible and frequently performed transformations in synthetic organic chemistry laboratories. The resulting oximes serve as valuable intermediates for further transformations, including Beckmann rearrangements, reduction to amines, or as protecting groups for carbonyl functionalities.

In 2014, we reported a novel and practical method for the synthesis of organonitriles via organoselenium-catalyzed dehydration of aldoximes under mild conditions (Scheme 25, Equation (1)) [101]. Organonitriles are valuable intermediates in organic synthesis, pharmaceuticals, and materials science, but traditional methods often rely on toxic reagents like sodium cyanide or harsh conditions, limiting their applicability [102]. In our cases, we found that ArSeOH, generated in situ from the related diaryl diselenides via the in situ oxidation by hydrogen peroxide, served as efficient and recyclable catalysts for the dehydration of aldoximes to produce organonitriles (Scheme 25, Equation (2)). The reaction proceeds at 65 °C in air, tolerates a wide range of substrates, and achieves yields of up to 85%. Notably, the method is scalable and avoids the use of transition metals or strong dehydrating agents. The proposed mechanism involves selenoxide syn-elimination, supported by control experiments. This work highlights the potential of organoselenium catalysis as a greener alternative to conventional nitrile synthesis, addressing both environmental and practical concerns. The recyclability of the catalyst further enhances its appeal for sustainable chemistry.



Scheme 25. Organoselenium-catalyzed aldoxime dehydration to produce organonitriles.

PhSe(O)OH could be employed as a stable and efficient catalyst precursor (Scheme 26) [103]. Compared to the previous system, which relied on in situ generation of $3\text{-}FC_6H_4SeOH$ from $(3\text{-}FC_6H_4Se)_2$ and H_2O_2, this method eliminates the need for unstable H_2O_2, offering milder conditions and broader functional group tolerance. The key innovation lies in the direct use of PhSe(O)OH, which avoids side reactions caused by H_2O_2 and simplifies the reaction setup. Air acts as a sustainable oxidant to regenerate the active catalytic species, PhSeOH, ensuring high efficiency (e.g., 85% yield for benzonitrile) without strong oxidants. Mechanistic studies confirm that PhSeOH is the true catalytic intermediate, formed via reduction of PhSe(O)OH by the aldoxime substrate, while air reoxidizes $(PhSe)_2$ back to the active form. This method demonstrates superior practicality, especially for sensitive substrates like thiophene derivatives. The technique has been successfully applied in the production of anisonitrile [104].

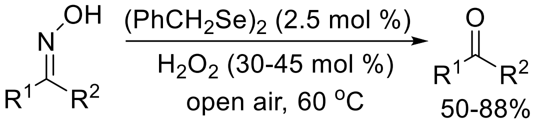


Scheme 26. Aldoxime dehydration to organonitriles using PhSe(O)OH as the catalyst precursor.

Deoximation reactions are pivotal in organic synthesis, serving as a key strategy for the protection, characterization, and purification of carbonyl compounds. Oximes, derived from ketones or aldehydes, are stable and easily prepared, making them versatile intermediates in synthetic routes, such as in the total synthesis of complex molecules like erythronolide A [105]. Additionally, deoximation enables the transformation of non-carbonyl functionalities into carbonyl groups, as exemplified in the industrial production of carvone [106].

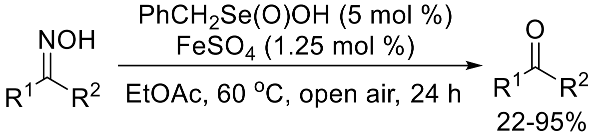
Traditional deoximation methods, however, often rely on metal catalysts, hazardous solvents, or generate significant waste, highlighting the need for greener alternatives [107–111]. Developing efficient, metal-free, and environmentally benign deoximation protocols is thus of great importance for sustainable chemistry [112–119].

In 2017, we reported an organoselenium-catalyzed deoximation method employing dibenzyl diselenide [$(PhCH_2Se)_2$] as the catalyst precursor with hydrogen peroxide as the oxidant (Scheme 27) [120]. While traditional deoximation can proceed without oxidants, such methods typically require acidic conditions generating a lot of waste [121]. In contrast, oxidative deoximation represents an emerging trend toward milder reaction conditions, as the oxidation process provides additional driving force for the transformation, according to the element transfer reaction theory [122–124]. This organoselenium-catalyzed system demonstrates excellent functional group tolerance, efficiently converting both ketoximes and aldoximes to their corresponding carbonyl compounds under mild conditions with good to excellent yields. The use of $(PhCH_2Se)_2$ as a recyclable catalyst aligns with green chemistry principles, enhancing the process's sustainability. Mechanistic studies, including control experiments and Se NMR analysis, support a catalytic cycle involving in situ generation of organoseleninic acid as the active species. This work expands the synthetic utility of organoselenium catalysis and provides a practical, metal-free alternative to conventional deoximation methods.



Scheme 27. Organoselenium-catalyzed deoximation.

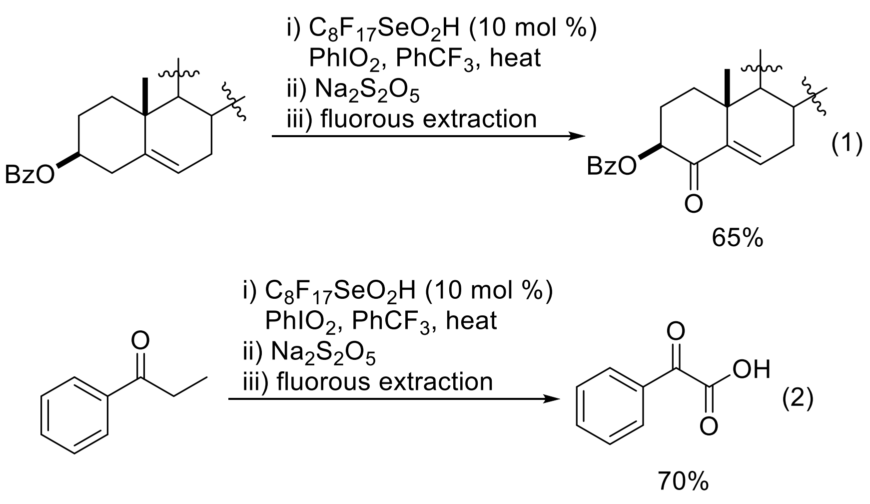
Iron-enabled aerobic oxidative deoximation of ketoximes represents a significant advance in organoselenium catalysis (Scheme 28) [125]. Unlike previous methods requiring hydrogen peroxide, this system employs a catalytic amount of Fe(II) to utilize air as the terminal oxidant, enhancing safety and sustainability. The reaction leverages $PhCH_2Se(O)OH$ as the selenium catalyst, with $FeSO_4$ playing a critical role in regenerating the active high-valent selenium species from reduced diselenides via aerobic oxidation-a mechanism corroborated by XPS analysis. Operationally simple, the transformation proceeds under mild conditions in ethyl acetate, accommodating diverse electronic and steric substituents with excellent yields. Notably, this approach eliminates hazardous reagents and minimizes waste, aligning with green chemistry principles. While highly effective for ketoximes, the method proves less suitable for aldoximes, which predominantly undergo dehydration to nitriles. These findings underscore the synergistic role of iron in sustaining catalytic activity and expand the scope of aerobic organoselenium catalysis. Further optimizations to improve substrate generality and reduce reaction times would enhance its industrial applicability.



Scheme 28. Se/Fe-catalyzed aerobic oxidative deoxmiation.

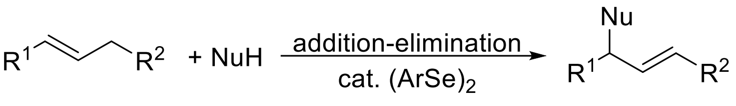
4. Oxidation of C-H

Organoselenium catalysts have emerged as powerful tools for selective C-H bond activation, particularly in the oxidation of vinylic hydrogens and α-hydrogens adjacent to carbonyl groups. These transformations enable the efficient synthesis of valuable α,β-unsaturated carbonyl compounds and β-keto acids, respectively. In 2004, Crich and Zou developed a catalytic system employing fluorous seleninic acid for the allylic oxidation of steroidal substrates. Their innovative approach not only achieved high selectivity but also incorporated a practical catalyst recovery protocol through fluorous extraction (Scheme 29, Equation (1)) [126]. This method represented an important advancement in sustainable organoselenium catalysis. Building upon this work, the same research group subsequently demonstrated the versatility of fluorous seleninic acid catalysts in the oxidation of aryl ketones to α-carbonyl carboxylic acids, obtaining these products in excellent yields (Scheme 29, Equation (2)) [127]. These studies collectively established fluorous organoselenium compounds as efficient and recyclable catalysts for selective C-H oxidation reactions.



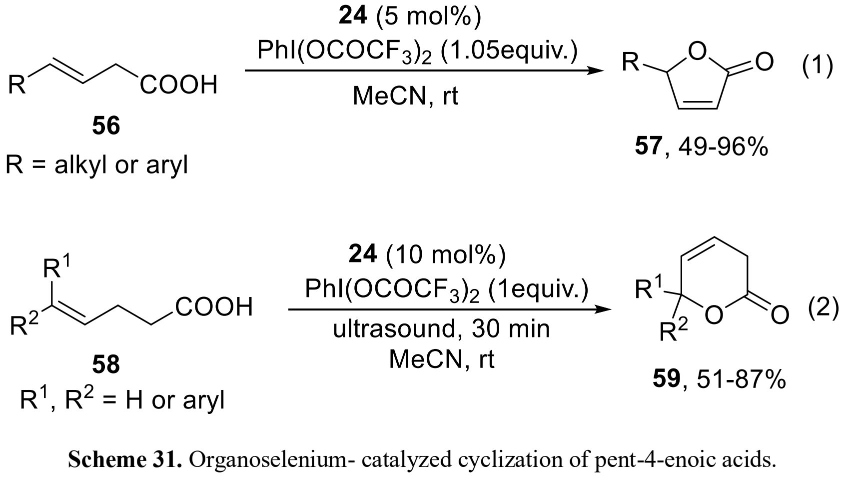
Scheme 29. Organoselenium- catalyzed allylic oxidation and carbonyl α-H oxidation.

Wirth et al. presented an electrochemical approach to organoselenium catalysis, demonstrating the efficient generation of selenium electrophiles from catalytic diphenyl diselenide (10 mol %) via anodic oxidation (Scheme 30) [128]. The method enables a tandem methoxyselenenylation–elimination sequence, converting alkenes into valuable allylic ethers under mild conditions while avoiding stoichiometric oxidants. The reaction exhibits good functional group tolerance for electron-deficient alkenes, though non-activated substrates suffer from competing side reactions. The authors also explore asymmetric variants using chiral diselenides, achieving modest enantioselectivities (up to 66% ee), suggesting room for optimization in stereocontrol.



Scheme 30. Electrochemically driven oxidation of allylic C-H.

The biologically relevant butenolides (**57**) could be synthesized from β,γ-unsaturated acids (**56**) using only 5 mol% diphenyl diselenide as the catalyst precursor and [bis(trifluoroacetoxy)iodo]benzene as the oxidant (Scheme 31, Equation (1)) [129]. The method offers operational simplicity, good yields (up to 70%), and broad substrate compatibility. Similarly, 3,6-dihydro-2*H*-pyran-2-ones (**59**) can be synthesized from γ,δ-unsaturated carboxylic acids (**58**, Scheme 31, Equation (2)) [130].

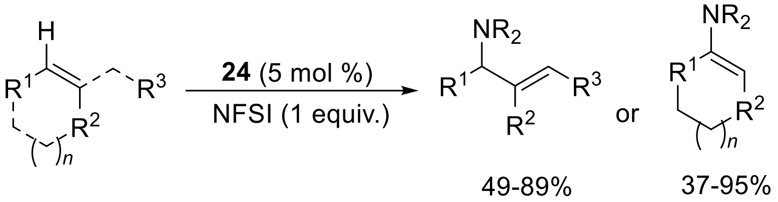


Scheme 31. Organoselenium- catalyzed cyclization of pent-4-enoic acids.

Organoselenium-catalyzed halogenations of allylic C–H bonds have also been extensively explored. For instance, phenylselenyl chloride effectively mediates the chlorination of allylic compounds, yielding the corresponding allylic chlorides in high efficiency (Scheme 32) [131]. The same research group later extended this methodology to encompass halolactonizations and α-halogenations, demonstrating the versatility of selenium catalysis in selective halogenation reactions [132]. Further advancing this field, solid-phase organoselenium-catalyzed systems were developed for the selective allylic chlorination of polyprenoids, providing a streamlined route to biologically significant terpenoid derivatives [133]. Recently, Zhao et al. reported an efficient organoselenium-catalyzed oxidative allylic fluorination method using TMFP-OTf as the oxidant/fluorine source and TEMPO as a key additive, enabling the synthesis of diverse allylic fluorides in high yields [134]. These studies collectively highlight the broad utility of organoselenium reagents in facilitating diverse and selective halogenation transformations under mild conditions.

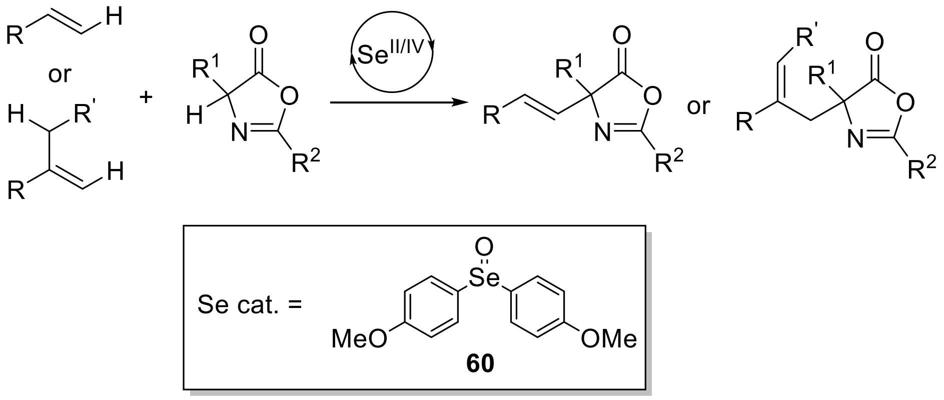
Scheme 32. Organoselenium- catalyzed allylic chlorination.

Breder and colleagues developed an organoselenium-catalyzed oxidative amination of alkenes, enabling direct allylic and vinylic C-H amination using *N*-fluorobenzenesulfonimide (NFSI) as both the oxidant and nitrogen source (Scheme 33) [135]. This method offers an efficient route for directly incorporating amine groups into organic molecules under mild catalytic conditions. In 2015, Zhao et al. reported an organoselenium-catalyzed, hydroxy-directed regio- and stereoselective amination of terminal alkenes using NFSI, enabling efficient synthesis of 3-amino allylic alcohols with broad substrate scope and excellent functional group tolerance [136].



Scheme 33. Organoselenium-catalyzed allylic and vinylic amination of alkenes.

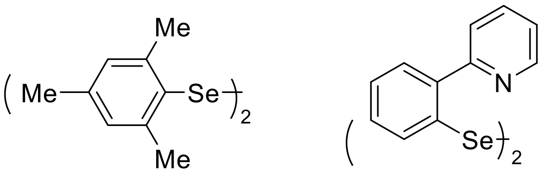
In 2022, Zhao et al. introduced an innovative organoselenium-catalyzed cross-dehydrogenative coupling (CDC) of alkenes and azlactones, leveraging a high-valent para-methoxyphenyl selenium species to achieve C–C bond formation with exceptional regioselectivity (Scheme 34) [137]. The method efficiently synthesizes α,α-disubstituted α-amino acid derivatives via vinyl or allylic C–H functionalization, accommodating a broad substrate scope including inactivated and multi-substituted alkenes. Key to the success is the synergistic use of selenoxide catalyst **60** and NFSI/Tf_2O, which generates a highly electrophilic selenium intermediate to activate the alkene-azlactone coupling. The protocol also extends to electron-rich arenes and oxindoles, demonstrating versatility. While the mechanism involves selenium(IV)-mediated activation, the exact role of Tf_2O in suppressing side reactions warrants further study. This work significantly advances selenium catalysis by enabling challenging C-C bond formations under mild conditions. Besides, selenium-π-acid-catalyzed oxidative alkyne functionalization [138] and the construction of C-SCF_3 stereogenic molecules via C-H activation/functionalization [139] were also developed by the same group.



Scheme 34. Organoselenium-catalyzed cross-dehydrogenative coupling (CDC) of alkenes and azlactones.

5. Oxidation of Heteroatoms

In 1982, Kuwajima et al. reported the oxidation of alcohols with *tert*-butyl hydroperoxide (TBHP) in the presence of catalytic bis(2,4,6-trimethylphenyl) diselenide (**61**, Figure 4), yielding carbonyl compounds in moderate to excellent yields. However, in some cases, **61** should be employed equivalenty [140]. Bis[2-(2-pyridyl)phenyl] diselenide (**62**, Figure 4) was found to be a more efficient catalyst precursor for alcohol oxidation with N-chloro-4-chlorobenzenesulfonamide sodium salt as the oxidant, and its dosage was reduced to only 0.2–1 mol % [141]. Arends et al. supposed the mechanisms of organoselenium-catalyzed alcohol oxidation with TBHP. Through comparative experiments, they concluded that benzeneseleninic anhydride (BSA) was the active oxidative imtermediate [142].

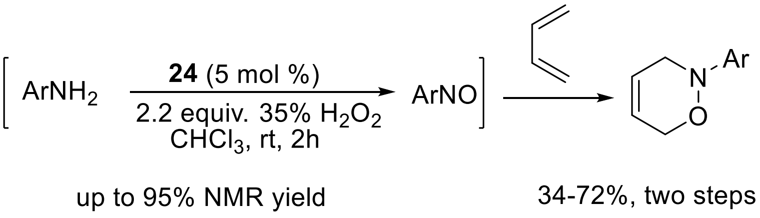


61 **62**

Figure 4. Organoselenium pre-catalyst **61** and **62.**

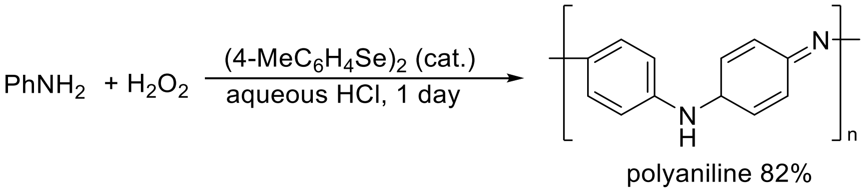
Beyond alcohols, organoselenium catalysis has also been successfully applied to the selective oxidation of phenols-a transformation of significant industrial relevance. For instance, the organoselenium-catalyzed oxidation of phenol to p-benzoquinone offers a sustainable route to this high-value intermediate, widely used in agrochemicals, pharmaceuticals, and polymer production [143]. Unlike conventional methods that rely on stoichiometric oxidants, this catalytic approach employs environmentally benign oxidants like hydrogen peroxide and achieves high selectivity under mild conditions.

Selenium-catalyzed amine oxidations have also been well-documented. As early as 1987, Murahashi et al. reported the oxidation of secondary amines to nitrones using hydrogen peroxide in the presence of SeO_2 as the catalyst [144]. Later, in 2007, Bäckvall and coworkers demonstrated an organoselenium-catalyzed oxidation of primary amines, affording nitroso compounds in excellent NMR yields. These in situ-generated nitroso species further reacted with dienes to form oxazines (Scheme 35) [145]. Selenium-catalyzed oxidation reaction has also been extended to other nitrogen-containing functional groups. For example, the oxidation of 1,1-dimethylhydrazines could produce nitriles using hydrogen peroxide or *m*-chloroperoxybenzoic acid (MCPBA) as the oxidant [146].



Scheme 35. Organoselenium catalyzed oxidation of primary amines.

In 2019, we reported a significant advancement in organoselenium catalysis by demonstrating its first successful application in polymer materials fabrication. In the work, a green, efficient method for synthesizing polyanilines (PANIs) was developed via organoselenium-catalyzed oxidative polymerization of anilines using hydrogen peroxide as the oxidant (Scheme 36) [147]. Compared to known methods [148], the adavantages of this work include the mild reaction conditions (20 °C, aqueous HCl), low catalyst loading (1.1 mol% $(4\text{-TolSe})_2$), and high yield (82%), with water as the sole byproduct.



Scheme 36. Organoselenium catalyzed oxidative polymerization of aniline.

The study stands out as the first application of organoselenium catalysis in aniline polymerization, offering a sustainable alternative to conventional metal-catalyzed or stoichiometric oxidant-based methods. It highlights selenium's versatility in materials chemistry, combining environmental benefits (low toxicity, atom economy) with practical scalability, making it a notable example of catalytic method development for functional polymer synthesis. Moreover, PANI is a widely used material that can support catalyst [149–154]. Compared to inorganic support materials, the electronegativity of nitrogen in polyaniline (PANI) can be precisely modulated through substituent engineering, enabling fine-tuning of the catalytic activity of supported metal species [155–158]. This unique tunability makes PANI a versatile support material with significant potential for advanced catalytic applications. Thus, the organoselenium-catalyzed synthesis of polyaniline (PANI) is expected to grow in prominence as PANI-supported catalysts gain wider adoption in reactions with industrial application potential [159].

The oxidation of sulfides is a well-established process. As early as 1978, Reich et al. demonstrated that seleninic acids (**1** or **2**) can efficiently catalyze sulfide oxidation, yielding significant amounts of sulfones[43]. Later studies revealed that ortho-amide-functionalized seleninic acid derivatives (**63**–**65**, Figure 5) enable selective oxidation, allowing the reaction to be controlled at the sulfoxide stage [160]. Further advancement was achieved by immobilizing these catalysts on silica, yielding recyclable systems (e.g., **66**, Figure 5). These heterogeneous catalysts proved effective for diverse transformations, including the oxidation of alkyl arenes to ketones, aromatic aldehydes to carboxylic acids, and sulfoxides to sulfones [161].

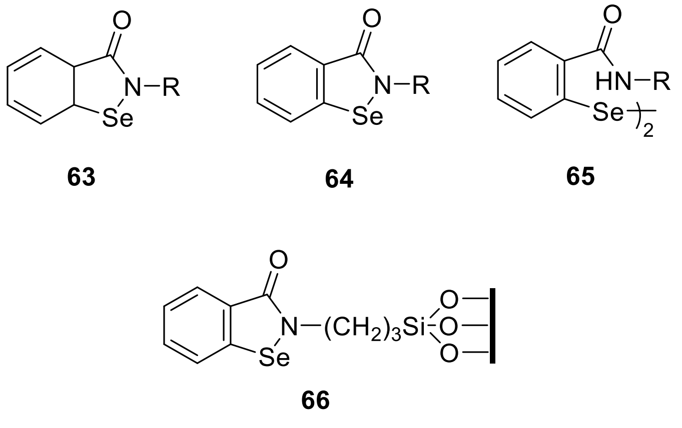
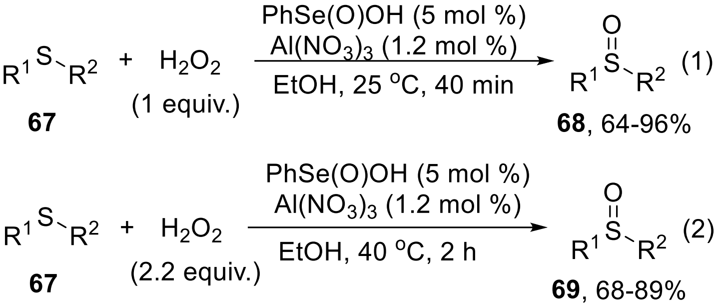


Figure 5. Chemical structures of the organoselenium catalysts **63**–**66**.

In our work, the $PhSe(O)OH/Al(NO_3)_3$ catalytic system was demonstrated to be a highly efficient and tunable platform for the selective oxidation of sulfides (**67**), enabling controlled conversion to either sulfoxides (**68**) or sulfones (**69**) using hydrogen peroxide as a green oxidant under mild reaction conditions (Scheme 37) [162]. The synergistic interplay between Se, Al^{3+}, and nitrate enables precise control over reaction selectivity—sulfoxides dominate with stoichiometric H_2O_2 (Scheme 37, Equation (1)), while excess oxidant drives the formation of sulfones (Scheme 37, Equation (2)). Mechanistic studies suggest a dual-pathway process involving ionic oxidation for sulfoxides and radical intermediates for sulfones, supported by TEMPO quenching experiments. The system's practicality is underscored by its broad substrate scope, including electron-rich and electron-deficient aryl sulfides, and its successful application in the synthesis of omeprazole, where the catalyst could be recycled without significant loss of activity. Compared to traditional methods relying on stoichiometric oxidants or transition metals, this approach offers a greener alternative with high atom economy and minimal waste.



Scheme 37. $PhSe(O)OH/Al(NO_3)_3$ catalyzed oxidation of sulfides.

6. Heterogeneous Selenium Catalysis: Engineering Perspectives

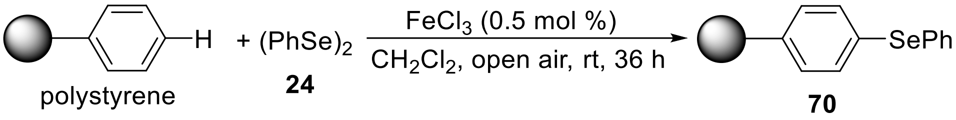
Selenium is a scattered element. Although selenium is far less expensive than precious metals such as gold, platinum, and rhodium, it remains relatively costly compared to common metals like copper and iron. Currently, the price of selenium powder with a purity of 99.99% is approximately $55 per kilogram. From an engineering perspective, the recycling and reuse of selenium-based catalysts is essential for large-scale production. While some reported homogeneous organoselenium catalytic reactions allow for the recovery of selenium catalysts through extraction or other methods, heterogeneous catalysts are undoubtedly critical for achieving continuous production in industrial settings. Consequently, since the inception of selenium catalysis research, heterogeneous catalytic systems are continuously being developed.

Over the past decade, advancements in materials science have led to significant breakthroughs in heterogeneous catalyst design. These developments not only facilitate process scalability and engineering feasibility but have also yielded unique scientific insights, substantially advancing the field of selenium catalysis. Integrating novel support materials, nanostructured selenium composites, and optimized immobilization techniques has further enhanced catalytic efficiency, stability, and recyclability, paving the way for broader industrial applications. Thus, the transition from homogeneous to heterogeneous selenium catalysts represents both a practical necessity for sustainable production and a promising avenue for fundamental research in catalytic mechanisms and material innovation.

A key advantage of polymer-supported selenium catalysts lies in their ability to stabilize reactive selenium species that are otherwise transient in homogeneous systems. Small-molecule organoselenium catalysts often undergo comproportionation or decomposition due to the high reactivity of Se^{2+} and Se^{6+} intermediates. However, as demonstrated in the polystyrene-supported selenium-catalyzed oxidation of cyclohexene, polymer matrices can isolate these active species, preventing their deactivation [163]. XPS analysis confirmed the presence of Se^{2+} and Se^{6+} on the polymer support, which facilitated the activation of molecular oxygen—a rare phenomenon in homogeneous catalysis. This stabilization enhances catalytic efficiency and enables unconventional reaction pathways, such as the aerobic oxidation of cyclohexene with sub-stoichiometric H_2O_2, achieving yields exceeding theoretical limits. Such phenomena underscore the unique mechanistic opportunities afforded by heterogeneous selenium systems, bridging the gap between industrial practicality and fundamental discovery.

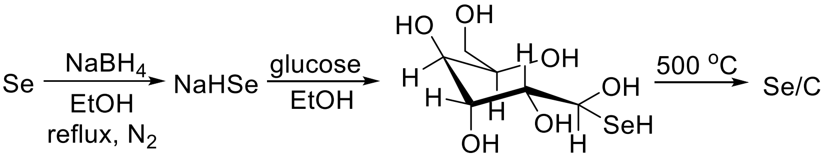
While steric hindrance in polymer-supported catalysts was historically viewed as a limitation, recent studies reveal its unexpected benefits. Polyselenides, once considered poor catalysts due to restricted reactant access [164], exhibit remarkable activity in oxidative cracking reactions [165]. For instance, polyselenide catalyzes the cleavage of alkenes under mild conditions (80 °C, ethanol), utilizing a combination of hydrogen peroxide and O_2 to minimize peroxide residues-a critical advantage for industrial safety. Mechanistic studies attribute this to a "hydroxyl radical pump" mechanism [33]: the Se-O bonds in oxidized polyselenides thermally decompose, generating hydroxyl radicals that drive the reaction. The cycle involves continuous regeneration of Se-H and Se-O states, similar to that of enzymatic catalysis. This discovery challenges traditional assumptions about steric effects and highlights how polymer-supported selenium can exploit constrained environments to achieve selective, sustainable transformations unattainable with small-molecule catalysts. Notably, the polyselenide catalyst has been successfully applied in the dihydroxyl reaction of cyclohexene to produce 1,2-cyclohexadiol, a reaction with industrial application potential [166].

The economic viability of polymer-supported selenium catalysts hinges on scalable synthesis methods. Traditional approaches, such as polystyrene lithiation followed by selenization, are resource-intensive [163]. Recent advances leverage the heterolytic cleavage of Se-Se bonds (e.g., using $FeCl_3$) to generate electrophilic $PhSe^+$ species, which directly selenize polystyrene via aromatic C-H substitution (Scheme 38) [167]. This method, exemplified by the synthesis of selenized polymer (**70**), reduces costs by avoiding expensive reagents and multi-step protocols. The resulting catalysts exhibit robust activity in pharmaceutical applications, such as the oxidation of Ulfiprazole to Omeprazole (73% yield), without requiring transition metals. Furthermore, the $FeCl_3$-catalyzed process is inherently sustainable, regenerating the diselenide reagent via aerobic oxidation of PhSeH. These innovations align with green chemistry principles while addressing the cost barriers to industrial adoption, demonstrating how tailored synthetic strategies can unlock the full potential of heterogeneous selenium catalysis.



Scheme 38. $FeCl_3$-catalyzed selenization of polystyrene with diphenyl diselenide.

In 2018, we reported an example of developing heterogeneous selenium catalysts from renewable resources. By employing carbohydrates such as glucose, fructose, and even agricultural waste (e.g., potato starch and willow sawdust) as carbon precursors, a Se/C catalyst was developed (Scheme 39) [168]. This approach utilizes renewable feedstocks and demonstrates the potential for valorizing low-cost biomass materials in catalysis applications. Remarkably, despite the sterically constrained environment of the carbon support—which would traditionally be expected to hinder access to the endocyclic C=C bond of *β*-ionone-the Se/C catalyst achieves highly regioselective epoxidation of *β*-ionone with exceptional efficiency (TON up to 3.9×10^5). This unexpected reactivity challenges conventional assumptions about steric limitations in heterogeneous catalysis. It is proposed that the carbon support's unique structure facilitates close contact between *β*-ionone's cyclic framework and the active selenium sites, as evidenced by adsorption experiments showing significant substrate uptake (72% after 24 h). The proposed mechanism involves electrophilic addition of the endocyclic C=C bond to selenium sites, forming a fused 1,2,3-dioxaselenolane intermediate that decomposes to yield the epoxide. Notably, the carbon matrix's steric bulk prevents competing Baeyer-Villiger oxidation at the ketone group-a transformation typically favored in homogeneous selenium catalysis-by physically blocking the nucleophilic attack required for carbonyl activation. This steric gating effect, combined with the thermodynamic favorability of the epoxidation pathway (releasing ~210 kJ/mol overall), underscores how heterogeneous systems can enforce reaction selectivity through structural design rather than electronic tuning. The work thus provides both a practical biomass-based catalytic platform and fundamental insights into steric control in selenium-mediated oxidations.



Scheme 39. Synthesis of Se/C.

The Se/C catalyst was then improved by introducing potassium bromide (KBr) as a dopant during the calcination process [169]. Subsequent water washing removed the inorganic salts, generating well-defined lattice vacancies within the carbon matrix. This modification resulted in a highly crystalline K-intercalated Se/C catalyst with improved structural properties. Remarkably, the optimized material exhibited superior activity in the epoxidation of *β*-ionone, achieving higher yields and selectivity compared to the undoped counterpart. Additionally, the modified catalyst demonstrated exceptional versatility by enabling the use of molecular oxygen (O_2) as a green oxidant, eliminating the need for hydrogen peroxide and further enhancing the sustainability of the process. This advancement highlights the tunability of biomass-derived Se/C catalysts and provides a promising strategy for designing efficient and eco-friendly oxidation systems. It was also found that iron doping could enhance the catalytic activity of Se/C [170]. The Se/C catalyst has been successfully employed in the derivation of Cefixime intermediates, demonstrating its significant potential in medicine development [171]. Beyond catalysis, carbohydrate-derived selenium materials demonstrate versatile applications spanning agriculture, medicine, and animal husbandry [172–182]. They are also employed in heavy metal removal for environmental protection [183].

Metal and non-metal oxide-supported selenium catalysts have emerged as highly promising materials for industrial applications due to their cost-effectiveness, durability, and environmental compatibility. Compared to polymer- or carbon-supported selenium catalysts, oxide supports offer distinct advantages, such as resistance to solvent swelling (unlike polymers) and enhanced stability under harsh conditions (unlike carbon materials). Silica (SiO_2)-supported selenium, prepared by calcining selenium powder with silica, demonstrates efficient catalytic activity in β-ionone epoxidation using O_2 as a green oxidant, achieving a turnover number (TON) of 393 when fluorine-doped [184]. Alumina (Al_2O_3)-supported selenium, combined with manganese, shows synergistic effects in selectively oxidizing alcohols to aldehydes without over-oxidation, with yields up to 83% [185]. Iron oxide (FeO_x)-supported selenium, formed via Fe-Se bonds, exhibits magnetic properties, enabling easy separation and reuse, and catalyzes oxidative cleavage of alkenes and degradation of β-carotene [186–188]. Zirconia (ZrO_2)-supported selenium, with its high density, facilitates catalyst recovery and is effective in alkene oxidative cracking [189] and phenol oxidation to p-benzoquinone [190]. It is also employed as catalyst in the oxidative polymerization of aniline to produce PANI [191]. These oxide supports are not only inexpensive and robust but also enhance catalytic performance through unique interactions with selenium, such as electron density modulation (e.g., F-doping in SiO_2) or synergistic metal effects (e.g., Mn in Al_2O_3). Overall, metal and non-metal oxide-supported selenium catalysts outperform polymer and carbon counterparts in industrial scalability, recyclability, and versatility, making them ideal for sustainable chemical processes.

In addition to metal oxide-supported selenium catalysts, certain metals can directly react with selenium to form catalytic materials. For example, silver selenide (Ag/Se), prepared by simple calcination of selenium and silver powders under mild conditions (120–150 °C), demonstrates remarkable catalytic performance in oxidation reactions, highlighting its industrial potential. In alcohol oxidation, Ag/Se activates molecular oxygen (O_2) to selectively convert primary and secondary alcohols to aldehydes and ketones with moderate to high yields (up to 91%), while avoiding over-oxidation [192]. Notably, it also catalyzes the selective epoxidation of β-ionone's endocyclic C=C bond using O_2 as a green oxidant, yielding β-ionone epoxide-a key pharmaceutical intermediate—without requiring hazardous additives like NHPI [193]. The catalyst's heterogeneous nature allows easy recovery and reuse, and its components (Ag, Se) can be recycled into fertilizers, minimizing waste. Similarly, the Fe/Se catalyst is prepared by direct calcination of selenium and iron powders at 350 °C, forming a soft magnetic material that efficiently catalyzes phenol oxidation to *p*-benzoquinone with high selectivity (88% yield) [194]. Compared to costly alternatives (e.g., Pd@C, Ru@C etc.), Ag/Se and Fe/Se combine cost-effectiveness, operational simplicity, and environmental benefits, making it highly promising for scalable industrial applications in fine chemical and pharmaceutical synthesis.

7. Conclusions

Organoselenium catalysis has emerged as a transformative field that bridges fundamental chemistry with sustainable industrial applications. This review highlights the remarkable versatility of selenium-based catalysts in facilitating a wide array of organic transformations, including epoxidations, dihydroxylations, halogenations, Baeyer-Villiger reactions, and C-H functionalization reactions. The unique redox properties of selenium [195] enable these reactions to proceed under mild conditions, often with high selectivity and minimal environmental impact. Notably, the ability of organoselenium catalysts to utilize green oxidants such as hydrogen peroxide and molecular oxygen aligns perfectly with the principles of sustainable engineering, offering a cleaner alternative to traditional transition metal catalysts that rely on toxic or scarce metals. From an industrial perspective, selenium catalysis presents significant advantages, including cost-effectiveness, recyclability, and compatibility with large-scale processes. The development of heterogeneous selenium catalysts, such as polymer-supported, carbon-based, and metal oxide-immobilized systems, has further enhanced their practicality for continuous production. These advancements not only address the challenges of catalyst recovery and reuse but also unlock novel reactivity patterns that are unattainable in homogeneous systems. For instance, the stabilization of high-valent selenium species in polymer matrices or the synergistic effects observed in bimetallic Se/Fe or Se/Cu systems exemplify the innovative potential of this field. Organoselenium catalysts may be applied in continuous-flow systems, but the leaching of selenium is a challenge that bottlenecks the technology. To avoid selenium leaching, a catalyst with strong X-Se bond (X = support) is required, and it may be better if there is a methyl on selenium site to avoid the selenoxide *syn*-elimination, i.e., the end-capping strategy [177].

It is important to note that while this review focuses on systems where selenium directly participates in catalytic cycles, selenium also plays a crucial role in modifying catalyst surfaces to enhance activity and selectivity in broader contexts [196,197]. Although such applications fall outside the scope of this discussion, their industrial significance (particularly in improving catalytic performance in energy conversion, environmental remediation, and fine chemical synthesis) should not be overlooked. Future research exploring these indirect roles of selenium could further expand its utility in sustainable engineering. The sustainability of organoselenium catalysis extends beyond synthetic efficiency. By minimizing hazardous waste, reducing energy consumption, and enabling the use of renewable feedstocks (e.g., biomass-derived catalysts), this technology contributes to the broader goals of green chemistry and circular economy [198,199]. Applications such as the oxidative degradation of pollutants, the synthesis of biodegradable polymers, and the production of high-value pharmaceuticals underscore its relevance to environmental protection and human health.

In future, the integration of organoselenium catalysis into industrial workflows holds immense promise for achieving sustainable chemical manufacturing. Future research should focus on optimizing catalyst design, expanding substrate scope, and exploring novel reactor configurations to further enhance efficiency and scalability. Collaborative efforts between academia and industry will be essential to translate laboratory breakthroughs into real-world solutions. In conclusion, organoselenium catalysis represents a paradigm shift in sustainable engineering, combining scientific ingenuity with practical applicability. Its ability to deliver high-performance, eco-friendly solutions (both through direct catalytic action and indirect catalyst enhancement) positions it as a cornerstone of modern green chemistry, paving the way for a more sustainable and resource-efficient future.

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Conflicts of Interest

The authors declare no conflict of interest.

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