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Artículo de revisión

Copper(II) triflate in Catalysis: A benchmark tool for Organic Synthesis

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Abstract

Copper(II) triflate ($Cu(OTf)_2$), whose early mechanistic foundations were established by the pioneering studies of Jay K. Kochi in 1972 and subsequently popularized in the field of catalysis, has emerged as a powerful tool in modern synthetic chemistry. Its physicochemical properties, well-defined Cu(II)/Cu(I) redox behavior, stability in organic media, and compatibility with a wide range of functional groups make it a highly effective platform for homogeneous transformations. This review examines its preparation, reactivity profile, and role in a broad spectrum of transformations, including coupling reactions (Ullmann, Sonogashira, Chan–Lam), Friedel–Crafts reactions, Lewis-acid-mediated cyclizations, aminations, cycloadditions, and radical processes. In addition, its utility in multicomponent reactions (MCRs), asymmetric synthesis, and heterogeneous catalytic systems supported on silica, zeolites, or nanotubes (HTNT) is examined. Applications in unconventional media such as ionic liquids, deep eutectic solvents, and solvent-free conditions, as well as in microwave- and ultrasound-assisted reactions and in photocatalysis, further highlight its catalytic versatility. Recent bibliometric analyses indicate a steady rise in publications involving $Cu(OTf)_2$, reinforcing its position as a benchmark catalyst. Moreover, its successful use in total syntheses and one-pot procedures, often consistent with green chemistry principles, underscores its potential as a valuable system for diverse catalytic transformations in contemporary organic synthesis.

Keywords: Copper(II) triflate; Homogeneous catalysis, C–H activation; C–C bond formation; Green chemistry

Resumen

El triflato de cobre (II) en catálisis: una herramienta de referencia para la síntesis orgánica. El triflato de cobre(II) ($Cu(OTf)_2$), cuyas bases mecanísticas fueron establecidas por los estudios pioneros de Jay K. Kochi en 1972 y posteriormente popularizado en el campo de la catálisis, se ha consolidado como una herramienta poderosa en la síntesis química moderna. Sus propiedades fisicoquímicas, un comportamiento redox Cu(II)/Cu(I) bien definido, su estabilidad en medios orgánicos y su compatibilidad con una amplia gama de grupos funcionales lo convierten en una plataforma altamente eficaz para transformaciones homogéneas. Esta revisión examina su preparación, su reactividad y su papel en un amplio espectro de transformaciones, incluyendo reacciones de acoplamiento (Ullmann, Sonogashira y Chan–Lam), reacciones de Friedel–Crafts, ciclaciones mediadas por ácidos de Lewis, aminaciones, ciclo-adiciones y procesos radicalarios. Asimismo, se analiza su utilidad en reacciones multicomponente (MCRs), síntesis asimétrica y sistemas catalíticos heterogéneos soportados sobre sílice, zeolitas o nanotubos (HTNT). Sus aplicaciones en medios no convencionales, como líquidos iónicos, disolventes eutécticos profundos y condiciones libres de disolvente, así como en reacciones asistidas por microondas y ultrasonido y en procesos de fotocatálisis, ponen de manifiesto su versatilidad catalítica. Estudios bibliométricos recientes indican un incremento sostenido de las publicaciones que involucran al $Cu(OTf)_2$, lo que refuerza su posición como catalizador de referencia. Además, su uso exitoso en síntesis totales y procedimientos tipo *one-pot*, frecuentemente de acuerdo con los principios de la química verde, subraya su potencial como un valioso sistema para diversas transformaciones catalíticas en la síntesis orgánica contemporánea.

Palabras clave: Triflato de cobre(II); catálisis homogénea; activación C–H; formación de enlaces C–C; química verde

Introduction

Catalysis plays a central role in the development of efficient, sustainable, and economically viable chemical processes[1]. More than 80%[2] of modern industrial operations, as well as a substantial proportion of synthetic transformations in fine chemistry[3], rely at some stage on catalytic activity. In the field of organic synthesis, catalysis has enabled selective access to diverse classes of compounds through covalent bond activation, the controlled formation of new C–C and C–X bonds (X = N, O, S), and the development of reaction pathways governed by regio- and stereoselectivity. Within this wide range of catalytic tools, Lewis's acids, whether employed as additives or co-catalysts, have been particularly valued for their ability to activate substrates and steer reaction pathways in complex organic transformations[4].

In this context, copper(II) triflate, $Cu(OTf)_2$ (Fig. 1a), combines the redox versatility of copper with the advantages of the trifluoromethanesulfonate anion (OTf^-), which, although often described as weakly coordinating, can exhibit moderate coordination and generate HOTf *in situ*, thereby enhancing the electrophilicity of the metal center and facilitating the generation of catalytically active species in solution[5]. The accessible oxida-

tion states Cu(0), Cu(I) and Cu(II) (with possible Cu(III) intermediates under oxidative conditions), together with its stability in organic media, have established $Cu(OTf)_2$ as an efficient, economical, and selective catalyst for a broad array of transformations (Fig. 1b)[6,7], including cross-couplings, mild oxidations, cyclization, and radical reactions[8]. These features contribute to its broad applicability, although direct replacement of noble-metal catalysts must be evaluated case-by-case.

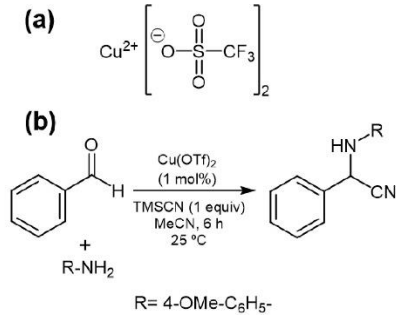


Fig. 1: **(a)** Structure of copper(II) trifluoromethanesulfonate, $Cu(OTf)_2$. **(b)** Representative three-component synthesis of α-aminonitriles catalyzed by $Cu(OTf)_2$, performed under mild conditions with a high yield (95%). Note: This reaction involves Cu(II) specifically and should not be confused with Cu(I) triflate.

The development of copper(II) triflate as a catalyst traces back to the pioneering work of Jay Kazuo Kochi[9] (1927–2008), who in 1972, at Indiana University, demonstrated its efficacy in olefin oxidation[10], highlighting a distinctive redox behavior compared to other copper compounds. His studies clarified the involvement of ionic and radical pathways in Cu(II)/Cu(I) redox processes; however, the specific role of the trifluoromethanesulfonate counterion was not explicitly recognized at that stage. Subsequent investigations revisited this assumption and showed that the anion can actively modulate catalytic behavior, thereby setting the stage for later developments in homogeneous copper catalysis.

$Cu(OTf)_2$ has demonstrated remarkable versatility in homogeneous catalysis, enabling C–C and C–N couplings (Ullmann[11] and Chan–Lam[12] variants), C–H activation in arylation[13], alkylation[14], and amination[15], as well as intramolecular cyclizations and heterocyclizations relevant to the synthesis of bioactive heterocycles[16]. It has also proven effective in nucleophilic addition and substitution reactions, allowing the formation of acetals, ethers, esters, and azides in the presence of diverse functional groups, including multicomponent transformations under mild Lewis-acid conditions[17,18].

This review aims to provide a comprehensive perspective on copper(II) triflate as a homogeneous catalyst, addressing its preparation, physicochemical characteristics, and representative catalytic applications, from the mechanistic insights established by Kochi to more recent developments. Current trends in homogeneous, heterogeneous, and asymmetric catalysis are also discussed, emphasizing its potential in emerging synthetic strategies within the context of milder and more sustainable reaction conditions[19]. The goal is to provide an updated framework for future research on $Cu(OTf)_2$ catalysis.

Methodology

The methodology of this review was based on a structured literature analysis, with the aim of examining copper(II) triflate and its relevance in catalysis applied to the synthesis of high-value organic compounds. Databases and recognized academic sources were consulted, including ACS Publications, Google Scholar, ScienceDirect, Scopus, Wiley Online Library, as well as technical catalogs from Strem Chemicals and Sigma-Aldrich (Merck KGaA®). Priority was given to original research articles, specialized reviews, and book chapters published between 1972 and 2024, starting from the seminal study of Jay K. Kochi (1972)[10]. The literature selection considered both experimental and theoretical studies providing relevant information on its catalytic behavior. Search terms included combinations such as "copper triflate", "copper(II) triflate catalysis", "$Cu(OTf)_2$ organic synthesis", "copper triflate reactions", and "copper-catalyzed C–N/C–C bond formation", adjusted according to the filters of each database. Boolean operators (AND, OR, quotation marks) were applied for exact searches, along with filters for language and document type. Additionally, a keyword co-occurrence analysis was carried out using the VOSviewer software (version 1.6.20)[20] based on a Scopus database search with "copper(II) triflate" as the keyword. A total of 760 records were retrieved, filtered by relevance, and clustered using the program's algorithm. The resulting map revealed color-coded thematic clusters, highlighting research areas associated with copper triflate catalysis.

Results and Discussion

Copper as a catalyst: strategic foundations

The appeal of copper as a catalytic metal arises from a well-balanced combination of structural, electronic, and economic factors that make it an attractive option in catalysis[21]. From a chemical standpoint, copper belongs to the d block, which in catalytic systems gives access predominantly to Cu(I) ($3d^{10}$) and Cu(II) ($3d^{9}$) species. Nevertheless, recent advances have demonstrated that higher oxidation states, including Cu(III) ($3d^{8}$)[22], can be stabilized in well-defined molecular complexes under specific ligand and solvation environments, thereby broadening the range of mechanistic scenarios proposed for copper-mediated transformations[23], although the precise nature of high-valent copper intermediates under catalytic conditions remains the subject of ongoing discussion[24,25].

The Cu(II)/Cu(I) redox couple has a standard reduction potential of +0.16 V in aqueous solution, indicating the relative ease with which Cu(I) can be oxidized to Cu(II), although these values are strongly influenced by solvent effects and ligand coordination under catalytic conditions. As a consequence, Cu(I) is thermodynamically unstable in aqueous media and tends to disproportionate into Cu(0) and Cu(II), with an overall potential of $E° = -0.37$ V[26]. However, in organic media or in the presence of stabilizing ligands such as Cl^-, Br^-, CN^-, OTf^-, or OR^-,

Cu(I) species can be effectively stabilized and actively participate in catalytic cycles, as evidenced in numerous copper-mediated C–N and C–C bond-forming reactions.

Remarkably, this redox flexibility of copper, combined with its ability to engage in both single-electron transfer processes (as in radical reactions) and two-electron mechanisms (such as Chan–Lam couplings[27,28]), renders it a particularly efficient and adaptable transition metal for diverse catalytic contexts.

On the other hand, the ability of copper to form coordination compounds with oxygenated ligands[29] (e.g., salen-type[30]), nitrogenated[31], sulfur-based[32], phosphine (as in the Stryker reagent[33]), or N-heterocyclic carbene ligands[34], together with its behavior as a soft Lewis acid in the Cu(I) state and as a borderline Lewis acid in the Cu(II) state, depending on the ligand field, according to the Pearson scale[35], favors the selective activation of multiple bonds, heteroatoms, and leaving groups. Moreover, unlike noble metals such as palladium or platinum, copper is relatively abundant in the Earth's crust (~100 ppm)[36], its salts are inexpensive[37] and display lower toxicity[38], reinforcing its position as an excellent candidate for catalyst-based strategies.

Catalytic role of trifluoromethanesulfonate as a non-coordinating ligand

Trifluoromethanesulfonate ($[CF_3SO_3]^-$, OTf^-, triflate) is derived from trifluoromethanesulfonic acid (CF_3SO_3H, triflic acid), a superacid ($pK_a = -12$)[39] stronger than pure sulfuric acid. While it must be handled with extreme care, it provides unique opportunities for the generation of valuable products[40,41]. Owing to its structural features, the triflate anion is bulky, highly electronegative, and of low nucleophilicity, properties that make it ideal for homogeneous catalysis, particularly when highly electrophilic and reactive metal species are required in solution. Although traditionally regarded as a non-coordinating ligand, several studies[42] have highlighted that its influence can extend beyond simple ionic equilibria and may involve transient or weak inner-sphere interactions with the metal center or substrate, depending on the medium and the catalytic environment.

From a coordination chemistry perspective, the triflate anion is classified as a non-coordinating or weakly coordinating ligand, whose interaction with the metal center is predominantly electrostatic rather than covalent. This lability is one of its most valued features in synthesis, as it keeps the metal center coordinatively unsaturated, thereby facilitating the entry of auxiliary ligands (e.g., water, pyridine, or phosphines) through displacement of OTf^- (e.g., $M(OTf) + L \rightarrow M(L) + OTf^-$). Its low nucleophilicity and limited tendency to form covalent bonds also make it an excellent counterion, particularly useful for stabilizing highly electrophilic cationic species, as commonly observed in reactions requiring highly electrophilic or coordinatively unsaturated metal centers, such as in heterolytic H_2 activation processes[43]. Moreover, its perfluorinated structure confers high solubility in both aqueous and organic media[44], good thermal stability, and low reactivity toward atmospheric moisture, thereby preserving a high Lewis acidity at the metal center, an aspect crucial in homogeneous catalysis, especially in redox transformations.

Taken together**,** these features make OTf^- a suitable substitute for perchlorate, tetrafluoroborate, and hexafluorophosphate anions in catalysis. Nevertheless, it has been documented that in highly polar media or in the absence of competitive ligands, OTf^- may remain within the inner coordination sphere, as observed in complexes of Cu(II), Ru(II), and other d-block metals[45]. In the specific case of copper(II) trifluoromethanesulfonate, OTf^- modulates the reactivity of the catalytic center by maintaining the metal center coordinatively accessible, thereby favoring the formation of active species in solution and enabling C–N and C–C couplings, C–H activations, and radical transformations under mild conditions with broad functional group tolerance.

Synthesis of copper(II) triflate: strategies and experimental considerations

A commonly employed method for preparing metal triflates involves the direct reaction of metal chlorides (MCl_x) with trifluoromethanesulfonic acid (CAS: 1493-13-6) under anhydrous conditions, followed by precipitation of the product with dry diethyl ether. This procedure is successfully applied to Cu(II) salts as well as triflates of other transition metals, including Pd(II), Pt(II), M(III) (M = Co, Rh, Ir, Ru, Os), and Pt(IV), among others[46], as illustrated in reaction 1.

$$MCl_x + xCF_3SO_3H \rightarrow M(CF_3SO_3)_x + xHCl\uparrow \text{ …..} \textbf{(1)}$$

The synthesis is typically carried out under a nitrogen atmosphere and in a fume hood owing to the release of HCl vapors. The product is isolated by careful addition of dry diethyl ether, which induces precipitation of the corresponding triflate salt. The resulting solids are typically crystalline, soluble in polar organic solvents such as acetonitrile (although in some cases the triflate anion may be displaced by this ligand), and display good stability.

A practical route to metal trifluoromethanesulfonates, particularly useful for acid-sensitive compounds, involves the reaction of a metal sulfate ($M(SO_4)_x$) with a stoichiometric amount of barium triflate (CAS: 2794-60-7) in aqueous solution, as shown in reaction 2.

$$M(SO_4)_x + xBa(CF_3SO_3)_2 \rightarrow M(CF_3SO_3)_{2x} + xBaSO_4\downarrow \quad \textbf{(2)}$$

Barium sulfate, being insoluble, precipitates and is removed by filtration, while the metal triflate remains in solution. The solvent is removed by rotary evaporation under reduced pressure, yielding the product as a solid that can be purified by recrystallization if necessary. This methodology avoids the use of strong acids and is compatible with thermally or chemically sensitive systems, making it especially valuable for substrates prone to decomposition under acidic conditions.

An alternative route involves treatment of metal halides (MCl_x)

with silver triflate (CAS: 2923-28-6) in aqueous solution, as shown in reaction 3.

$$MCl_x + xAg(CF_3SO_3) \rightarrow M(CF_3SO_3)_x + xAgCl\downarrow \quad \textbf{(3)}$$

When the dissolved metal halide is mixed with a stoichiometric amount of $Ag(CF_3SO_3)$, a silver chloride precipitate forms immediately and is removed by vacuum filtration. The metal triflate remains in solution and is recovered by solvent evaporation. This method is particularly useful for preparing metal triflates from poorly water-soluble halides because it avoids the need for strong acids and is compatible with acid-sensitive substrates.

The procedure originally introduced by Jay K. Kochi[10] for the preparation of $Cu(OTf)_2$ involves the acid–base reaction of copper carbonate (5 g, 0.0405 mol) with trifluoromethanesulfonic acid (12 g, 0.080 mol) in 200 mL of acetonitrile, as shown in reaction 4.

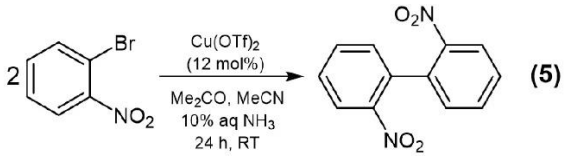
$$CuCO_3 + 2CF_3SO_3H \rightarrow Cu(CF_3SO_3)_2 + CO_2\uparrow + H_2O \quad \textbf{(4)}$$

The trifluoromethanesulfonic acid is added slowly owing to vigorous CO_2 release. After 0.5 h of stirring, the mixture is filtered and the blue solid is concentrated to dryness. The crude product is washed with petroleum ether, redissolved in acetonitrile, and precipitated by addition of diethyl ether. Cooling to −20 ºC affords a light-blue solid, which is dried under vacuum at 130 ºC for 8 h to yield 8 g of purified $Cu(OTf)_2$.

Currently, copper(II) triflate is commercially available at reasonable cost from major chemical suppliers. Its CAS number is 34946-82-2, with catalog entries such as Sigma-Aldrich 45,908-9 (99.99+%), 28,367-3 (98%), and Strem Chemicals 29-5000 (98%). It is typically supplied as an anhydrous light-blue solid with purities above 98%, soluble in polar organic solvents such as acetonitrile and dichloromethane. The compound is corrosive and hygroscopic and should be handled under an inert atmosphere, as it readily absorbs moisture and undergoes slow hydrolysis, which can compromise stability and catalytic performance.

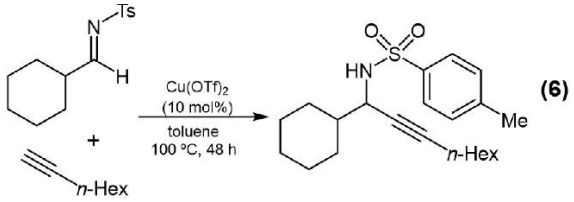
Selected catalytic applications of copper(II) triflate in organic synthesis

During the last five decades, copper(II) triflate has proven to be a versatile and efficient catalyst across a broad range of organic transformations, particularly in homogeneous catalysis. Its ability to activate C–C and C–N bonds under mild conditions, together with its compatibility with diverse functional groups, has driven its application in the synthesis of high-value products, including pharmaceuticals, functional materials, and natural products. Among these, C–C coupling reactions represent a prominent field of application. For instance, Ullmann-type couplings, which typically involve the formation of C–C, C–N, C–O, or C–S bonds and are traditionally catalyzed by metallic copper or Cu(I) species[47] under harsh conditions at elevated temperatures (>200 °C), can also be carried out efficiently with $Cu(OTf)_2$ under milder conditions. Notably, the $Cu(OTf)_2$-catalyzed homocoupling of 2-bromonitrobenzene at room temperature affords the corresponding nitro-substituted biphenyl in 79% yield, as shown in reaction 5[48].



(5)

Another notable case is the Sonogashira-type coupling[49], which traditionally involves the reaction of terminal alkynes with aryl or vinyl halides to form conjugated C≡C–C bonds, typically requiring Pd/Cu catalytic systems. Importantly, a palladium-free variant has been developed in which $Cu(OTf)_2$ serves as the sole catalyst, efficiently promoting C(sp)–C(sp^2) coupling under milder and more economical conditions. The catalytic activity of $Cu(OTf)_2$ is attributed to its Lewis acidity, which facilitates aryl halide activation and alkyne deprotonation, generating key copper–acetylide intermediates for transmetalation. As illustrated in reaction 6[50,51], this strategy enables the synthesis of sulfonyl-substituted propargylamines, with the product obtained in 63% yield, underscoring the ability of $Cu(OTf)_2$ to activate alkynes under neutral conditions without the need for palladium.

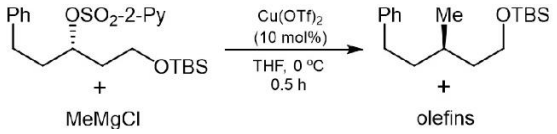


(6)

A synthetic approach of particular interest involves cross-coupling reactions between aryl halides (or their functional equivalents) and highly reactive carbon nucleophiles. These transformations enable efficient couplings between readily available nucleophiles (e.g., Grignard reagents) and activated alkyl electrophiles, thereby facilitating the construction of C(sp^3)–C(sp^3) bonds, even at stereogenic centers. In this context, $Cu(OTf)_2$ has proven to be an effective catalyst, capable of activating both the halide and the nucleophile simultaneously. Its high electrophilicity, combined with the lability of the trifluoromethanesulfonate anion, favors the transient formation of organocopper species that participate in the coupling step, even in the absence of strong bases or strictly anhydrous conditions.

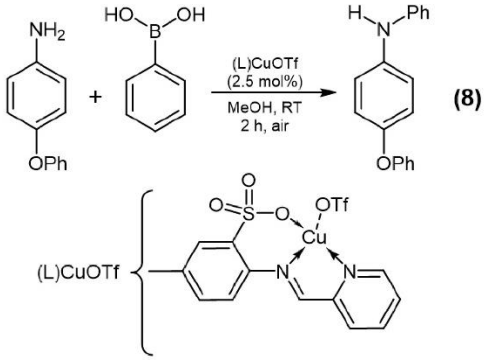
A representative example is the coupling between an O-alkyl-2-pyridinesulfonate and the Grignard reagent MeMgCl, as exemplified by reaction 7[52], forming a C–C bond via an S_N2[53] substitution with inversion at the chiral center. The transformation proceeds with high yields and enantioselectivities in short reaction times. Interestingly, the OSO_2-2-Py group acts as a pseudohalogen. The reaction also generates a mixture of olefins ($PhCH_2CH{=}CH(CH_2)_2OTBS$ and $Ph(CH_2)_2CH{=}CHCH_2OTBS$; OTBS = O-tert-butyldimethylsilyl). Remarkably, no additives such as TMEDA (N,N,N',N'-tetramethylethylenediamine) or LiOMe are required, highlighting the intrinsic ability

of $Cu(OTf)_2$ to promote the coupling without the assistance of external ligands or bases.



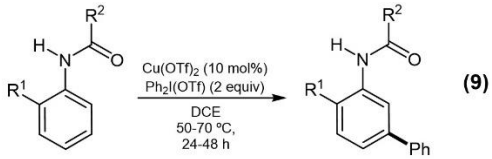
(7)

Copper-catalyzed aminations represent one of the most effective strategies for C–N bond formation under mild conditions. Among them, Chan–Lam reactions[54] have gained particular prominence for their ability to couple nitrogen nucleophiles (e.g., amines, amides, or azoles) with arylboronates or other organic nucleophiles, using copper(II) triflate catalysts under air and without auxiliary ligands or additional oxidants. A particularly effective strategy in these transformations is the preformation of LCu(OTf) complexes, in which an appropriate ligand (L) stabilizes the metal center while OTf^- serves as a non-coordinating counterion. These preformed complexes modulate the reactivity of the system, enabling highly selective and efficient couplings. As demonstrated in reaction 8[55,56], a Chan–Lam amination between 4-phenoxyaniline and phenylboronic acid catalyzed by preformed LCu(OTf) achieves conversions above 99%, demonstrating the high reactivity of well-defined Cu(II)–ligand complexes in oxidative coupling pathways.



(8)

In addition to coupling processes, $Cu(OTf)_2$ has also been employed in oxidative C–H functionalization reactions that are not accessible through purely Lewis acidic triflate systems. A representative example is the arylation of simple arenes catalyzed by copper(II) triflate using diphenyliodonium triflate as the arylating agent[57]. As illustrated in reaction 9, the catalyst (typically 10 mol%) was used in combination with $Ph_2I(OTf)$ (2 equiv), enabling direct arylation of electron-rich arenes. The reactions were conducted at 50–70 °C in 1,2-dichloroethane (DCE) and afforded the corresponding arylated products in moderate to good yields, with a marked preference for substitution patterns governed by the electronic nature of the substrate.



(9)

The mechanistic proposal[58], as shown in Fig. 2, underscores the involvement of high-valent organocopper species and suggests that interaction between the diaryliodonium salt and a reduced copper species leads to the formation of a formal aryl Cu(III) intermediate. A key feature of this transformation is the direct transfer of an aryl group to a C–H bond at the *meta* position of the arene ring, a site that is difficult to functionalize by conventional Friedel–Crafts reactions (Gaunt's proposal)[59]. The initial mechanistic interpretation invoked an anti-oxycupration pathway involving aryl Cu(III) species; however, subsequent, and more detailed DFT studies disfavored this scenario and instead supported an alternative mechanism involving initial metal attack at the *ortho* position, followed by a four-membered transition state that ultimately delivers arylation at the *meta* position (Wu's proposal)[60]. Further studies demonstrated that the presence of a carbonyl group plays a decisive role in controlling regioselectivity, enabling *meta* arylation even in electronically neutral arenes, whereas substrates lacking such directing groups preferentially undergo para or *ortho* functionalization. This transformation illustrates a key advantage of $Cu(OTf)_2$ over non-redox-active triflates (e.g., $Zn(OTf)_2$ or $X(OTf)_3$, where X = La, Sc, Bi), while also indicating that important questions remain regarding the nature and lifetime of high-valent copper intermediates in copper mediated oxidative and C–H functionalization processes.

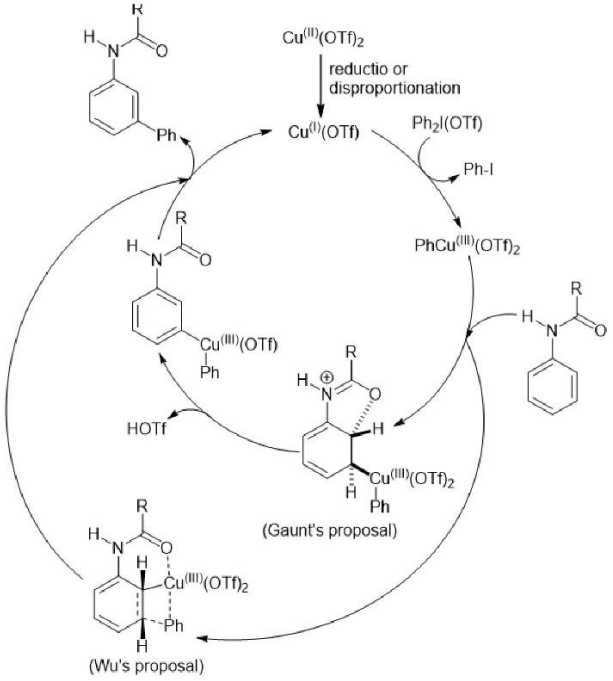
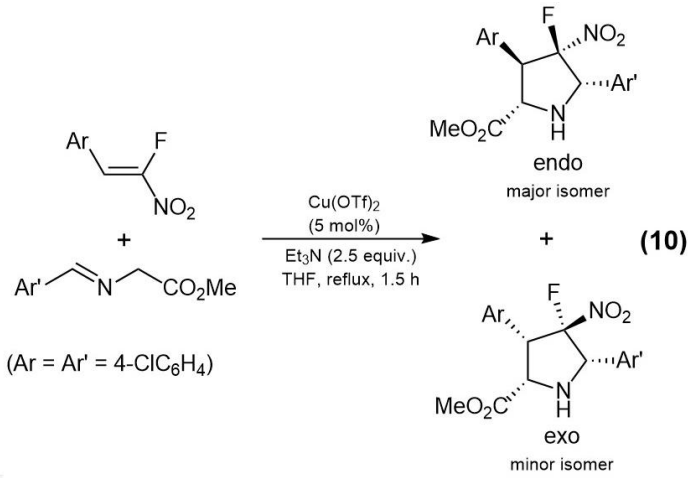


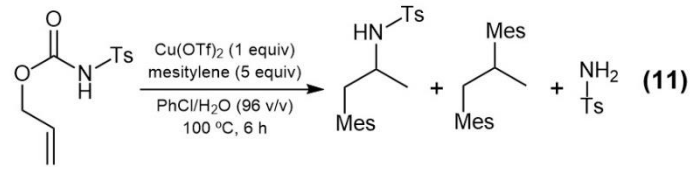
Fig. 2: Mechanistic proposals for the *meta* arylation of arenes catalyzed by $Cu(OTf)_2$. The originally proposed antioxycupration pathway (Gaunt) and the alternative DFT-supported *ortho* metalation mechanism leading to *meta* functionalization (Wu) are shown. Adapted from Ref. 58. R = Me, OMe, NEt_2, Ph.

Beyond the couplings discussed above, copper(II) triflate has also proven to be a remarkably versatile catalyst in other synthetically valuable transformations. Among these, the [3+2] cycloaddition of diazo compounds with alkenes or alkynes enables the efficient generation of nitrogen heterocycles under

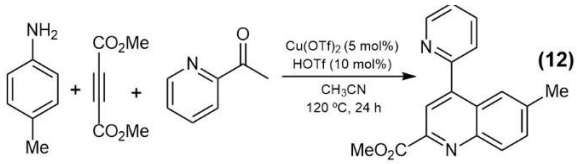
mild conditions with high diastereo- and enantioselectivity. In the example shown in reaction 10[61], the [3+2] cycloaddition of a nitrostyrene and an N-aryldiazo ester affords the corresponding pyrrolidines in 88% yield with excellent diasteroselectivity (dr = 10:1 endo:exo). This transformation represents an efficient strategy for the construction of tetrasubstituted pyrrolidines with potential pharmacological value.



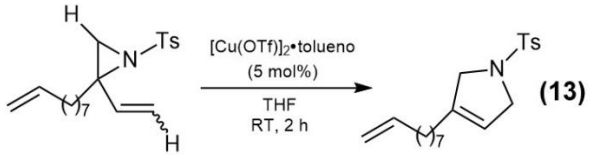
Copper(II) triflate has successfully replaced classical Lewis acid catalysts such as $AlCl_3$ or BF_3 in Friedel–Crafts-type reactions, offering milder conditions and greater functional group compatibility. A representative example is a cascade sequence promoted by $Cu(OTf)_2$, initiated by a decarboxylative and acid-mediated dealkylative Friedel–Crafts alkylation, followed by cationic rearrangements whose course depends on the substrate. In reaction 11[62], $Cu(OTf)_2$ catalyzes the alkylation of a tosyl-protected allyl carbamate with mesitylene (Mes = 1,3,5-trimethylbenzene), delivering the product in 70% overall yield without the need for intermediate steps.



$Cu(OTf)_2$ has also found application in multicomponent reactions (MCRs), such as Mannich-type processes[63], enabling the one-step construction of complex nitrogen-containing scaffolds with high regio- and stereoselectivity. As demonstrated in reaction 12[64,65], the synthesis of 2,4-disubstituted quinolines from *p*-toluidine, DMAD (dimethyl acetylenedicarboxylate), and 2-acetylpyridine in acetonitrile proceeds in 97% yield, underscoring the ability of copper triflate to orchestrate sequential condensation and cyclization steps within a single multicomponent process.



In some catalytic protocols, copper(I) triflate is preferably used in the form of complexes with aromatic solvents, such as $[Cu(OTf)]_2$•toluene (CAS: 48209-28-5). This formulation improves experimental handling, enhances solubility in organic media, and prevents the formation of inactive aggregates. In specific systems[66], such as the one shown in reaction 13[67], this form provides higher yields, reaching 90%, compared to anhydrous $Cu(OTf)_2$, underscoring its technical advantages under demanding catalytic conditions.



These and many other applications of $Cu(OTf)_2$[68], well documented in the literature, not only consolidate its role as a frontline catalyst in organic synthesis but also open up new opportunities for the construction of complex molecular architectures through advanced synthetic strategies aimed at the preparation of compounds of biomedical, pharmaceutical, and agrochemical interest[69]. Notably, a significant number of mechanistic proposals for $Cu(OTf)_2$ catalysis invoke Cu(III) intermediates[70–78], although their precise role under catalytic conditions remains a matter of ongoing discussion, defining an open mechanistic landscape that warrants further investigation[24,25].

Copper(II) triflate in the total synthesis of bioactive molecules

As outlined above, copper(II) triflate catalyzes a wide variety of coupling and functional group transformation reactions, making it a valuable alternative for the total synthesis of high-value molecules. Numerous alkaloids with antioxidant, anxiolytic, antimicrobial, anti-HIV, antiparasitic, anti-inflammatory, and antidepressant activities have been reported whose synthesis relies on copper(II) catalysis, particularly $Cu(OTf)_2$. Notable examples include calothrixins A and B, (+)-cladoniamide F and G, (+)-naseseazines A and B, and quebrachamine[79].

The scope of $Cu(OTf)_2$ catalysis further extends to (−)-alliacol A[80], a sesquiterpene of interest for its antimicrobial activity; anibamine B[81], a natural product with potent antiplasmodial activity; members of the azepane family[82]; cephalostatin 1[83], a powerful antitumor agent; and barringtogenol C, noted for its anti-inflammatory and vasoprotective properties. Additional applications include lissodendrolide A[84], with potential activity against Parkinson's disease, and the antibiotic tiacumicin B[85], of therapeutic interest in central nervous system (CNS) disorders as well as for its antitumor and antibiotic activities.

Products synthesized using $Cu(OTf)_2$ also include (+)-brasilenyne[86], investigated for its antiproliferative activity; diazonamide A[87], a natural product with cytotoxic and antitumor properties; himalensine A[88], an alkaloid studied for potential antioxidant, antitumor, and anti-HIV activity; (−)-lycoperine A[89], with potential against neurodegenerative diseases; (±)-merrilactone A[90], a natural product of therapeutic interest for Alzheimer's and Parkinson's disease; mescengricin[91], a metabolite

with potential neuroprotective activity; spirooxindole derivatives[92], valued for their antitumor, antimicrobial, anti-HIV, and anti-inflammatory properties; onoseriolide-lactone derivatives[93], a sesquiterpenoid with antitumor potential; oplopandiol[94], a natural product with antimicrobial activity; and (+)-pleuromutilin[95], a diterpenoid antibiotic.

The chemical structures of selected high-value bioactive molecules whose total synthesis features copper(II) triflate catalysis are shown in Fig. 3.

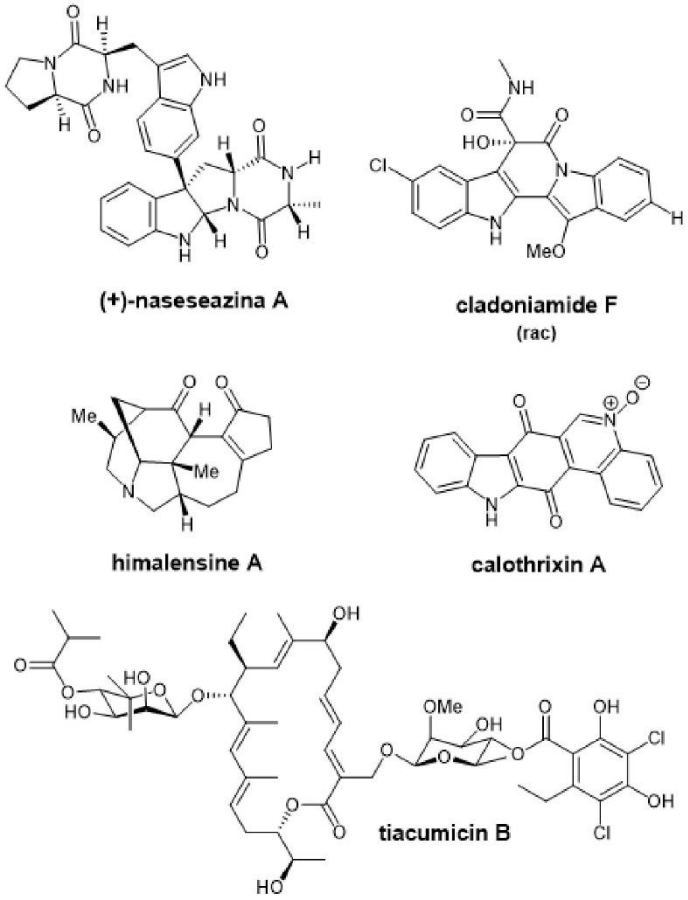


Fig. 3: High-value bioactive molecules that have featured copper(II) triflate catalysis in their total synthesis.

Copper(II) triflate in emerging applications

The chemistry of metal triflates extends well beyond $Cu(OTf)_2$, with several other species proving useful in organic synthesis as Lewis acid catalysts[96]. These include copper(I) triflate (CuOTf)[48], silver (AgOTf; CAS 2923-28-6)[97], iron(III) ($Fe(OTf)_3$)[98], lanthanum ($La(OTf)_3$; CAS: 52093-26-2)[99], scandium ($Sc(OTf)_3$; CAS: 144026-79-9)[100], zinc ($Zn(OTf)_2$; CAS: 54010-75-2)[101], indium ($In(OTf)_3$)[102], bismuth ($Bi(OTf)_3$)[103], and several rare-earth triflates[104]. Nevertheless, copper(II) triflate has emerged as one of the most versatile and effective, owing to its balanced combination of reactivity and stability together with its broad catalytic scope.

Reflecting current directions in sustainable catalysis, new modes of applying $Cu(OTf)_2$ have been developed, including heterogeneous systems in which it is supported on solid materials as well as its use in unconventional reaction media. These strategies improve recyclability, selectivity, and efficiency in synthetic processes. For instance, $Cu(OTf)_2$ supported on silica (SiO_2•$Cu(OTf)_2$) has proven effective in the cationic polymerization of styrene[105], Mannich reactions[106], and Diels–Alder cycloadditions[107]. It has also been combined with zeolite Y for the enantioselective aziridination of styrene[108]. In the field of nanotechnology, $Cu(OTf)_2$ has been incorporated into trititanate nanotubes (HTNT) for the synthesis of furo[2,3-b]quinoxalines[109], and used to prepare *N*-(cycloalkyl)aziridinofullerenes[110].

Further catalytic applications include the hydration of arylacetylenes[111] and Friedel–Crafts acetylation, both performed under microwave irradiation[112]. $Cu(OTf)_2$ has also been applied in ultrasound-assisted reactions, such as the synthesis of indenonaphthopyrans[113]. In addition, its use in ionic liquids ([BMIM]X, X = $[BF_4]$, $[PF_6]$) has been explored for transformations including the asymmetric cyclopropanation of styrene with ethyl diazoacetate[114], the benzoylation of anilides[115], and the synthesis of 1,3,5-triarylpyrazoles[116]. Moreover, the possibility of employing deep eutectic solvents (DES)[117] remains an established and valid option for many metal triflates.

Under solvent-free conditions, $Cu(OTf)_2$ has been applied in the synthesis of quinolines[118], vinyl sulfones[119], α-acetoxyphosphonates[120], aryl/heteroaryl-4-quinolones[121], and as a metal source in chiral Schiff-base complexes for the preparation of β-nitroalcohols[122]. In photocatalysis, it has been employed in the synthesis of quinoline derivatives, where $Cu(OTf)_2$ acts as an additive and the photocatalyst is a $Ru(bpy)_3Cl_2$ complex[123].

In terms of alignment with green chemistry, the various catalytic methodologies developed for $Cu(OTf)_2$ catalysis address several core concepts of sustainable synthesis, including efficiency, process intensification, and reduced waste generation. Given the diversity of catalytic platforms, reaction media, and activation modes described above, quantitative green metrics such as E-factors[124] are not systematically reported for $Cu(OTf)_2$ systems, which limits direct numerical comparison across studies. Nevertheless, these systems may be regarded as suitable candidates for future comparative sustainability studies, particularly when heterogeneous approaches, solvent-free conditions, deep eutectic solvents or ionic liquids, and alternative energy inputs (microwave and ultrasound) are employed, as discussed in this section.

Taken together, these strategies illustrate the synthetic potential of $Cu(OTf)_2$ and justify its position as a valuable tool in the design of increasingly efficient, selective, and sustainable catalytic processes.

Bibliometric analysis of copper(II) triflate research

A review of bibliometric data for copper(II) triflate during the period 1972–2024 reveals sustained growth in the number of scientific publications reporting its use as a catalyst across a

wide variety of reaction systems, as illustrated in Fig. 4. The graph, based on data from Google Scholar, ScienceDirect, ACS Publications, and Scopus, reflects a steady increase in research activity starting in 1972, followed by a pronounced acceleration from the early 2000s onward and reaching a peak between 2019 and 2024. This evolution can be broadly divided into three phases: an initial exploratory stage (1972–1990), characterized by sporadic reports following the seminal work of Kochi; a consolidation phase (1990–2010), during which $Cu(OTf)_2$ became increasingly adopted as a reliable Lewis acid and redox-active catalyst; and a rapid expansion phase after 2010, coinciding with its incorporation into multicomponent reactions, asymmetric catalysis, heterogeneous systems, and reactions conducted under unconventional or green conditions. Google Scholar reports the highest number of entries due to its broader coverage, which includes journal articles, books, theses, patents, and preprints. ScienceDirect and Scopus display similar growth trends with lower absolute counts, reflecting their more selective indexing criteria, while ACS Publications shows a more limited but consistent representation that nevertheless mirrors the same overall increase in research output. The sharp rise observed in the last decade points to a diversification and maturation of research on $Cu(OTf)_2$, with increasing emphasis on complex reaction manifolds, multicomponent processes, and advanced catalytic strategies, rather than solely on its initial use as a classical Lewis acid.

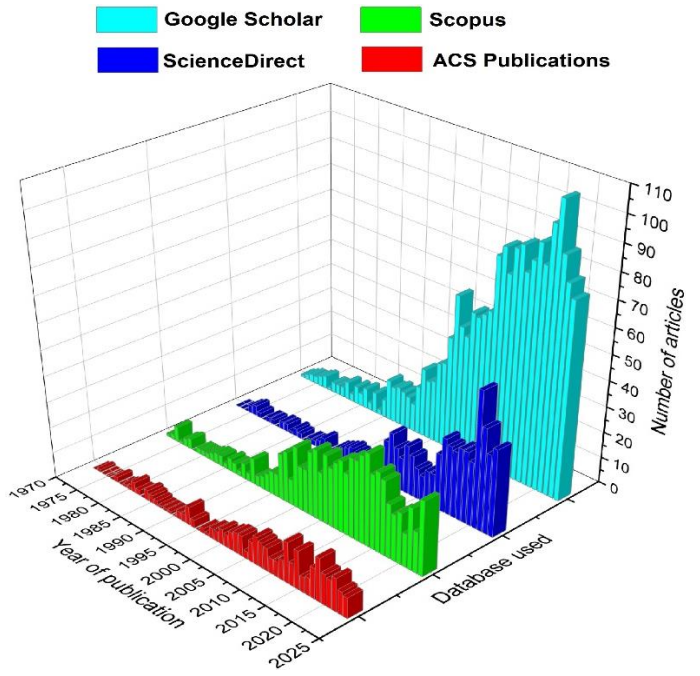


Fig. 4. Evolution of scientific publications involving $Cu(OTf)_2$ between 1972 and 2024, based on data retrieved from multiple bibliographic databases. After filtering duplicate records, 1955 entries were obtained from Google Scholar, 587 from ScienceDirect, 760 from Scopus, and 280 from ACS Publications, using "copper(II) triflate" as the search term.

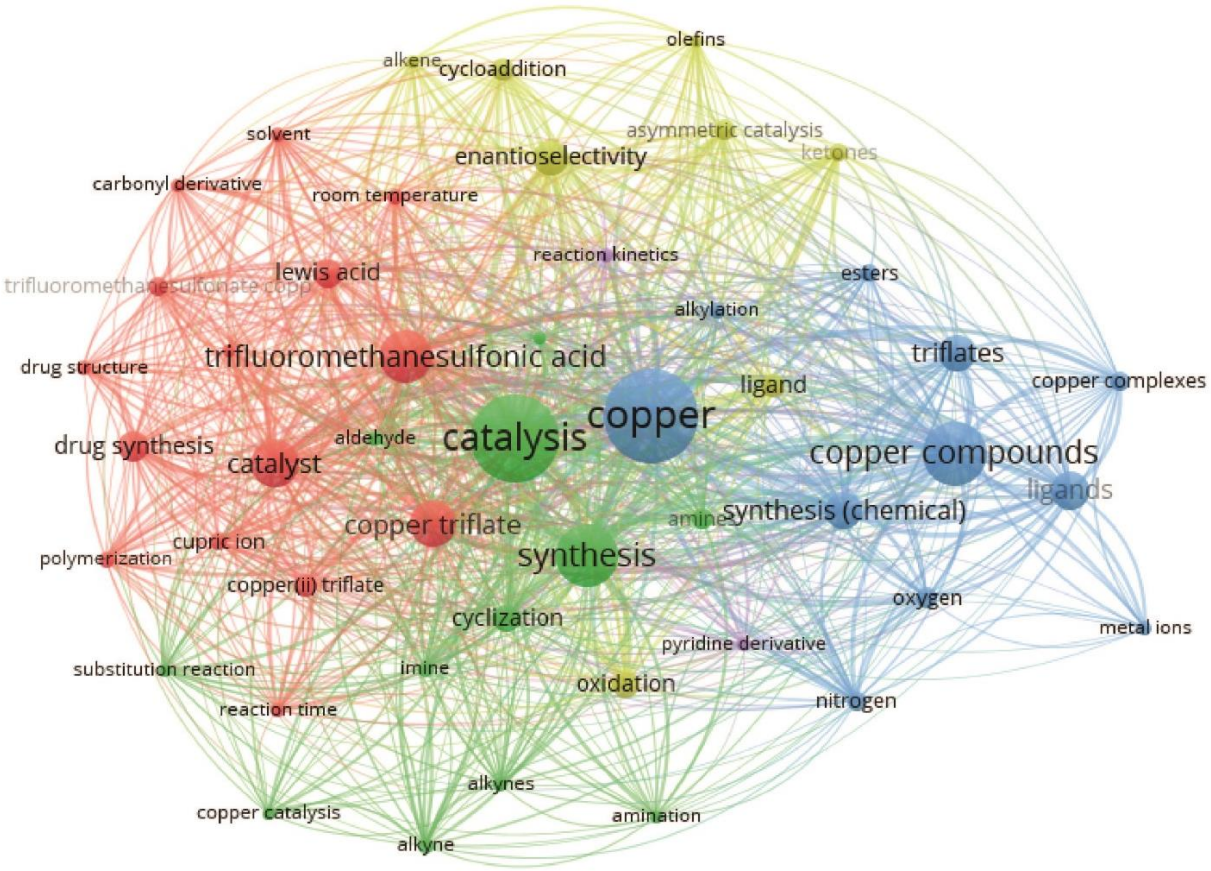


Fig. 5. Keyword co-occurrence map for "copper(II) triflate", generated with VOSviewer using 760 Scopus records. Colors indicate thematic clusters: red (catalysis in organic synthesis), green (oxidations), blue (coordination chemistry), and yellow (asymmetric catalysis). Node size reflects term frequency, and connecting lines visualize co-occurrence.

Based on the 760 Scopus records, a keyword co-occurrence map was generated using the VOSviewer software (Fig. 5). The analysis revealed four main thematic clusters. The red cluster highlights applications of $Cu(OTf)_2$ as a Lewis acid in drug synthesis and in catalysis in organic media. The green cluster groups terms related to homogeneous catalysis, oxidations, and cyclization reactions. The blue cluster focuses on coordination chemistry, emphasizing the association of the triflate with ligands, complexes, or metal ions. Finally, the yellow cluster links the use of $Cu(OTf)_2$ to enantioselective processes, cycloadditions, and asymmetric catalysis. The distribution of co-occurrences shows that copper(II) triflate is a key reagent both in the development of synthetic methodologies and in the mechanistic study of reactions, spanning coordination chemistry, catalysis, pharmaceutical synthesis, and fine chemistry. The analysis supports the positioning of $Cu(OTf)_2$ as a reference catalytic system across multiple fronts of contemporary organic synthesis.

Conclusions

Since the seminal mechanistic studies of Jay K. Kochi five decades ago, copper(II) triflate has established itself as a highly versatile and relevant catalytic tool in modern organic synthesis. Its combination of Lewis acidity, redox capability, stability in organic media, functional group tolerance, and ease of experimental handling makes it an especially attractive catalyst when compared with other, more costly or less sustainable catalytic systems. As outlined in this review, $Cu(OTf)_2$ participates in a wide range of transformations, including Ullmann-, Sonogashira-, and Chan–Lam-type couplings, intramolecular cyclizations, Mannich, Friedel–Crafts, and Ugi reactions; cycloadditions, oxidations, C–H activation, aziridination, and multicomponent and asymmetric syntheses. Its efficiency under mild conditions, with excellent substrate-to-catalyst ratios (typically 0.5–20 mol%), together with its ability to modulate reactivity through preformed complexes or supported systems, reinforces its role as a benchmark catalyst and a valuable platform for the total synthesis of structurally complex and high-value molecules. Emerging trends highlight a shift toward more sustainable and reusable media, including heterogeneous systems on silica, zeolites, or nanotubes (HTNT), alternative solvents such as ionic liquids and deep eutectic solvents, solvent-free reactions, and its integration into microwave- and ultrasound-assisted reactions, as well as photocatalysis. The bibliometric analysis confirms its sustained growth as both a subject of study and a versatile catalytic system, reflecting the increasing interest of the scientific community in methodological developments based on this compound. In summary, copper(II) triflate emerges as a catalyst well suited to the demands of more efficient and selective organic synthesis, in accordance with the principles of green chemistry. Its study and application will continue providing valuable opportunities for the rational construction of complex molecular architectures, both in fundamental research and in the development of compounds of pharmacological, agrochemical, and materials interest.

Acknowledgements

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