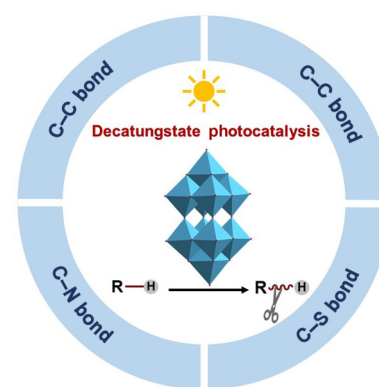


Decatungstate-based photocatalysts for organic transformations

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ABSTRACT: The functionalization of C–H bonds is critical in organic syntheses. However, their direct functionalization under mild conditions is complicated by their inherent inertness. To address this challenge, decatungstates ($W_{10}O_{32}^{4-}$), as versatile, inexpensive, and easily accessible hydrogen-atom transfer (HAT) photocatalysts, have emerged as powerful catalysts that can activate inert C–H bonds under ultraviolet irradiation to generate carbon-centered radicals for constructing C–C, C–N, C–S, and C–F bonds. This review highlights recent advances in $W_{10}O_{32}^{4-}$ -based photocatalysts and their applications in organic transformations. Overall, this article explores various $W_{10}O_{32}^{4-}$ -photocatalyzed organic transformations. In addition to summarizing the reported literatures, it critically discusses the current challenges and offers insights for future developments in this promising research field.



KEYWORDS: polyoxometalates, decatungstate, organic transformation, photocatalysis

1 Introduction

The functionalization of C–H bonds represents a significant methodology for realizing organic transformations. However, the high bond strength of these bonds significantly complicates their cleavage/functionalization, typically requiring harsh reaction conditions, such as elevated temperatures, and the use of noble-metal catalysts or oxidants [1–6]. The photocatalytic transformation of organic substrates, owing to its environmental benignity and high efficiency, has been attracting interest as a promising approach for realizing C–H bond cleavage/functionalization. For example, recent decades have witnessed widespread investigation of POMs as efficient photocatalysts for C–H bond activation under mild conditions.

POMs, which are anionic metal–oxygen clusters with well-defined structures, typically comprise W, Mo, V, Nb, and Ta in their high oxidation states [7–21]. Furthermore, POMs exhibit unique photoinduced charge-transfer properties [22], redox properties [23, 24], excellent electron-reservoir capacities [25, 26], and thermal/oxidative stability [27, 28], which make them ideal catalysts for water oxidation [29–31], hydrogen-evolution reaction (HER) [19, 32, 33], carbon dioxide reduction [34–39], and organic syntheses [9, 40–43]. Additionally, they exhibit intense O-to-W

ligand-to-metal charge transfer (LMCT) bands under ultraviolet (UV) and/or near-UV light. Therefore, when photoexcited, POMs undergo intramolecular charge transfer from the oxide ion (O^{2-})-based highest-occupied molecular orbital (HOMO) to the tungsten(VI) ion (W^{6+})-based lowest-unoccupied molecular orbital (LUMO), generating photoexcited states and functioning as oxidizing and reducing agents. These capabilities enable the application of POMs in diverse photocatalytic organic transformations [44–46]. Consequently, POMs have been systematically investigated as photocatalysts for the transformation of organic substrates, such as alcohols, phenols, benzenes, alkanes, and alkenes [47–51]. As a fascinating POM type, decatungstate ($[W_{10}O_{32}]^{4-}$) has attracted considerable attention for its unique photocatalytic activity [51–53].

The decatungstate anion ($[W_{10}O_{32}]^{4-}$) is a highly stable anionic cluster that is formed by the corner-, edge-, or face-sharing of simple tungstate units. Structurally, it is a dimer of two $[W_6O_{19}]^{2-}$ defect fragments that are connected by nearly linear W–O–W bridging bonds (Fig. 1(a)). Further, $W_{10}O_{32}^{4-}$ exhibits unique photophysical and photochemical properties that render it an exceptional photocatalyst. Under UV irradiation, the anion's photoactivation leads to the formation of an excited state, $[W_{10}O_{32}]^{4-*}$, via intramolecular O-to-W ligand-to-metal charge transfer (LMCT). Extensive mechanistic investigations have established the following mechanism for $W_{10}O_{32}^{4-}$ -based photocatalysis [54–61]: Under UV irradiation, the photoactivation of $[W_{10}O_{32}]^{4-}$ yields an excited state ($[W_{10}O_{32}]^{4-*}$) via intramolecular O-to-W LMCT. This species, $[W_{10}O_{32}]^{4-*}$, rapidly transforms into reactive species exhibiting an actual reactive state (wO), i.e., a relaxed excited state with a quantum yield of 0.5–0.6. Furthermore,

Received: August 6, 2025; Revised: August 21, 2025

Accepted: August 21, 2025

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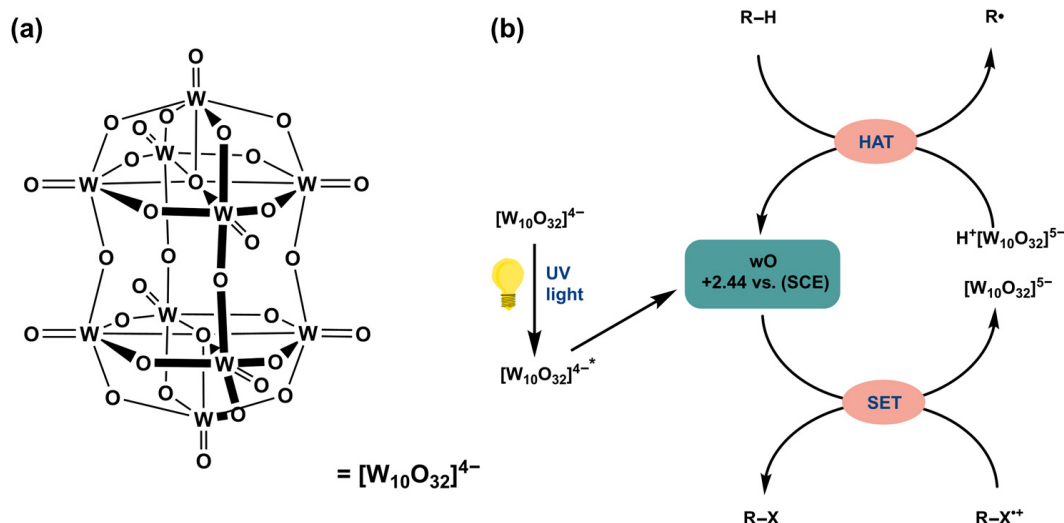


Figure 1 (a) Decatungstate anion structure and (b) the photocatalytic mechanism ($X = \text{Cl}, \text{Br}, \text{I}$) [45].

the redox potential of the actual reactive state, wO, is approximately +2.44 V vs. SCE, which is suitable for activating the C–H or C–X bonds of organic substrates through two plausible reaction pathways, namely single-electron transfer (SET) and hydrogen-atom transfer (HAT) [45] (Fig. 1(b)). By following SET, the R–X bond can be oxidized into R–X^+ species by wO; conversely, by following the HAT process, the R–H bond can be activated by transferring H, thus generating a carbon-centered radical ($\text{R}^\bullet$) for subsequent reactions. Notably, $\text{W}_{10}\text{O}_{32}^{4-}$ mediates the photocatalytic oxidation/mineralization of diverse organic substrates in an oxygen atmosphere. Conversely, it facilitates the cleavage of unactivated C–H bonds to generate carbon-centered $\text{R}^\bullet$ in the absence of oxygen [62]. These radicals are subsequently trapped by organic substrates, yielding C–C, C–N, C–S, and C–F bonds among others [63, 64]. Additionally, POMs demonstrate exceptional structural tenability, which is achieved by a deliberate modification of their counterion systems and constituent metal centers, including maintaining a hydrophilic/hydrophobic balance, across various solvent environments [65, 66].

In this review, we systematically categorized different $\text{W}_{10}\text{O}_{32}^{4-}$ photocatalyst-mediated C–X ($X = \text{C}, \text{N}, \text{S}, \text{F}$) bond-forming reactions [45, 52, 67–69]. This review also summarizes recent advances in $\text{W}_{10}\text{O}_{32}^{4-}$ -based photocatalysts for organic transformation based on the reported literature works, discussing the current challenges and providing insights into the future development of this promising research field.

2 Decatungstate-mediated photocatalytic oxidation under aerobic conditions

Under UV irradiation, the catalytic oxidation of organic compounds can be accomplished by POMs in the presence of oxygen [70, 71], particularly $\text{W}_{10}\text{O}_{32}^{4-}$. By combining laser flash photolysis, pulse radiolysis, and continuous photolysis, Tanielian and colleagues [54] investigated the mechanism of the $\text{W}_{10}\text{O}_{32}^{4-}$ -photocatalyzed oxidation of alcohols and alkanes. In their investigation, most of the organic substrates, including aliphatic alcohols and alkanes, typically underwent reactions via the aforementioned HAT process. In the presence of oxygen, wO reacted with propan-2-ol to produce the one-electron-reduced species ($\text{H}^+[\text{W}_{10}\text{O}_{32}]^{5-}$), whereas propan-2-ol was converted into

acetone. Notably, production distribution was significantly influenced by the oxygen concentration. In 1997, Maldotti et al. [72] demonstrated that the catalytic hydroxylation of cyclohexane yields cyclohexanol and cyclohexanone as main products at low and high oxygen pressures, respectively (Fig. 2(a)). In 2007, Orfanopoulos and coworkers [73] systematically investigated the mechanism of the $\text{W}_{10}\text{O}_{32}^{4-}$ -photocatalyzed oxidation of aromatic alcohols in acetonitrile through time-resolved techniques and kinetic isotope-effect studies (Fig. 2(b)). The combined experimental evidence demonstrated that the reaction proceeds exclusively via the HAT mechanism.

Our group recently developed tetrabutylammonium decatungstate (TBADT) as a photocatalyst for the oxidation of p-xylene into terephthalic acid (TPA) in acetonitrile under 365 nm light-emitting diode (LED) irradiation under ambient conditions. By exploiting the facile separation of TPA and the exceptional recyclability of TBADT, we engineered a continuous-flow photocatalytic system and demonstrated the potential of achieving its industrial-scale production. Further mechanistic studies revealed that the presence of an additive, HCl, contributed to the structural integrity of the $[\text{W}_{10}\text{O}_{32}]^{4-}$ and facilitated the transformation of photoexcited $[\text{W}_{10}\text{O}_{32}]^{4-*}$ into wO, thereby enhancing photo-oxidation performance [74].

3 Decatungstate-photoinduced carbon–carbon single-bond formation

3.1 Alkanes, alcohols, and ethers as radical precursors

Organic-compound alkylation is among the pivotal research directions in organic synthesis. Alkylated products, for their inexpensiveness and wide availability, can be efficiently synthesized via the selective C–H bond activation of alkanes, catalyzed by $\text{W}_{10}\text{O}_{32}^{4-}$. Employing TBADT as a photocatalyst, Hill and coworkers investigated the radical addition reaction of alkanes with ethylene, acetylene, and carbon monoxide (CO) under UV irradiation, which yielded the corresponding alkylated products (Fig. 3(a)) [75, 76]. The same group subsequently realized the temperature-controlled selective synthesis of nitrile ($T = 90^\circ\text{C}$) or α -iminoester ($T = 22^\circ\text{C}$) from alkanes and methyl cyanofornate through the precise regulation of the reaction conditions

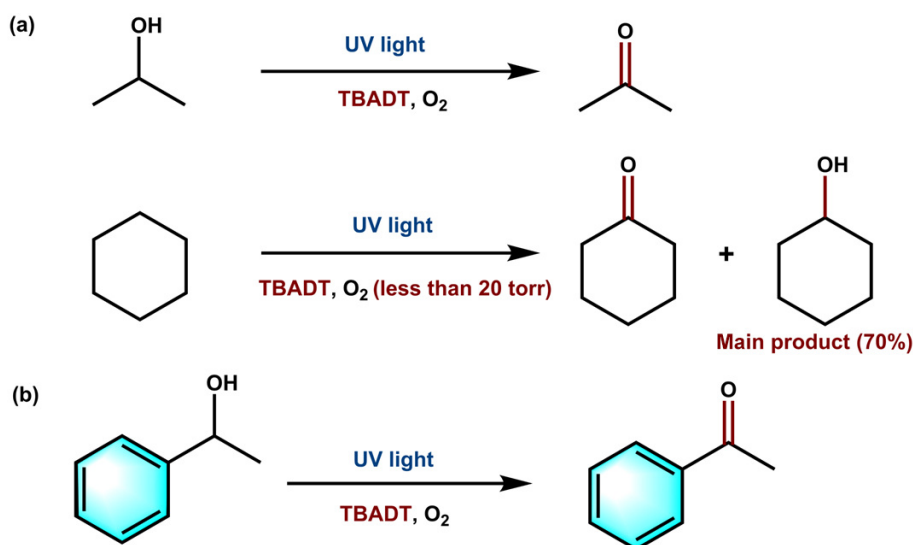


Figure 2 Oxidation of aliphatic alcohols, alkanes and aromatic alcohols [73, 74].

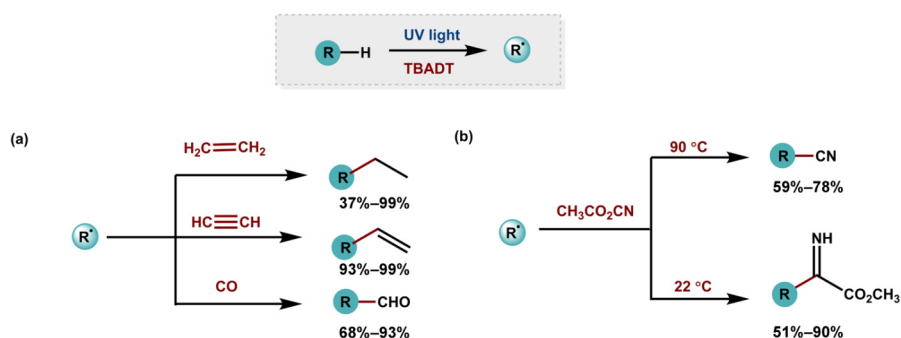


Figure 3 Functionalization of alkanes. (a) Addition reaction of alkanes with alkenes, alkynes and CO [75, 76]. (b) Addition reaction of alkanes with methyl cyanoformate [77].

(Fig. 3(b)) [77].

Based on present studies, Albini and colleagues [78–80] demonstrated the TBADT-photosensitized UV-irradiated alkylation of electrophilic alkenes (unsaturated nitriles, esters, ketones, etc.) using alkanes, alcohols, and ethers (Fig. 4(a)). In 2011, Ryu et al. [81] generated an alkyl radical from an activated alkane using a catalytic amount of TBADT. This radical was subsequently allowed to react with CO and an electron-deficient alkene to yield an unsymmetrical ketone via a three-component coupling process (Fig. 4(b)). In 2014, Ravelli's group [82] reported the activation of the C–C single bond ($\text{C}(\text{sp}^3)\text{--H}$) in oxetanes via TBADT-mediated photocatalysis under mild conditions. The resulting radical was captured by electron-deficient olefin, facilitating the synthesis of 2-substituted oxetanes (Fig. 4(c)).

Notably, the direct activation of gaseous hydrocarbons is still a grand challenge owing to their inherent inertness, typically requiring extreme reaction conditions to achieve $\text{C}(\text{sp}^3)\text{--H}$ bond cleavage. In 2020, Timothy Noël's group [83] developed a continuous-flow platform for activating gaseous alkanes under mild reaction conditions. The system, which was photocatalyzed by inexpensive TBADT at room temperature, activated $\text{C}(\text{sp}^3)\text{--H}$ bonds in methane, ethane, propane, and isobutane. The resulting carbon-centered radicals were subsequently transformed into corresponding alkylated products in excellent yield through the Michael addition reaction, exhibiting remarkable selectivity (Fig. 4(d)).

Although the cross-dehydrogenative coupling of alkanes, alcohols, and ethers with aromatic compounds is feasible, it requires exogenous oxidants. In 2017, Ryu's group [84] employed the persulfate anion as an oxidant for the cross-dehydrogenative coupling of aromatic compounds with hydrogen donors, mainly yielding radical precursors from alkanes, alcohols, and ethers (Fig. 5(a)). Additionally, TBADT can photocatalyze alkane cyanation under mild conditions. In 2021, Soon Hyeok Hong and coworkers [85] developed an efficient, mild cyanation protocol employing a TBADT-mediated catalytic system with tosyl cyanide as the cyanide source. This system effectively facilitated the catalytic cyanation of unactivated aliphatic $\text{C}(\text{sp}^3)\text{--H}$ bonds. Their cyanation protocol could be applied to a remarkably broad substrate scope, ranging from simple aliphatic hydrocarbons to structurally complex bioactive compounds (Fig. 5(b)).

Moreover, alkylarenes functionalization can be achieved by generating benzylic radicals, leveraging the inherent instability of benzylic hydrogens. In 2013, Fagnoni and coworkers [86] reported the TBADT-photocatalyzed benzylation of electrophilic alkenes with alkylbenzenes in a high-ionic-strength medium (5:1 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$, 0.5 M LiClO_4), as illustrated in (Fig. 6(a)). Notably, this protocol applies to a wide range of substituted toluene ($-\text{Cl}$, $-\text{F}$, $-\text{CN}$, etc.) and alkylbenzene derivatives. In 2017, Ryu's group [87] investigated the TBADT-photocatalyzed C–H functionalization of alkylpyridines. They achieved site-selectivity in 2-propylpyridine alkylation, with functionalization proceeding preferentially at β -

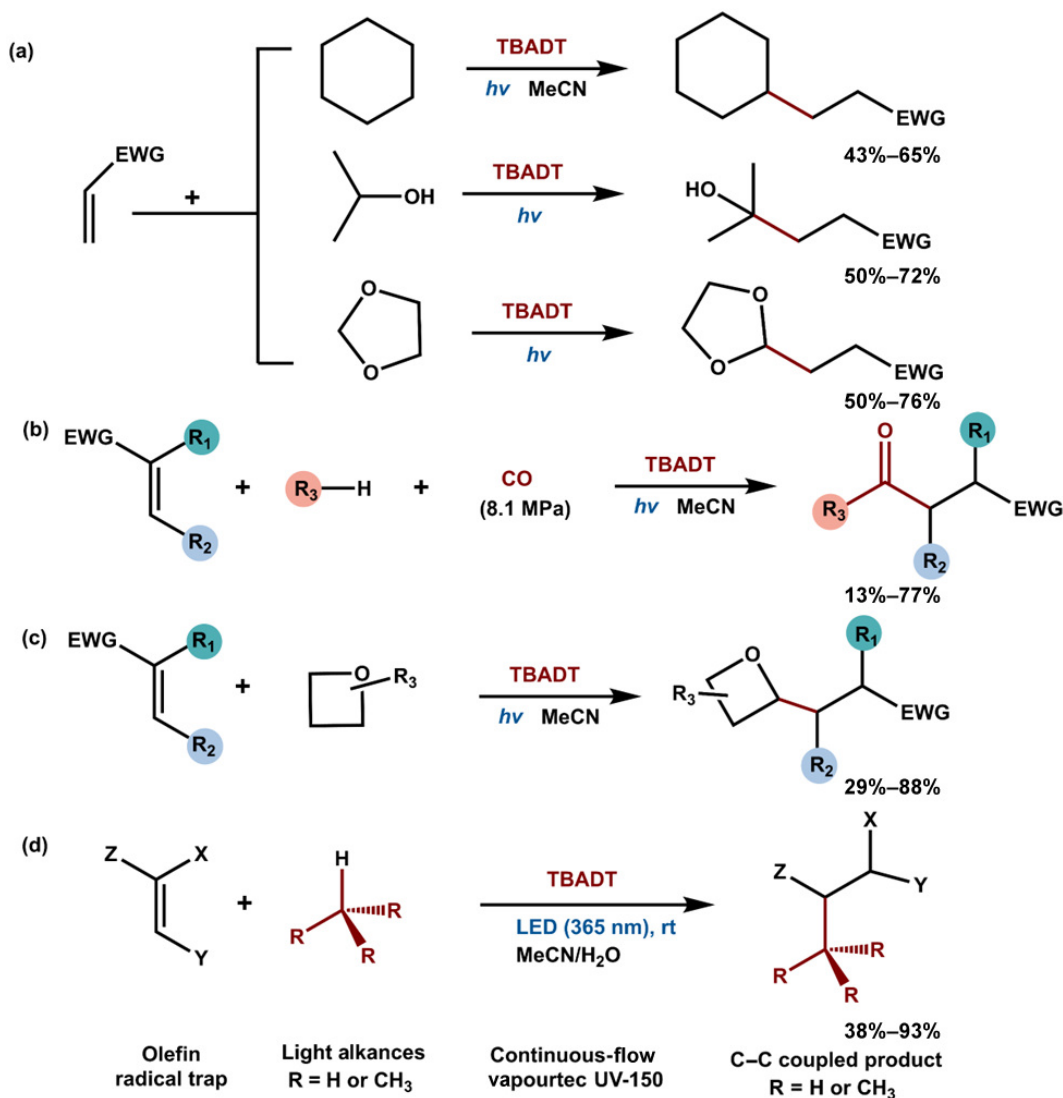


Figure 4 Addition reaction of electrophilic alkenes (EWG = electron withdrawing group). (a)–(c) Addition reaction of electrophilic alkenes with alkanes, alcohols, and ethers [78–82]. (d) Addition reaction of electrophilic alkenes with light hydrocarbons [83].

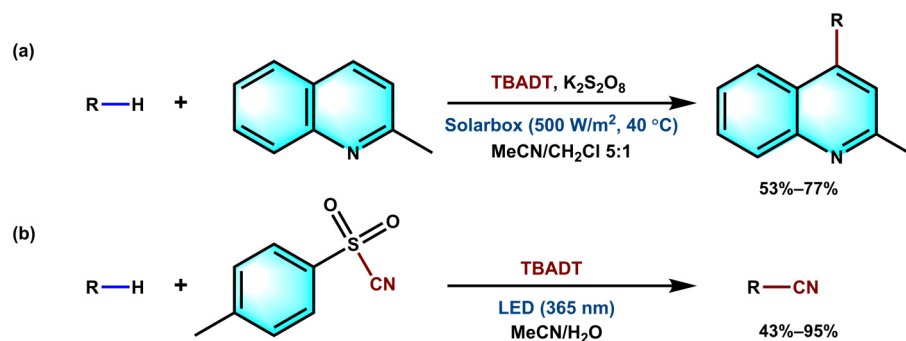


Figure 5 (a) Cross-coupling of alkanes with aromatic compounds [84]. (b) Cyanation of alkanes with aromatic compounds [85].

$C(sp^3)$ –H positions while the benzylic positions did not react (Fig. 6(b)). In 2022, Kuninobu and colleagues [88] developed a protocol for controlling the site-selective $C(sp^3)$ –H functionalization of 2-methylanilinium salts through radical intermediates (Fig. 6(c)). Leveraging electrostatic interactions, TBADT reacted with the ammonium group of 2-methylanilinium salts, abstracting a hydrogen atom from the proximal benzylic $C(sp^3)$ –H bond under

UV light. The product was converted into the corresponding alkylated compound via an addition reaction with an electron-deficient alkene.

3.2 Aldehydes and ketones as radical precursors

As summarized in Section 3, the $C(sp^3)$ –H bonds in saturated alkanes, alkylarenes, alcohols, and ethers can generate their

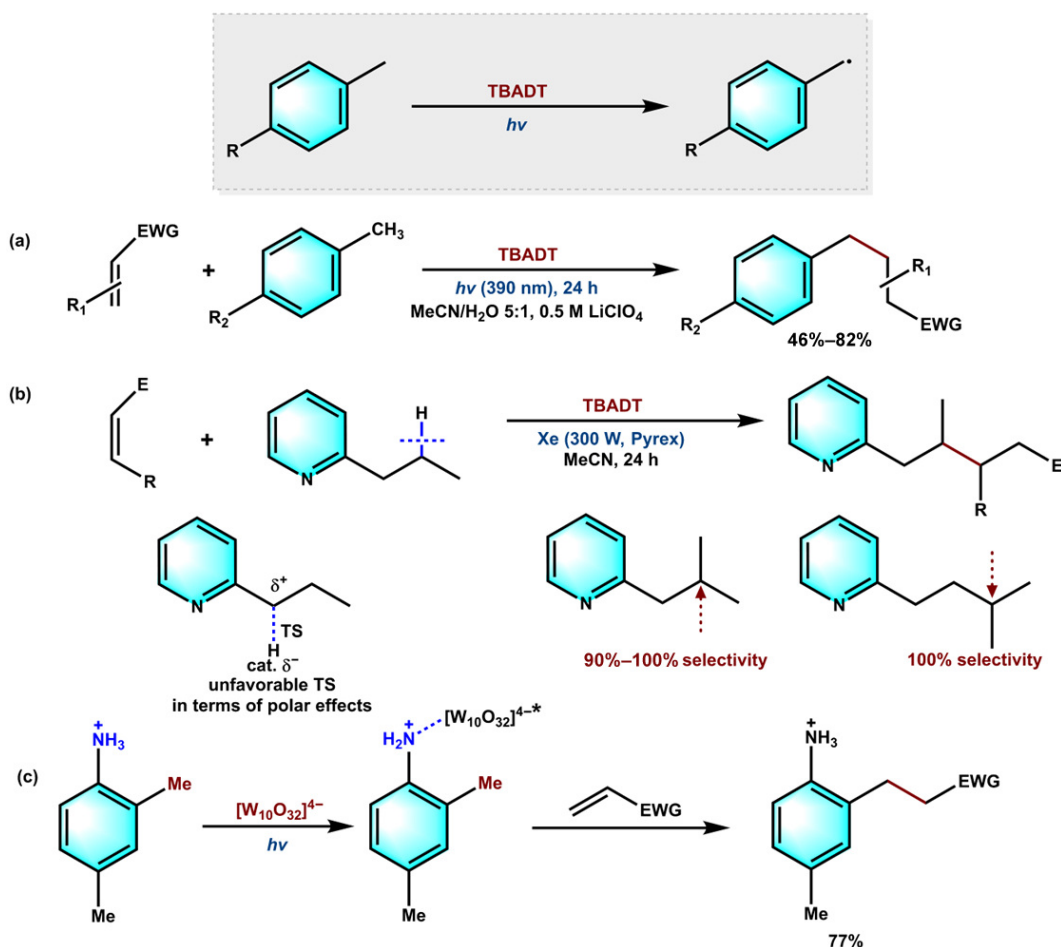


Figure 6 Addition reaction of alkylarenes with alkenes [86–88].

corresponding radicals through HAT. Similarly, the C(sp²)–H bonds of aldehydes and ketones can form carbon-centered radicals via HAT for subsequent transformations. In 2007, Albini et al. [89] synthesized ketones through the TBADT-mediated reaction of electrophilic alkenes with acyl radicals (Fig. 7(a)). In 2009, Orfanopoulos and coworkers [90] realized the direct acylation of [51] fullerene through the photocatalytic generation of carbonyl radicals from aldehydes, followed by their trapping with C₆₀

(Fig. 7(a)). Fagnoni's group [91] efficiently synthesized unsymmetrical ketones in 2017 by reacting acylsilane-generated acyl radicals with Michael acceptors (Fig. 7(b)).

Notably, the hydroacylation of trifluoromethyl (CF₃) alkenes is still greatly complicated by its requirement for nucleophilic addition, followed by β-F elimination. In 2019, Chuan Wang and colleagues [92] achieved the photocatalytic hydroacylation of CF₃ alkenes using TBADT as a catalyst, thereby avoiding β-F

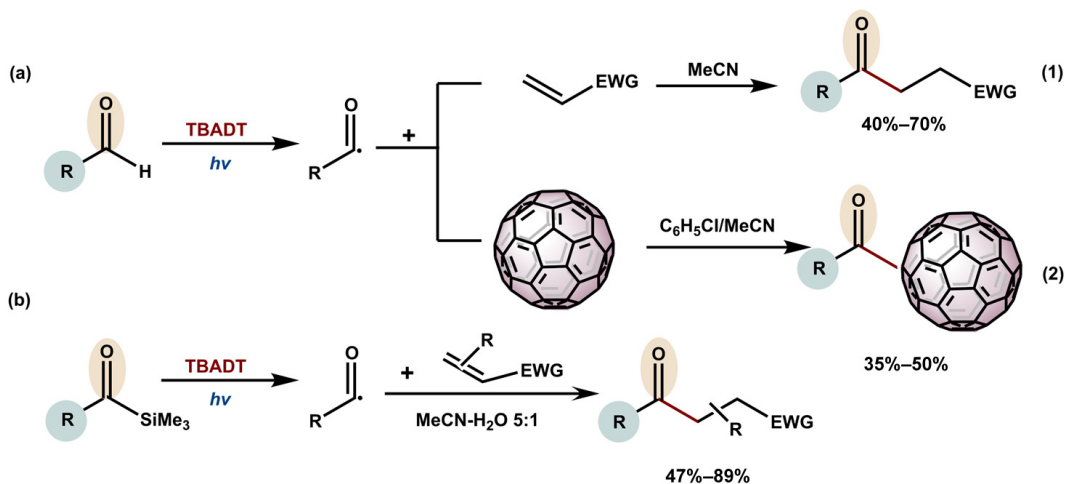


Figure 7 Acylation of organic compounds. (a) Acylation of electrophilic alkenes and [60]fullerene with aldehydes [89, 90]. (b) Acylation of electrophilic alkenes with acylsilanes [91].

elimination (Fig. 8(a)). Generally, natural amino acids exhibit poor biostability, and this makes the synthesis of unnatural amino acids a long-standing focus in chemical research. Recent advances in radical chemistry have yielded novel synthetic strategies for preparing unnatural amino acids. In 2021, Qingmin Wang's group [93] developed a method for synthesizing acyl radicals from readily available aldehydes; in this method, the aldehyde hydrogen was abstracted by $W_{10}O_{32}^{4-}$ under illumination (Fig. 8(b)). Thereafter, the generated acyl radicals were subjected to an addition reaction with dehydroalanine to yield γ -carbonyl unnatural amino acids.

Additionally, the $W_{10}O_{32}^{4-}$ -mediated photocatalytic system can be applied to β -C–H bond activation in cyclopentanones for the β -alkylation of electron-deficient alkenes. In 2014, Fagnoni and coworkers [68] realized the β -alkylation of cyclopentanones via the TBADT-mediated reaction of cyclopentanones with electron-deficient alkenes (Fig. 9(a)). A highly polar bimolecular-homolytic-

substitution transition state, such as that generated during TBADT-mediated hydrogen abstraction, facilitates β -selective C–H bond cleavage via a polar effect. Notably, replacing artificial xenon-lamp illumination with sunlight irradiation produced comparable or even superior results. Moreover, the three-component β -acylated product was obtained in a good yield in the presence of CO (Fig. 9(b)). Ryu's group [94] reported $W_{10}O_{32}^{4-}$ -catalyzed site-selective $C(sp^3)$ -H alkenylation in 2022 (Fig. 9(c)). The key reaction step involved an efficient proton-coupled electron transfer or HAT between $H^+W_{10}O_{32}^{5-}$ and a benzenesulfonyl radical to generate benzenesulfinic acid, which sustained the catalytic cycle.

3.3 Formation of carbon–carbon single bonds mediated by decatungstate and other catalysts

Decatungstate has been utilized in organic syntheses because of its dual roles: as a photosensitizer that promotes SET, and as an HAT

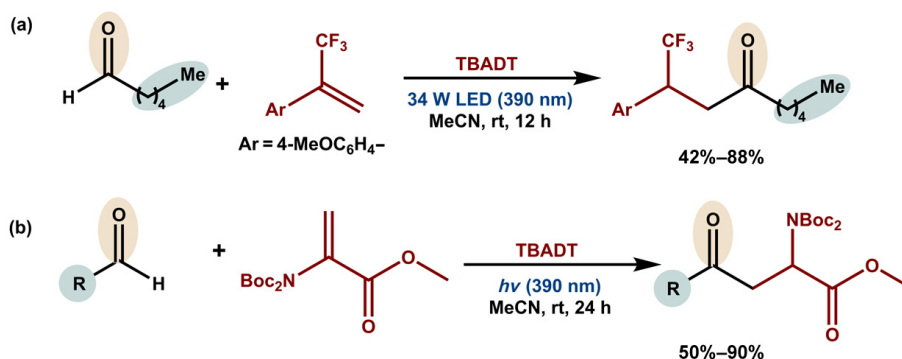


Figure 8 (a) Acylation of trifluoromethyl alkenes with aldehydes [92]. (b) Acylation of dehydroalanine with aldehydes [93].

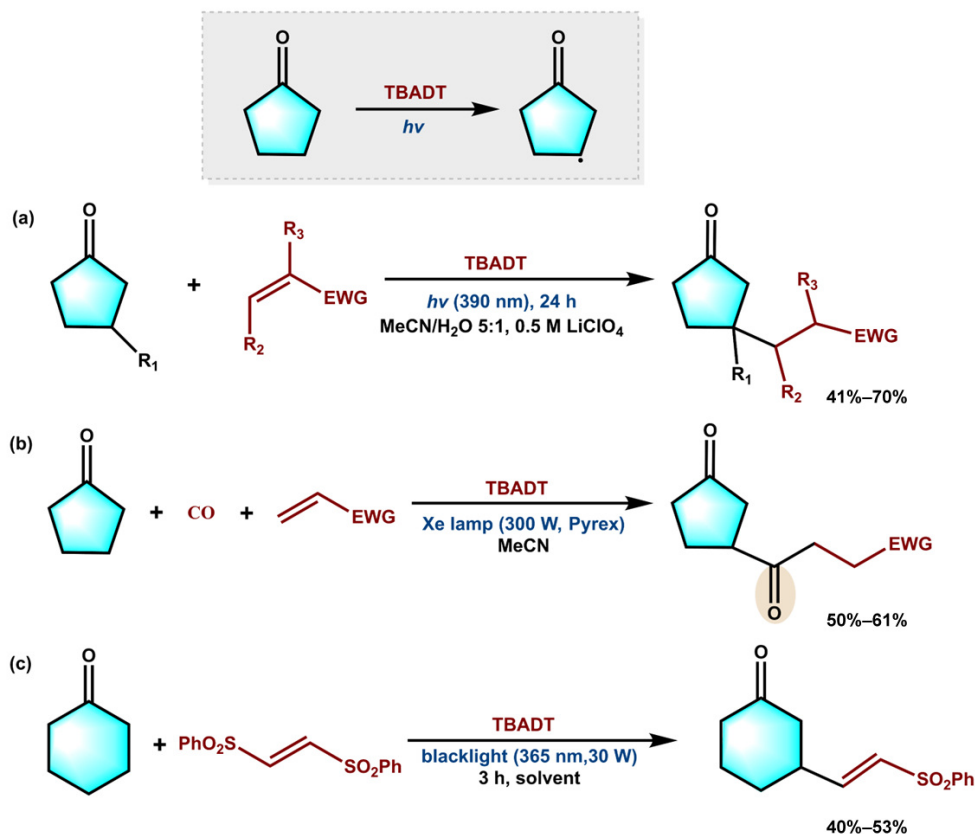


Figure 9 Reactions of cyclopentanones with electron-deficient alkenes [68, 94].

catalyst that cleaves the C–H bonds to generate alkyl radicals. However, the inherent high reactivity of these TBADT-generated alkyl radicals often induces uncontrolled side reactions, resulting in poor product selectivity. To address this drawback, the introduction of auxiliary catalysts has emerged as an effective strategy to stabilize radical intermediates, concurrently enabling the expansion of substrate scope and the development of novel organic transformations.

3.3.1 Synergistic catalysis by decatungstate and organic catalysts

Merging $W_{10}O_{32}^{4-}$ and organic catalysts offers potent strategies for accessing and synthesizing chiral products from simple molecules, thus significantly shortening synthetic routes. Further, the construction of quaternary stereocenters primarily relies on organometallic-catalyzed carbon-group addition to conjugated carbonyl compounds. However, this approach suffers from substantial side reactions and the requirement of expensive catalysts. In 2016, Melchiorre and coworkers [63] adopted a radical-trapping strategy for constructing quaternary stereocenters (Fig. 10). During the reaction based on this strategy, the amino moiety of the organic catalyst interacted with the cyclohexenone substrate to generate a chiral iminyl cation. Thereafter, the unstable radical intermediate was formed by a TBADT-mediated radical addition to the C=C double bond. Next, the intermediate was reduced by the redox-active carbazole moiety of the organic

catalyst, effectively suppressing its decomposition. Subsequently, the rapid tautomerization of the reduced product yielded the corresponding quaternary stereocenters, and the catalyst was regenerated.

The direct asymmetric functionalization of $C(sp^3)$ –H bonds enables the transformation of readily accessible chemicals into complex chiral molecules. In 2020, Pusheng Wang's group [95] developed a protocol for the asymmetric C–H functionalization of unactivated hydrocarbons with exocyclic enones in the presence of TBADT and chiral phosphoric acid (Fig. 11). In this process, a light-mediated decatungstate anion first facilitated the generation of alkyl radicals via HAT, after which these radicals were added to the enones to form the enol intermediates. Next, these enol intermediates were converted into chiral alkyl ketones via a covalent interaction between the intermediates and the chiral phosphoric acid. This protocol can be used for a broad variety of hydrocarbons, including benzylic hydrocarbons, cycloalkanes, and allylic hydrocarbons, with high enantioselectivity.

3.3.2 Synergistic catalysis using decatungstate and transition metal catalysts

In addition to SET, photosensitive metal catalysts exhibit broader applicability. Notably, the direct arylation/acylation of inert alkane C–H bonds can be realized using $W_{10}O_{32}^{4-}$ as hydrogen-atom-abstracting photosensitizers in combination with metal catalysts.

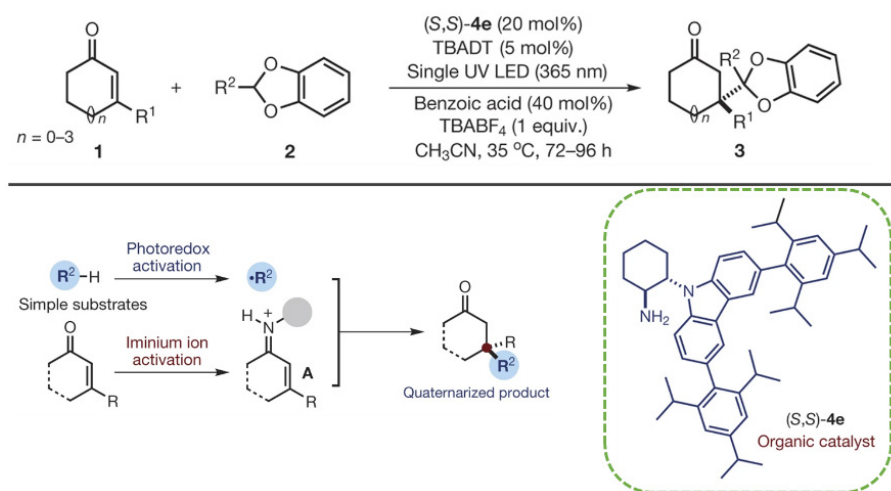


Figure 10 Construction of quaternary stereocenters through alkanes reaction with ketenes. Reprinted with permission from Ref. [63], © Macmillan Publishers Limited 2016.

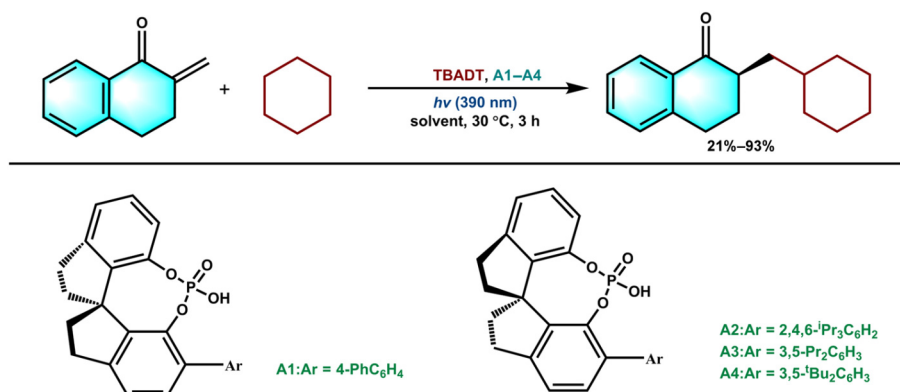


Figure 11 Synthesis of chiral alkyl ketones via the reaction of alkanes with exocyclic enones. Reprinted with permission from Ref. [95], © American Chemical Society 2020.

MacMillan and coworkers [96] demonstrated the direct C–H arylation of aliphatics in 2018, with high selectivity and generality (Fig. 12). In this synergistic system integrating photoinduced TBADT-mediated HAT with nickel catalysis, they generated carbon-centered radicals from strong, neutral C–H bonds. These radicals subsequently acted as nucleophiles in nickel-mediated cross-coupling with aryl bromides to construct C(sp³)–C(sp²) bonds. The methodology obviates the requirement for complex synthetic routes, achieving the desired product through a single synthetic step.

Moreover, the merging of TBADT with a nickel-phosphinooxazoline (PHOX) complex can induce the asymmetric acyl-carbamoylation of alkenes. In 2020, Wang Chuan et al. [97] selectively synthesized diverse 3,3-disubstituted oxindoles from aryl carbamoyl chloride-tethered alkenes and aldehydes, and the synthesis was driven by the synergistic catalysis of TBADT and a

nickel-PHOX complex (Fig. 13). The preliminary mechanistic studies revealed that the nickel-mediated catalytic process might account for the enantiodetermining step in the catalytic cycle, whereas the TBADT-catalyzed acyl C–H activation of the aldehydes might account for the synthesis of the acyl radicals. The catalytic system displays remarkable generality, including for aliphatic and (hetero)aromatic aldehydes, with consistently high yields.

In 2021, Noël's group [98] developed a protocol for the acylation/arylation of unfunctionalized alkyl derivatives by synergistic TBADT–nickel catalysis under flow conditions (Fig. 14(a)). The protocol integrated a continuous-flow environment with a high photon-flux light source. It employed TBADT for hydrogen-atom abstraction and generated nucleophilic carbon-centered radicals that were trapped by nickel catalysts to construct C(sp³)–C(sp²) bonds. This method enables the uniform,

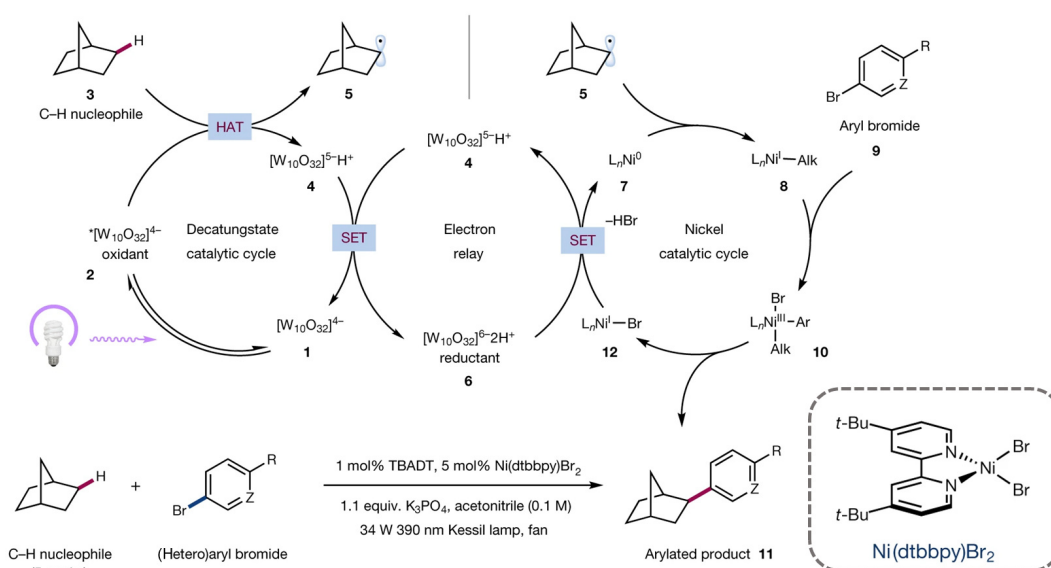


Figure 12 Cross-coupling of alkanes with aryl bromides. Reprinted with permission from Ref. [96], © Springer Nature Limited 2018.

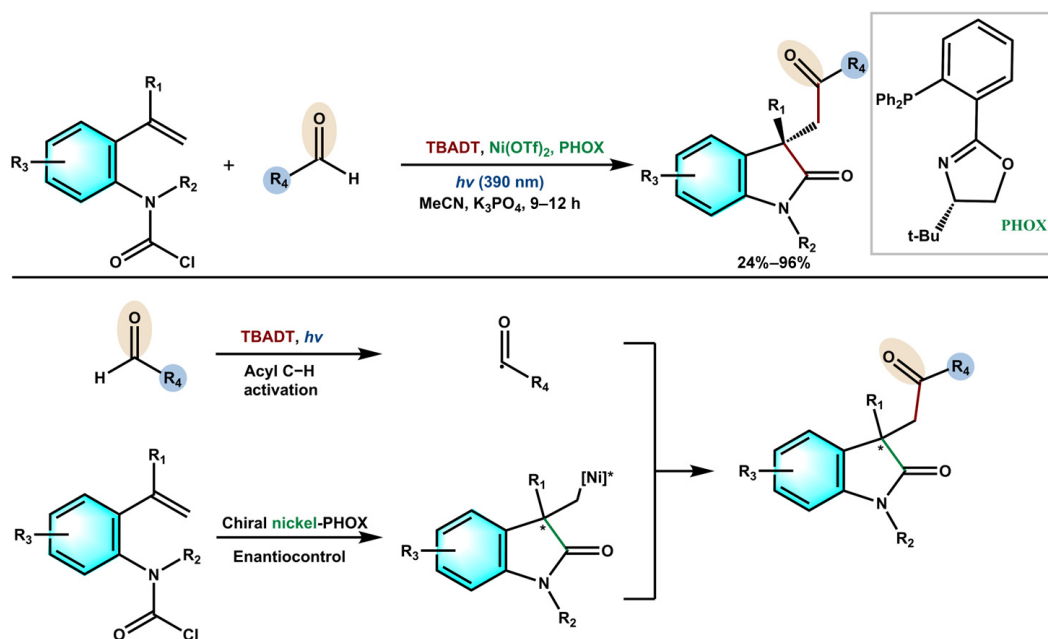


Figure 13 Formylation of alkenes with aldehydes [97].

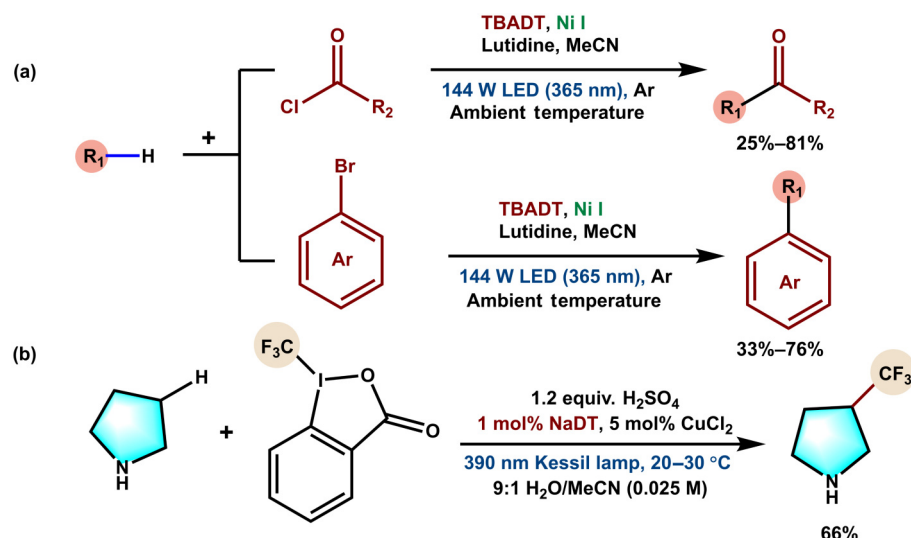


Figure 14 (a) Acyl/aryl functionalization of C–H bonds [98]. (b) The C–CF₃ bonds construction [99].

high-intensity photoirradiation of the entire reaction mixture, achieving dramatic rate acceleration, which reduces the reaction time to only 5–15 min.

Synergistic W₁₀O₃₂^{4–}-copper catalysis can mediate the direct trifluoromethylation of alkyl C–H bonds. Additionally, the introduction of a CF₃ moiety can dramatically improve the pharmacokinetic properties and activity of compounds. In 2020, MacMillan and colleagues [99] developed a W₁₀O₃₂^{4–}-photocatalyzed strategy for activating C(sp³)–H bonds toward generating carbon radicals. Employing Togni's reagent as the CF₃ source, they efficiently generated C–CF₃ via copper(II) chloride-mediated reductive elimination (Fig. 14(b)). This methodology establishes a platform for synthesizing complex aliphatic trifluoromethylated compounds, demonstrating extensive applicability in natural products and pharmaceuticals.

Beyond benefiting C–C bond formation, synergistic W₁₀O₃₂^{4–}-transition metal catalytic systems can effectively promote other organic transformations. In 2025, our research group developed a photoinduced catalytic-transfer-hydrogenation system by integrating a W₁₀O₃₂^{4–}-generated reductive species (H⁺[W₁₀O₃₂]^{5–}) with Pd/C to facilitate the selective conversion of furfural (FF) into a biofuel, furfuryl ethyl ether [100]. The subsequent mechanistic studies revealed that H⁺[W₁₀O₃₂]^{5–} generated active hydrogen species on the Pd nanoparticles and that this species can participate

in HER or the FF hydrogenation (Fig. 15).

4 Decatungstate-photoinduced formation of carbon–fluorine bonds

Typically, incorporating a fluorine atom or fluorinated substituent into organic molecules significantly modifies their physical/chemical properties, as well as pharmacophysiological activities. Thus, fluorinated compounds are indispensable in the fields of pharmaceuticals, agrochemicals, and functional materials. Consequently, the efficient construction of C–F bonds is a critical objective in synthetic methodology [101]. In 2014, Britton et al. [64] reported the direct fluorination of unactivated alkanes by combining TBADT (as a hydrogen-atom abstractor) with a fluorine-transfer reagent (*N*-fluorobenzenesulfonimide; Fig. 16(a)). One year later, they [102] also utilized a W₁₀O₃₂^{4–} photocatalyst to synthesize γ-fluoroleucine, a key intermediate for preparing odanacatib (a preclinical anti-osteoporotic compound). Additionally, the use of sodium decatungstate (NaDT) as the photocatalyst for the direct fluorine-18 fluorination of aliphatic amino acids holds significant implications, as it enables the one-step synthesis of oncological positron-emission-tomography imaging agents (Fig. 16(b)) [103, 104].

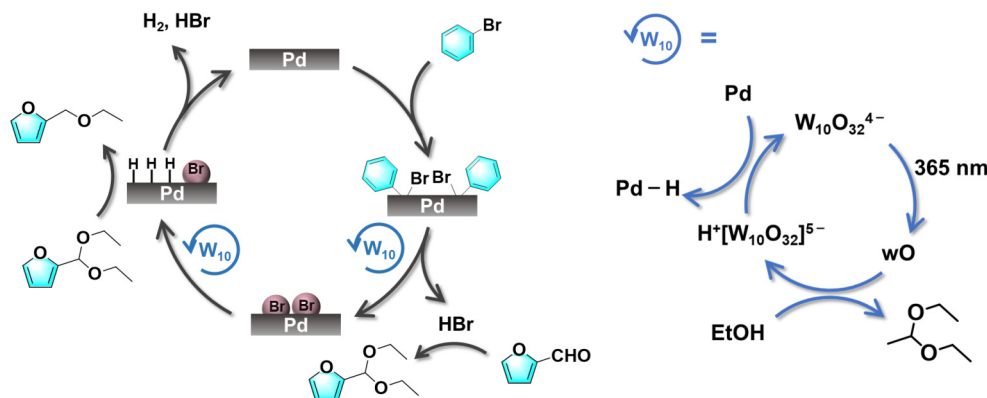


Figure 15 Synergistic catalytic system by decatungstate and Pd/C for the photocatalytic synthesis of furfuryl ethyl ether. Reprinted with permission from Ref. [100], © Dalian Institute of Chemical Physics, the Chinese Academy of Science. Published by Elsevier B.V. 2025.

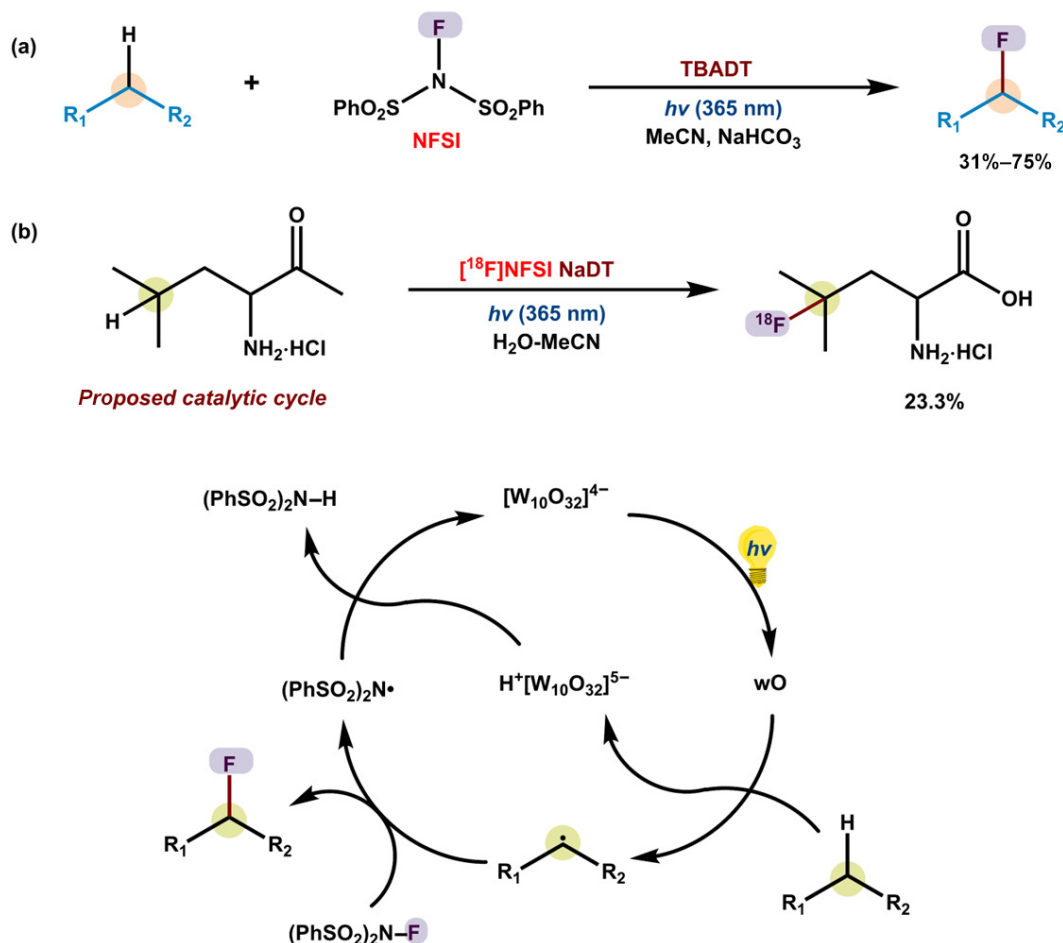


Figure 16 C–F bonds formation of aliphatic compounds with NFSI [64, 103].

5 Decatungstate-photoinduced formation of carbon–nitrogen bonds

Despite extensive studies on the amination of C(sp³)–H bonds, the corresponding functionalization of aliphatic C(sp³)–H bonds remains significantly underdeveloped. To address this drawback, photocatalytic C(sp³)–H functionalization has emerged as a key strategy in synthetic chemistry, where $[W_{10}O_{32}]^{4-}$ effectively mediates C(sp³)–H bond activation to form C–N bonds. In 2013, Fagnoni and coworkers [105] demonstrated that the strongly electrophilic N=N bond in diisopropyl azodicarboxylate could act as a Michael acceptor for Giese-type addition to produce hydrazides (Fig. 17(a)), which reacted with alkane-, ether-, and aldehyde-generated carbon-centered radicals to form C–N bonds. Notably, the same conditions readily apply to the three-component coupling between cyclic alkanes, CO, and diisopropyl azodicarboxylate to form C–CO–N bonds.

In 2021, Noël's group [67] employed TBADT to generate a carbon-centered nucleophilic radical, which was subsequently oxidized into a carbocation by tert-butylhydroperoxide via an oxidative radical–polar crossover process. The resulting carbocation was trapped by N-heteroaryl-based nucleophiles to form the desired C–N bond (Fig. 17(b)). Further, they employed the Microflow technology (continuous-flow technology), which shortened the reaction times and boosted conversion efficiency. In 2022, they [106] implemented a newly developed flow photoreactor (featuring high-power LED) to initiate regioselective C(sp³)–H amination

mediated by $W_{10}O_{32}^{4-}$ photocatalysts to produce protected hydrazine, pyrazole, and free amine (Fig. 17(c)). This high-intensity reactor system facilitated simultaneous rapid data acquisition and scalable production within a single device, effectively bridging the gap between laboratory-scale research (mmol scale) and industrial implementation (mmol scale).

In 2022, Wang et al. [107] demonstrated a facile and efficient strategy for constructing C–N bonds. In their protocol, a broad array of C–H substrates, including gaseous, linear, cyclic, and benzylic hydrocarbons, can be used to efficiently synthesize the corresponding alkylamines (Fig. 17(d)). This transformation leveraged the dual catalytic role of POMs: (I) alkane activation to generate alkyl radicals and (II) nitroarenes reduction into nitrosoarenes, which trap alkyl radicals to produce the target alkylated amines. The protocol presents an economic strategy for the rapid synthesis of alkylamines from industrial feedstock.

6 Decatungstate-photoinduced carbon–sulfur bond formation

Organosulfur compounds, such as sulfonamides, sulfones, and sulfides, are extensively utilized in modern materials, agrochemicals, and pharmaceuticals. Despite their paramount significance, as well as the remarkable progress in C–H functionalization, the direct conversion of C(sp³)–H bonds into C–S bonds still constitutes a major challenge. In 2021, MacMillan and coworkers [66] reported the transformation of aliphatic C(sp³)–H bonds into corresponding

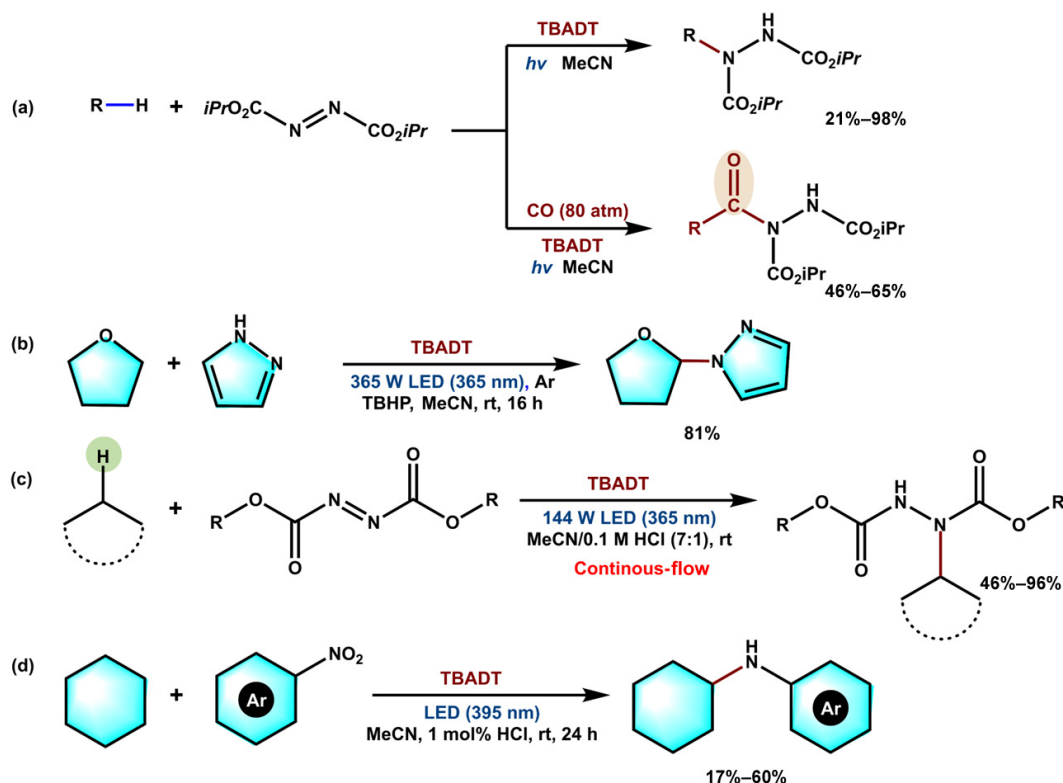


Figure 17 Decatungstate-photoinduced formation of C–N bonds in different reactions (a)–(d) [67, 105–107].

alkyl sulfinic acids using NaDT as the catalyst. Their study paved the way for the syntheses of a variety of valuable organosulfur compounds (Fig. 18). Under UV irradiation and in the presence of a $[W_{10}O_{32}]^{4-}$ catalyst, cyclopentanones are converted into alkyl

radicals, which are rapidly trapped by sulfur dioxide to generate sulfonyl radicals, ultimately forming the $C(sp^3)-S$ bond. Taken together, these studies provide a general strategy for related transformations, illustrating the feasibility of using sulfur dioxide to

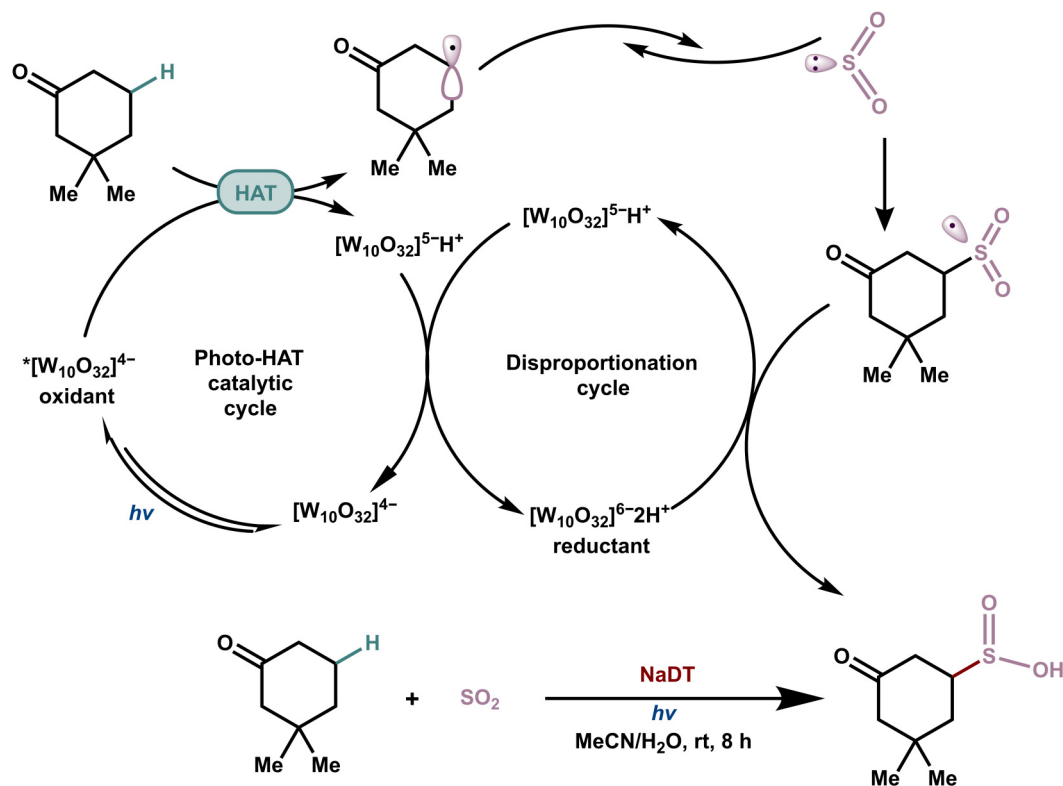


Figure 18 C–S bonds formation of cyclopentanones with SO_2 [66].

efficiently trap diverse aliphatic radicals to form C–S bonds.

7 Conclusions and outlook

The inherent stability of C–H bonds typically poses a significant challenge for their functionalization, often necessitating harsh conditions, such as elevated temperatures, and the use of additives, such as precious metal catalysts and oxidants. Therefore, developing methodologies for C–H bond functionalization under mild conditions holds significant synthetic value. As a versatile, inexpensive, and environmentally benign HAT photocatalyst, $W_{10}O_{32}^{4-}$ can activate inert C–H bonds to generate carbon-centered radicals under UV irradiation, thereby facilitating the functionalization of organic molecules. This protocol has been extensively deployed in $C(sp^3)$ –H functionalization, including oxidations, dehydrogenations, aminations, fluorinations, and conjugate additions. In this tutorial review, we outlined some of the progress recorded in $W_{10}O_{32}^{4-}$ -mediated photocatalytic syntheses. Although numerous studies primarily explored C–C bond formation, only a few explored the construction of C–N, C–F, and C–S bonds.

Despite the remarkable advantages of $W_{10}O_{32}^{4-}$ in organic transformations, its photocatalytic activation typically requires UV irradiation owing to the large energy gap between its O^{2-} -based HOMO and W^{6+} -based LUMO orbitals. As UV light constitutes only a minor fraction of natural sunlight, developing functionalized visible-light-responsive $W_{10}O_{32}^{4-}$ photocatalysts is crucial for efficient solar-energy utilization. To address these challenges, the following strategies are proposed: (I) integrating $W_{10}O_{32}^{4-}$ catalysts with soluble visible-light-active photosensitizers and (II) introducing transition metal ions into the $W_{10}O_{32}^{4-}$ skeleton to modulate its electronic structures. Additionally, the recyclability of $W_{10}O_{32}^{4-}$ catalysts from homogeneous catalytic systems presents another key concern that must be resolved. Therefore, future studies must consider the immobilization of $W_{10}O_{32}^{4-}$ catalysts into porous photoactive substrates to enhance light-activity, dispersibility, and reusability. In summary, $W_{10}O_{32}^{4-}$ -based photocatalysts have demonstrated remarkable advantages in organic synthesis owing to their inherent unique properties. Thus, we anticipate that many excellent related studies will be reported.

Data availability

Not applicable.

Acknowledgements

This work was supported by the Hebei Natural Science Foundation (No. B2024105003), the National Natural Science Foundation of China (Nos. 22471017 and 21831001), the Recruitment Program of Global Experts (Young Talents) and BIT Excellent Young Scholars Research Fund. The instrumental support from the Analysis and Testing Center of Beijing Institute of Technology is also highly appreciated.

Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article. Author Guo-Yu Yang is the advisory board member of this journal, but he is not involved in the peer-review or decision of this article.

Author contribution statement

Y. R. L.: Data curation, visualization, writing – original draft. Z. L.: Validation, writing – original draft. J. L.: Writing – original draft. T. F. L.: Supervision, validation. H. J. L.: Funding acquisition, project administration, conceptualization, supervision, writing – reviewing & editing. G.-Y. Y.: Funding acquisition, project administration, supervision. All the authors have approved the final manuscript.

Use of AI statement

None.

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