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Recent advance in carbocation-catalyzed reactions

Wei Xiao[a], Jie Wu[a,b,c,*]

[a] School of Pharmaceutical and Materials Engineering & Institute for Advanced Studies, Taizhou University, Taizhou 318000, China
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China
[c] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, China

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ABSTRACT

Carbocations such as tropylium and trityl cation, can be stable enough to be isolated and used without inert conditions. They can act as Lewis acids to lower the LUMO of electrophile, thus promoting reactions with nucleophiles. Additionally, the interaction between carbocations and alcohols can form Brønsted acids with enhanced acidity. Furthermore, electrophoto activation of TAC^+ (trisaminocyclopropenium ion) delivers the excited radical dication $TAC^{\bullet 2+*}$, which is a strong oxidant and capable of oxidizing a range of challenging substrates. Moreover, ^{n}Pr-DMQA$^+$ is disclosed as a versatile photoredox catalyst as its excited state can be quenched through both oxidation and reduction. This review summarizes recent advance in carbocation-catalyzed reactions. These developed methods provide an environmentally friendly pathway for the synthesis of valuable compounds and will inspire chemists to discover more interesting transformations promoted by carbocations.

1. Introduction

Discovery of novel catalysts that are efficient and environmentally-friendly is highly desirable. Carbocations are normally considered as unstable and nonisolable intermediates in fundamental transformations such as E1, S_N1 and rearrangements [1]. However, this is only partially true as delocalized carbocations can be stable enough to be isolated and utilized without inert conditions or even in aqueous medium [2]. The first stable carbocation discovered was the tropylium cation in 1891 [3]. Since then, several types of carbocations have been extensively studied in terms of reactivity, properties and stability [2]. Despite the fact that carbocations have been known for more than 130 years, it's rather surprising that their applications in organic transformations have been investigated only in recent decades. To date, carbocations, such as tropylium and trityl cation, are commonly used as Lewis acids to activate electrophiles by lowering their LUMO [4]. The utilization of carbocations as Lewis acids can provide a metal-free way to facilitate reactions without precious metals since Lewis acids are normally metals or metalloids [5]. Additionally, the combination of carbocation with other components such as water and alcohol can furnish a stronger Brønsted acid to promote various transformations [6]. Furthermore, electrophoto activation of TAC^+ (trisaminocyclopropenium ion) delivers the excited radical dication $TAC^{\bullet 2+*}$, which is a strong oxidant and capable of oxidizing a range of challenging substrates [7]. Recently, a newly developed carbocation, ^{n}Pr-DMQA$^+$, can be employed as a versatile photocatalyst to catalyze reactions under red light irradiation [8].

In spite of the emergence of carbocation promoted organic reactions in the past decade, few reviews have been published in this area [9,10]. Herein, this review is aimed to summarize the recent advance in carbocation-catalyzed organic reactions published since 2017, and focuses on the role of carbocation in the reaction process.

2. Carbonyl groups activation

Carbonyl groups are one of the most synthetically important classes of organic substrates due to their versatile and ubiquitous chemical reactivity in organic transformations [11], and acetalization reactions are the popular masking protocol for aldehydes and ketones. In 2017, Nguyen and coworkers reported the tropylium cation catalyzed acetalization reaction with a wide range of aldehydes **1** and trialkyl orthoformate **2** [12]. This metal-free process worked efficiently in both batch and flow conditions. A plausible mechanism is depicted in Scheme 2. It was reasoned that initially, tropylium cation served as a Lewis acid to activate the carbonyl group to form intermediate **4**, which went through a nucleophilic addition with trialkyl orthoformate **2** to generate intermediate **5**. Subsequently, alkyl group transfer intramolecularly of intermedi-

* Corresponding author.
E-mail address: jie_wu@fudan.edu.cn (J. Wu).

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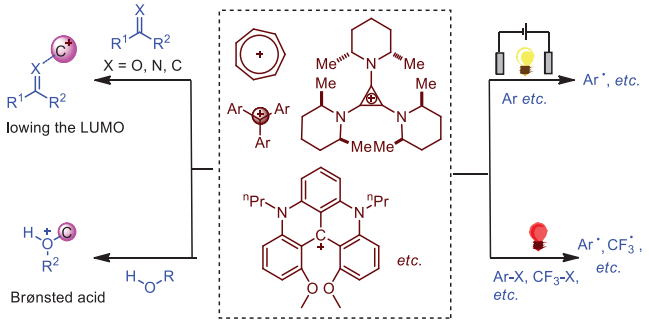
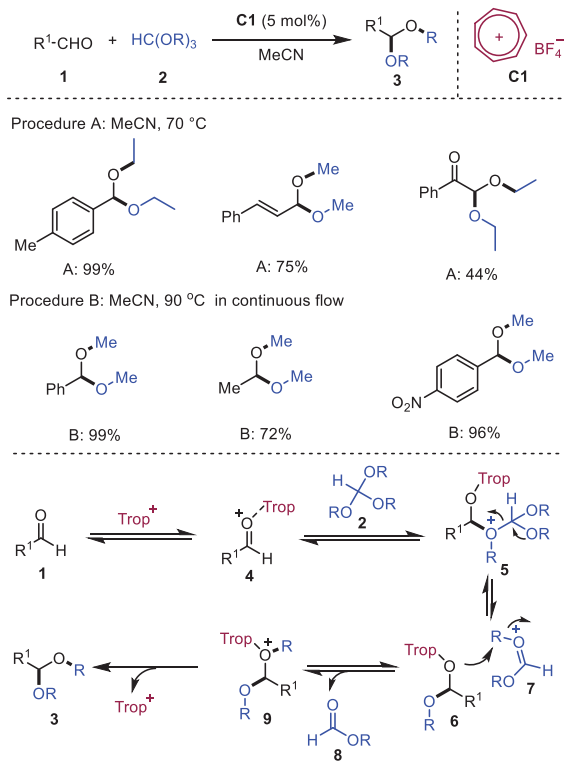
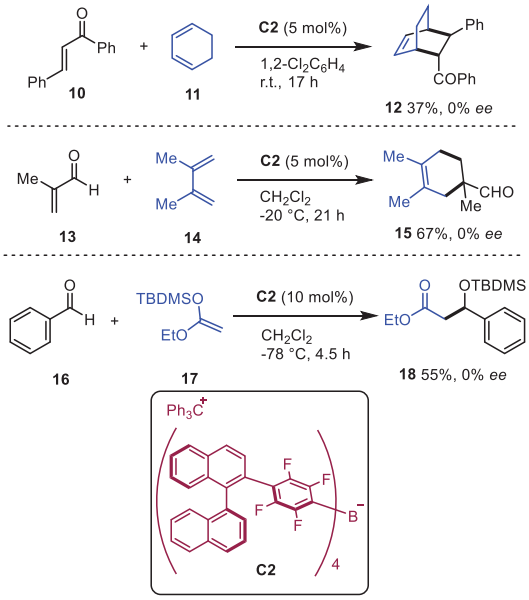


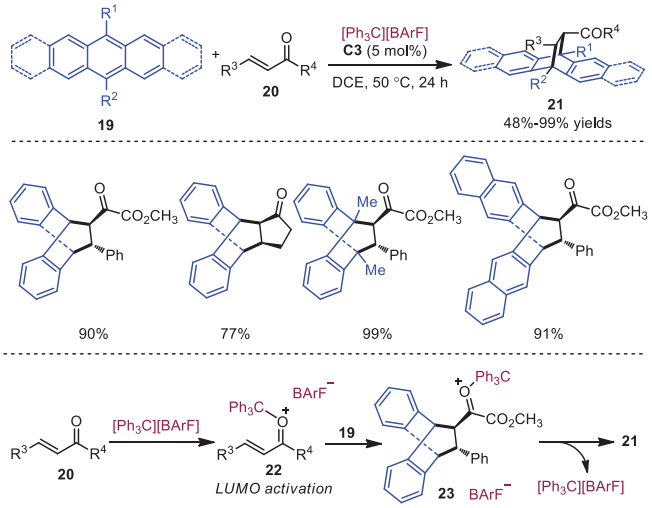
Scheme 1. Activation pattern of carbocations.



Scheme 2. Tropylium cation catalyzed acetalization reactions.



Scheme 3. Application of chiral trityl salts.



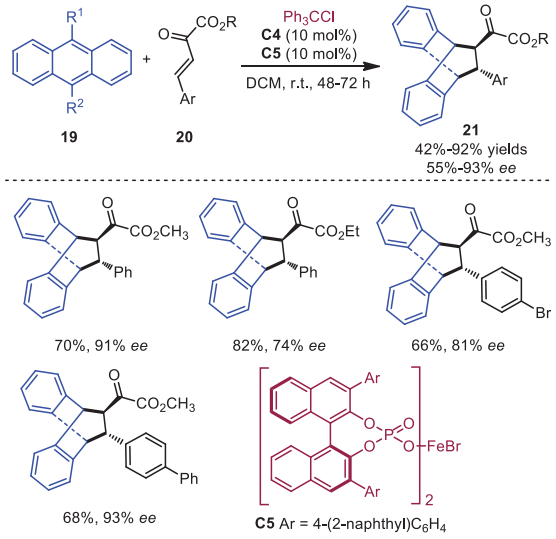
Scheme 4. Diels-Alder reactions.

ate **5** gave rise to intermediate **6**. Followed by alkyl transfer intermolecularly, intermediate **9** would be provided along with the elimination of alkyl formate **8**. Finally, release of tropylium cation in intermediate **9** afforded product **3**. This method described an alternative metal-free pathway for the acetalization of carbonyl compounds.

In 2017, Oestreich and coworkers prepared a chiral derivative of $[B(C_6F_5)_4]^-$ in which the *p*-F of each C_6F_5 was replaced by a 1,1′-binaphthalen-2-yl group (Scheme 3) [13]. The counteranions were provided as its sodium, lithium and trityl salts. Subsequently, this chiral trityl salt **C2** was utilized as a catalyst in counteranion-directed Diels-Alder reactions and Mukaiyama aldol addition. However, no asymmetric induction was achieved.

Stoichiometric or excess Lewis acid catalysts were required to promote Diels-Alder reactions of anthracenes *via* LUMO activation of dienophiles. Luo and coworkers developed a Diels-Alder reaction between α,β-unsaturated carbonyl compounds **20** and anthracene derivatives **19** in 2017 in the presence of a catalytic amount of trityl cation [14]. α,β-Unsaturated ketones **20** bearing various aromatic substituents and cyclic α,β-unsaturated ketones were readily tolerated in this transformation, affording the corresponding cyclic products **21** in good to excellent yields. Pentacene derivatives could also participate smoothly in this reaction. A plausible mechanism is outlined in Scheme 4. The coordination of trityl cation to unsaturated carbonyl compounds **20** formed intermediate **22**, which could lower the LUMO of dienophile to enable the Diels-Alder reaction with anthracene derivatives **19**. The final product **21** was delivered with the release of catalyst from intermediate **23**. In 2019, the same group disclosed that the combination of trityl cation and a chiral weakly coordinating Fe^{III} based bisphosphate anion **C5** could act as a highly active carbocation Lewis acid catalyst to promote the asymmetric Diels-Alder reaction of anthracenes **19** with α,β-unsaturated carbonyl compounds **20** (Scheme 5) [15]. Control experiments showed that only chiral iron salt **C5** or carbocation **C4** would be ineffective to promote the reaction, indicating the reaction was catalyzed by the combination of trityl cation and Fe^{III} complexed bisphosphate.

Despite the fact that olefin-olefin metathesis reactions have been extensively studied, the similar carbonyl-olefin metathesis has been rarely investigated. In 2018, Nguyen and coworkers dis-

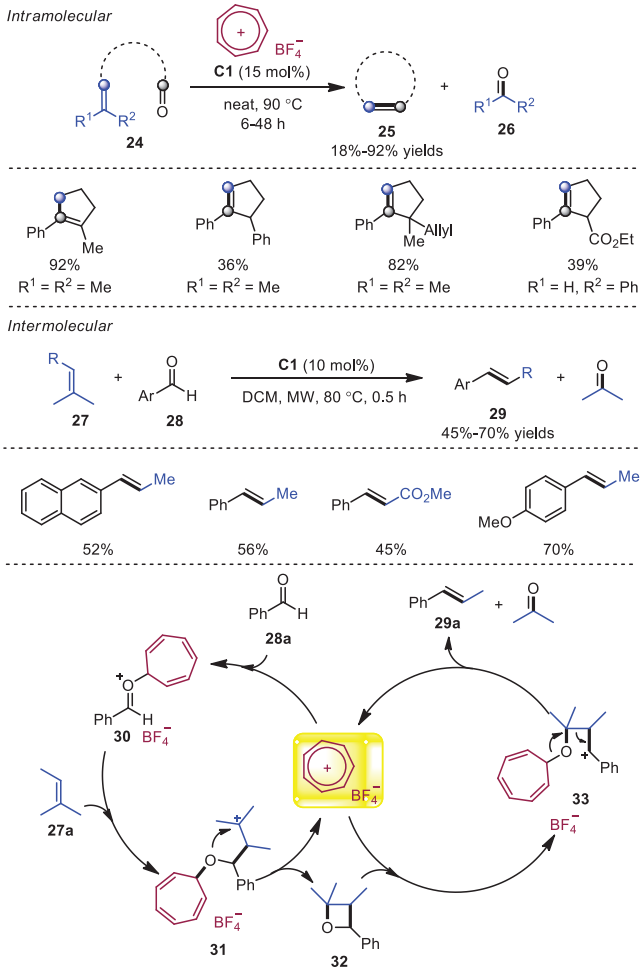


Scheme 5. Asymmetric Diels-Alder reactions.

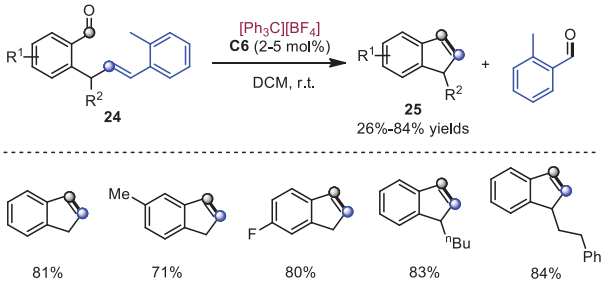
closed tropylium cation catalyzed carbonyl-olefin metathesis reactions [16]. A broad range of substrates were applicable to intramolecular and intermolecular reactions. A plausible mechanism was presented in Scheme 6 on the basis of DFT calculations. At the beginning, activation of aldehyde **28a** through tropylium cation would form intermediate **30**, which lowered the LUMO of aldehyde to enable the electrophilic addition with alkene **27a** to furnish intermediate **31**. Next, intermediate **31** underwent intramolecular cyclization to generate intermediate **32** along with the release of tropylium cation. Subsequently, tropylium cation would coordinate to the oxygen of intermediate **32** leading to cation intermediation **33**, which went through retro [2 + 2] cycloaddition to produce the final product **29a**. In the same year, Franzén and coworkers developed analogous trityl cation catalyzed aldehyde-olefin metathesis (Scheme 7) [17]. These methods featured high yields, low catalyst loading, good functional group tolerance and mild reaction conditions.

Brominated aromatic compounds are highly valuable in organic synthesis and material science. However, their synthesis usually requires high temperature and toxic radical initiators. In 2018, Franzén and coworkers developed trityl cation catalyzed chemoselective bromination reaction of alkyl arenes under mild conditions [18]. In this contribution, benzylic C(sp^3)-H bromination products could be efficiently accessed under common hood light in the presence of trityl cation as the catalyst and *N*-bromosuccinimide (NBS) as the brominating agent. On the other hand, for electron-rich alkyl arenes, the arene C(sp^2)-H bromination products could be obtained by simply alternating the solvent. A possible mechanism is showed in Scheme 8. For the benzylic C(sp^3)-H bromination, trityl cation was proposed to assist the production of bromine from NBS and HBr by activation of NBS toward the nucleophilic attack of bromide. For the arene C(sp^2)-H bromination, trityl cation was believed to involve in the Lewis acid activation of NBS, leading to a more potent electrophile.

Retro-Claisen rearrangement provides an alternative way to access ester products from carbonyl compounds. This type of reaction usually is promoted by transition metal Lewis acids. In 2018, Nguyen and co-workers developed tropylium cation catalyzed retro-Claisen-type reaction for C−C bond cleavage of diketones **39** under metal-free conditions [19]. A wide range of synthetically valuable esters and amines **41** could be easily afforded through solvolysis of 1,3-dicarbonyl compounds **39**. Furthermore, thio-enol ether product **43** was afforded by using thiols as nucle-



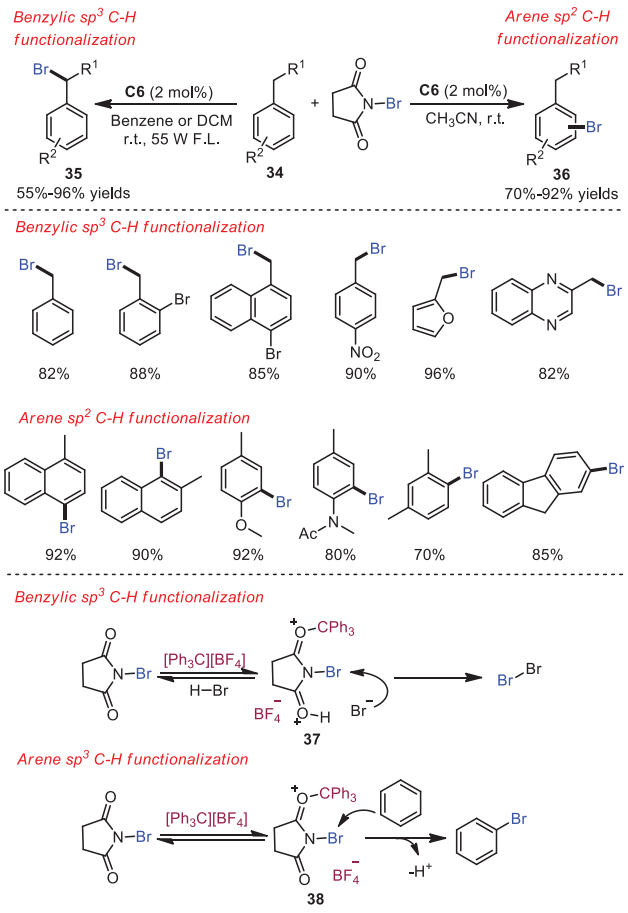
Scheme 6. Tropylium cation catalyzed carbonyl-olefin metathesis.



Scheme 7. Trityl cation catalyzed carbonyl-olefin metathesis.

ophiles. A plausible mechanism was proposed as shown in Scheme 9. Firstly, tropylium cation would activate 1,3-diketones to form intermediate **44**. Subsequently, intermediate **44** reacted with nucleophile **40a** to generate intermediate **45**, which underwent proton transfer and C−C bond cleavage to deliver cation intermediate **46**. Next, C−C bond cleavage of intermediate **46** gave rise to intermediate **47**, which was followed by isomerization with the release of tropylium cation to furnish the final product **41a**.

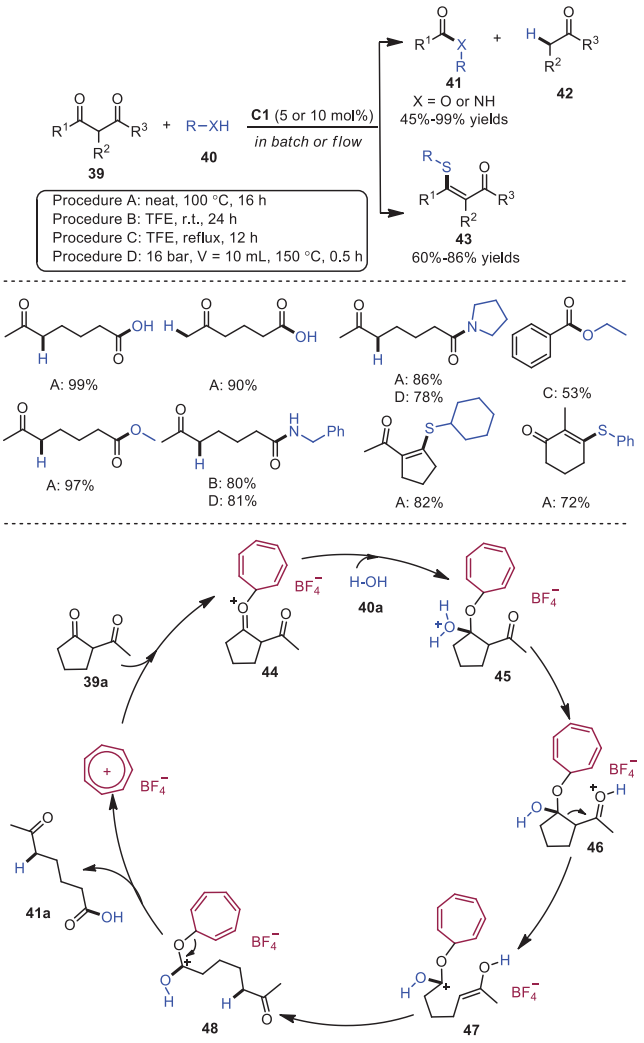
In 2019, Lv and coworkers reported trityl cation catalyzed Roskamp reaction of aldehydes **50** and α-alkyldiazoacetates **49** leading to diverse α-branched β-ketocarbonyls **51** in moderate yields (Scheme 10) [20]. In 2021, Koenigs and coworkers developed an analogous transformation involving tropylium cation catalyzed O−H insertion of diazoalkanes **49** with carboxylic acids **52** [21].



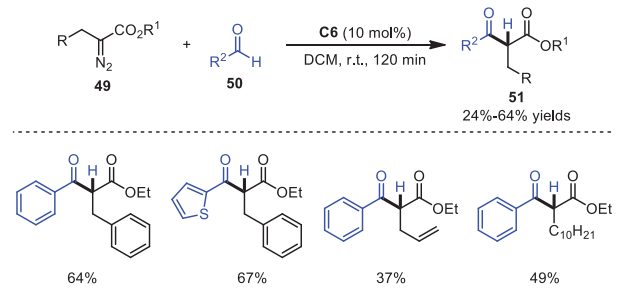
Scheme 8. Synthesis of brominated arenes.

This reaction featured a wide range of carboxylic acid derivatives and diazoalkanes to form α-functionalized esters **53** with high efficiency. A proposed mechanism is depicted in Scheme 11. It was postulated that tropylium cation initially activated diazoalkane **49** *via* coordination to the carbonyl group or the diazo group to form intermediate **54** or **55**, which underwent tautomerization to deliver intermediate **56**. Subsequently, an activated carbene intermediate **57** was furnished from intermediate **56** along with the expulsion of N_2. Then, carboxylic acid **52** interacted with carbene intermediate **57** to provide intermediate **58**, which underwent proton transfer giving rise to the final product **53**.

Although cyclopropenium ions are known in the past several decades, their potential as organocatalysts has been investigated only recently. The hydrogen atom attached to the cyclopropane ring is acidic and can serve as a hydrogen-atom donor in organic transformations. In 2021, Anand's group successfully realized bis(amino)cyclopropenium (BAC) ion catalyzed 1,6-conjugate addition reaction of *p*-QM with nucleophiles *via* hydrogen-bonding catalysis [22]. A variety of nucleophiles including indoles, thiols, 2-naphthols and phenols participated in this reaction smoothly, leading to the corresponding products in high yields. The deuterium isotope labeling studies as well as spectropic studies indicated that the hydrogen-atom in the catalyst was indeed responsible for facilitating this transformation. A plausible mechanism is outlined in Scheme 12. Initially, activation of *p*-QM by catalyst **C7** *via* hydrogen-bonding would provide complex **63**. Nucleophilic addition in a 1,6-fashion with indole **61a** would occur *via* complex **64** to afford intermediate **65**, which would then release product **62a** and catalyst **C7**.



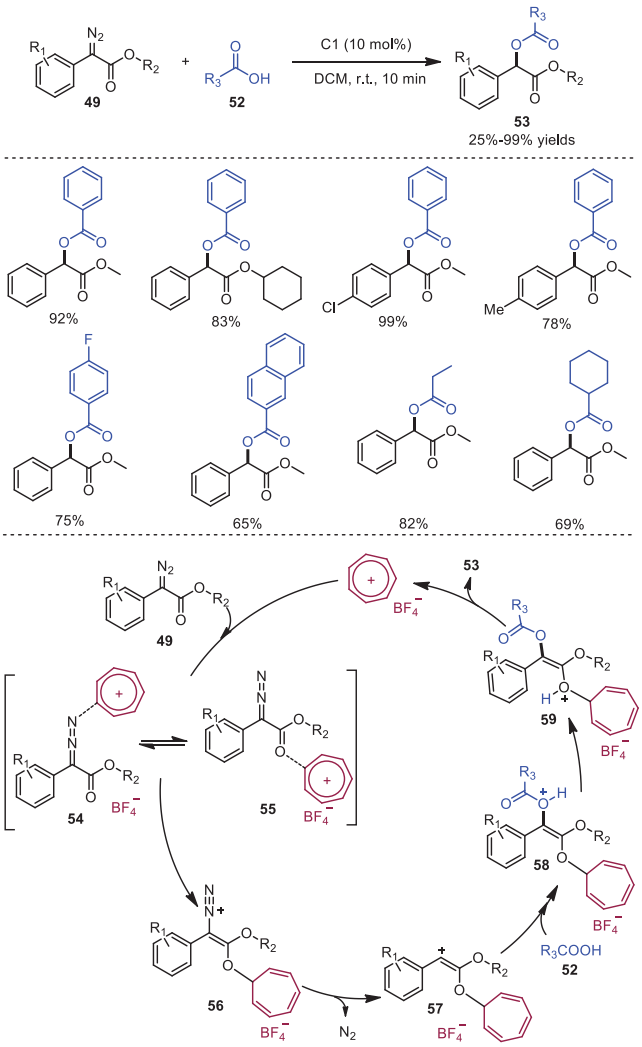
Scheme 9. Retro-Claisen rearrangement.



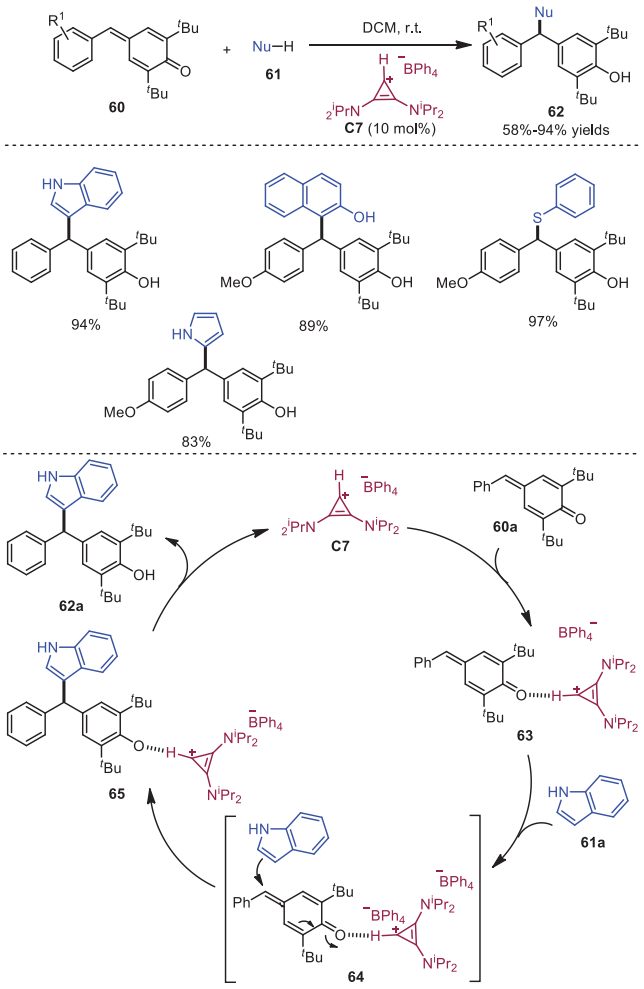
Scheme 10. Roskamp reaction of aldehydes and α-alkyldiazoacetates.

The first asymmetric intermolecular Stetter reaction catalyzed by a chiral bis(amino)cyclopropenium ion **C8** was developed by Gravel and coworkers in 2021 (Scheme 13) [23]. A novel C2-symmetric precatalyst possessing restricted rotation around the C–N bond enabled the outcome of high enantioselectivity. Notably, a catalytic amount of water was essential to obtain high enantioselectivities.

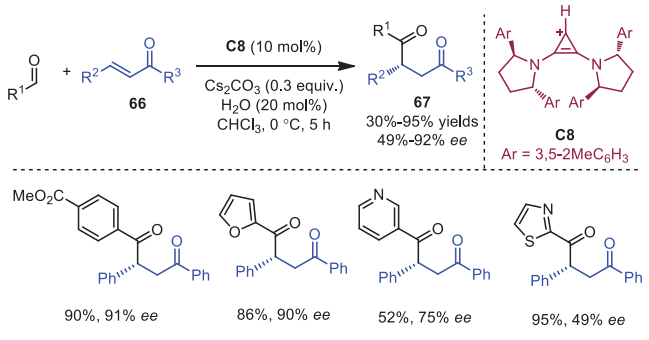
In 2022, Anand and coworkers disclosed tropylium cation catalyzed vinylogous aza-Michael addition of carbamates **68** to *p*-quinone methides **60** [24]. A wide range of α,α'-diarylmethyl carbamates **68** were afforded in moderate to excellent yields. Two plausible mechanisms involving a hidden Brønsted acid and a



Scheme 11. Synthesis of α-functionalized esters.



Scheme 12. Bis(amino)cyclopropenium catalyzed 1,6-conjugate addition reaction of *p*-QM.



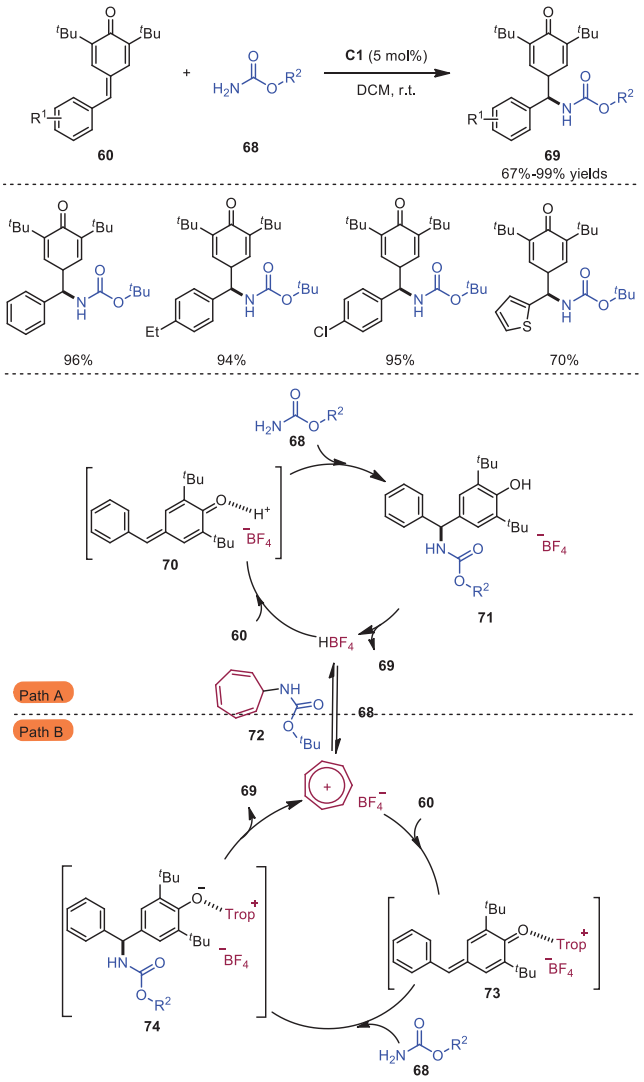
Scheme 13. Asymmetric intermolecular Stetter reaction.

Lewis acid catalysis were proposed as outlined in Scheme 14. Path A was based on the hidden Brønsted acid catalysis. At the beginning, tropylium salt reacted with carbamate **68** to provide tropylium-carbamate complex **72** along with the formation of Brønsted acid HBF_4, which activated *p*-QM through hydrogen-bonding to deliver intermediate **70**. Subsequently, 1,6-conjugate addition of carbamate **68** would occur to produce intermediate **71**, which decomposed to produce the final product **69** with the regeneration of HBF_4. Another alternative possibility was that tropylium cation would coordinate with *p*-QM through a weak interaction, which resulted in the formation of complex **73**. Followed by 1,6-conjugate addition of carbamate **68**, intermediate **74** would be generated, which further underwent proton exchange giving rise to the final product **69** with the release of tropylium cation to complete the catalytic cycle.

3. Imines activation

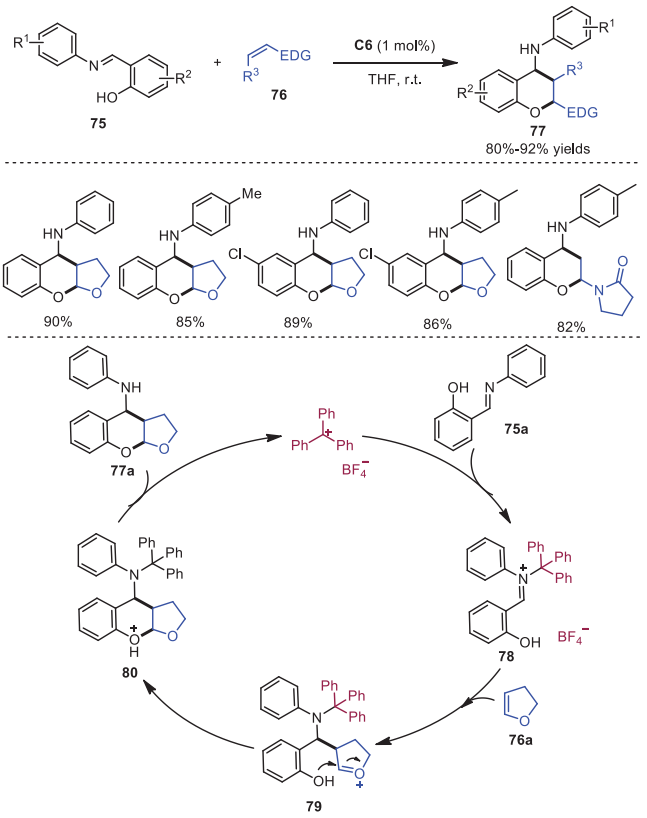
In 2017, Guo and coworkers developed trityl cation promoted interrupted Povarov reactions, affording a series of *cis*-4-aminobenzodihydropyrans **77** in good yields within 10 min with low catalyst loadings (Scheme 15) [25]. In this reaction, trityl cation performed as a Lewis acid catalyst to activate salicylaldimine **75a**, delivering intermediate **78** with increased electrophilicity. Next, intermediate **78** reacted with electron rich 2,3-dihydrofuran **76a** leading to intermediate **79**, which went through an intramolecular nucleophilic attack from the hydroxyl group to oxocarbenium carbon giving rise to intermediate **80**. Finally, proton transfer of intermediate **80** provided product **77a** along with trityl cation to complete the catalytic cycle. This reaction provided an efficient way to access benzodihydropyran skeletons under mild conditions, which were widely existed in bioactive molecules.

In 2021, Brindle and coworkers developed triarylmethyl cation catalyzed one-pot, three component synthesis of unsymmetrical bisindolylmethanes from two different indoles with *N*-arylimines **82** (Scheme 16) [26]. This reaction featured commercially available



Scheme 14. Vinylogous aza-Michael addition of carbamates to *para*-quinone methides.

catalyst, high efficiency and mild reaction conditions. The single addition product **83** could be achieved by tuning the stability of carbocation. Followed by one-pot interaction with another molecular indole, unsymmetrical bisindolylmethanes **84** would be formed in moderate to excellent yields.

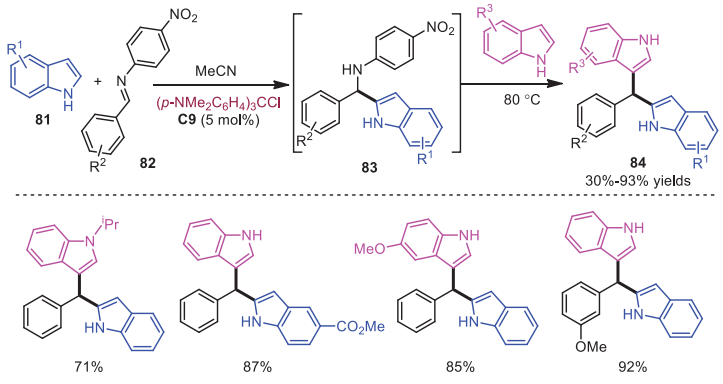


Scheme 15. Interrupted Povarov reactions.

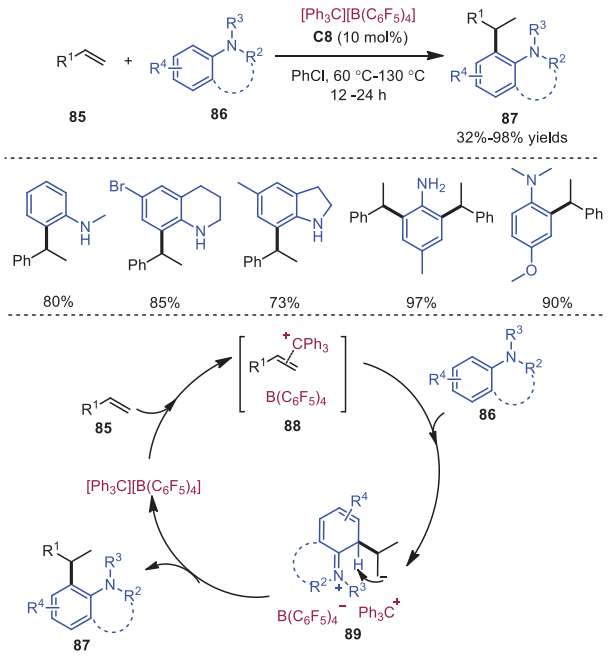
4. Alkenes and alkynes activation

In 2018, Yao and coworkers developed a trityl cation catalyzed hydroarylation reaction of a wide range of alkenes with aromatic primary, secondly and tertiary amines [27]. A broad scope of aniline derivatives **87** were provided in moderate to good yields. A plausible mechanism is shown in Scheme 17. Trityl cation acted as a Lewis acid to activate alkene **85**, rendering alkene **85** electron-deficient to allow for the electrophilic attack with aniline **86** leading to intermediate **89**. Further proton transfer of intermediate **89** would result in the formation of product **82**.

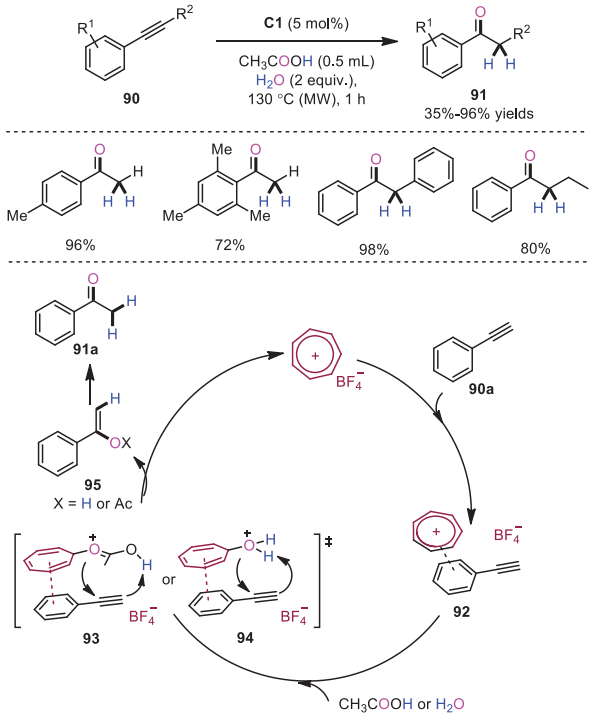
In 2018, Nguyen and coworkers developed tropylium cation promoted hydration reactions of alkynes **90** [28]. A broad scope of alkynes was readily demonstrated in this transformation, providing the corresponding ketone products **84** in moderate to excellent yields. A plausible mechanism based on mechanistic studies



Scheme 16. Synthesis of unsymmetrical bisindolylmethanes.

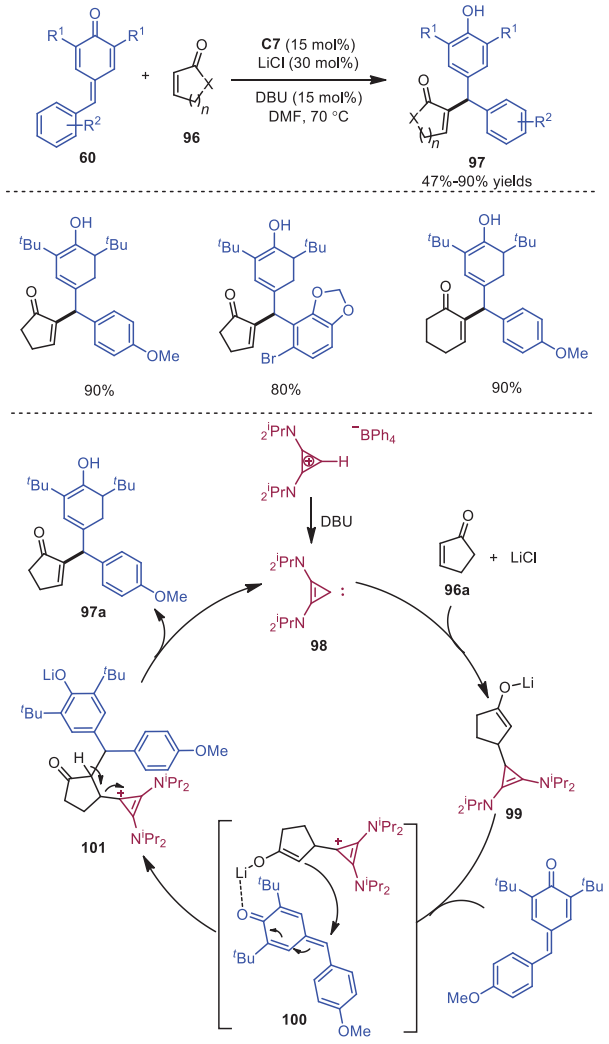


Scheme 17. Trityl cation catalyzed hydroarylation reaction of alkenes with aromatic amines.



Scheme 18. Hydration reactions of alkynes.

was depicted in Scheme 18. It was reasoned that initially, complex **92** was formed through π-π interaction between tropylium cation and phenylacetylene **90a**. Subsequently, the covalent interaction between tropylium cation and acetic acid or water would produce intermediate **93** or **94** with enhanced Brønsted acidity, respectively. An intermolecular proton transfer from water or acetic acid with spontaneous acetate addition and hydroxyl addition gave rise to intermediate **95** along with the regeneration of tropylium cation. Finally, enolate species **95** would isomerize to afford ketone

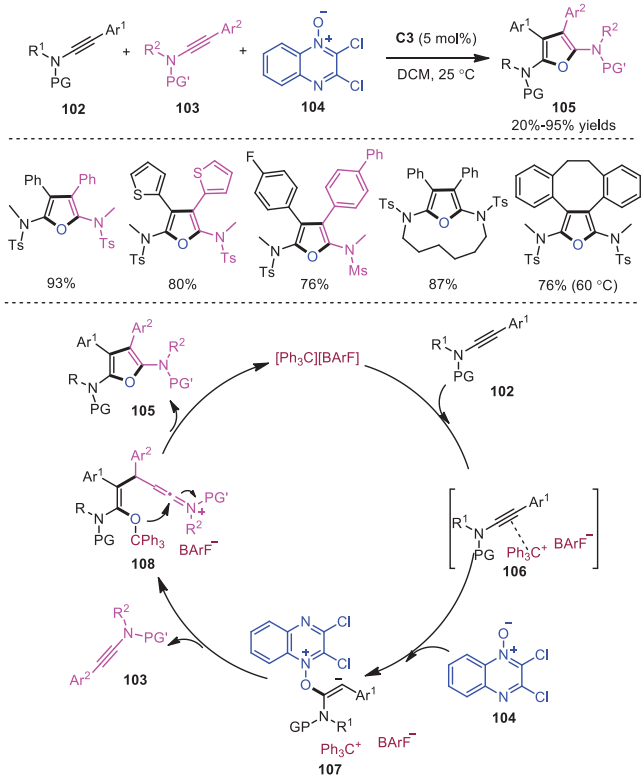


Scheme 19. Rauhut-Currier reaction.

products **91a**. This protocol provided an alternative way for the hydration of alkynes under metal-free and mild reaction conditions.

Anand and coworkers explored the intermolecular Rauhut-Currier reaction between *p*-QM and α,β-unsaturated carbonyl compounds catalyzed by bis(amino)cyclopropenium ion **C7** (Scheme 19) [29]. Diverse vinyl diarylmethane derivatives **97** were afforded in moderate to good yields. The reaction started by the abstraction of acidic proton with DBU from **C7** to generate carbene intermediate **98**, which would react with α,β-unsaturated carbonyl compounds **96a** giving rise to enolate **99**. The transition state **100** would be formed with *p*-QM in which the presence of lithium stabilized the enolate and coordinated with the carbonyl group of *p*-QM to bring it closer to the reaction center. After that, the reaction between enolate and *p*-QM would take place to form intermediate **101**, which further went through proton elimination to furnish the final product **97**.

In 2019, Hashmi and coworkers reported trityl cation catalyzed oxidative [2 + 2 + 1] cycloaddition of two molecules of ynamides with 2,3-dichloroquinoxaline-*N*-oxide **104** [30]. Various fully substituted symmetric and unsymmetric furan derivatives **105** were rapidly constructed. This protocol could further go through intramolecular macrocyclization of diynamides to convergent assembly of macrocyclic furan derivatives. A plausible mechanism is presented in Scheme 20. At the beginning, the triple bond of ynamide **102** was activated by trityl cation to generate interme-



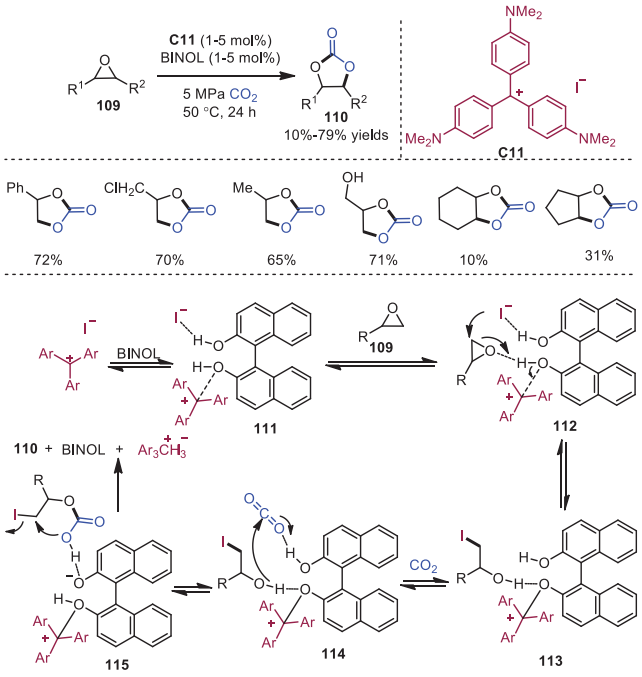
Scheme 20. [2 + 1 + 1] Cycloaddition of ynamides with quinoxaline *N*-oxides.

diate **106**, which was verified by NMR experiments. Subsequently, electrophilic addition of intermediate **106** with *N*-oxide occurred to produce "umpoled" enolate **107**, which underwent an intermolecular C−C coupling with another molecular of ynamide **103** to provide enolonium species **108**. Finally, enolonium species **108** went through intramolecular cycloaddition giving rise to fully substituted furans **105** accompanied with the regeneration of trityl cation.

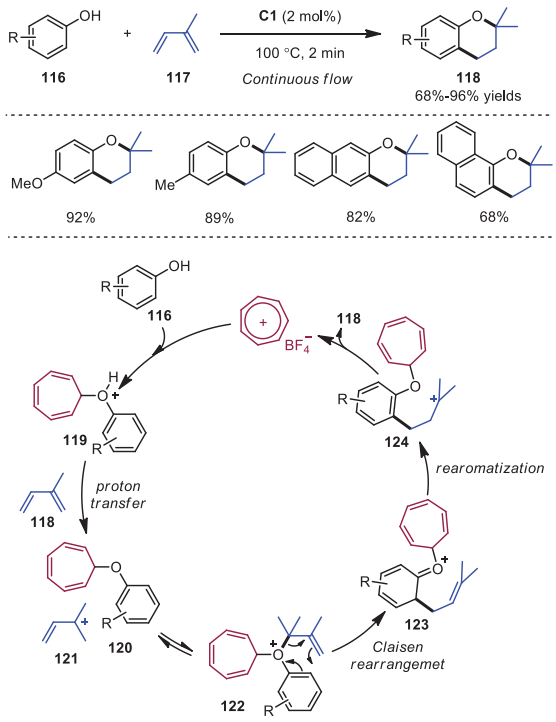
5. Alcohols and epoxides activation

Cyclic carbonates are an important class of industrial intermediates and solvents, and they can be utilized as electrolytes in lithium-ion batteries. In 2017, Belokon and coworkers developed the synthesis of cyclic carbonates from epoxides **109** and carbon dioxide catalyzed by carbocation/polyol. In this transformation, the catalysts were commercially available and less toxic than metal complexes (Scheme 21) [31]. The catalyst system of crystal violet **C11** and BINOL could be recycled five times without loss of activity. Mechanistically, carbocation initially acted as a Lewis acid to activate BINOL, forming a stronger Brønsted acid **111**. The increased acidity of BINOL allowed the formation of a stronger hydrogen bond between hydroxyl group and epoxide, triggering the epoxide ring opening through the addition of iodide ion leading to intermediate **113**. Subsequently, the remaining hydroxyl group in intermediate **113** would coordinate with CO_2 to produce intermediate **114**, which went through addition and cyclization to provide product **110**.

In 2020, Nguyen and coworkers described tropylium cation promoted prenylation reactions of phenols (Scheme 22) [32]. This method was amenable to continuous flow chemistry, enabling an inexpensive pathway to obtain 2,2-dimethylchromans **118** on multiple-gram scale with high efficiency, short reaction times and simple product purification. Mechanistically, a nucleophilic attack

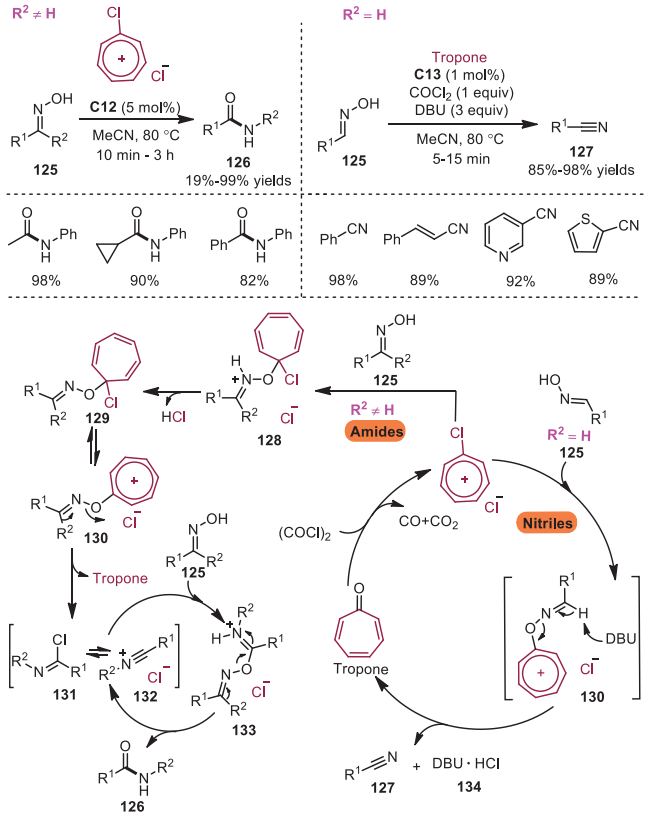


Scheme 21. CVI/BINOL catalyzed synthesis of cyclic carbonates.



Scheme 22. Synthesis of 2-dimethylchromans.

of phenol **116** to tropylium cation afforded the active Brønsted acid **119**, which underwent a proton transfer to diene **118** affording intermediates **120** and **121**. Subsequently, interaction between intermediates **120** to **121** gave rise to intermediate **122**, which went through a Claisen rearrangement and re-aromatization to produce intermediate **124**. Further cyclization of intermediate **124** would occur leading to product **118**, accompanied with the formation of tropylium cation. This method provided a metal-free and highly efficient approach to access compounds possessing 2-

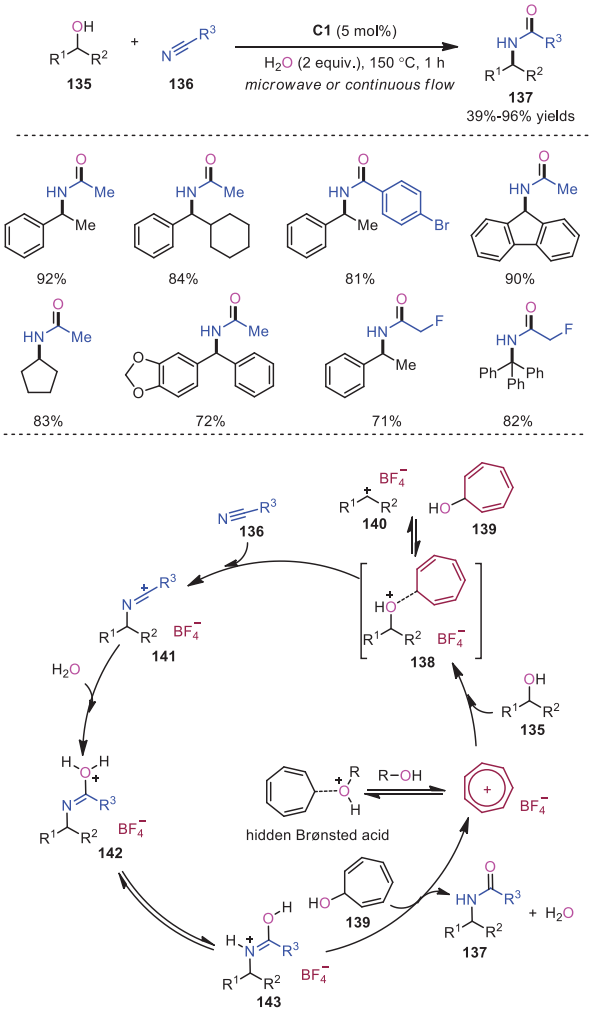


Scheme 23. Synthesis of amides and nitriles.

dimethylchroman framework, which was widely existed in bioactive compounds with antitumor, antihypertensive and antithrombotic activities.

In 2020, Guo and coworkers reported the synthesis of amides and nitriles through chlorotropylium cation promoted transformations of ketoximes and aldoximes, respectively [33]. Amides and nitriles were rapidly assembled in short reaction time with excellent yields. A plausible mechanism is presented in Scheme 23. For the reactions with ketone oximes, complex **128** would be formed with chlorotropylium cation, which eliminated a molecule of HCl to generate intermediate **129**. Subsequently, chloride anion was released from intermediate **129** to furnish the key tropylium oxime ether **130**. Next, R^2 group would migrate to the N atom with the cleavage of O−N bond and formation of C=O bond at the same time. The intermediate nitrilium cation **132**, in equilibrium with isomer imidoyl chloride **131**, would be attacked by ketoxime leading to intermediate **133**. Intermediate **132** was regenerated along with the release of amide product **126**. On the other hand, DBU abstracted a proton from the key intermediate **130** to form nitrile product **127** with the explusion of precatalyst tropone. Oxalyl chloride would react with tropone giving rise to chlorotropylium chloride, which would be employed in the catalytic cycle for the synthesis of nitriles. This method provided a mild and efficient way to access amides and nitriles.

Ritter reactions haven't been frequently used in modern organic synthesis due to the employment of harsh and strong acidic reaction conditions, which may lead to complicated side reactions. In 2021, Nguyen and coworkers developed a new protocol using tropylium cation as a Lewis acid to promote the Ritter reaction, which was amenable to microwave and continuous flow reactors . A variety of alcohol **135** and nitrile substrates **136** were well tolerated, affording the corresponding amides **137** in good to excellent yields. A possible mechanism was proposed as shown

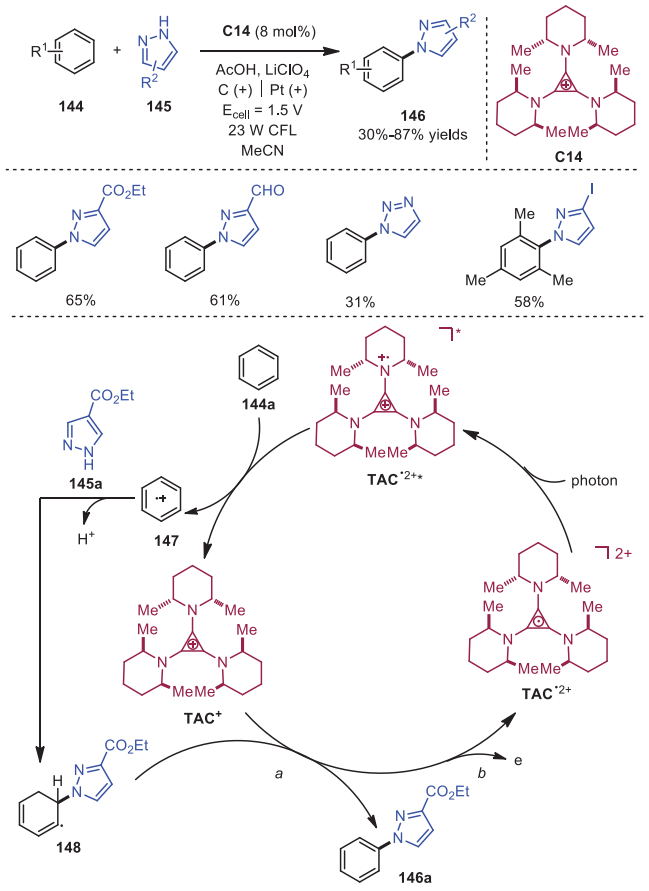


Scheme 24. Synthesis of amides.

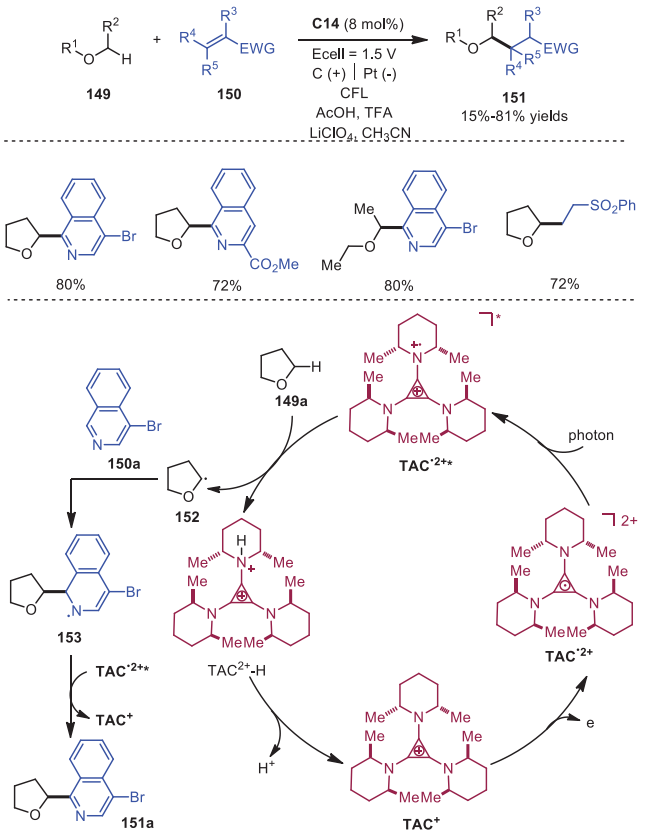
in Scheme 24. Tropylium cation coordinated with the oxygen of alcohol, rendering the adjacent carbon electron-deficient to enable the nucleophilic attack of nitrile **136** on alcohol **135**. Subsequently, a hydrolysis process would occur, which resulted in the conversion of iminium intermediate **141** into amide intermediate **142**. Amide intermediate **142** would further undergo proton transfer and isomerization affording amide product **143**. The hidden Brønsted acid, generated from tropylium cation with either alcohol or water, might also promote the reaction.

6. Electrophotocatalysis

Recently, vigorous activity in the areas of electrocatalysis has enabled a variety of powerful oxidative protocols. TAC^+ could be electrochemically oxidized to the air-stable dication $TAC^{\bullet 2+}$, which could further be excited by visible light irradiation to form the excited radical dication $TAC^{\bullet 2+*}$. Notably, the reduction potential of $TAC^{\bullet 2+*}$ is 3.33 V (*vs.* SCE), which is higher than the excited-state reduction potentials of 9-mesityl-10-methylacridinium ($E^*_{1/2} = 2.06$ V), 3-cyano-1-methylquinolinium ($E^*_{1/2} = 2.72$ V) and even DDQ ($E^*_{1/2} = 3.18$ V). As a result, $TAC^{\bullet 2+*}$ is capable of oxidizing a wide range of challenging substrates. In 2019, Lambert's group realized the electrophotocatalytic coupling of arenes and nitrogen heteroaromatics catalyzed by TAC^+ (Scheme 25) [34]. The reaction started with electrochemical oxidation of TAC^+ to produce $TAC^{\bullet 2+}$, which was then excited by light irradia-



Scheme 25. Electrophotocatalytic coupling of arenes and nitrogen heteroaromatics.



Scheme 26. C–H functionalization of ethers.

tion to generate reactive $TAC^{\bullet 2+*}$. Subsequently, $TAC^{\bullet 2+*}$ would oxidize benzene **144a** *via* single electron transfer (SET) to afford radical cation **147** with the regeneration of catalyst. The interaction of **147** and pyrazole **145a** followed by deprotonation would provide intermediate **148**, which would be oxidized by TAC^{+} or directly at the anode leading to product **146**.

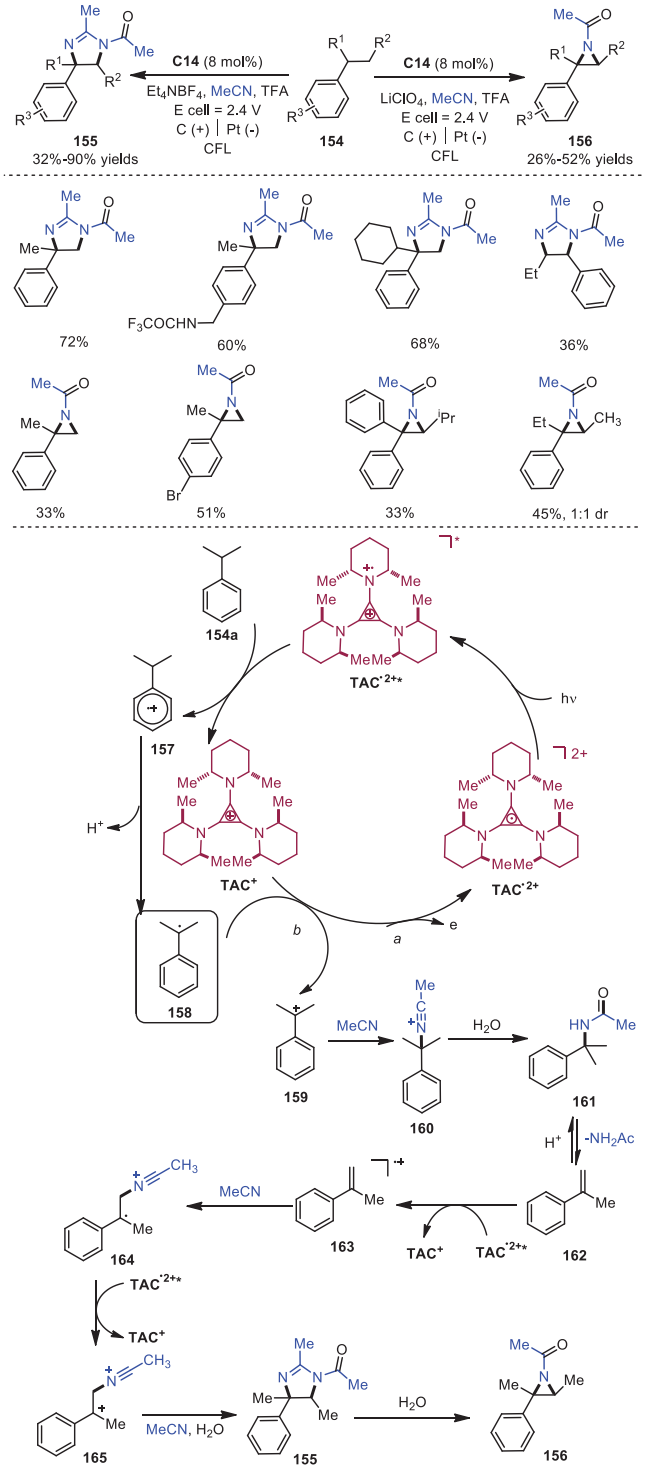
Later in 2020, TAC^{+} was also demonstrated to serve as a hydrogen-atom-transfer catalyst to promote the CH functionalization of ethers *via* electrophotocatalysis [35]. A variety of ethers **149** went through oxidant-free coupling with isoquinolines and alkenes, leading to the corresponding products **151** with high regioselectivity at the less-hindered α-position. A possible mechanism is described in Scheme 26. Initially, TAC^{+} went through electrochemical oxidation to form $TAC^{\bullet 2+}$, which was then excited by light irradiation to provide $TAC^{\bullet 2+*}$ possessing an aminyl radical character. This $TAC^{\bullet 2+*}$ would abstract a hydrogen from ether substrate **149a** leading to radical **152** accompanied with the protonated TAC^{2+}–H. After that, radical **152** would react with isoquinoline **150a** to generate radical intermediate **153**. Followed by a second oxidation and loss of proton, product **151a** would be produced. In the meantime, deprotonation of TAC^{2+}–H would regenerate TAC^{+} to close the catalytic cycle. This method revealed a new reactivity mode for this electrophotocatalyst.

As the first amination diminishes the reactivity of neighbor CH bonds, it remains challenging to access diaminated products *via* twice CH activation. Electrophotocatalytic diamination of vicinal CH bonds *via* CH activation catalyzed by TAC^{+} was realized by Lambert and coworkers in 2021 (Scheme 27) [36]. The reaction started with the generation of photoexcited intermediate $TAC^{\bullet 2+*}$ with high oxidizing potential, which could oxidize compound **154a** to radical cation **157**. Deprotonation of radical cation **157** would produce radical intermediate **158**, which would further undergo oxidation to afford carbocation intermediate **159**. Cation **159** would react with MeCN leading to intermediate **160**, which went through hydrolysis to provide acetamide compound **161**. Compound **161** would proceed through a reversible, acid-catalyzed elimination to generate α-methylstyrene **162**, which would then undergo a single-electron oxidation, solvent trapping and oxidation giving rise to dihydroimidazole product **155** or aziridine **156**. Later, the same group also described Ritter-type CH bond amination *via* electrophotocatalysis by using TAC^{+} as the catalyst (Scheme 28) [37].

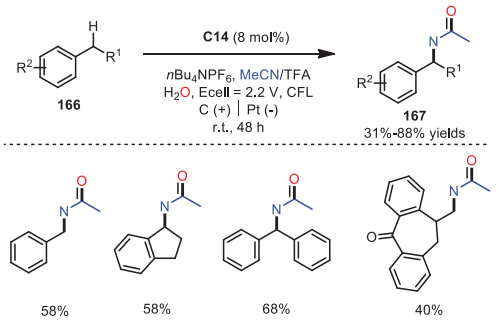
Acetoxyhydroxylation of olefins with high *syn* selectivity *via* TAC^{+} catalysis under electrophotocatalytic conditions was developed by Lambert's group in 2021 (Scheme 29) [38]. The success of this reaction was that the electrochemical potential by itself was unable to oxidize olefin, and the reaction took place only by combination with light irradiation. It was reasoned that TAC^{+} could be oxidized to radical dication $TAC^{\bullet 2+}$. Upon photoexcitation, $TAC^{\bullet 2+*}$ with strongly oxidizing potential was formed, which could oxidize olefin substrate **168a** to radical cation **171**. Then acid nucleophile **169** trapped **171** leading to radical **172**, which was further oxidized to oxocarbenium intermediate **173** and hydrolyzed to provide dioxygenated **170a**. This transformation offered an attractive and alternative way for olefin dioxygenation without utilizing transition metal reagents or catalysts.

7. Photoredox catalysis

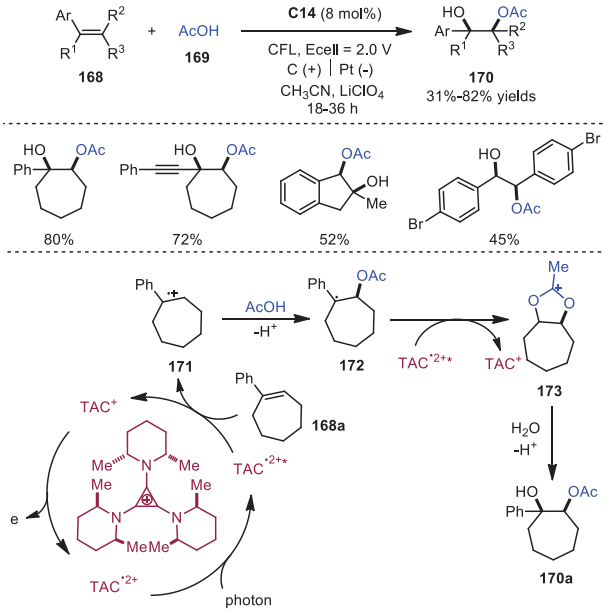
Photoredox catalysis and has emerged as an effective and environmentally friendly synthetic tool to promote SET process in organic transformations [39,40]. Compared with the commonly



Scheme 27. Electrophotocatalytic diamination of vicinal C–H bonds.



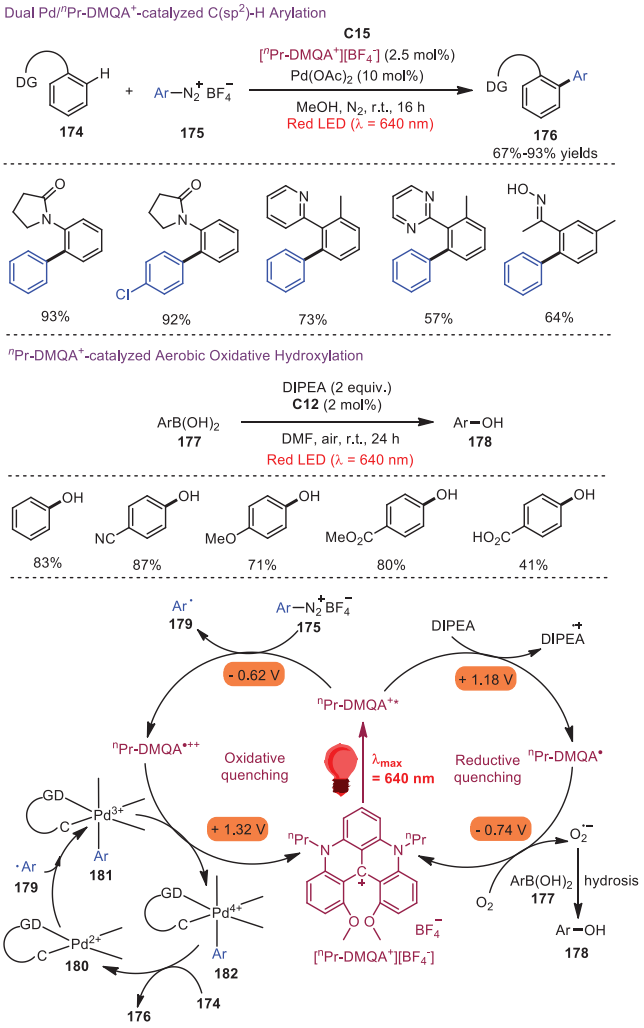
Scheme 28. Electrophotocatalytic amination C–H bonds.



Scheme 29. Acetoxyhydroxylation of olefins.

used high-energy white, blue or green light, low-energy red light has advantages including fewer side reactions and less health risks. In 2020, Gianetti and coworkers disclosed that helical carbenium ion **C15** could act as a versatile organic photoredox catalyst for red-light-mediated photoredox transformations [41]. Red-light-mediated dual transition-metal/photoredox-catalyzed arylation reaction could be catalyzed by ^{n}Pr-DMQA through oxidative quenching. Additionally, the potential of ^{n}Pr-DMQA in photo-oxidation catalysis could be demonstrated by application in red-light-mediated aerobic oxidative hydroxylation of arylboronic acids. Two catalytic cycles involving oxidative or reductive quenching are showed in Scheme 30. The oxidative quenching catalytic cycle was proposed for Pd/^{n}Pr-DMQA^{+} catalyzed C(sp^2)-H arylation. At the outset, photoexcitation of ^{n}Pr-DMQA^{+} produced ^{n}Pr-DMQA^{+*}, which reduced aryldiazonium salt **176** to generate an aryl radical **179** with the formation of ^{n}Pr-DMQA$^{\bullet+}$. Subsequently, addition of aryl radical **176** to Pd^{II} intermediate **180**, which was generated by CH activation of aryl substrate **174**, afforded Pd^{III} species **181**. This Pd^{III} species **181** was oxidized by ^{n}Pr-DMQA$^{\bullet+}$ to regenerate ^{n}Pr-DMQA^{+}, accompanied with Pd^{IV} species **182**. The final product **176** was obtained by reductive elimination of Pd^{IV} species **182**. On the other hand, a reductive quenching cycle was proposed for ^{n}Pr-DMQA^{+}-catalyzed aerobic oxidative hydroxylation. Initially, $^{i}Pr_2$NEt was oxidized to ammonium radical cation by the excited state ^{n}Pr-DMQA^{+*} along with ^{n}Pr-DMQA$^{\bullet}$. Then, ^{n}Pr-DMQA$^{\bullet}$ reacted with oxygen to form an $O_2^{\bullet-}$ and regenerated ^{n}Pr-DMQA^{+}. Followed by oxidative attack on aryl boronic acid **177** and hydrolysis, phenol **178** would be produced.

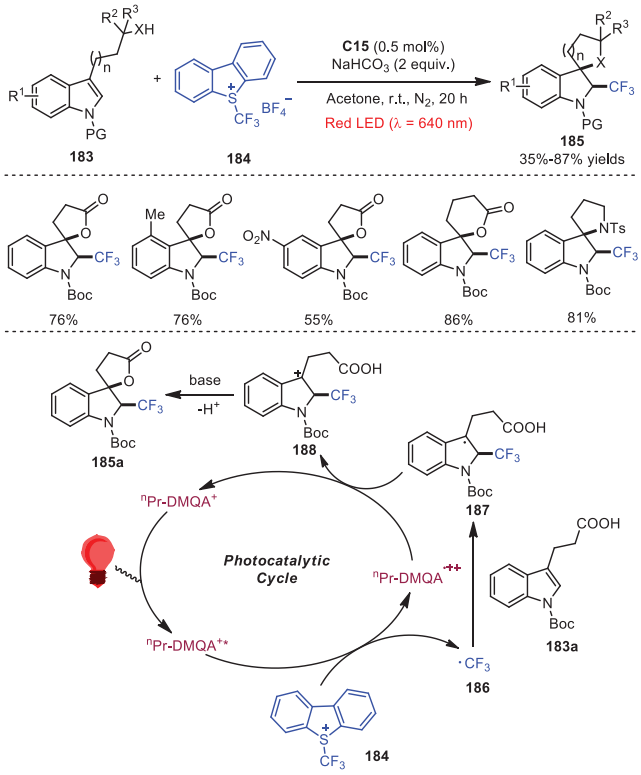
Gianetti and coworkers further extended the above strategy to the construction of CF_3-containing spirocyclic indolines in 2021 [42]. A variety of functionalized CF_3-containing 3,3-spirocyclic indoles **185** were afforded in moderate to good yields through a red-light-mediated ^{n}Pr-DMQA^{+} catalyzed trifluo-



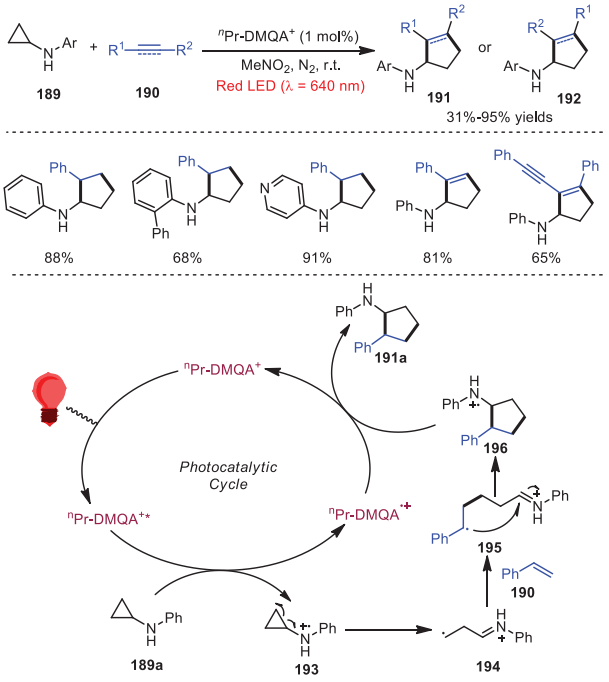
Scheme 30. Helical carbenium ion catalyzed C–H arylation and aerobic oxidative hydroxylation reactions.

romethylation/dearomatization cascade process. A plausible mechanism is presented in Scheme 31. It was proposed that excitation of ground state ^{n}Pr-DMQA^{+} would provide ^{n}Pr-DMQA^{+*} under red light irradiation, which would reduce Umemoto's reagent **184** to generate CF_3 radical **186**. Subsequently, CF_3 radical **186** reacted with indole **183a** leading to dearomatized benzyl radical species **187**, which went through a SET with ^{n}Pr-DMQA$^{\bullet+}$ to afford benzyl carbocation intermediate **188**. Further deprotonation of intermediate **188** gave rise to product **185a**.

[3 + 2] Cycloaddition of alkenes or alkynes with cyclopropylamines could be achieved as well under red light irradiation by using ^{n}Pr-DMQA^{+} as the organic photocatalyst [43]. Diverse cyclopentane and cyclopentene derivatives possessing various functional groups were readily afforded in moderate to good yields under mild conditions. A plausible mechanism is proposed, as shown in Scheme 32. Firstly, red light irradiation of ground state ^{n}Pr-DMQA^{+} would produce excited state ^{n}Pr-DMQA^{+*}, which proceeded through a SET process with cyclopropylamine **189a** to provide nitrogen radical cation intermediate **193**. Subsequently, intermediate **193** underwent β-scission of cyclopropane ring giving rise to β-carbon radical iminium ion **194**, which attacked styrene **190** leading to stabilized radical cation **195**. Intramolecular addition of radical to iminium ion of intermediate **195** produced nitrogen radical cation **196**, which went through reduction to provide product **191a**.



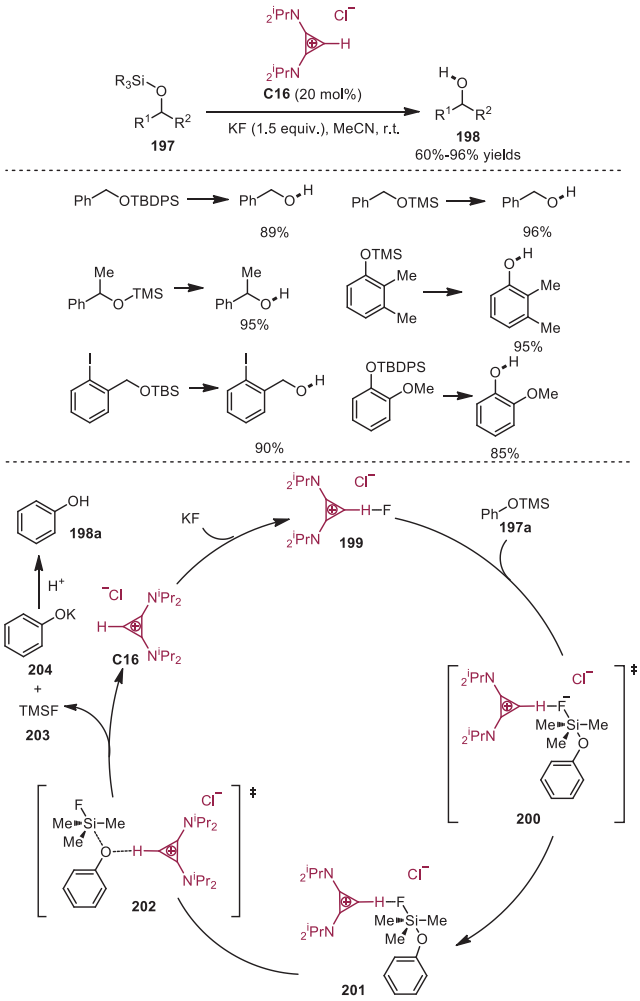
Scheme 31. Synthesis of CF_3-containing spirocyclic indolines.



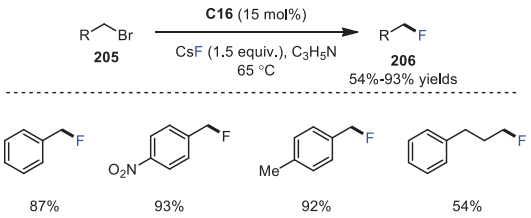
Scheme 32. [3 + 2] Cycloaddition of alkenes or alkynes with cyclopropylamines.

8. Miscellaneous

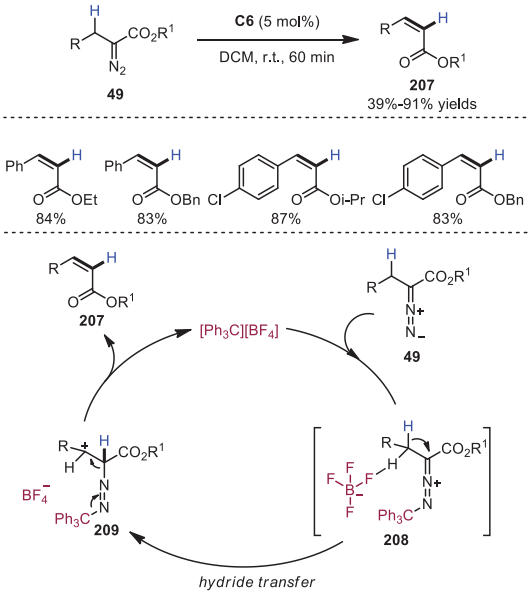
O-silyl ethers are one of the most utilized protecting groups due to the stability under various conditions, functional group tolerance and commercial availability. However, there are several shortcomings employing "naked F^{-}" for silyl deprotection,



Scheme 33. *O*-Silyl ether deprotection.



Scheme 34. Benzylic fluorination.



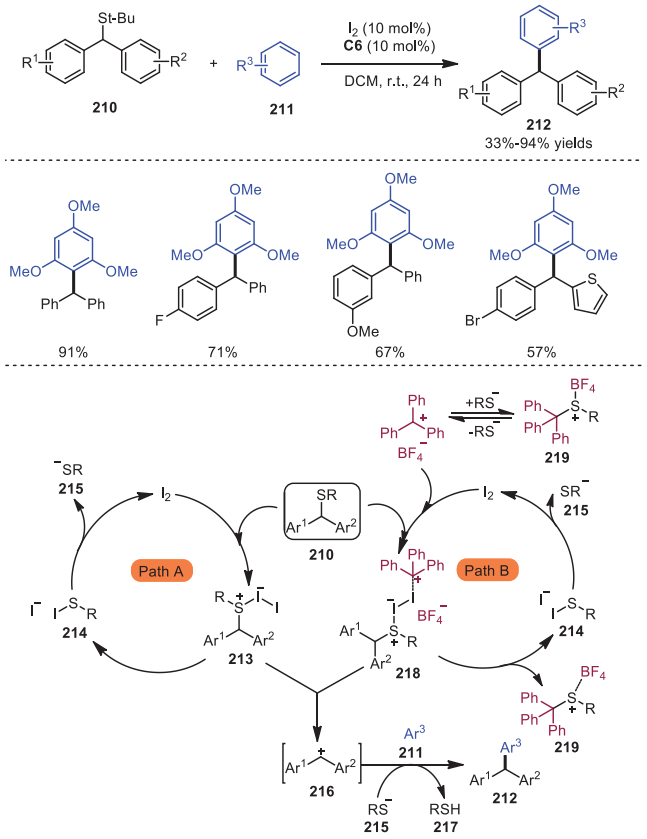
Scheme 35. Synthesis of *Z*-α,β-unsaturated esters.

such as side reactions and requirement of greater amount of "naked F^-". In 2017, Dudding and coworkers developed the *O*-silyl ether deprotection with "naked F^-" *via* bis(amino)cyclopropenium (BAC) ion catalysis [44]. The corresponding deprotection products **198** were afforded in good yields. A plausible mechanism supported by DFT calculation is outlined in Scheme 33. The catalytic cycle was initiated by the counterion ion exchange between bis(amino)cyclopropenium (BAC) ion catalyst **C16** with KF leading to active catalyst **199** possessing the H···F^- bond, in which the cyclopropenium catalyst served as the phase-transfer catalyst. After that, the fluoride added to the Si to form intermediate **201** *via* transition state **200**. Then the Si-O bond cleavage would occur *via* transition state **202** to furnish the **204**, TMSF and regeneration of the catalyst **C16**. The potential of this H-bonding motif to attenuate fluoride basicity and nucleophilicity might be applicable to other catalytic modes. Later in 2018, the same group further extended the strategy in which the cyclopropenium catalyst served as the phase-transfer catalyst to the benzylic fluorination, the corresponding fluorinated products were provided in high yields (Scheme 34) [45].

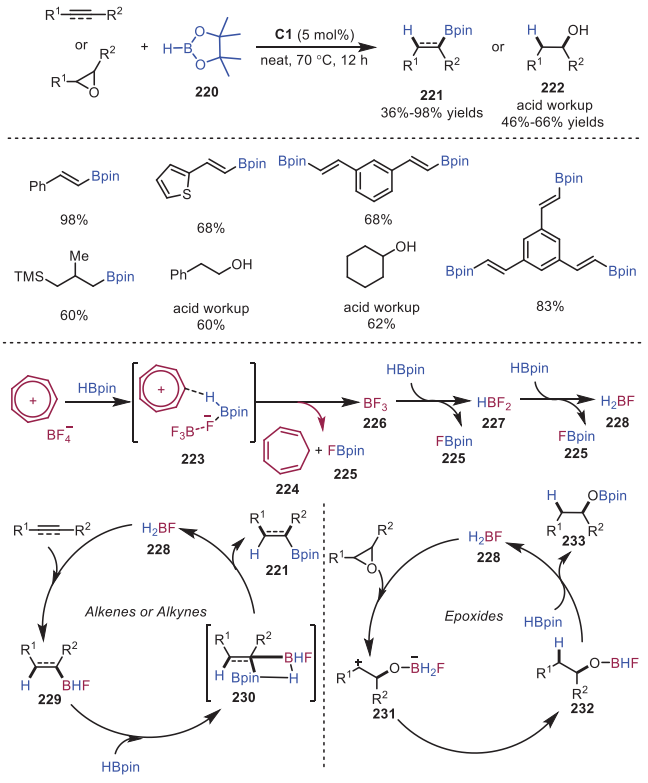
In 2019, Lv and coworkers developed trityl cation catalyzed 1,2-hydride migration of α-alkyldiazoacetates **49** leading to α,β-unsaturated esters **207** in moderate to excellent yields with high *Z* selectivity (Scheme 35) [20]. In this reaction process, intermediate **208**, generated by coordination of trityl cation with diazene moiety and hydrogen-bonding between fluorine atoms on $[BF_4]^-$, converted to intermediate **209** *via* hydride transfer. Further intramolecular *syn* elimination of intermediate **209** would afford product **207**, with the release of a molecule of N_2 and trityl cation.

In 2020, Masson and coworkers discovered that the combined Lewis acid catalytic system, formed by molecular iodine and trityl cation, could efficiently catalyze Friedel-Crafts arylation of diarylmethyl triarylmethanes leading to various unsymmetrical triarylmethanes **212** [46]. Two plausible mechanisms are presented in Scheme 36. In the absence of trityl cation, the sulfur atom of compound **210** was attacked by iodine, resulting in the formation of cationic iodosulfonium intermediate **213**. Subsequently, cationic iodosulfonium intermediate **213** underwent elimination giving rise to sulfenyl iodide **214** and carbocation **216**. Then, sulfenyl iodide went through nucleophilic addition with iodine to produce thiolate **215**. Meanwhile, carbocation **215** reacted with electron rich arene **211**, with further hydrogen atom abstraction mediated by thiolate **215**, affording the desired Friedel-Crafts products **212** and thiol **216**. On the other hand, trityl cation might activate iodosulfonium ion *via* possible Lewis acid assisted Lewis acid model **217** when trityl cation was added in the reaction, thus facilitating the cleavage of C–S bond leading to cation **216** and triphenylmethylium thiolate **219**. Triphenylmethylium thiolate **219** could be in equilibrium with thiolate **214** and tritylium tetrafluoroborate to allow the regeneration of co-catalyst.

Hydroboration reaction is one of the most frequently used reactions in organic synthesis. Normally, hydroboration was catalyzed by transition-metal or main group element. Therefore, method development of metal-free hydroboration reaction is highly important. In 2021, Nguyen and coworkers reported hydroboration reactions by using tropylium cation as an efficient catalyst [47].



Scheme 36. Friedel-Crafts arylation of diarylmethyl triarylmethanes.



Scheme 37. Hydroboration reaction.

Alkynes, alkenes and epoxides could be readily tolerated, affording the corresponding products in moderate to good yields. DFT calculations and experimental studies suggested that BH_2F was the hidden boron catalyst. A proposed mechanism is depicted in Scheme 37. The reaction was triggered by a hydride abstraction of HBpin with tropylium cation to provide cycloheptatriene **224**, FBpin **225** and BF_3 species **226**. Subsequently, BF_3 species **226** reacted with HBpin twice leading to BH_2F species **228**. Next, 1,2-*syn*-addition to alkynes or alkenes from BH_2F took place giving rise to boron alkene or alkane intermediate **229**, which underwent transborylation with HBpin in a stepwise fashion to provide the final product **221**. On the other hand, epoxide would undergo ring-opening process with BH_2F species **228** to produce zwitterionic species **231**, which proceeded through a hydride transfer from boron moiety to the carbocationic center affording intermediate **232**. Subsequently, transborylation between intermediate **232** and HBpin gave rise to BH_2F species **228** and compound **233**, which went through acid workup to generate product **222**.

9. Summary and outlook

In summary, carbocations such as tropylium and trityl cation, can act as Lewis acids to lower the LUMO of electrophile, thus promoting reactions with nucleophiles. Additionally, interaction between alcohols and carbocations can form Brønsted acids with enhanced acidity. Furthermore, electrophoto activation of TAC^+ can furnish $TAC^{\bullet 2+*}$, which is a strong oxidant and capable of oxidizing a variety of challenging substrates. Moreover, ^{n}Pr-DMQA$^+$ is disclosed as a versatile photoredox catalyst as its excited state can be quenched by both oxidation and reduction. These reported results show that carbocations exhibit great ability toward the activation of various groups, such as carbonyl groups, imines, hydroxyl groups and epoxides. These developed methods provide an environmentally friendly pathway for the synthesis of valuable compounds and will inspire chemists to discover more interesting transformations promoted by carbocations.

Despite the significant achievements of carbocation-catalyzed organic reactions, there are still some challenges to be solved. For example, chiral carbocation catalysts are rarely studied and limited to central, planar chiral cations or chiral counterions. Therefore, developing diverse chiral carbocations such as axial carbocations are highly desirable. We believe that in the near future, more achievements will be obtained for the carbocation-catalyzed organic transformations, and enantioselective reactions involving novel chiral carbocation catalysts will be developed rapidly.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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References

[1] J. Clayden, N. Greeves, S. Warren, Organic Chemistry, 2nd Ed., University Press, Oxford, 2012.
[2] G.A. Olah, G.K.S. Prakash, Carbocation Chemistry, Wiley, Hoboken, 2004.
[3] G. Merling, Ber. Dtsch. Chem. Ges. 24 (1891) 3108–3126.
[4] O. Sereda, S. Tabassum, R. Wilhelm, Top. Curr. Chem. 291 (2010) 349–393.

[5] H. Yamamoto, Lewis Acids in Organic Synthesis, Wiley-VCH, Weinheim, 2000.
[6] J.J. Koenig, M. Breugst, Catalysis by Molecular Iodine, in: S. Huber (Ed.), Halogen Bonding in Solution, Wiley-VCH, Weinheim, 2021, pp. 237–268.
[7] L. Capaldo, L.L. Quadri, D. Ravelli, Angew. Chem. Int. Ed. 58 (2019) 17508–17510.
[8] L. Mei, T. Gianetti, Synlett 32 (2021) 337–343.
[9] V.R. Naidu, S.J. Ni, J. Franzen, ChemCatChem 7 (2015) 1896–1905.
[10] J. Bah, J. Franzen, Chem. Eur. J. 20 (2014) 1066–1072.
[11] W. Xiao, J. Wu, Chin. Chem. Lett. 32 (2021) 2751–2755.
[12] D.J.M. Lyons, R.D. Crocker, D. Enders, T.V. Nguyen, Green Chem. 19 (2017) 3993–3996.
[13] P. Pommerening, J. Mohr, J. Friebel, M. Oestreich, Eur. J. Org. Chem. 2017 (2017) 2312–2316.
[14] Q.C. Zhang, J. Lv, S.J. Li, S.Z. Luo, Org. Lett. 20 (2018) 2269–2272.
[15] Q. Zhang, J. Lv, S. Luo, Beilstein J. Org. Chem. 15 (2019) 1304–1312.
[16] U.P.N. Tran, G. Oss, D.P. Pace, J. Ho, T.V. Nguyen, Chem. Sci. 9 (2018) 5145–5151.
[17] S.J. Ni, J. Franzen, Chem. Commun. 54 (2018) 12982–12985.
[18] S.J. Ni, M. El Remaily, J. Franzen, Adv. Synth. Catal. 360 (2018) 4197–4204.
[19] M.A. Hussein, V.T. Huynh, R. Hommelsheim, R.M. Koenigs, T.V. Nguyen, Chem. Commun. 54 (2018) 12970–12973.
[20] W.S. Shang, D.P. Duan, Y.J. Liu, J. Lv, Org. Lett. 21 (2019) 8013–8017.
[21] S.H. Doan, M.A. Hussein, T.V. Nguyen, Chem. Commun. 57 (2021) 8901–8904.
[22] P.K. Ranga, F. Ahmad, P. Nager, et al., J. Org. Chem. 86 (2021) 4994–5010.
[23] M. Rezazadeh Khalkhali, M.M.D. Wilde, M. Gravel, Org. Lett. 23 (2021) 155–159.
[24] S.Sharma Rekha, G. Singh, R. Vijaya Anand, ACS Org. Inorg. Au 2 (2022) 186–196.
[25] J.J. Liu, J.X. Xu, Z.J. Li, et al., Eur. J. Org. Chem. 2017 (2017) 3996–4003.
[26] W.J. Patterson, K. Lucas, V.A. Jones, et al., Eur. J. Org. Chem. 2021 (2021) 6737–6742.
[27] W.G. Zhu, Q. Sun, Y.R. Wang, D. Yuan, Y.M. Yao, Org. Lett. 20 (2018) 3101–3104.
[28] G. Oss, J. Ho, N.Thanh Vinh, Eur. J. Org. Chem. 2018 (2018) 3974–3981.
[29] P. Goswami, S. Sharma, G. Singh, et al., J. Org. Chem. 83 (2018) 4213–4220.
[30] H.M. Jin, M. Rudolph, F. Rominger, A.S.K. Hashmi, ACS Catal. 9 (2019) 11663–11668.
[31] Y.A. Rulev, Z.T. Gugkaeva, A.V. Lokutova, et al., ChemSusChem 10 (2017) 1152–1159.
[32] K. Omoregbee, K.N.H. Luc, A.H. Dinh, T.V. Nguyen, J. Flow Chem. 10 (2020) 161–166.
[33] J. Xu, Y. Gao, Z. Li, et al., Eur. J. Org. Chem. 2020 (2020) 311–315.
[34] H. Huang, Z.M. Strater, M. Rauch, et al., Angew. Chem. Int. Ed. 58 (2019) 13318–13322.
[35] H. Huang, Z.M. Strater, T.H. Lambert, J. Am. Chem. Soc. 142 (2020) 1698–1703.
[36] T. Shen, T.H. Lambert, Science 371 (2021) 620–626.
[37] T. Shen, T.H. Lambert, J. Am. Chem. Soc. 143 (2021) 8597–8602.
[38] H. Huang, T.H. Lambert, J. Am. Chem. Soc. 143 (2021) 7247–7252.
[39] W. Xiao, X. Wang, R. Liu, J. Wu, Chin. Chem. Lett. 32 (2021) 1847–1856.
[40] W. Xiao, J. Wu, Chin. Chem. Lett. 31 (2020) 3083–3094.
[41] L. Mei, J.M. Veleta, T.L. Gianetti, J. Am. Chem. Soc. 142 (2020) 12056–12061.
[42] L. Mei, J. Moutet, S.M. Stull, T.L. Gianetti, J. Org. Chem. 86 (2021) 10640–10653.
[43] S.M. Stull, L. Mei, T.L. Gianetti, Synlett 33 (2022) 1194–1198.
[44] R. Mir, T. Dudding, J. Org. Chem. 82 (2017) 709–714.
[45] K. Dempsey, R. Mir, I. Smajlagic, et al., Tetrahedron 74 (2018) 3507–3511.
[46] T. Courant, M. Lombard, D.V. Boyarskaya, L. Neuville, G. Masson, Org. Bio. Chem. 18 (2020) 6502–6508.
[47] N.N.H. Ton, B.K. Mai, T.V. Nguyen, J. Org. Chem. 86 (2021) 9117–9133.