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光诱导的自由基脱氰反应研究进展

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摘　要

脱氰基是药物研究、医学和材料科学研究中芳香分子合成的重要过程。在过去几十年中，由于氰基的热力学稳定性，很少有人将其认为是一个好的反应位点。随着科学技术的进步，光化学反应发展迅速，凭借其绿色、可持续、高效降解等优势，正日益成为环境修复领域的研究热点。近些年来，化学中备受争议的氰基转化问题也在光化学中取得了重大进展。本文综述了通过可见光介导的氰基作为离去基团的芳基自由基脱氰反应研究最新进展。

关键词

光催化，自由基反应，脱氰

Research Progress on Light-Induced Radical Decyanation Reactions

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Abstract

Decyanation is an important process in the synthesis of aromatic molecules in drug research, medicine, and materials science. In the past few decades, due to the thermodynamic stability of the CN, it has rarely been considered a favorable reaction site. With advances in science and technology, photochemical reactions have developed rapidly, and thanks to their advantages such as being green, sustainable, and highly efficient in degradation, they are increasingly becoming a research hotspot in the field of environmental remediation. In recent years, the long-debated issue of cyano group transformation in chemistry has also seen significant progress in photochemistry. This article reviews the latest developments in the study of visible-light-mediated aryl radical decyanation

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reactions using CN as leaving groups.

Keywords

Photocatalysis, Radical Reaction, Decyanation

1. 引言

腈经常被用作多个领域的原料，包括制药、先进材料、农用化学品和工业化学品[1]。它们也广泛存在于天然产物和生物活性分子中，以及在化学合成中作为不同羰基化合物、胺和杂环的不同前体[2]，或作为催化芳烃 C-H 官能化反应中的导向基团[3]-[5]。将氰基引入到有机分子中是相对比较容易的[6]，同时 C-CN 键作为产生其他有价值有机基团的反应位点也是有利的。氰基的强吸电子能力通过增加相邻 C-H 键的酸性来改变反应性。因此，苯甲腈的邻位和烷基腈中 C-H 键的 α 位经常被认为是脱质子化或官能化的反应位点，并为进一步多样化开辟了可能性[7]。自由基介导的 C-CN 键断裂最近几年才成为合成转化中的一种新方法。自在 2011 年 MacMillan 团队的开创性工作以来，有机化学家通过直接自由基偶联脱氰的方式实现了 $Ir(ppy)_3$ 催化的叔胺与 C-CN 键官能化的光氧化 C-H 芳基化反应[8]。到目前为止，由自由基介导的 C-C 和 C-X 键断裂途径被证明是合成复杂有机化合物的有效方法，同时该过程也是非常具有挑战性的，仍吸引着科研工作者去进一步探索。

2. 光诱导自由基脱氰

通过自由基偶联策略和过渡金属催化方案构建 C-C 键的新方法的发展一直是近年来有机化学的一个突出研究课题[9]-[13]。几个研究小组已经证明了光催化 α-胺、醇和羧酸 C-H 芳基化反应方案。其中，芳基氰化物的使用频率最多，特别是 1,4-二氰基苯和氰基取代的氮杂芳环。吡啶是一种重要的杂环化合物，广泛应用于药物、农用化学品、生物活性天然产物和功能材料中[14]，而吡啶基腈的脱氰反应也为制备重要吡啶衍生物提供了一种的有效途径。

3. C_{sp3}-H 键活化的光氧化还原催化自由基脱氰芳基化

2011 年，MacMillan 团队报道了一项关于 $Ir(ppy)_3$ 光氧化催化 C-H 芳基化反应的开创性工作(图 1)，该反应可以以市售的芳基腈作为基础原料，通过光氧化催化的方式使叔胺与芳基氰直接自由基偶联脱氰，得到相应的芳基化产物。

机理方面，首先光敏剂被光激发将对苯二腈还原生成 InI，随后被氧化的光敏剂将三级胺氧化生成 InII，同时完成催化循环，InII在碱的作用下脱质子生成 InIII，此后与 InI发生自由基偶联并脱除一分子氰基负离子，由此得到相应产物。

未激活的 C_{sp3}-H 键的功能化仍然是有机研究人员最具挑战性的任务之一[15]-[18]。这种吸引力源于它们能够从简单和其他容易获得的惰性有机分子中创造更为复杂的有机化合物[19]。此后，许多研究小组发现了如何通过光氧化还原催化直接实现 C_{sp3}-H 的芳基化[20] [21]。

2015 年，麦克米兰[22]等人发现了烯丙基 C_{sp3}-H 键与缺电子芳腈直接芳基化的可见光驱动条件(图 2)，利用该反应可以得到多种烯丙基芳基化的产物。

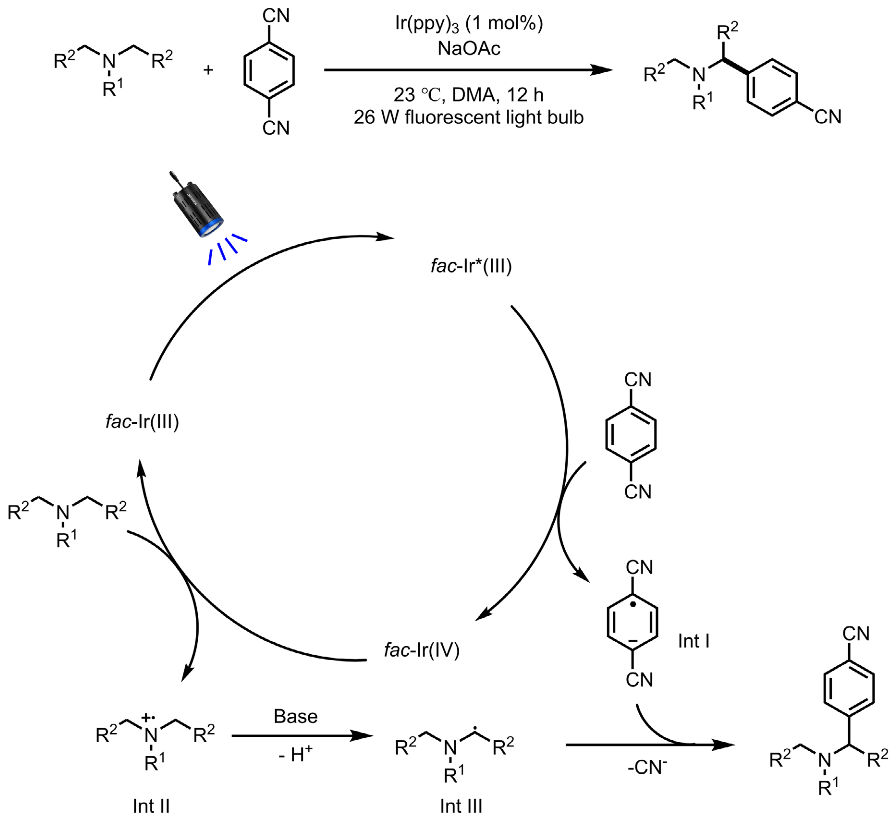

Figure 1. Photo-catalyzed C-H arylation reaction between amines and aryl cyanides
图 1. 胺和芳基氰化物之间的光催化 C-H 芳基化反应

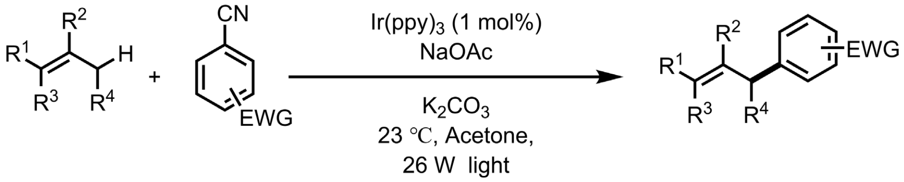

Figure 2. The direct arylation of allylic C_{sp3}-H bonds via organic and photoredox catalysis
图 2. 通过有机和光氧化还原催化进行烯丙基 C_{sp3}-H 键的直接芳基化

2016，汪清民团队[23]通过使用光氧化还原和有机催化，实现了可见光驱动的直接 α-C_{sp3}-H 键芳基化合成 N-酰基保护的四氢异喹啉(图 3)。光敏剂可以氧化 HAT 催化剂，如硫醇，然后可用于从特定底物中提取·H，以产生匹配的自由基中间体[24]。因此，在这种自由基－自由基偶联反应中，各种缺电子的杂芳腈或芳腈可以用作芳基化试剂。

随后，众多团队[25]进一步将该技术扩展到多取代哌啶衍生物与杂芳腈的光催化脱氰氨基 C_{sp3}-H 芳基化反应(图 4)。该反应利用了具有多达四个立体中心的各种哌啶衍生物作为合适的底物，与现有的立体中心相比，该反应为产物提供了通常较高的非对映选择性。

2021，段春迎团队[26]开发了一种构建双功能配位聚合物的方法，该方法能够使用络合物(Cd-MIX)作为催化剂使 C_{sp3}-H 键芳基化(图 5)。定制的铱络合物和小分子有机染料已被证明是均相光氧化还原催化反应中必不可少的。这种新的 C-C 键形成策略在温和条件下和操作简单的反应方案下广泛用于合成苄基和异苄基胺。在结构范围探索中，吡咯烷、哌啶、氮杂环庚烷、吗啉和哌嗪都可以提供了很好的结果。除了

上述反应之外，用同类的芳基氰化物也可以与其他种类的三级胺、一级胺、烯烃、肟等底物发生自由基偶联脱氰反应[17]-[31]。

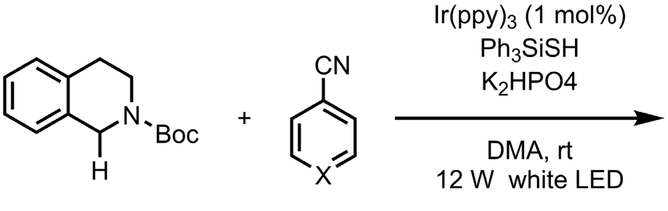

Figure 3. Photoredox-catalyzed direct α-C$_{sp3}$-H arylation reaction
图 3. 光氧化还原催化的直接 α-C$_{sp3}$-H 芳基化反应

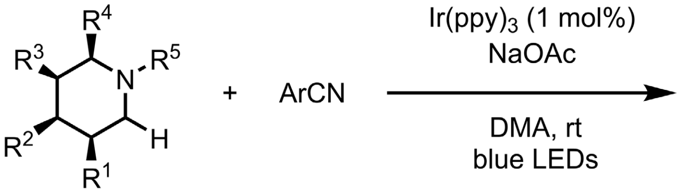

Figure 4. Photo-catalyzed α-amino C-H arylation of highly substituted piperidine derivatives with aryl nitriles
图 4. 光催化高度取代哌啶衍生物的 α-氨基 C-H 芳基化

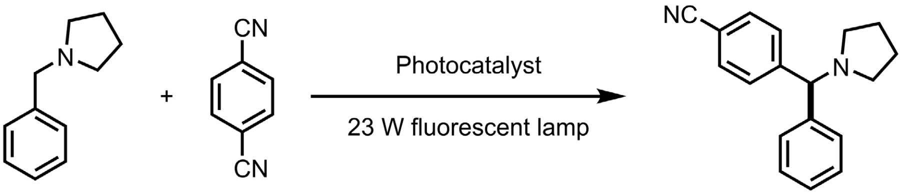

Figure 5. Photo-catalyzed C-H arylation reaction between amines and aryl cyanides
图 5. 胺类与芳基腈之间的光催化 C-H 芳基化反应

由此，通过光氧化还原催化途径可以有效活化 C$_{sp3}$-H 键，产生相应的烷基自由基中间体，参与后续偶联脱氰过程。

4. 通过 C-C 键活化实现的光氧化还原催化自由基脱氰芳基化

由于 C-C 键热力学稳定性和低极化程度，所以 C-C 键的活化仍然是最困难的挑战之一[32]。裂解这种强键的一种可能策略是自由基阳离子的裂解[33]。Till Opatz 团队[34]在 2017 年报道了一种紫外光介导的通过激活非活性的 C_{sp3}-C_{sp3} 键的杂芳基腈烷基化(图 6)。其中，包括二氰基苯和氰基吡啶在内的芳基腈被紫外线辐射激发后，成为一种非常好的电子受体，有利于进一步参与反应[35]。该反应比较有趣的是在反应过程中会生成 InII，InII会发生 C-C 键的断裂，生成 InIII，进而与 InI发生自由基偶联脱氰，生成目标产物。

2022 年卢戢团队[36]发现了环丙醇与氰基芳烃通过自由基介导的光催化芳基化反应，该反应可以通过换用不同的环丙醇得到各种相应的 β-芳基化酮(图 7)。

随后，Till Opatz 团队报道[37]了一种无金属光氧化合成 γ-杂芳基酮的方法，该方法从传统合成的环丙基酮作为底物，使用 Hantzsch 酯作为光还原剂，同样可以得到芳基偶联的产物(图 8)。

自由基化学领域的不断扩大有助于脱羧反应自由基策略的发展。脱羧反应的一种革命性方法是众所

周知的巴顿脱羧反应，它通常由紫外线辐射或高温启动[38]。

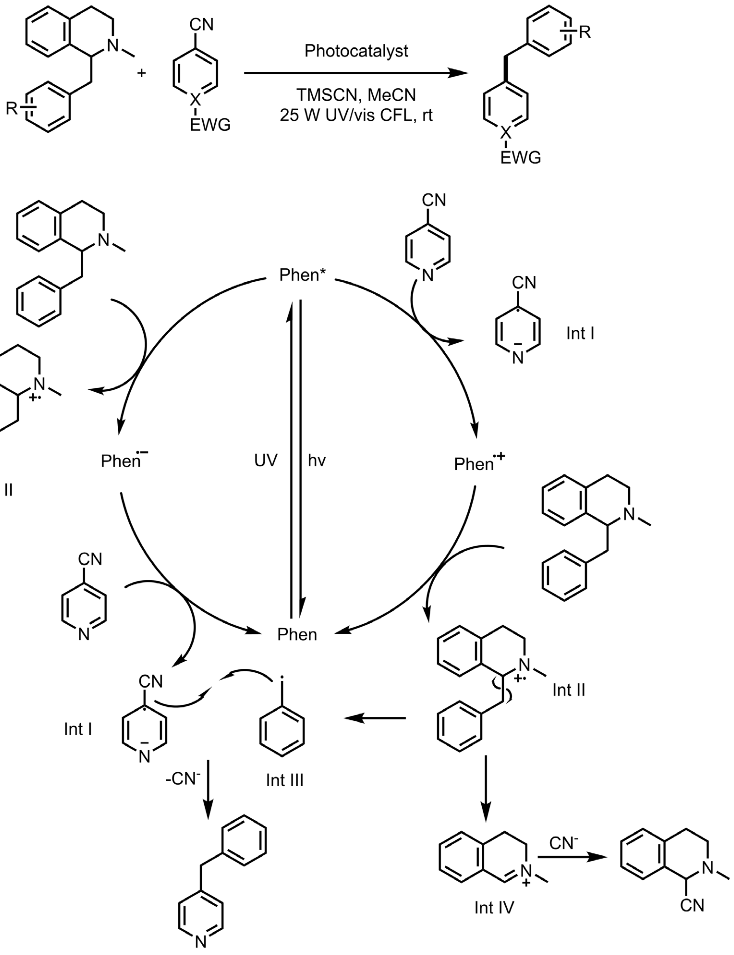

Figure 6. Photo UV light-induced alkylation of (hetero) arylnitriles
图 6. 紫外光介导的(杂)芳基腈烷基化反应

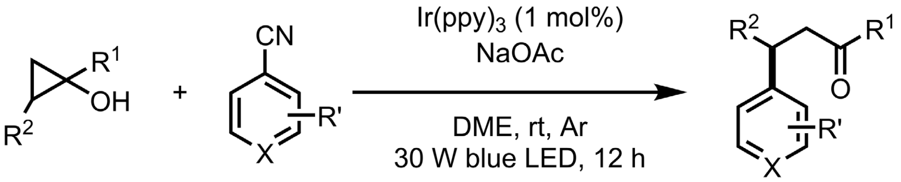

Figure 7. Photo-catalyzed arylation of cyclopropanols with aryl nitriles
图 7. 光催化环丙醇与芳基腈的芳基化反应

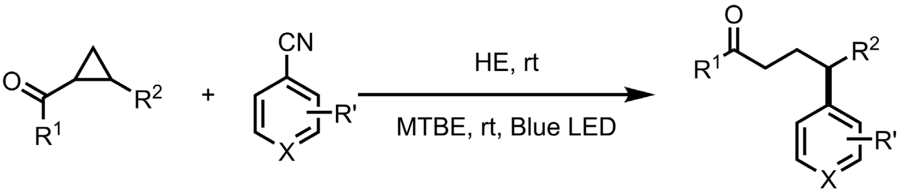

Figure 8. Photocatalytic arylation reaction of cyclopropyl ketones with Aryl Nitriles
图 8. 光催化环丙基酮与芳基腈的芳基化反应

2014 年 MacMillan 团队[39]通过利用 *N-Boc* 氨基酸进行了扩展，这些氨基酸在光催化剂的存在下被活化，通过脱羧过程产生碳自由基物种，从而与还原形式的芳基氰化物反应，得到相应的芳基化产物(图 9)。2016 年 Till Opatz 团队，将底物拓展到了 *α*-氨基酸[40]。

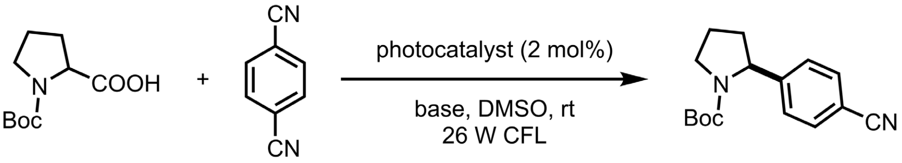

Figure 9. Photo-catalyzed decarboxylative arylation of *α*-amino acids with aryl nitriles
图 9. *α*-氨基酸与芳基腈的光催化脱羧芳基化反应

环丙烷、烷基羧酸等底物可以通过光催化途径发生 C-C 键的断裂或直接脱羧实现 C-C 键的活化，同时产生可以与芳基氰化物偶联兼容的自由基。

5. 通过 C_{sp3}-X (X = B、N 和 C)键断裂实现的光氧化还原催化自由基脱氰芳基化

苄基频哪醇酯是易于获得的前体，因为它们可以从合成和商业来源广泛获得[41]-[43]。

2016 年 Steven V. Ley 团队[44]报道了一种新的活化模式，该模式在铱的催化条件下，通过流动化学技术使硼酸酯与杂芳基腈发生偶联脱氰反应(图 10)。后来，Hirohisa Ohmiya 报道了一种新的烷基硼酸盐试剂，用于产生烷基自由基，该试剂可以在直接光激发下通过 C-B 键断裂与 4-氰基吡啶反应[45] [46]。之后 Amos B. Smith, III 团队通过光催化单电子转移引发的高价硅中间体鉴定出氧化[1,2]-Brook 重排过程[47]。

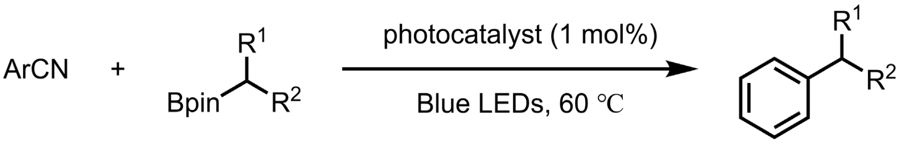

Figure 10. Photoredox-catalyzed activation of boronic esters enables C_{sp2}-C_{sp3} cross-couplings in flow
图 10. 光氧化还原催化活化硼酸酯，实现流动反应中的 C_{sp2}-C_{sp3} 交叉偶联

2019 年，余达刚团队[48]发现了一种不寻常的脱氰反应，该反应使用季铵盐作为偶联底物，季铵部分作为离去基团，在可见光介导的还原偶联方案下与杂芳腈偶联，得到二芳基甲烷(图 11)。机理研究表明，在这种转化过程中可能会产生苄基自由基和一个持久的自由基阴离子。该方法具有底物范围广、易于扩展、反应条件温和等特点，为 C-C 键的构建提供了一种实用的策略。

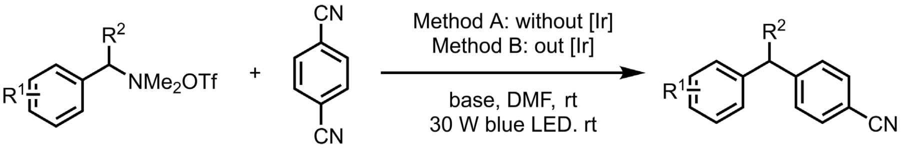

Figure 11. Visible-light-mediated cross coupling of benzylammonium salts with (hetero)aryl nitriles
图 11. 可见光介导的苄基铵盐与(杂)芳腈的交叉偶联反应

2022 年 Varinder K. Aggarwal 团队[49]报道了伯、仲和叔硼酸酯与叔胺和芳基腈的可见光诱导自由基偶联进行了具有里程碑意义的研究(图 12)。

丙二腈在离子和自由基反应中都有很好的应用[50] [51]。使用丙二腈作为单腈的原料，通过去除多余

的腈基团具有先天优势。尽管与类似的丙二酸酯，如乙酰乙酸酯和磺酰基乙酸酯相比，丙二腈的 C-CN 裂解存在困难，但通过使用特殊的引发剂，已经建立了丙二腈还原脱氰反应[52] [53]。

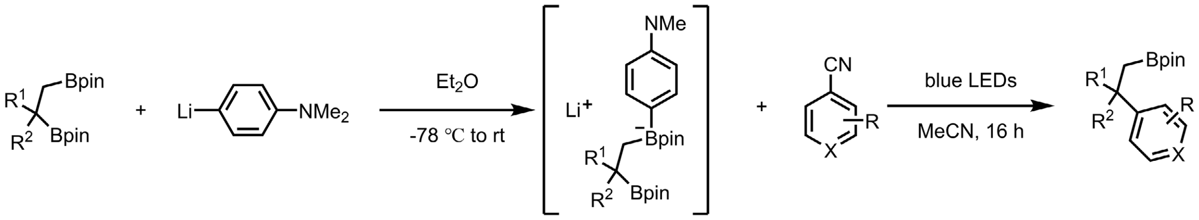

Figure 12. Visible light-induced coupling of 1,2-bis-boronic esters and (hetero) aryl nitriles
图 12. 可见光诱导的 1,2-双硼酸酯与(杂)芳基腈的偶联反应

2012 年 John A. Murphy 团队[54] [55]通过使用有机光活化有机电子供体作为催化剂，开发了单腈的选择性自由基 C-C 键断裂(图 13)。

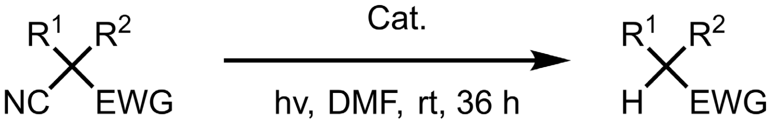

Figure 13. Photo-catalyzed organic superelectron-donors promoted hydrodecyanation of nitrile derivatives
图 13. 光催化有机超电子供体促进腈类衍生物的脱氰反应

含有碳杂键或者特殊官能团的 C-C 的底物是一种优良的自由基前体，通过光催化的方式可以有效地释放自由基并参与自由基反应。

6. C_{sp2} 键官能化实现的脱氰芳基化

除了 C_{sp3} 键官能化外，C_{sp2} 键官能化也可以实现自由基偶联脱氰反应。2017 年夏吾炯团队[56]开发的一种简单方案实现了可见光促进的羰基或亚氨基的自由基脱氰芳基化，并产生了各种仲醇、叔醇和胺(图 14)。

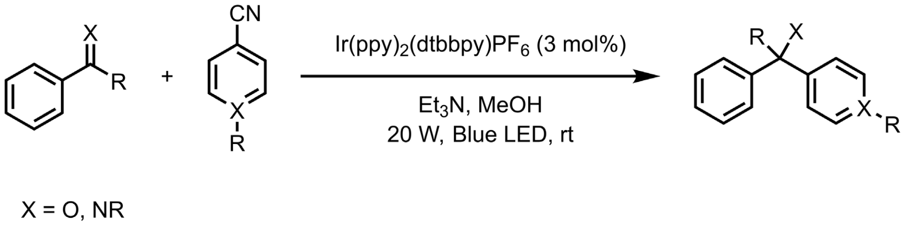

Figure 14. Photoredox-catalyzed directly reductive arylation of carbonyl or iminyl derivatives
图 14. 光催化直接还原羰基或亚胺衍生物的芳基化反应

与这一结果类似的是 2018 年 Karl A. Scheidt 团队报道了亚芳基丙二酸酯与氰基芳烃的可见光驱动的光氧化还原芳基化反应，该反应可以得到各种官能化的二芳基丙二酸酯[57]。

烯烃－吡啶交叉偶联是获得具有化学和区域选择性的烷基吡啶的可行途径[58]。

2018 年储玲玲[59]开发了一种无金属的方法，用于苯乙烯和 Togni 试剂的分子间三组分卡吡啶化，在不使用外源催化剂的情况下，通过依次形成两个 C-C 键，提供了一系列 *β*-CF_3 吡啶(图 15)。在该反应中使用了 90 W 的蓝色 LED 并由 Hantzsch ester 作为还原剂，可以得到三氟甲基吡啶化产物以及高产率的天然产物类似物。

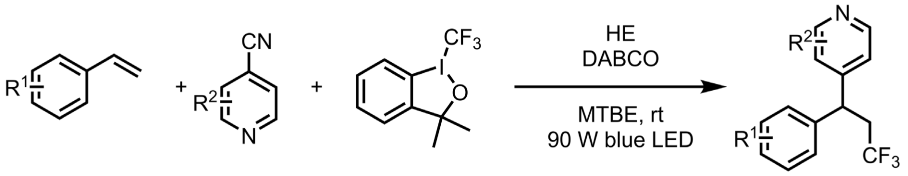

Figure 15. Visible light-induced photoredoxcatalyzed three-component carbopyridylation of styrenes
图 15. 可见光诱导的光红氧化催化三组分苯乙烯羧基化吡啶反应

基于这项工作，储玲玲团队[60]还报道了一种可见光诱导和 IrIII 催化的策略，用于用氰基吡啶和 $TMSN_3$ 对多取代苯乙烯进行分子间三组分氧化还原中性叠氮杂芳基化，以产生具有中等到高度区域选择性的相应 *β*-叠氮吡啶(图 16)。

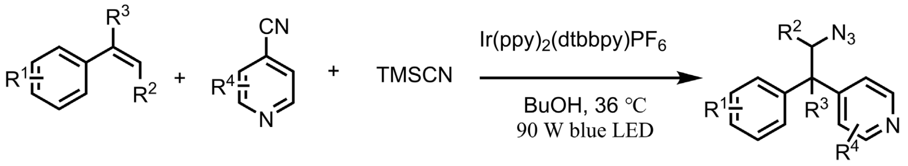

Figure 16. Photoredox-catalyzed azidopyridylation of styrenes
图 16. 光氧化还原催化的苯乙烯叠氮吡啶化反应

2021 年沈佳轩团队[61]描述了一种有用的可见光诱导光氧化还原催化苯乙烯与氰基吡啶和二苯基氧化膦的膦吡啶化反应，以产生相应的 *β*-膦吡啶(图 17)。对于类似的烯烃双官能化反应，林禄清团队[62]和邓红平团队[63]也分别通过脱氰策略开发了未活化烯烃的光诱导多组分双官能化。

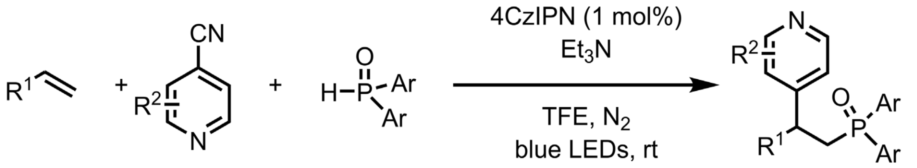

Figure 17. Visible light-induced photoredoxcatalyzed three-component phosphinicpyridylation of styrenes
图 17. 可见光诱导光氧化还原催化的苯乙烯三组分膦基吡啶化反应

2022 年江智勇团队[64]通过使用不对称磷酸作为手性氢键(氢键)催化剂实现了烯酮的光催化脱氰还原氮杂芳基化(图 18)，这种方法的稳健性已经通过使用无数种候选药物得到了证明，所有候选药物都显示出高对映选择性和优异的产量。

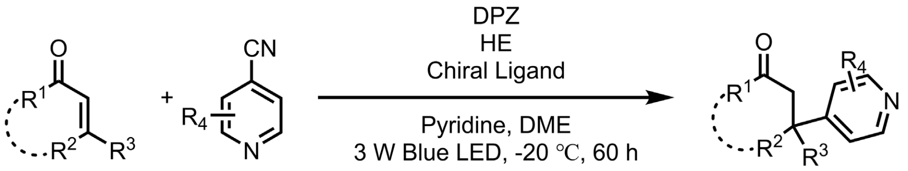

Figure 18. Visible-light-driven photocatalytic reductive aza-arylation of enones
图 18. 可见光驱动的光催化还原氮芳基化烯酮反应

胺的制备是一个广阔的研究领域，旨在通过新的 C-N 键形成、C=N 加成或胺的 *α*-C-H 官能化产生新的产品或合成方法[65]。在这方面，需要形成伯胺，特别是具有完全取代的 *α*-碳的伯胺。

2020 年，Tomislav Rovis 团队[66]开发了一种使用光氧化还原催化将现成的 *O*-苯甲酰肟(或氯化亚铵)与氰基芳烃结合形成具有完全取代的季碳中心的伯胺的反应(图 19)。

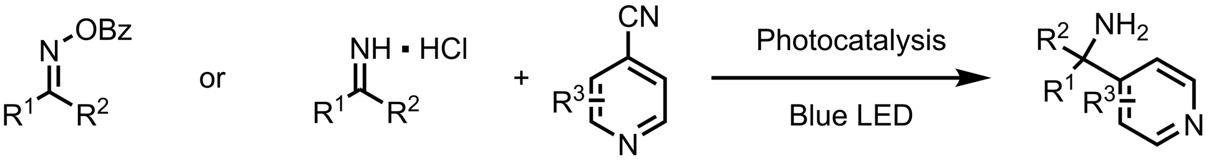

Figure 19. Photoredox-catalyzed syntheses of primary amines from O-benzoyl oximes (or iminium chlorides) with cyanoarenes
图 19. 光催化氧化还原反应合成原胺的方法，从 O-苯甲酰肟(或亚胺氯化物)与氰基芳烃反应获得

光催化的电子转移质子耦合(PECT)途径适用于酮、亚胺等底物，而单电子转移(SET)过程生成的自由基也可以与烯烃加成，两种方式均可以使含有 C_{sp2} 键的底物生成活性自由基，并顺利进行偶联脱氰反应。

7. 光氧化还原催化自由基脱氰胺化

芳胺，特别是杂芳胺，是非常有价值的片段，广泛存在于农用化学品、药品、先进材料和工业化学品中[67]-[69]。因此，构建 C-N 键合成芳胺已成为学术界和工业界的重要反应之一[70] [71]。

2020 年，吴骊珠团队[72]发现了一种无金属位点选择性脱氰胺化反应，用于在可见光照射下直接访问光催化剂催化的杂芳基胺(图 20)。各种芳基或烷基胺可以与(杂)芳基腈(如异喹啉、吡啶、嘧啶等)偶联，以高产率生产有价值的药用芳胺。

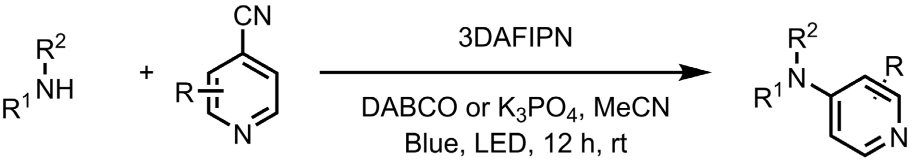

Figure 20. Visible light-induced the formation of heteroaryl amines via a SET process
图 20. 可见光诱导下通过单电子转移(SET)过程形成杂芳基胺

8. 总结

本文综述了近些年来自由基介导的光催化脱氰反应。自 MacMillan 团队首次报道了 $Ir(ppy)_3$ 催化的叔胺与 C-CN 键活化的自由基偶联脱氰反应以来，该反应引起了众多化学家的兴趣。即使有了这些发展，但仍然有许多科学挑战，如用有机腈作底物时，脂肪族腈与自由基脱氰方案不相容；芳基(杂)腈，如苯甲腈、1,4-二氰基苯或氰基取代的氮杂芳环，是最近大多数发现的基础底物，这种限制大大减少了产物的芳基或杂芳基部分的种类。上述问题既是挑战，也是机遇，在新的科研环境下，探索新的催化体系和自由基前体将是进一步拓展自由基偶联脱氰反应应用范围的一个可行方向。

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