Brønsted酸催化的2-萘偶氮邻位胺化反应

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摘要 独特的分子结构和理化性质使得 N -芳基咪唑类化合物在有机发光半导体(OLED)材料以及药物化学领域展现出了重要的应用潜力。因此, 发展高效的、条件温和的合成策略实现 N -芳基咪唑类骨架的构建具有十分重要的意义。传统过渡金属催化的 N -芳基偶联策略需要芳烃原料的预官能化, 同时副产物的产生也显著影响了该方法的合成效率。已报道的 $C-H/N-H$ 脱氢偶联方法一般需要大量的氧化剂, 而且存在反应条件剧烈、化学选择性差和底物普适性不足等诸多问题。本研究基于芳烃极性翻转策略, 实现了一种Brønsted酸催化的芳烃 $C-H$ 胺化途径用于 N -芳基咪唑的高效构建, 该方法反应条件温和、原子经济性高, 且避免了对于金属催化剂的依赖。实验结果表明, 磷酸与底物间的氢键作用以及催化剂上大共轭芳香基团与底物间的 $\pi-\pi$ 堆积作用对该转化的化学选择性调控起到了至关重要的作用。

关键词 N -芳基咪唑, Brønsted酸, 芳基偶氮, $C-H$ 胺化

N -芳基骨架是一类在天然产物、药物分子和有机功能材料中广泛存在的重要分子结构^[1~3]。其中, N -芳基咪唑结构因为具有高三重态能量和竞争性空穴传输能力, 成为近年来在有机发光半导体(OLED)的材料中应用较为广泛的化学结构单元之一^[4~9]。此外, 具有独特平面结构的咪唑可以与DNA双螺旋结构有效结合从而抑制DNA复制过程, 使得 N -芳基咪唑类化合物成为抗肿瘤、抗菌和治疗精神类疾病等药物的有效成分^[10]。这些领域的快速发展极大刺激了对 N -芳基咪唑骨架多样性的需求。因此, 发展条件温和、绿色高效的催化合成策略进行 N -芳基咪唑的多样性构建已成为合成化学领域重要的研究方向之一。

基于分子结构和原料来源的综合分析, $C-N$ 键的直接构筑无疑是合成 N -芳基咪唑结构的最有效方式。通常来说, 过渡金属催化的交叉偶联反应, 包括Ullmann偶联、Buchwald-Hartwig偶联和Chan-Lam-Evans

偶联, 已成为构建 $C-N$ 键的最可靠、也是最常用的方式(图1)^[11~17]。然而, 该过程需要使用芳基卤代物或芳基硼酸等预官能化底物, 原子经济性降低的同时还会伴随卤化物等环境不友好物质的产生, 同时还不可避免地存在重金属残留问题。与之对比, 具有高原子经济性的 $C-H/N-H$ 氧化脱氢偶联成为近年来构筑 $C-N$ 键的主要发展方向。高价碘试剂^[18,19]和过渡金属^[20~23]是实现该氧化胺化过程的常规方式。此外, 光催化^[24,25]和电催化^[26~28]策略成为近年来用于该类型转化的新兴手段。而在有机发光半导体材料领域常用的 N -芳基咪唑类化合物的构建中, 咪唑则常被用作胺化试剂于较高的反应温度条件下, 与(杂)芳基氟类底物通过芳环的亲核取代反应构筑 $C-N$ 键^[29~31]。尽管在该方面已经取得了重要的进展, 但上述的方法在氧化剂用量、反应温度、化学选择性和底物普适性等方面仍面临着诸多问题。

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有机催化具有反应条件温和、官能团兼容性强等优点,同时能够从根本上解决重金属残留问题,因此有机小分子催化的C-H胺化反应被认为是构建C-N键的理想方式。但是,有机催化对于惰性C-H键较低的活化能力对该策略的发展提出较大的挑战。为了解决这个科学难题,我们提出基于芳烃极性翻转的非常规Michael加成策略,通过底物设计采用共轭体系将Meisenheimer中间体的高能量进行快速转移,开创性实现了有机催化偶氮芳烃和亚硝基芳烃C-H键的不对称官能化,包括吡啶、2-萘酚、2-萘胺和硼酸等碳亲核试剂都可以高效适用于该催化模式^[32-34]。在此基础上,我们于近期实现了手性磷酸催化2-萘偶氮酯与吡啶/吡啶的不对称C-H胺化反应,高效构筑了一系列C-N键轴手性化合物^[35]。这一研究已经初步证实了该C-H胺化策略具有在温和条件下实现N-芳基吡啶构筑的应用潜力,但研究中轴手性控制的因素使得在吡啶底物普适性方

面的考察还相对有限。因此,本工作将在前期研究的基础上,摒弃轴手性元素,着重考察该磷酸催化的C-H胺化过程的底物普适性和化学选择性,以期为N-芳基吡啶的合成提供一种高效实用的策略(图2)。考虑到本课题组的消旋磷酸种类较少,为了便于进行化学选择性的筛查,实验过程仍使用手性磷酸进行。

1 实验

(i) 试剂与仪器。¹H NMR、¹³C NMR、¹⁹F NMR核磁共振谱由Bruker 400 M核磁共振仪测定。高分辨率质谱仪(HRMS)由Thermo Scientific Q Exactive组合型四级杆Orbitrap质谱仪测定。所有空气敏感化合物均在DPI-LAB HE493或者MBRAUN Lab Star手套箱中称量,并在真空线上按照标准Schlenk技术(SST)操作。二氯甲烷、1,2-二氯乙烷(DCE)、氯仿经氢化钙回流干燥,重蒸;乙醚、四氢呋喃(THF)、甲苯经钠-二苯甲酮

图1 (网络版彩色) 构筑C-N键常用方法

Figure 1 (Color online) Common methods for constructing C-N bonds

图2 (网络版彩色) 手性磷酸对2-萘偶氮的活化模式猜想

Figure 2 (Color online) Conjecture on the activation mode of chiral phosphate acid to azo

回流干燥,重蒸、其他溶剂如无特殊说明为直接使用。所有试剂均从安耐吉、百灵威或Alfa公司以及国内的试剂公司购买。2-萘偶氮、咪唑底物与手性磷酸的合成均参考已报道的方法^[29-32]。

(ii) 碳氢键胺化反应的经典实验操作。称取2-萘偶氮(0.2 mmol)、咪唑(0.3 mmol)以及催化剂(10%(mol))于10 mL Schlenk管中。抽换气3次,使得管中气体被置换为氩气。在氩气氛围下加入2 mL氯仿,反应在35°C下进行直至原料完全消耗。将反应体系浓缩后经硅胶柱层析(石油醚和乙酸乙酯的体积比为9:1~2:1),得到*N*-芳基咪唑产物**3**。相应产物的表征数据如下。

产物**3a**: 固体, 收率87%。¹H NMR(400 MHz, DMSO-*d*₆) δ 9.24(s, 1H), 8.38~8.25(m, 2H), 8.06(d, *J* = 9.1 Hz, 1H), 7.90(d, *J* = 8.1 Hz, 1H), 7.46(d, *J* = 9.1 Hz, 1H), 7.29(m, 5H), 7.20(m, 1H), 7.08(m, 1H), 6.90(d, *J* = 7.9 Hz, 2H), 6.25(d, *J* = 8.5 Hz, 1H), 3.58(s, 3H); ¹³C NMR(100 MHz, DMSO-*d*₆) δ 157.85, 145.97, 141.57, 132.12, 130.70, 128.87, 128.69, 127.81, 126.38, 123.69, 123.18, 120.94, 120.74, 120.16, 115.11, 111.62, 110.68, 52.34; HRMS(ESI) *m/z*: 计算值[M+H]⁺ C₂₄H₂₀N₃O₂, 382.1550, 实测值[M+H]⁺, 382.1548。

其他产物的核磁共振氢谱、碳谱、高分辨质谱与液相色谱图详见补充材料。

2 结果与讨论

基于前期的研究基础,我们选择2-萘偶氮酯**1a**与咪唑**2a**为模板底物,氯仿为反应溶剂,在50°C条件下对催化剂Brønsted酸的类型和反应参数进行了详细考察。研究初期对于常规易得的质子酸(包括醋酸、三氟乙酸、磺酸等)的考察均得到较低的收率,其中三氟乙酸为催化剂时能以34%的核磁收率得到目标产物**3a**(表1, 实验1)。考虑到有机磷酸在催化过程中能够通过酸性质子对偶氮基团进行活化,同时P=O的碱性位点还能与亲核试剂形成氢键作用(图2)。这种双功能的协同作用过程有利于反应化学选择性的控制^[36-38],接下来的研究系统考察了磷酸对于该转化的促进作用。通过对带有不同芳基取代基的SPINOL衍生磷酸进行筛选,结果表明改变6,6'-位置芳基的电性和位阻并不能改善反应结果(表1, 实验4~7)。进一步的研究表明带有如1-萘、9-蒽、9-菲和1-芘等大共轭芳环体系取代基团的磷酸能够显著提高转化效率(表1, 实验8~11),其中9-菲

和1-芘取代基的磷酸Cat-7、Cat-8催化效果最为明显,能够分别以70%和75%的分离收率获得产物**3a**(表1, 实验10, 11)。这可能是因为具有大共轭体系的多芳环取代基团与底物之间存在较强的 π - π 堆积作用,使得催化剂与底物间的结合更为紧密,能够更好地诱导转化的进行。发现 π - π 堆积作用对该转化的潜在促进作用后,对9-菲和1-芘取代的BINOL和8H-BINOL骨架磷酸进行了考察,遗憾的是并没有得到更好的结果(表1, 实验13~16)。确定磷酸Cat-8为最优催化剂后,进一步对反应的温度进行优化。研究表明反应温度对该转化的收率影响较大,室温下产物的收率下降到59%(表1, 实验17)。当反应在35°C进行时,能够以87%的分离产率得到目标产物(表1, 实验18),进一步提高反应温度并不能改善该转化的选择性(表1, 实验19)。

在获得反应的最优转化条件后(表1, 实验18),在该条件下对该转化的底物适用性进行了考察。图3的结果表明,偶氮上吸电子基团的位阻和类型(酯基或酰胺基, **3a**~**3f**)对反应产率有较大的影响。位阻较大的偶氮异丙酯的反应速率变慢,延长反应时间至68 h能够以72%的收率得到产物**3b**,而位阻更大的叔丁酯底物进行反应时,产物**3c**的收率明显下降;将酯基改变为酰胺基团后底物的活性明显降低,将反应温度升高到60°C,用20%(mol)的催化剂用量时,反应产率只有37%(**3f**)。萘环上的取代基对反应也有一定的影响,但整体上呈现出较好的官能团兼容性,能够以良好的收率获得*N*-芳基咪唑化合物(**3g**~**3i**)。接下来,对咪唑底物的兼容性进行了考察。3,6-位带有供电子基团的咪唑呈现出更高的反应活性,均能顺利地参与转化并以优异的收率获得目标产物(**3j**~**3o**),其中产物**3k**产率达到了96%;甚至与亲电能力减弱的偶氮异丙酯反应时,仍能以84%的收率得到产物**3n**。咪唑2-位的甲氧基由于同时存在供电子的共轭效应和吸电子的诱导效应,二者相互抵消后呈现出的净电子效应不是很明显(**3p**)。与之相反,吸电子基团降低了咪唑氮原子上的电子云密度,导致咪唑的亲核性降低,仅能以中等的收率获得相应的产物(**3q**~**3t**)。此外,增加咪唑芳环的共轭体系同样降低了氮上电子的亲核能力,使得转化的收率变差,如7*H*-苯并咪唑参与反应时仅能以38%的收率得到产物**3w**。与电子效应相比,取代基的位阻效应对该底物的活性有着更加直接的影响,如2-溴和3-溴咪唑在转化中均能得到中等的收率(**3q**, **3r**),而1-溴咪唑在提高反应温度和增加催化剂用量的情况下仍不能参与反应(**3v**)。同时,选择2-叔丁

表1 Brønsted酸催化2-萘偶氮的邻位胺化反应条件筛选

Table 1 Screening of the conditions for the *ortho* amination of 2-naphthalazo catalyzed by Brønsted acid

实验	催化剂	温度(°C)	时间(h)	收率(%) ^{a)}
1	TFA	50	18	34
2	$\text{C}_6\text{H}_5\text{SO}_3\text{H}$	50	18	15
3	$(\text{PhO})_2\text{P}(\text{O})\text{OH}$	50	18	7
4	Cat-1	50	18	13
5	Cat-2	50	18	12
6	Cat-3	50	18	痕量
7	Cat-4	50	18	9
8	Cat-5	50	18	64
9	Cat-6	50	18	55
10	Cat-7	50	18	72(70 ^{b)})
11	Cat-8	50	18	78(75 ^{b)})
12	(Rac)-Cat-9	50	18	11
13	Cat-10	50	18	19
14	Cat-11	50	18	痕量
15	Cat-12	50	18	19
16	Cat-13	50	18	26
17	Cat-8	25	48	59
18	Cat-8	35	48	83(87 ^{b)})
19	Cat-8	60	18	79

a) ^1H NMR产率, 2,4,5-三氯嘧啶为内标; b) 分离产率

基咪唑与2-苯基咪唑作为考察对象, 初步研究了该反应体系的立体选择性. 结果发现, 在50°C下反应96 h后, 该反应能够分别以中等的产率与对映选择性获得相应的C–N轴手性化合物(**3x**, **3y**).

3 结论

本研究报道了一例Brønsted酸催化2-萘偶氮与咪

唑的高区域选择性C–H胺化反应, 实现了温和条件下N-芳基咪唑的高效构建. 研究表明磷酸与底物形成的双氢键作用, 以及催化剂上大共轭芳香基团与底物间的 π - π 堆积作用对该转化的选择性调控起到了至关重要的作用. 该方法原子经济性高, 且避免了对于金属催化剂的依赖, 为N-芳基咪唑的多样性构建提供了一种有效途径.

图3 (网络版彩色)底物适应性探究
 Figure 3 (Color online) Substrate scope

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补充材料

附录 产物核磁表征数据*N*-芳基咪唑类化合物结构表征

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Summary for “Brønsted酸催化的2-萘偶氮邻位胺化反应”

Brønsted acid catalyzed *ortho*-amination of azonaphthalene

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Because of the unique molecular structure as well as physical and chemical properties, organic compounds containing the *N*-arylcarbazole moiety exhibit significant potential in functional organic light-emitting diode (OLED) materials and the pharmaceutical chemistry domain. The direct construction of a C–N bond through cross-coupling reactions is undoubtedly the most effective way to synthesize *N*-arylcarbazole moieties. Conventional transition-metal-catalyzed cross-coupling reactions, including Ullmann, Buchwald-Hartwig, and Chan-Lam-Evans couplings, have become the most reliable and commonly used methodologies to construct C–N bonds directly. Nevertheless, there remain several unavoidable shortcomings of these practical protocols. For instance, functionalized aryl halides or aryl boronic acid substrates need to be preprepared, which may be impossible with different functional groups. Besides, excessive waste production, including detrimental byproducts, also heavily hamper their efficiencies, and there would inevitably be the problem of heavy-metal residues. To overcome these disadvantages, reactions through C–H/N–H oxidative dehydrogenation coupling have become hot areas to accomplish the construction of C–N bonds. Thus, hypervalent iodine reagents or transition metals are utilized to promote the vital oxidative amination process. In addition, recently, novel photocatalysis and electrocatalysis strategies put forward by Nicewicz and Ackermann to establish amine-arene coupling has also drawn much attention. However, the abovementioned protocols still face many problems in terms of the additional oxidant, harsh reaction conditions, restricted substrate generality, etc. In contrast, organocatalyzed reactions have been well-developed, giving the advantages of mild reaction conditions, good functional group compatibility, and transition-metal-free catalyzed process. Therefore, the organocatalyzed C–H amination reaction is considered an ideal manner to build C–N bonds. However, the low reactivity of C–H bonds in organic molecules presents a great challenge to the development of this strategy in direct C–H amination reactions. Therefore, based on the aromatics polarity reversal strategy, we designed a substrate with a conjugated system to accomplish the rapid transformation of the high energy of Meisenheimer intermediates, and a Brønsted acid-catalyzed aromatic C–H amination pathway for efficient construction of *N*-arylcarbazoles was developed. This method features mild conditions, a high atom economy, and avoids the use of transition metals.

In the exploration of this reaction system, a series of experiments on the organocatalysts, reaction temperature, reaction time, and other parameters was investigated in detail. The experimental results showed that the noncovalent interactions, including multiple hydrogen-bond interactions and π – π -stacking effect between the catalyst and substrates, played essential roles for the chemoselectivity of this transformation. After screening for the optimal reaction conditions, the substrate generality was evaluated with various substitutions on both azonaphthalenes and arylcarbazoles. As a whole, the substituents on the azonaphthalene ring exhibited good functional group compatibility, and the *N*-arylcarbazole compounds could be obtained with a good yield. The experimental results showed that the steric hindrance and electron cloud density on the N atom of arylcarbazole with different electron-withdrawing substituents would have a notable impact on the yield of the transformations, and basically, these substituent groups reduced the yield to some extent. When the 3,6-position of the carbazole substrate was replaced by an electron-donating group, the yield was obviously boosted, and the highest yield reached 96%. In contrast, when arylcarbazoles modified by an electron-withdrawing group were tested, only moderate yields of the desired products were obtained due to the lower electron cloud density on the nitrogen atom as well as its corresponding nucleophilicity. Moreover, the steric hindrance effect of the substituent on the carbazole presented a more obvious impact on the reactivity of the nucleophilicity when 1-bromocarbazole was chosen as the nucleophile that could not participate in the reaction even though the reaction temperature and amount of catalyst were greatly increased. Furthermore, 2-*tert*-butylcarbazole and 2-phenylcarbazole were initially chosen to evaluate the stereoselectivity of the reaction system, and finally, corresponding products with moderate yield and enantioselectivity were obtained.

***N*-arylcarbazole, Brønsted acid, arylazo, C–H amination**doi: [10.1360/TB-2020-1697](https://doi.org/10.1360/TB-2020-1697)