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# Nickel-Catalyzed Decarboxylative Cycloaddition of Isatoic Anhydrides with Alkenes

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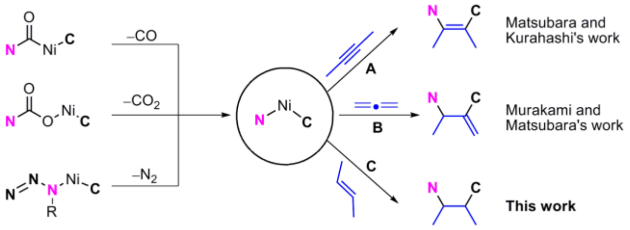
## ABSTRACT

A new method for the synthesis of tricyclic 2, 3-dihydro-4-quinolones by the $NiCl_2(PMe_3)_2$-catalyzed carboamination of alkenes by intermolecular decarboxylative cycloaddition reaction is reported here. Isatoic anhydrides were reacted with various norbornenes to afford the novel structure of quinolones. This protocol is simple and easy to handle.

Tricyclic 2,3-dihydro-4-quinolones are found in a number of bioactive small molecules, including the acronycine family of alkaloids that possess potent anticancer properties.[1] As a result, strategies have been developed in order to synthesize this framework. The [4+2] cycloadditions reaction is one of the most straightforward methods of synthesis.[2] Another popular synthetic route is the intermolecular Diels–Alder reaction.[3] Moreover, decarboxylative reactions is also to be a powerful method.[4] Other methods also involve palladinum-catalyzed enolate arylation.[5] However, despite a number of innovative synthetic approaches to such *N,O*-polyheterocycles have been reported, existing compound collections occupy only a small fraction of biogenic chemical space. Thus, in order to enable the discovery of bioactive chemotypes, the development of new and more efficient methods for synthesis of novel heterocyclic molecules is crucial. Recently, a nickel(0)-catalyzed direct insertion of an unsaturated carbon-carbon bond into a carbon-nitrogen bond has offered a useful transformation. This process takes into account an atom and step economy which undertakes to prepare more complicated azacytclic compounds in a single step, namely the addition of C and N fragments to form C-C and C-N bonds simultaneously (**Scheme 1**).[6-10] It has been shown that heterocyclic compounds such as triazoles, phthalimides, phthalic anhydride, and isatoic anhydrides can work with Ni(0) through oxidative addition and then extrusion of gaseous molecules such as CO, $CO_2$ and $N_2$ to generate an active species (C-Ni-N). This process leads to the carboamination of alkynes or allenes and can be applied to the synthesis of different new heterocyclic compounds (**Scheme 1**, **A** and **B**).[11-13] However, only two precedents exist for such a potentially valuable methodology with alkenes;[11f,13c] the easy elimination of $\beta$-hydride elimination when alkenes are added or a process of rapid self-oligomerisation may be the reason. Herein, we disclose a Ni(0), generated in situ, catalyzed cycloadditon of isatoic anhydrides with norbornenes by carboamination to synthesize quinolone derivatives (**Scheme 1**, **C**).

**Scheme 1**. Different Pathways of Nickel-Catalyzed Carboamination



Our initial experiment began with *N*-methylisatoic anhydride (**1a**), which was treated with norbornene (**1b**),[14] 5 mol % $Ni(cod)_2$, and 10 mol % $PCy_3$ in toluene at 100 ºC for 24 h. Although only a trace of the desired product of **2a** was obtained, this result hinted to us that the reaction was practical. Therefore, we screened different trialkylphosphine ligands such as $PMe_3$, $P^{t-}Bu_3$, $PPh_3$ or *N*-heterocarbnen ligands, but no good result was found (Table 1, entry 2-5). Generally, some pioneering reports have shown that the addition of appropriate Lewis acid (LA) will effectively improve the conversion and yield of reactions.[15] Results of investigating diverse Lewis acids served to correct our tactics: the addition of $Zn(OTf)_2$ or Zn promoted the reaction,

**Table 1**. Reaction Condition Screening [a,b,c]

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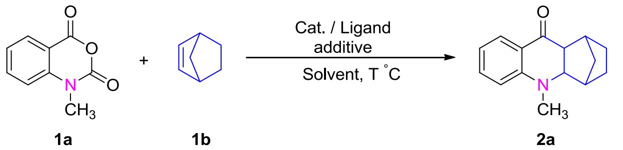
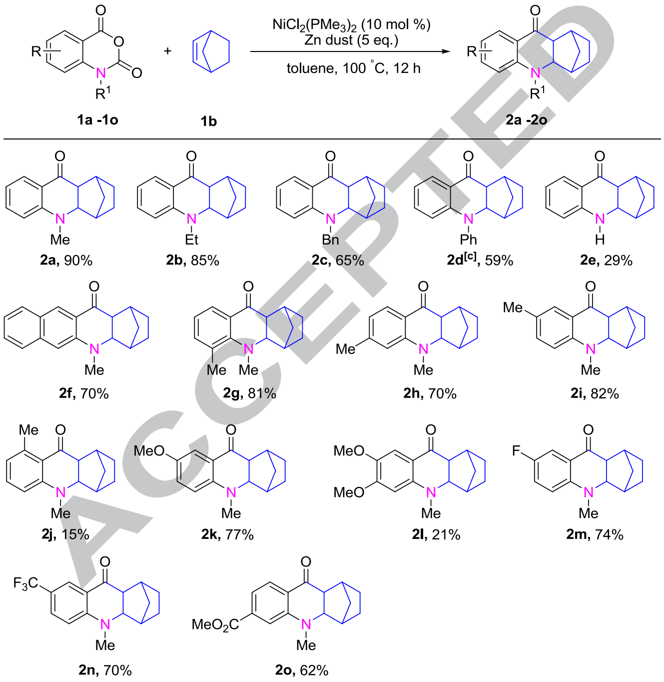


**1a** **1b** **2a**

| Entry | Cat. [mol %] | Ligand [mol %] | Additive [equiv] | Solvent | Yield [%][b] |
|---|---|---|---|---|---|
| 1 | Ni(cod)$_2$ 5% | PCy$_3$ | | toluene | <5% |
| 2 | Ni(cod)$_2$ 5% | PPh$_3$ | | toluene | trace |
| 3 | Ni(cod)$_2$ 5% | Pt-Bu$_3$ | | toluene | trace |
| 4 | Ni(cod)$_2$ 5% | Me$_3$P | | toluene | n. r. |
| 5 | Ni(cod)$_2$ 5% | IMes | | toluene | n. r. |
| 6 | Ni(cod)$_2$ 5% | HOAc | AlMe$_2$Cl (0.2) | toluene | n. r. |
| 7 | Ni(cod)$_2$ 5% | PCy$_3$ | BPh$_3$ (0.2) | toluene | n. r. |
| 8 | Ni(cod)$_2$ 5% | PCy$_3$ | Cu(OTf)$_2$ (0.2) | toluene | 12% |
| 9 | Ni(cod)$_2$ 5% | PCy$_3$ | Mg(OTf)$_2$ (0.2) | toluene | 9% |
| 10 | Ni(cod)$_2$ 5% | PCy$_3$ | Yb(OTf)$_3$ (0.2) | toluene | 17% |
| 11 | Ni(cod)$_2$ 5% | PCy$_3$ | Zn(OTf)$_2$ (0.2) | toluene | 20% |
| 12 | Ni(cod)$_2$ 5% | PCy$_3$ | ZnCl$_2$ (0.2) | toluene | n. r. |
| 13 | Ni(cod)$_2$ 5% | PCy$_3$ | FeCl$_3$ (0.2) | toluene | n. r. |
| 14 | Ni(cod)$_2$ 5% | PCy$_3$ | Zn (5.0) | toluene | 51% |
| 15 | NiCl$_2$(PMe$_3$)$_2$ 5% | | Zn (5.0) | toluene | 49%[c] |
| 16 | NiCl$_2$(PMe$_3$)$_2$ 5% | | Zn (5.0) | toluene | 90% |
| 17 | NiCl$_2$(PCy$_3$)$_2$ 5% | | Zn (5.0) | toluene | n. r. |
| 18 | NiCl$_2$(dppf) 5% | | Zn (5.0) | toluene | n. r. |
| 19 | NiCl$_2$(PPh$_3$)$_2$ 5% | | Zn (5.0q) | toluene | n. r. |
| 20 | NiCl$_2$(PMe$_3$)$_2$ 5% | | Zn (5.0) | dioxane | 82% |
| 21 | NiCl$_2$(PMe$_3$)$_2$ 5% | | Zn (5.0) | THF | 74% |
| 22 | NiCl$_2$(PMe$_3$)$_2$ 5% | | Zn (5%) | toluene | n. r. |
| 23 | NiCl$_2$(PMe$_3$)$_2$ 5% | | Zn (10%) | toluene | n. r. |
| 24 | NiCl$_2$(PMe$_3$)$_2$ 5% | | Zn (1.0) | toluene | trace |
| 25 | NiCl$_2$(PMe$_3$)$_2$ 5% | | Zn (2.0) | toluene | 21% |

[a] All the reactions were carried out in the presence of 0.5 mmol of **1a** and 0.75 mmol of **1b** in 5.0 mL toluene at 100 ºC; [b] Isolated yields; [c] 80 ºC.

**Table 2.** Nickel-Catalyzed Annulations of Norbornene with Different Isatoic Anhydrides [a,b,c]

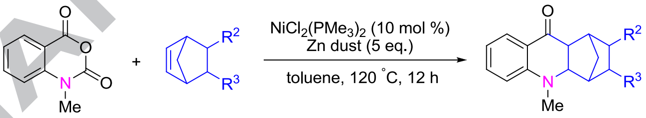


[a] All the reactions were carried out in the presence of 0.5 mmol of 1a and 0.75 mmol of 1b in 5.0 mL toluene at 100 ºC; [b] Isolated yields. [c] NiCl$_2$(PMe$_3$)$_2$ was replaced with Ni(cod)$_2$ and PCy$_3$.

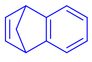
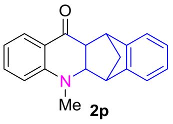
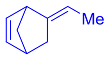
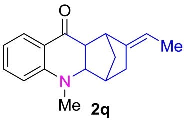
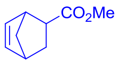
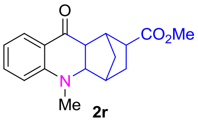
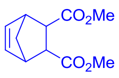
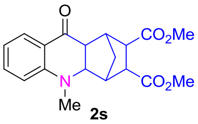
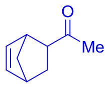
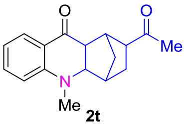
thus improving the yield 20% or 51% (Table 1, entry 6-14). This unsatisfying result prompted us to consider other accounts. We all know that the nickel(0) species is very active and prone to oxidation if stored improperly or imposed on an ill-defined operation. With this in mind, we subsequently concentrated our screening on the nickel (0) catalyst generated in situ and guaranteed its genuine and high activity. To our delight, when we selected NiCl$_2$(PMe$_3$)$_2$ and activated Zn powder as an additive in the reaction, the quinolone **2a** was obtained in 90% isolated yield (Table 1, entry 16). In addition, the product was also obtained in moderate yield under the condition of Ni(cod)$_2$ with PMe$_3$ and Zn. Lastly, the solvent screening showed that toluene is the best choice.

With the optimized conditions in hand, we next investigated the scope of various isatoic anhydrides in the reactions. Initially, a variety of *N*-protected isatoic anhydrides **1b-1d** were surveyed, which were readily prepared from isatoic anhydride **1e.**[16] Reaction of the isatoic anhydrides **1b-1d** with norbornene resulted in the corresponding *N*-substituted derivatives **2b-2d** with good-to-excellent yields (Table 2). The results demonstrated that steric hindrance is not crucial to the cycloaddition reaction, although the corresponding yields were depressed with the increasing size of the *N*-substituted groups. It was encouraging that isatoic anhydrides **1e** also took part in this reaction, although the quinolones product was only isolated in a 29% yield. In order to study the impact of varying isatoic anhydride aromatic substituents in the reaction of decarboxylative annulation, a wide variety of *N*-methyl benzo-substituted isatoic anhydrides **1f-1o** were subjected to optimized conditions. The isatoic anhydrides, which possess electron-donating groups at the aromatic ring, proceeded to completion. High yields of quinolones compounds were therefore obtained. In particular, **1g** and **1i,** which had methyl substituents at the para-position or ortho- position of amides, provided quinolones **2g** and **2i** in 81% and 82% yields, respectively. However, lower amounts of **2j** and **2l** were obtained because of the high steric hindrance of **1j** and the decomposition of **1l** in reaction conditions. On the other hand, the quinolones were also isolated in good yields. The quinolones were originally

**Table 3.** Nickel-Catalyzed Cycloaddition Reaction of Isatoic Anhydride with Various Norbornenes [a,b]



**1a** **2p -2t**

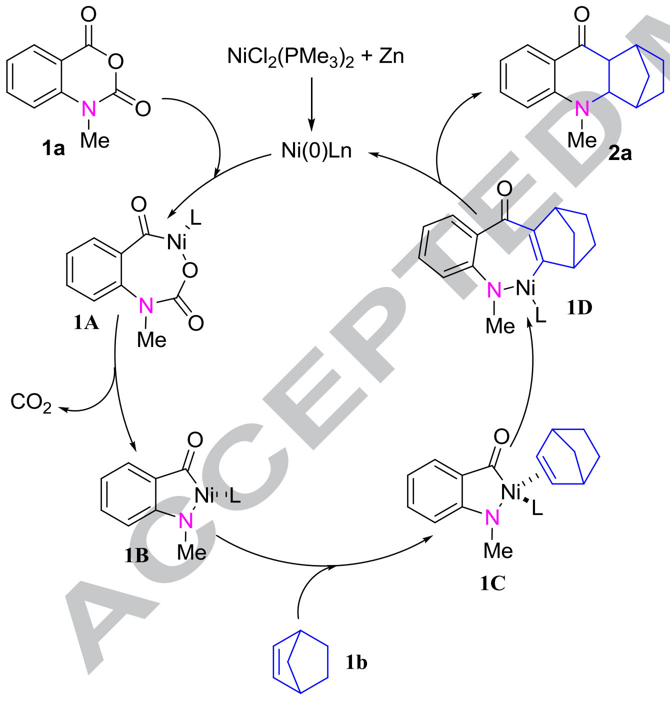
| Entry | Alkenes | Products | Yields [%][b] |
|---|---|---|---|
| 1 |  |  **2p** | 40 |
| 2 |  |  **2q** | 43 |
| 3 |  |  **2r** | 88 |
| 4 |  |  **2s** | 66 |
| 5 |  |  **2t** | 55 |

[a] All the reactions were carried out in the presence of 0.5 mmol of 1a and 0.75 mmol of norbornenes in 5.0 mL toluene at 120 ºC; [b] Isolated yields.

isatoic anhydrides, which we substituted with electron-withdrawing groups as fluoro, trifluoromethyl, and methoxycarbonyl groups. The addition of norbornene across **1m** and **1n** afforded organofluorine quinolones in 74% and 70% yields. Moreover, we attributed the moderate yield obtained for **2o** to the separation of cycloadditon product, which was sensitive to the flash column.

Encouraged by these promising results, we further examined the scope and limitations of the reaction using various substituted norbornenes. The decarboxylative cycloaddition was also compatible with electron-donating norbornenes, although the corresponding yields were moderate (Table 3, entry 1-2). The treatment of benzonorbornadiene and 5-ethylidene-2-norbornene at a higher temperature gave annulation products **2p** and **2q** in 40% and 43% yields under the same conditions. To our delight, the insertion of electron-deficient norbornenes afforded the products in good yields. We were pleased to observe that the reaction of **1a** with the methyl-5-norbornene-2-carboxylate gave the quinolones **2r** in 88% yield. (Table 3, entry 3). In addition, dimethyl-5-norbornene-2, 3-dicarboxylate, and 5-acetyl-2-norbornene were both tolerated and provided the novel quinolones **2s** and **2t** in moderate yields, respectively (Table 3, entry 4-5). However, other alkenes, such as styrene and methyl acrylate, failed to participate in the reaction due presumably to rapid oligomerization or $\beta$-hydride elimination.

**Scheme 2.** The Proposed Mechanisms of Nickel-Catalyzed Cycloaddition Reactions via Decarboxylation.



Scheme **2** illustrates a plausible mechanism of the present reaction. In the initial step, similar to the nickel-catalyzes carboamination of alkynes or allenes,[17] it is reasonable to assume that the oxidative addition of an anhydride O-CO bond to nickel occurs first, forming a seven-membered ring azanickelacycle **1A**. Then decarboxylation occurs and the release of $CO_2$ produces the intermediate of **1B**, which coordinates with norbornene to result in the Ni(II) intermediate **1C**. Quinolones **2a** is afforded when the norbornene inserts into the acyl-nickel bond to give nickelacycle **1D**, followed by reductive elimination to regenerate the catalyst Ni(0). The activated Zn powder is the key to the success of this reaction which has three important functions: 1) Zn powder reduces the Ni(II) to Ni(0), which generates in situ with a high reactivity; 2) the Lewis acid of $ZnCl_2$, which is formed in situ by the reaction of $NiCl_2(PMe_3)_2$ and activated Zn powder, might coordinate a carbonyl moiety to facilitate oxidative addition steps; 3) the Lewis acid of $ZnCl_2$ promotes the reductive elimination steps in this transformation. To the best of our knowledge, Zn has been applied as an reductant or addition in a variety of contexts,[18] but it has not been employed in the cycloaddition reactions of isatoic anhydrides.

In conclusion, we have developed a novel nickel-catalyzed decarboxylative cycloaddition of alkenes with isatoic anhydrides, which provide a new method to synthesize quinolone derivatives. Nickel(0) catalyst generated in situ from $NiCl_2(PMe_3)_2$ and activated Zn powder is found to be very important to ensure the success of the reaction. Further efforts to expand the scope of the chemistry and studies of the detailed mechanism are currently underway in our laboratories.

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## Graphical Abstract

### Nickel-Catalyzed Decarboxylative Cycloaddition of Isatoic Anhydrides with Alkenes

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