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Mo(VI)-Catalyzed Synthesis of 2-Aryl-2*H*-Indazoles Using Pinacol Mediated Deoxygenation of Nitroaromatics

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Mo(VI)-Catalyzed Synthesis of 2-Aryl-2*H*-Indazoles Using Pinacol Mediated Deoxygenation of Nitroaromatics

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A molybdenum(VI)-catalyzed protocol for the synthesis of 2-aryl-2*H*-indazoles using pinacol as a reducing agent under neat reaction conditions has been demonstrated. The developed method gives an easy access to wide range of 2-aryl-2*H*-indazoles in excellent yields. The present strategy excludes the use of P(III)-reagents as deoxygenating agents.

Keywords: $MoO_2Cl_2(dmf)_2$, Pinacol, 2-Aryl-2*H*-Indazoles.

Indazole containing molecules received considerable attention in medicinal chemistry and drug discovery research.[1] Due to their broad spectrum of useful pharmacological properties, these molecules have found wide applications in an extensive range of biological disorders, such as anti-HIV,[2] anti-cancer,[3] anti-pyretic,[4] anti-inflammatory,[5] contraceptive activities,[6] and anti-microbial activities.[7] Scaffolds embedded with 2-substituted indazoles have been identified as potent 5-HT_{1A} receptors,[8] imidazoline I_2 receptor,[9] estrogen receptor β[10] and viral polymerase inhibitor.[11] The biological importance of these structural motifs (Figure 1) has been also witnessed in marketed drugs such as pazopanib[12] and lonidamine,[13] those act as VEGF inhibitor and anti-cancer agent respectively.

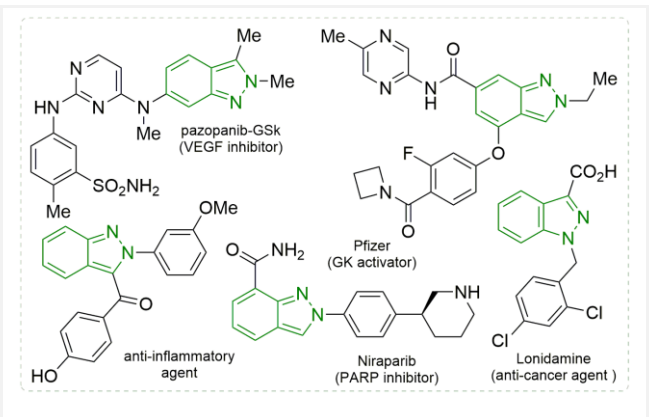
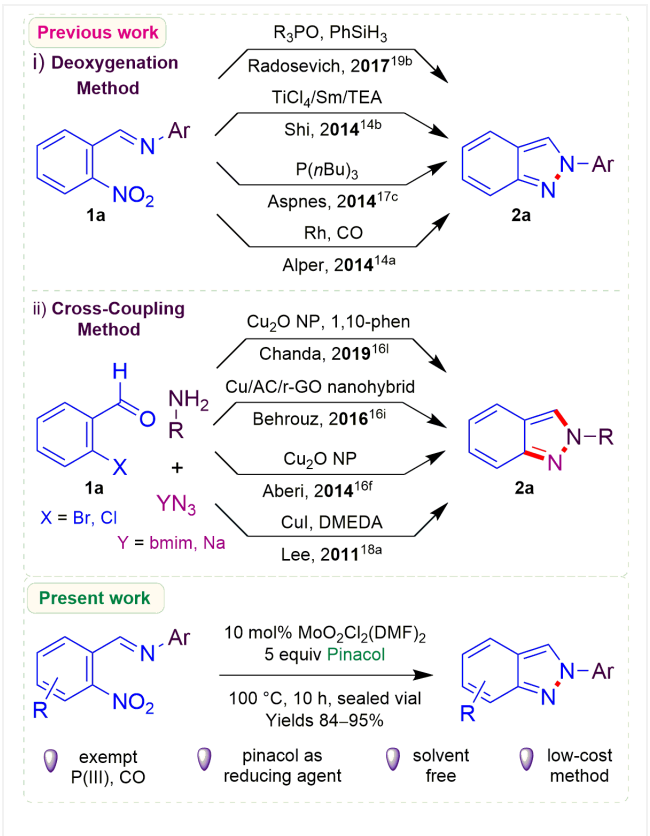


Figure 1. Bioactive molecules embedded with indazole moiety.

Hence, owing to their diverse range of activities and analytical properties, during the past years, the indazole derivatives have found enormous industrial and agricultural applications.[14] The potent bioactivities of these scaffolds have evidenced a number of synthetic tools in the literature towards their effective preparation. Most of these methods admit the synthesis of 1*H*-indazoles.[15] Whereas, the efforts concerned towards the development of novel protocols for the synthesis of 2*H*-indazoles are still limited and remains desired due to the difficulties in their preparation.[16] Among these reported methods, the reductive cyclization of nitroaromatics,[17] the transition metal catalysed C-N[18] and N-N[19] bond formations, and the low-valent titanium mediated cyclization[14b, 20] reactions have been described (Scheme 1).



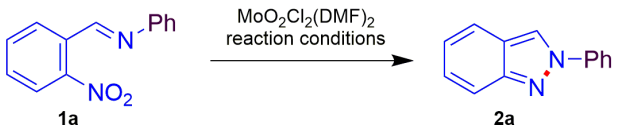
Scheme 1. Approaches for the synthesis of indazoles.

Albeit, these protocols are promising and endorsed pervasive practices, their major disadvantages affiliated to namely the use of (i) excess amounts of P(III)-reagents,[16a, 17b-c, 19a] (ii) precious metals (Fe, Cu, Pd, Rh)[14a, 16c,f,j,l, 18, 19] and expensive ligands, (iii) carcinogenic reagents (Sn, CO),[16b, 17a] (iv) highly reactive low-valent Ti-reagents.[14b, 20] Beside these difficulties, the earlier reported methods agonize from the deficiencies such as narrow substrate scope, harsh and toxic reaction conditions, long-reaction times, and low yields. The selectivity for the formation of desired products remains supplementary challenge, while many of these reported approaches lead to the mixture of 1*H*- and 2*H*-

indazoles.[15g, 16d] In 2013, we contributed to the synthesis of 2-arylindazoles using the Mo(VI)-catalyzed reductive cyclization methodology.[21] These reactions were mediated by an excess amounts of P(III)-reagent under microwave irradiation at 150 °C that derived the subsequent complications in purification stage due to the presence of phosphorous reagents. Hence, a mild method which avoids the use of phosphorous reagents could be an effective surrogate for the preparation of these scaffolds. Over the past decades, *N*-heterocycles are perceived as capital assets in the class of organic compounds and are emerging as decisive ingredients in all facets of pure and applied chemistry.[22] Starting from their isolation from natural resources to the development of new methodologies and their operations in the fields of pharmaceutical and industry are the subjects of ongoing interest for chemists and biologists.[23] Among the various synthetic tools, the reductive cyclization of nitroaromatics has been used extensively for the synthesis of *N*-heterocycles.[24] The heteroannulation of nitroaromatics followed by deoxygenation for the preparation various *N*-heterocycles has been known since 1898, which may be realized via single or two steps process.[25] A variety of reducing agents have been experimented for this purpose.[26] Multiple reaction mechanisms and theories have been taken in accounts and several reactive intermediates have been suggested.[24h, 27] The major drawback related to these processes are associated to the hazardous deoxygenating agents and reaction conditions, and these demerits restrict the further application in modern synthesis.[16a, 17b-c, 19a, 28] It is evident that multiple metal-oxygen containing inorganic complexes are effective towards deoxygenation process.[29] Among these, $MoO_2Cl_2(DMF)_2$ complex has been used extensively due to its simple operation and preparation in laboratory including our recent reports.[21, 29a,c-d] These deoxygenation reactions have been executed in the presence broad range of reducing agents to accomplish the successful transformation. Recently, Sanz et al, Sagar et al and our group have successfully employed the combination of Mo(VI) and pinacol as deoxygenative agent for the synthesis of useful organic molecules.[29a,c-d] Here, we have described the protocol for the synthesis of *2H*-indazole derivatives using Mo(VI)-catalyzed reaction, in which pinacol acts as deoxygenating agent (Scheme 1).

The starting materials *ortho*-nitrobenzylidene amines **1a-n** were synthesized using previously reported method.[21] To examine the feasibility of this transformation, the substrate *N*-(2-nitrobenzylidene)aniline (**1a**) was investigated under the influence of 5 mol% $MoO_2Cl_2(DMF)_2$ as catalyst and pinacol as deoxygenative agent in toluene as solvent at 100 °C for 8 hours. It was observed that the desired product 2-phenyl-2*H*-indazole (**2a**) has been formed in 51% yield (Table 1, Entry 1). By inspiring with this result, the efficacy of a number of reducing agents (HFIP, Et_3SiH, Ascorbic acid, $NaBH_4$, $NaBH_3CN$, $N_2H_4{\cdot}H_2O$) have been explored in details (Table 1, Entries 2-7). Among the tested deoxygenating agents, $NaBH_3CN$ and $N_2H_4{\cdot}H_2O$ contributed similarly in the conversion of **1a** to **2a** (Table 1, Entries 6-7); however, the pinacol as reducing agent delivered the highest yield (51%) of the product **2a** (Table 1, Entry 1). Afterwards, the reaction of *N*-(2-nitrobenzylidene)aniline (**1a**) was performed in the presence of 5 mol% $MoO_2Cl_2(DMF)_2$ as catalyst and 5.0 equiv. of pinacol as deoxygenating agent under solvent free conditions at 100 °C for 8 hours, leading to the formation of the product **2a** in 69% yield (Table 1, Entry 8). Interestingly, the yield of the product **2a** has been improved, when 10 mol% of $MoO_2Cl_2(DMF)_2$ was employed as catalyst along with 5.0 equiv. of pinacol at 100 °C for 10 hours (Table 1, Entry 9). It was also observed that when the reaction was performed in absence of pinacol, the product **2a** has been observed in traces on TLC (Table 1, Entry 10). On the other hand, the formation of the product **2a** was restricted in absence of catalyst (Table 1, Entry 11). After extensive optimization of the reaction conditions, it was realized that the 10 mol% of $MoO_2Cl_2(DMF)_2$ and 5.0 equiv. of pinacol at 100 °C for 10 hours obtained highest yield (87%) of the desired product **2a** (entry 9).

Table 1. Screening of the conditions towards $MoO_2Cl_2(DMF)_2$ catalyzed reaction of **1a**.[a]



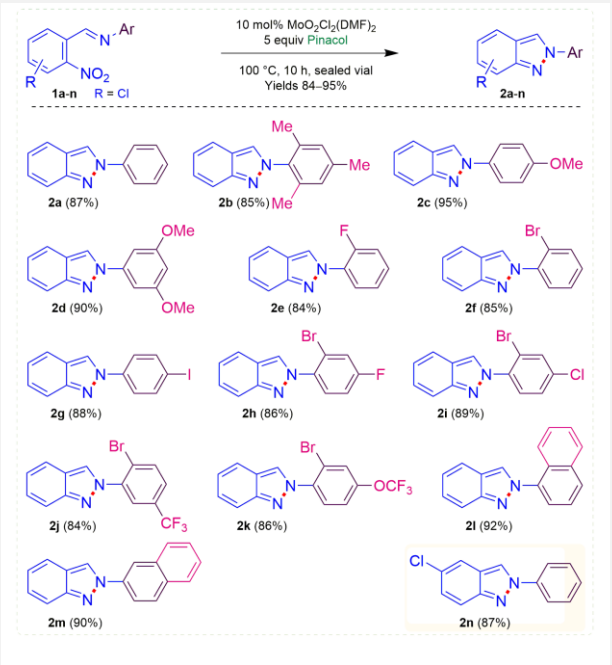
1a **2a**

Entry	Reducing agents	Conditions	2a, Yield %[b]
1	Pinacol (2.5 equiv.)	PhMe, 100 °C, 8 h	51
2	HFIP (20 equiv.)	100 °C, 8 h	17[c]
3	Et_3SiH (10 equiv.)	PhMe, 100 °C, 10 h	29[c]
4	Ascorbic acid (5 equiv.)	PhMe, 100 °C, 8 h	37
5	$NaBH_4$ (1.5 equiv.)	PhMe, 80 °C, 8 h	33
6	$NaBH_3CN$ (1.5 equiv.)	PhMe, 80 °C, 8 h	41
7	$N_2H_4{\cdot}H_2O$ (5 equiv.)	PhMe, 80 °C, 8 h	46
8	Pinacol (5 equiv.)	100 °C, 8 h	69[d]
9	Pinacol (5 equiv.)	100 °C, 10 h	87[d,e]
10	-	100 °C, 10 h	Trace[c,d,e]
11	Pinacol (5 equiv.)	100 °C, 10 h	0[c,d,f]

[a]Unless otherwise mentioned, all reactions were performed using 1.0 mmol **1a** and 5 mol% $MoO_2Cl_2(DMF)_2$ in 2 mL solvent in sealed vial. [b]Isolated yields. [c]Unreacted starting material **1a** was recovered. [d]Reactions were performed in neat condition. [e]Reactions were performed using 10 mol% $MoO_2Cl_2(DMF)_2$. [f]Reactions were performed in the absence of $MoO_2Cl_2(DMF)_2$.

With the optimized conditions, a series of *ortho*-nitrobenzylidene amines **1a-n** were examined to explore the scope of this methodology. The described protocol revealed a broad substrate scope and reaction conditions enabled the participation of a diversity of substituents in aromatic rings (*o*-, *m*- and *p*-substituted) containing both electron donating and electron withdrawing substituents (Scheme 2). Experimental results suggested that the yield of the products

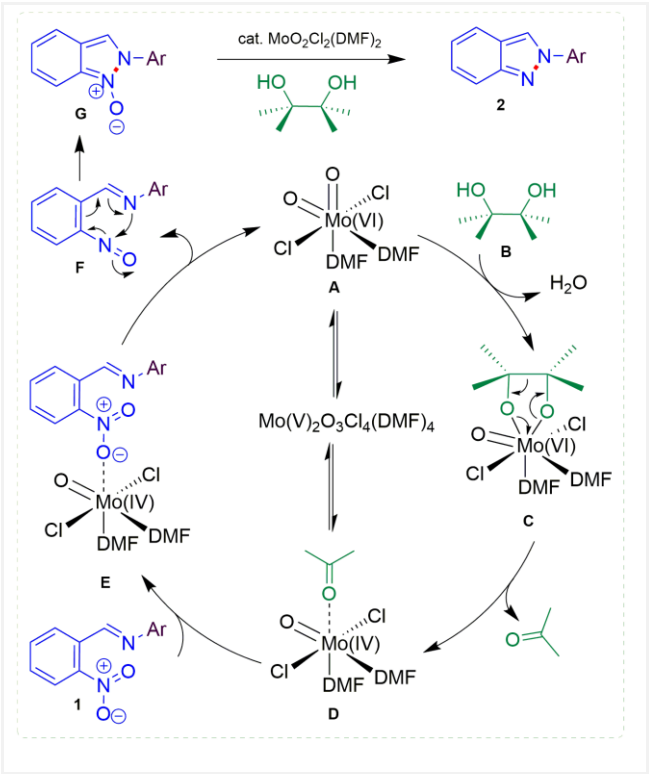
2a-n remains unaffected regardless of electronic nature of the functional groups. Interestingly, apart from mono-functionalized aromatic ring, di-substituted and tri-substituted aromatic residues tolerated rather well under the optimized reaction conditions to deliver the desired products **2b**, **d**, **h-k** in high yields ranging from 85-90%. Notably, the desired products **2l-m** embedded with polycyclic aromatic hydrocarbons can also be synthesized in high yields (90-92%) using this protocol. The resent protocol also enabled substitution on nitrobenzylidene ring to give desired product **2n** in 87% yield.



Scheme 2. Synthesis of indazoles **2a**–**n** using Mo(VI)-catalyzed reaction conditions.

After realizing the scope of the present protocol, we focused on demonstrating plausible reaction mechanism based on experimental results and literature evidences.[29a,c-d] The catalyst $MoO_2Cl_2(DMF)_2$ (**A**) on reaction with pinacol (**B**) generates a catalytic species MoO(pinacolate)$Cl_2(DMF)_2$ complex (**C**) by eliminating a molecule of water. The complex **C** undergoes oxidative cleavage leaving a Mo(IV) complex **D** along with two molecules of acetone. As one of the acetone molecule is in week coordination with Mo(IV) complex to obtain the geometric stability of molybdenum, the substrate **1** was inserted into the catalytic cycle to form an unstable intermediate **E**. Next, deoxygenation of intermediate **E** resulted in intermediate **F** and Mo(VI), which is restored into catalytic cycle. The derived nitroso intermediate undergoes 6π electrocyclization to produce *N*-oxide intermediate **G**. The catalytic cycle was repeated on intermediate **G** to furnish the desired product **2** (Scheme 3).

In summary, we have investigated a new, efficient and mild protocol towards the synthesis of substituted 2*H*-indazole derivatives using pinacol as a reducing agent. The present protocol excludes the use of P(III)-reagents as deoxygenating agents. The developed reaction conditions were realized using catalytic amount of Mo(VI) and pinacol as reducing agent under solvent free conditions. The method was screened on a variety of *ortho*-nitrobenzylidene amines having electron-donating and -withdrawing groups to obtain the desired product in the range of 84-95%.



Scheme 3. Plausible mechanism for the Mo(VI)-catalyzed indazole **2** synthesis.

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Supporting Information

A detailed supporting information is available which includes the experimental procedures, ^{1}H NMR and ^{13}C NMR of the final products.

Supporting Information is available on http://dx.doi.org/10.1246/cl.******.

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