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Ni(0)-Cu(I): A powerful combo catalyst for simultaneous coupling and cleavage of C-N bond with cyclization to valuable amide-based pyrroles and 4-pyridones

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An unprecedented ligand-tuned Ni(0)-Cu(I) combo catalysis is demonstrated *via* sequential bond activated domino C-N/C-C coupled annulation with C-N bond cleavage to afford valuable polysubstituted amide-based pyrroles and 4-pyridones selectively from β-ketoanilides.

The C-N[1] and C-C[2] coupling are fundamental chemical processes and have received considerable attention for easy construction of *N*-bearing ubiquitous cyclic frameworks.[3] The cleavage of C-N bond have attracted increasing attention recently because of their varied applications.[4] The development of a catalytic process for simultaneous cleavage and building of C-N bonds is a significant challenge in synthetic chemistry. It can be used for direct synthesis of valuable heterocyclic compounds[5] through designing of a suitable assembly of inexpensive precursors. In this regard, a combination of two catalysts may be employed for executing such two opposite chemical processes operating simultaneously. Interestingly, Ni(0)-Cu(0)[6a] and Ni(II)-Cu(0)[6e] combo catalysts[6] were reported for C-C coupling reactions. Herein, an unprecedented ligand-controlled Ni(0)-Cu(I) catalysis is communicated for executing diverse C-C/C-N coupled annulation with simultaneous cleavage of C-N bond through sequential activation of several bonds[7] to furnish highly substituted valuable pyrroles[8-11] and 4-pyridones[12] with outstanding selectivity.

Pyrrole is a characteristic structural motif of chlorophylls, vitamin B-12, haemoglobin and numerous other valuable natural products.[8] The substituted pyrroles-bearing amide functionality have found important applications.[9-11] For instance, pentasubstituted Storniamide A[10] is an antibiotic against Gram-positive bacteria and Atorvastatin[11] is the best-marketed cholesterol-lowering drug (Figure 1). Recently few synthetic strategies for pentasubstituted pyrroles are developed through cyclization of propargyl vinyl ethers and 1,3-enynes with amines, cycloaddition, Fe(III), Ce(III), Ni(II) and Rh(II)-catalyzed multicomponent reaction, C-H activation, sequential C-H activation, multistep processes and other strategies.[7a,b,13] The 4-pyridone moiety is an important building block of bioactive natural products and offers easy functionalization to furnish key intermediates, chiral organocatalyst, bioactive alkaloids, anti-HIV agent carbamoylpyridone (Figure 1),[12e] anticancer, antiviral and antibacterial drugs, and material for fabricating light-emitting devices, which led to development of few synthetic approaches.[12] Interestingly one direct synthetic approach for pyridones from acetoacetanilides is achieved recently through migration of substituents using one mole of sodium persulfate ($Na_2S_2O_8$) as an oxidant.[12c] However development of an catalytic process is desirable for synthesis of the valuable heterocycles.

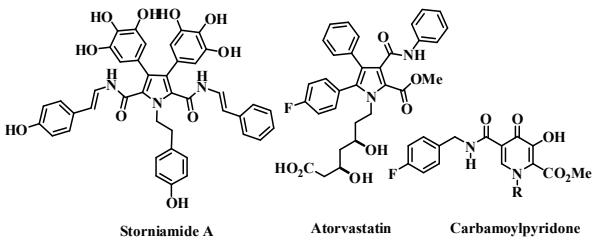

Figure 1. Useful pentasubstituted pyrrole and 4-pyridone

A general strategy for dual C-N/C-C coupled annulation cum cleavage of C-N bond was aimed at (proposed ***path a***, Scheme 1) utilizing readily available inexpensive 'two unit' insertion synthons acetoacetanilide[1e,14] (**1**) and 1-phenylpropargyl alcohol (**2**), and 'one unit' amine derivative (**3**) to afford directly the desired pentasubstituted pyrroles (**4**, Scheme 1). During screening of a suitable catalyst system acetanilide (**3a**, ***path a***) or acetoacetanilide (**1a**, ***path b***) was our amine of choice instead of aniline (**3b**) to avoid formation of undesired C-C triple bond-coupled byproduct(s). As a

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Scheme 1. Dual N-C/C-C coupled annulation *via N*-C bond cleavage

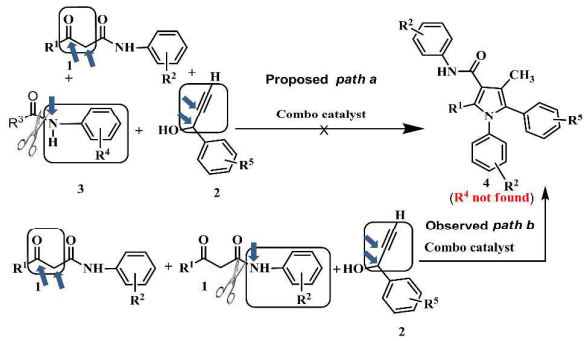


Table 1. Development and optimization of the reaction[a]

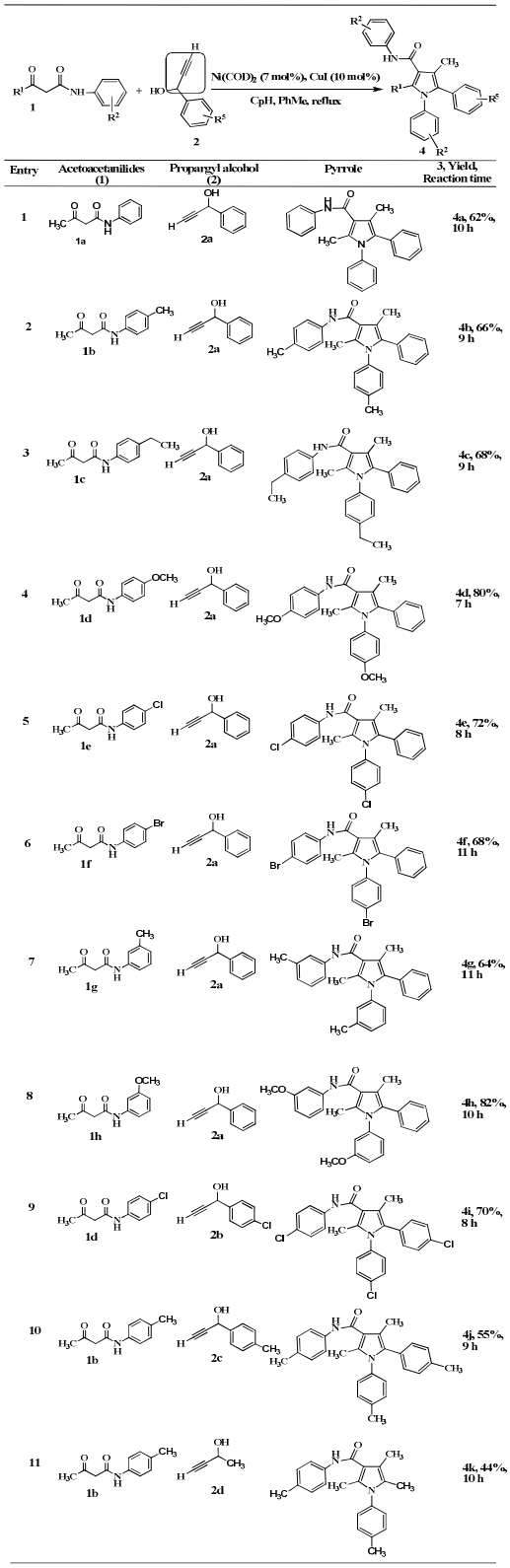
Entry	Catalyst[b]	Reaction Conditions[d]	4,Yield(%)[c]
1	$NiCl_2(PPh_3)_2$, Cu(0)	**3a**, PhMe, reflux, 24 h	-
3	$NiCl_2.6H_2O$, CuI	**3a**,PhMe, reflux, 22 h	-
4	$NiCl_2(PPh_3)_2$, $Cu(OTf)_2$	**3a**,PhMe, reflux, 24 h	-
5	$NiBr_2$, $CuBr_2$	**3a**,PhMe, reflux, 28 h	-
6	$Ni(OAc)_2.4H_2O$, $CuSO_4.5H_2O$	**3a**,PhMe, reflux, 20 h	-
7	$NiCl_2(PPh_3)_2$, $PhI(OAc)_2$	**3a**, PhMe, reflux, 24 h	-
8	$NiCl_2(PPh_3)_2$, $Pd(OAc)_2$	**3a**, PhMe, reflux, 21 h	-
9	$NiCl_2(PPh_3)_2$, $Ru(OAc)_2$	**3a**, PhMe, reflux, 21 h	-
10	RhCODCl, $Cu(OAc)_2.H_2O$	**3a**, PhMe, reflux, 24 h	-
11	$Ni(COD)_2$, $Cu(OTf)_2$	**3a**, PhMe, reflux, 23 h	-
12	$Ni(COD)_2$, CuI	**3a**, PhMe, reflux, 24 h	**4a**, 32
13	$Ni(COD)_2$,[e] CuI	CpH, PhMe, reflux, 10 h	**4a**,62
14	$Ni(COD)_2$, CuI	Ch, PhMe, reflux, 24 h	**4a**,55
15	$Ni(COD)_2$, CuI	Ind, PhMe, reflux, 24 h	**4a**,30
16	$Ni(COD)_2$, CuBr	Cp, PhMe, reflux, 24 h	**4a**,25
17	$Ni(COD)_2$,CuOTf	Cp, PhMe, reflux, 24 h	**4a**,30
18	$Ni(COD)_2$,CuOTf	PCy_3, PhMe, reflux, 24 h	**4a**,49
19	$Ni(COD)_2$,CuI	PhMe, reflux, 24 h	-
20	$Ni(COD)_2$, CuI	**3b**,[f] CpH, PhMe, reflux, 24 h	-
21	$Ni(COD)_2$,[e] CuI	**3a**, CpH, PhMe, reflux, 10 h	**4b**,30
23	$Ni(COD)_2$,	CpH, PhMe, reflux, 24 h	-
24	CuI	CpH, PhMe, reflux, 24 h	-

[a]One mmol of each precursor **1**-**3** was taken in 15 mL of toluene; [b]Catalyst (10 mol% each); [c]Product (**4a**) isolated after purification by column chromatography; [d]30 mmol% of ligand; [e]$Ni(COD)_2$ (7 mol%) along with **1a** and **2b** as substrates; [f]**3b**: Aniline.

part of our ongoing synthetic program for developing new combo catalyst,[6b] we initially attempted using Ni(II)-Cu(0)[6e] and several other potential combo catalysts. Unfortunately the reactions were unsuccessful (entries 1-11, Table 1). We were delighted to have the desired pentasubstituted pyrrole (**4a**, entry 1, Table 2) on use of Ni(0)-Cu(I) combo catalyst, although the yield was very low (32%, entry 12, Table 1). Surprisingly cleavage of C-N bond for generating amine partner was observed using one of the versatile synthon acetoacetanilide[1e,14] (**1a**, ***path b***, Scheme 1), but not with the acetanilide (**3a**, ***path a***). The optimization of the reaction was explored employing cyclopentadiene (CpH), 1,3-cyclohexadiene (Ch) and indene (Ind) ligands, variation of cuprous salts and solvent (entries 13-20), and best result was obtained using $Ni(COD)_2$-CuI combo catalyst with CpH ligand to afford **4a** in 62% yield after refluxing the reaction mixture in toluene for 10 h. On treatment of acetanilide (**3a**), 4-methyl acetoacetanilide (**1b**) and **2a** under the optimized conditions (entry 13) produced the product **4b** (Table 2), but not the proposed compound **4a** (***path a***, Scheme 1). In the catalyst controlled study desired product **4a** was not found using $Ni(COD)_2$ and CuI in two separate reactions (entries 23,24, Table 1).

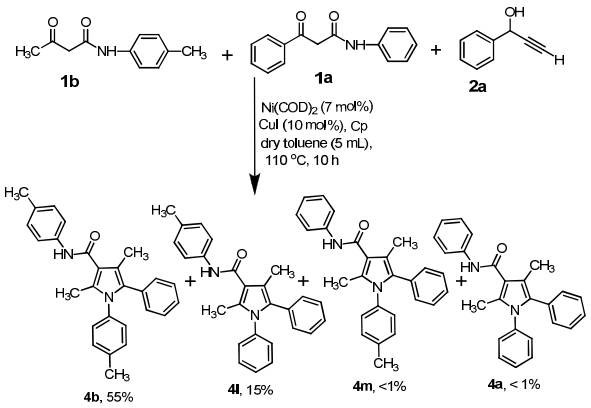
With the optimized conditions (entry 13, Table 1), we next examined the scope of this domino process with various acetoacetanilides **1b-g** (Table 2). Notably, moderate to high yields

Table 2. Synthesized amide-functionalized pentasubstituted pyrroles (**3**)



(44–82%) were obtained utilizing acetoacetanilide and its derivatives bearing alkyl and electron-donating groups to afford pentasubstituted pyrroles (**4b**-**k**) within 8-10 h. However, the reaction was unsuccessful when we replaced 1-phenylpropargyl alcohol by the unsubstituted propargyl alcohol and the yield was reduced (44%) on use of methyl substituted propargyl alcohol (**2d**, entry 11). A cross coupling reaction was executed using **1a** and **1b** in 1:1 molar ratio (Scheme 2) to understand the electronic requirement of this new cyclization process. Interestingly out of four possible products (**4a**,**b**, **4l** and **4m**), **4b** appeared as a major product (55%) with coupling of two molecules of **1b**-bearing activated aromatic amine moiety. Cross coupling product **4l** was found as a minor product (15%) through coupling of acetoacetanilide-bearing activated aromatic moiety (**1b**) and amine from relatively less activated acetoacetanilide (**1a**). However, other two possible isomers **4a** and **4m** were formed very negligible amount (~ 1%), which were not isolated from the post reaction mixture. The role of Cu(I) is expected towards selective activation of ≡C-*H* first and subsequently C≡C bond for annulation with the Ni-chelated acetoacetanilide.

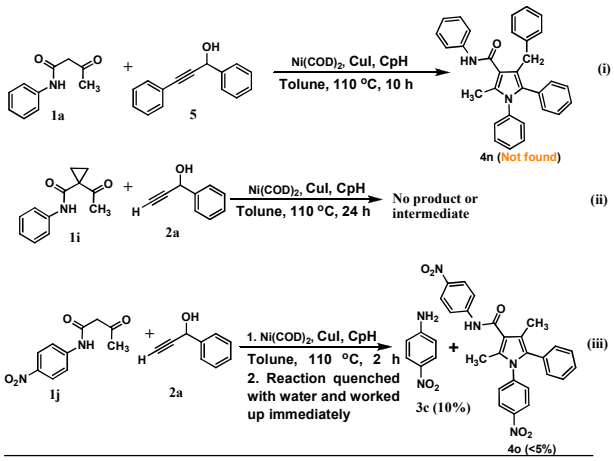
Scheme 2. Cross coupling reaction.



Our experiment using nonterminal alkyne (**5**) revealed terminal alkyne is necessary for the unprecedented annulation process (eq. i, Scheme 3). The reaction was completely blocked on use of aniline (**3b**, entry 20, Table 1). Involvement of activated C_3-H in the annulation process was confirmed using a designed acetoacetanilide (**1i**, eq. ii) bearing no such C-H bonds, which resulted no adduct, intermediate or any product under the reaction conditions. We have quenched most of the annulation reactions (Table 2) to trap the C-N bond cleaved free-amine intermediate, which were unsuccessful. However, treatment of acetoacetanilide-bearing strongly deactivated aromatic moiety (**1j**, 4-nitrophenyyl, eq. iii, Scheme 3) C-N bond breaking becomes easier and corresponding 4-nitroaniline (**3c**) was trapped from the reaction mixture, which confirms cleavage of C-N bond is an essential part of the new catalysis process.

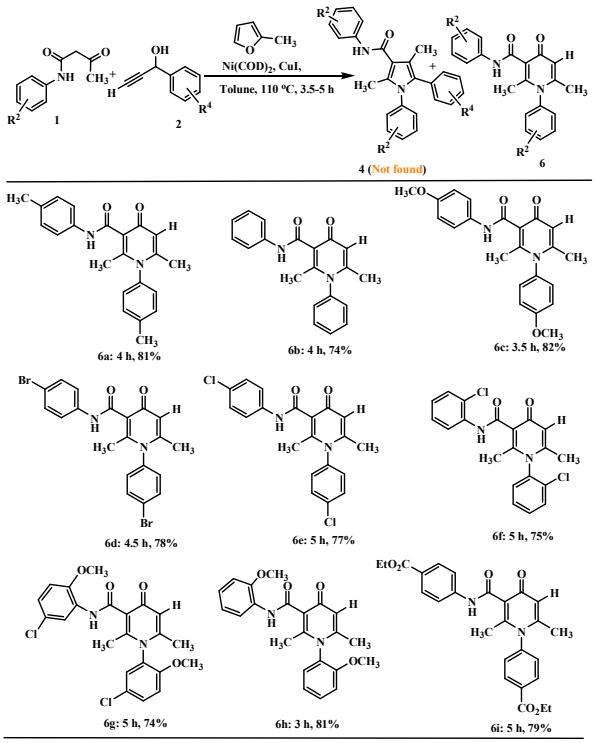
Next we turned our attention to explore versatility of the combo catalyst using various ligands under different reaction conditions. After screening with several ligands, 2-methyl furan was found effective for redirecting to the other annulation process to afford 4-pyridone (**6a**) as the sole product under the reaction conditions

Scheme 3. Investigating the possible reaction pathway



(Scheme 4). The C-C/C-N coupled annulation with cleavage of C-N bond proceeds through coupling between two molecules of acetoacetanilide (**1**), and the corresponding pyrrole (**4**) was not generated due to the steric and electronic forces exerted by the 2-methyl furan during the combo catalysis. The multidimensional application of 4-pyridone compounds led us to establish the catalytic approach for direct synthesis of highly substituted pyridones from acetoacetanilides in absence of any oxidant (Scheme 4). The syntheses of functionalised 4-pyridines **6a**-**i** were

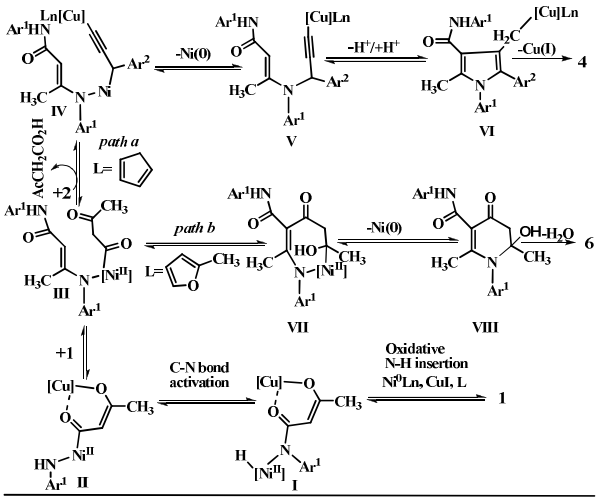
Scheme 4. 2-Methyl furan tuned synthesis of 4-pyridones



accomplished in the fast reaction rate (3.5-5 h) and high yield (74-82%) under the catalytic conditions.

The mechanism of the reactions is unknown to us. However, with these studies in hand, the possible mechanism of the unusual combo catalysis is depicted in Scheme 5. The oxidative insertion to N-H and chelation of the β-dicarbonly group occur first by the combo catalyst to generate intermediate **I**, which subsequently undergoes cleavage of the weak N-C bond (**II**). Coupling of β-ketoanilide (**1**) leads to formation of intermediate **III**. In presence of cyclopentadiene ligand it smoothly undergoes the ***path a*** through coupling of Cu(I)-activated propargyl alcohol (**2**) with release of acetoacetic acid. Successive N-C (**V**) and C-C coupled (**VI**) annulation of **IV** with regeneration of the combo catalyst furnishes the desired product **4**. The powerful steric and electronic influence of the 2-methylfuran ligand leads to formation of C-C coupled intermediate **VII** (***path b***), which immediately transformed to 4-pyridones (**6**) involving C-N coupling (**VIII**) with reductive elimination of Ni(0) catalyst followed by elimination of water.

Scheme 5. Plossible reaction pathways



In conclusion, for the first time we have devised an efficient ligand guided combo catalysis for dual N-C/C-C coupling with N-C bond cleavage leading to diverse annulation processes through sequential bond activation using readily available β-ketoanilides and 1-phenyl-2-propyn-1-ol to afford valuable amide-based polysubstituted pyrroles and 4-pyridones. This unprecedented compatibility and catalytic activity of Ni(0)-Cu(I) with various ligands will lead to new prospects and perspectives in the research for developing novel combo catalysis towards direct synthesis of functional molecules.

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