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ARTICLE TYPE

A co-operative Ni/Cu system for C_{sp}-C_{sp} and C_{sp}-C_{sp2} cross-coupling providing a direct access to unsymmetrical 1,3-diynes and en-ynes

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An efficient cross-coupling of alkynes with alkynyl and alkenyl halides catalyzed by Ni/Cu system without any ligand has been achieved. The reaction is suggested to proceed by Ni(0) catalysis assisted by Cu(I). A series of functionalised 10 diaryl, aryl-alkyl, aryl-heteroaryl, diheteroaryl 1,3-di-ynes and en-ynes are obtained in high yields.

The unsymmetric 1,3-diynes are of much interest as useful pharmaceuticals and materials.¹ They are widely present in a variety of naturally occurring biologically active molecules with 15 anticancer, antibacterial, and anti-HIV activities.² They are of high utility as optical materials, conductive plastic, high density fibres and liquid crystals.³ Thus development of an efficient procedure for their synthesis is of much importance. Although Glaser-Hay homocoupling of terminal alkynes is successful for ²⁰ the synthesis of symmetric 1,3-diynes,⁴ the synthesis of unsymmetric 1,3-diynes still remains a challenge. The oxidative coupling of terminal alkynes⁵ is one of the standard protocols for the synthesis of unsymmetric diynes. However, these procedures were limited to the synthesis of aryl-alkyl diynes and they 25 required use of a large excess of one of the alkynes with respect to other. This makes the separation and purification of product tedious. During last few years several methods involving nickel catalyzed cross-coupling of alkynyl Grignard reagent with acetylenic sulfones,^{6a} Cu(I) catalyzed coupling of alkynyl silanes ³⁰ and 1-chloroalkynes,^{6b} Cu(I)-catalyzed decarboxylative coupling

of alkynyl carboxylates with 1,1-dibromo-1-alkynes ^{6c} and propiolic acids with terminal alkynes,^{6d} were also reported among others.^{6e-i} However, so far the best alternative for the synthesis of unsymmetrical 1,3-diynes is the Cadiot-Chodkiewiez coupling 35 reaction of terminal alkynes and alkynyl halides in the presence

- of a Cu salt⁷, although this protocol too suffers from low efficiency and poor selectivity. To overcome the drawbacks of this protocol, recently Lei and co-workers demonstrated an improved procedure for the synthesis of unsymmetrical 1,3-
- 40 divnes by the reaction of terminal alkynes and 1-bromoalkynes in the presence of Pd/Cu- bimetallic catalyst with^{8a} or without the use of ligand.^{8b} Simultaneously Wang et al^{9a} and Jiang et al^{9b} reported a Cu-catalyzed protocol for the synthesis of unsymmetric 1,3-diynes by the coupling of 1-bromo alkyne and 45 terminal alkyne using phosphorus containing ligands9a which are
- usually toxic, and supercritical carbon dioxide.9b

Our initial success in the C_{sp2}-O bond formation¹⁰ using a combined Ni/Cu catalytic system motivated us to use the same

system for C_{sp}-C_{sp} cross-coupling (Scheme 1). In this report we 50 showcase successful synthesis of unsymmetric 1,3-diynes, where the Ni(0) works as an active catalytic species and Cu(I) assists in the transmetalation process in the absence of ligand.



55 Scheme 1 Cross-coupling of acetylene-halide and alkynes

To the best of our knowledge this coupling using Ni or its combination with other metal under ligand free condition is not reported. To explore the extended scope of our new protocol we consider it important to perform the cross-coupling of alkynes 60 with vinyl halides by using Ni/Cu catalytic system to provide 1,3envnes and their analogues which are present in many biologically active naturally occurring and synthetic molecules.11

To optimize the reaction conditions for C_{sp}-C_{sp} cross-coupling, a series of experiments were performed with variation of reaction 65 parameters such as catalyst, solvent, temperature and time for a representative reaction of phenylacetylene bromide and 4ethynylanisole. The results are summarized in Table 1. It was observed that Ni(acac)₂ or CuI alone cannot initiate the reaction (Table 1, entries 1 and 2). However, use of both Ni(acac)₂ and 70 CuI in the system delivered satisfactory result (Table 1, entry 6). N-Methyl-2-pyrrolidone (NMP) was found to be the best solvent compared to DMF and DMSO (Table 1, entries 7 and 8). The maximum yield of product was obtained using 5 mol % of Ni(acac)₂, 5 mol % of CuI, and 2.0 equivalents of Cs₂CO₃ at 100 75 °C for 9 h in NMP (Table 1, entry 6). Other copper salts such as CuBr and CuCl are found to be less active compared to CuI under identical conditions (Table 1, entries 3 and 4). The same trend was observed while using other nickel salts such as NiBr₂ (Table 1, entry 5). Lowering the reaction temperature (Table 1, entry 9) so and change of base from Cs₂CO₃ to Et₃N (Table 1, entry 10) reduced the yield. The use of weaker bases such as K₂CO₃ or K₃PO₄ did not initiate the reaction (Table 1, entries 11 and 12).

Yield of the reaction was significantly affected by changing

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catalyst loading from 5 mol % to 3 mol % (Table 1, entry 13). Shortening of reaction time lowered the yield too (Table 1, entry 14).

Entry	Catalyst	Solvent	Base	Yield(%) ^b
1	Ni(acac) ₂	NMP	Cs ₂ CO ₃	0
2	CuI	NMP	Cs_2CO_3	0
3	Ni(acac) ₂ / CuBr	NMP	Cs_2CO_3	48
4	Ni(acac) ₂ / CuCl	NMP	Cs_2CO_3	24
5	NiBr ₂ / CuI	NMP	Cs_2CO_3	trace
6°	Ni(acac) ₂ /CuI	NMP	Cs ₂ CO ₃	89
7	Ni(acac) ₂ /CuI	DMF	Cs_2CO_3	59
8	Ni(acac) ₂ /CuI	DMSO	Cs_2CO_3	33
9 ^d	Ni(acac)2/CuI	NMP	Cs_2CO_3	67
10	Ni(acac) ₂ /CuI	NMP	Et ₃ N	57
11	Ni(acac) ₂ /CuI	NMP	K ₂ CO ₃	0
12	Ni(acac) ₂ /CuI	NMP	K_3PO_4	trace
13 ^e	Ni(acac) ₂ /CuI	NMP	Cs_2CO_3	39
$14^{\rm f}$	Ni(acac)2/CuI	NMP	Cs_2CO_3	72

Table 1 Standardisation of reaction conditions^a

^aReaction conditions: phenyl acetylene bromide (1.0 mmol) and 4ethynylanisole (1.2 mmol), Cs₂CO₃ (2.0 mmol), 100 °C argon atmosphere, 9 h. bYields of isolated pure products. c5 mol % of Ni and Cu catalysts. ^d70 °C. ^e3 mol % of Ni and Cu catalyst. ^f6 h.

- Thus in a typical general procedure a mixture of alkynyl halide (1 mmol), terminal alkyne (1.2 mmol), and Cs₂CO₃ (2.0 mmol) was heated at 100 °C under argon in the presence of Ni(acac)₂ (5 mol %) and CuI (5 mol %) for a certain period of time to complete the reaction (TLC). A variety of diversely substituted 10 aromatic and heteroaromatic alkynyl bromides underwent reactions with several substituted aromatic, aliphatic and heterocyclic terminal alkynes to produce the corresponding crosscoupled products (Table 2). The reactions of alkynyl iodides furnished marginally higher yields compared to those with the 15 corresponding bromides (Table 2, 3aa, 3af, 3ad, and 3ab) although chlorides produced lower yields (3aa and 3aj). A series of aryl-aryl, aryl-alkyl, aryl-heteroaryl, heteroaryl-heteroaryl 1,3divnes were obtained by this procedure. Several terminal alkynes and alkynyl bromides containing electron donating groups, -
- 20 OMe, -Me, -'Bu, -pentyl, underwent clean reactions by this procedure (Table 2, 3aa, 3af, 3ad, 3fh, 3dc, and 3ea). The presence of -CF₃ at the ortho-position of aryl alkyne produced low yield presumably due to steric effect (Table 2, 3ae and 3gi). A similar trend was also observed with other aryl alkynes having
- 25 varied substituents at the ortho- position (Table 2, 3ab and 3aj). The aliphatic alkynes too including TMS acetylene underwent efficient reactions with alkynyl bromides (Table 2, 3ac, 3dc, 3ic and **3ik**). The terminal 1.3-divne containing TMS moiety (**3ik**) is of potential for further manipulation.^{8a}
- The coupling of heterocyclic alkynes and alkynyl halides also 30 proceeded with excellent yields (Table 2, 3ag, 3ca, and 3cg) extending the scope further. The ferrocene substituted alkynyl halide was compatible for this reaction too (Table 2, 3ha). Although the alkynyl iodides and bromides provided comparable
- 35 yields (Table 2, 3aa, 3af, 3ad and 3ab), the reaction with the corresponding chloride was not very encouraging (Table 2, 3aj). However, our attempts for the coupling of aliphatic alkynes with

aliphatic halides were not successful under varied reaction conditions.

40 Table 2 Ni/Cu catalyzed synthesis of unsymmetrical conjugated diynes^a



^a General reaction conditions: alkynyl halide (1 mmol), terminal alkyne (1.2 mmol), Ni(acac)₂ (0.05 mmol), CuI (0.05 mmol), Cs₂CO₃ (2 equiv.), NMP (3 mL), 100 °C, 9 h, argon atmosphere. ^b7 h. ^c10 h. ^dCs₂CO₃ (2.5 45 equiv.), 10 h. eterminal alkyne (4 mmol), Et₃N (1 mL) in place of Cs₂CO₃, NMP (1 mL), 25-100 °C, 12 h, in a sealed tube.

Table 3 Ni/Cu catalyzed synthesis of trans-enynes



^aReaction conditions: styrenyl, vinyl or 1,3-dienyl halide (1 mmol), 50 terminal alkyne (1 mmol), Ni(acac)₂ (0.05 mmol), CuI (0.05 mmol), Cs₂CO₃ (2 equiv.), NMP (3mL), 100 °C, 8 h, argon atmosphere. ^b10 h.

Furthermore this protocol has been successfully extended for the formation of en-yne and en-en-yne units by appropriate choice of styrenyl, vinyl and 1,3-dienyl bromides (Table 3). The 55 cross-coupling of (E)-1-naphthyl vinyl bromides with aliphatic, aromatic and heterocyclic alkynes led to the synthesis of a variety of en-ynes (Table 3, 5ac, 5aa and 5ag) and reaction of substituted aryl-1,3-dienyl bromide with 4-ethynylanisole produced the corresponding en-en-yne (Table 3, 5ca). The cis-vinyl bromides 60 led to homocoupled symmetric 1,3-divnes in place of usual product.10

Towards further extension, when 1,3-dienyl-gem-di-bromides were subjected to this reaction with a terminal alkyne the corresponding en-yne-yne derivatives were obtained (Scheme 2, 65 7aa and 7bj).

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Scheme 2 Ni/Cu catalyzed cross-coupling of 1,3-di-enyl-*gem* dibromides with terminal alkynes

Efforts were made to apply this protocol for Sonogashira ⁵ reaction. The C_{sp2}-C_{sp} cross-coupling of 4-ethynylanisole with diversely substituted iodo-benzenes led to the synthesis of unsymmetrical diaryl-acetylenes (Scheme 3, **9aa**, **9ba**, **9cl** and **9dl**). Several functionilities such as COMe, CO₂Me, CN are compatible with the reaction conditions. However, aryl iodides ¹⁰ containing OH and NH₂ underwent O- and N- arylations without providing any expected coupled product. This is not unusual as Ni/Cu system is known to catalyse such reactions.¹⁰



15 Scheme 3 Ni/Cu catalyzed Csp2-Csp cross-coupling

In general, the reactions are clean and high yielding. However, during alkyne-alkynyl halide cross-coupling reactions 2-5% of homocoupled products are formed. The reaction conditions are compatible with several functionalities and heteroaryl-, ferrocene-²⁰ substituted alkynes. Many of these compounds are new and reported for the first time with full characterization data (SI).

To ascertain the role of catalyst and the reaction pathway, a few experiments were performed. The reaction was carried out in the presence of nitroarene (electron acceptor), THF (electron $racceptor)^{12}$ and TEP (DQ (a kinch and a compared by the second acceptor) is the second acceptor of the s

- ²⁵ receptor)¹² and TEMPO (radical quencher) separately and it was found that the reaction rate and yield remained unaffected for a representative coupling of phenylacetylene bromide (1a) and 4ethynylanisole (2a) indicating a non-radical pathway. Moreover, the high stereo-selectivity in en-yne formation achieved in this
- ³⁰ process does not also support the radical mechanism as vinyl radical undergoes rapid inversion of configuration.¹³ Thus the possibility of radical pathway is unlikely. On the other hand, the decrease of reaction rate with increasing steric hindrance in aryl alkynes suggests that the reaction is more likely to follow an ³⁵ oxidative-addition and reductive-elimination pathway.

As the reaction did not proceed in the presence of $Ni(acac)_2$ or CuI alone the involvement of co-operative Ni/Cu catalytic system seems likely. As the redox potential of $Cu^{I-}Cu^{II}$ system is very high under ligand free condition the involvement of Cu in the

- ⁴⁰ oxidative addition step is a difficult proposition.¹⁴ Usually, in presence of a ligand the co-ordination of the nitrogen/phosphorus with the Cu^I center leads to the sharp decrease in redox potential value of the Cu^I-Cu^{III} system thus facilitating the oxidative addition step.¹⁵ Hence, the possibility of catalysis by Ni is
- $_{\rm 45}$ considered. To monitor the change of oxidation state of Ni(II) during the reaction an UV study of the $\rm C_{sp}\text{-}C_{sp}$ cross-coupling

reaction was undertaken. Immediately after initiation of reaction a peak appears at the range of 358-365 nm (Figure 1(a)) which indicates the generation of Ni(0) species.¹⁶ The formation of ⁵⁰ Ni(0) was also confirmed by the XPS data (Figure 1(b)) which clearly suggests the presence of Ni(0) and Ni(II) by their characteristic peaks at 852.23 and 854.1 eV respectively (12:88 area ratio).¹⁷ Furthermore, the TEM image (Figure 2(a), see SI) of a sample of reaction mixture also shows the presence of Ni(0) ⁵⁵ nanoparticles and it was supported by the lattice fringe calculation from the HRTEM image (Figure 2(b), see SI). The distance between two (011) planes of the Ni(0) nanoparticles was found to be 0.204 nm, which is very close to the reported values.¹⁸ The histogram from the TEM image reveals the average ⁶⁰ particle size diameter of the nanoparticles as 3.7 (\pm 0.7) nm (Figure 3) (see SI).



Figure 1 (a) UV spectra of Ni(0). (b) XPS spectra of Ni(0) and Ni(II).

⁶⁵ The UV experiment showed the generation of Ni(0) from Ni(acac)₂ in the presence of Cs₂CO₃ in NMP at 100 °C. To find the possible reducing agent for the formation of Ni(0) from Ni(II), a series of control experiments were performed (Scheme 4). In presence of nickel chloride as catalyst only a trace amount ⁷⁰ of coupled product was observed. However, addition of zinc along with NiCl₂ led to the corresponding product in 45% yield. In another experiment use of acetyl acetone in place of zinc as a reducing agent¹⁹ under identical conditions increased the yield of product substantially (79 %). These experimental observations ⁷⁵ firmly support the hypothesis that acetyl acetonate acts as a reducing species for the generation of the Ni(0) from Ni(acac)₂ in reaction medium.

Based on these results we proposed a mechanism as depicted in Scheme 5. The reaction was initiated by the formation of Ni(0) ⁸⁰ nanoparticle from Ni(acac)₂ in presence of Cs₂CO₃, which then undergoes oxidative addition with alkynyl bromide to form **A**. In another cycle Cu¹ interacts with alkyne to form Cu-acetylide **B**



Scheme 4 Control experiments

which transfers the alkyne moiety from Cu^{I} to Ni^{II} *via* transmetallation generating a reactive intermediate **C** which leads to the coupled product by reductive elimination. Furthermore the progress of the reaction was tracked by the UV-experiment where increase in the concentration of product was observed with time



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In conclusion, we have developed an efficient protocol for C_{sp}-C_{sp} and C_{sp}-C_{sp2} cross-coupling of alkynes with alkynyl/alkenyl halides catalysed by Ni/Cu co-operative system in absence of any ligand leading to the synthesis of a series of unsymmetrical ¹⁰ functionalised diaryl, aryl-alkyl, aryl-heteroaryl, diheteroaryl 1,3-diynes, en-ynes and 1,3,5-en-en-ynes and -en-yn-ynes. To the best of our knowledge, this is the first report where Ni/Cu catalytic system in absence of a ligand has been employed for Cadiot-Chodkiewiez coupling reaction overcoming its associated ¹⁵ limitations. Our catalytic system offers a great improvement to the known Pd/Cu⁸- or Cu⁹ (with ligand)-catalysed methods. The

enormous potential of this methodology relies on the use of inexpensive metals as catalyst, use of no ligand, excellent stereoselectivity and high yield. Further application of this 20 protocol for the synthesis of bioactive molecules bearing di-yne and en-yne units constitute our next goal.

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Notes and references

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