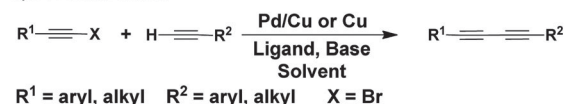# ChemComm

A co-operative Ni–Cu system for C_{sp}–C_{sp} and C_{sp}–C_{sp^2} cross-coupling providing a direct access to unsymmetrical 1,3-diynes and en-ynes†

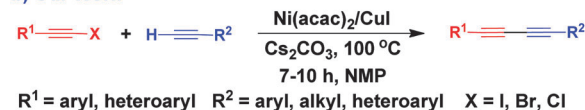Nirmalya Mukherjee, Debasish Kundu and Brindaban C. Ranu*

An efficient cross-coupling of alkynes with alkynyl and alkenyl halides catalysed by a Ni–Cu system without any ligand has been achieved. The reaction is suggested to proceed by Ni(0) catalysis assisted by Cu(ι). A series of functionalised 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 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 the synthesis of symmetric 1,3-diynes,[4] the synthesis of unsymmetric 1,3-diynes still remains a challenge. The oxidative coupling of terminal alkynes[5] 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 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 the last few years several methods involving nickel catalysed cross-coupling of alkynyl Grignard reagent with acetylenic sulfones,[6a] Cu(ι) catalysed coupling of alkynyl silanes and 1-chloroalkynes,[6b] Cu(ι)-catalysed 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 reaction of terminal alkynes and alkynyl halides in the presence of a Cu salt,[7] 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-diynes by the reaction of terminal alkynes

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

and 1-bromoalkynes in the presence of a 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-catalysed protocol for the synthesis of unsymmetric 1,3-diynes by the coupling of 1-bromo alkyne and terminal alkyne using phosphorus containing ligands[9a] which are usually toxic, and supercritical carbon dioxide.[9b]

Our initial success in the C_{sp^2}–O bond formation[10] 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 showcase successful synthesis of unsymmetric 1,3-diynes, where the Ni(0) works as an active catalytic species and Cu(ι) assists in the transmetalation process in the absence of ligand.

To the best of our knowledge this coupling using Ni or its combination with other metals under ligand free conditions is not reported. To explore the extended scope of our new protocol we consider it important to perform the cross-coupling of alkynes with vinyl halides by using a Ni–Cu catalytic system to provide 1,3-enynes 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 parameters such as catalyst, solvent, temperature and time for a representative reaction of phenylacetylene bromide and 4-ethynylanisole. 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 CuI in the system

Table 1 Standardisation of reaction conditions[a]

| Entry	Catalyst	Solvent	Base	Yield[b] (%)
1	Ni(acac)$_2$	NMP	Cs$_2$CO$_3$	0
2	CuI	NMP	Cs$_2$CO$_3$	0
3	Ni(acac)$_2$/CuBr	NMP	Cs$_2$CO$_3$	48
4	Ni(acac)$_2$/CuCl	NMP	Cs$_2$CO$_3$	24
5	NiBr$_2$/CuI	NMP	Cs$_2$CO$_3$	Trace
6[c]	Ni(acac)$_2$/CuI	NMP	Cs$_2$CO$_3$	89
7	Ni(acac)$_2$/CuI	DMF	Cs$_2$CO$_3$	59
8	Ni(acac)$_2$/CuI	DMSO	Cs$_2$CO$_3$	33
9[d]	Ni(acac)$_2$/CuI	NMP	Cs$_2$CO$_3$	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$_3$PO$_4$	Trace
13[e]	Ni(acac)$_2$/CuI	NMP	Cs$_2$CO$_3$	39
14[f]	Ni(acac)$_2$/CuI	NMP	Cs$_2$CO$_3$	72

[a] Reaction conditions: phenyl acetylene bromide (1.0 mmol) and 4-ethynyl-anisole (1.2 mmol), Cs$_2$CO$_3$ (2.0 mmol), 100 °C argon atmosphere, 9 h. [b] Yields of isolated pure products. [c] 5 mol% of Ni and Cu catalysts. [d] 70 °C. [e] 3 mol% of Ni and Cu catalyst. [f] 6 h.

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 Cs$_2$CO$_3$ at 100 °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 NiBr$_2$ (Table 1, entry 5). Lowering the reaction temperature (Table 1, entry 9) and change of base from Cs$_2$CO$_3$ to Et$_3$N (Table 1, entry 10) reduced the yield. The use of weaker bases such as K$_2$CO$_3$ or K$_3$PO$_4$ did not initiate the reaction (Table 1, entries 11 and 12). The yield of the reaction was significantly affected by changing the catalyst loading from 5 mol% to 3 mol% (Table 1, entry 13). Shortening of reaction time lowered the yield too (Table 1, entry 14).

Thus in a typical general procedure a mixture of alkynyl halide (1 mmol), terminal alkyne (1.2 mmol), and Cs$_2$CO$_3$ (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 aromatic and heteroaromatic alkynyl bromides underwent reactions with several substituted aromatic, aliphatic and heterocyclic terminal alkynes to produce the corresponding cross-coupled products (Table 2). The reactions of alkynyl iodides furnished marginally higher yields compared to those with the 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 1,3-diynes were obtained by this procedure. Several terminal alkynes and alkynyl bromides containing electron donating groups, –OMe, –Me, –^{t}Bu, –pentyl, underwent clean reactions in this procedure (Table 2, **3aa**, **3af**, **3ad**, **3fh**, **3dc**, and **3ea**). The presence of –CF$_3$ at the ortho-position of aryl alkyne produced low yield presumably due to the steric effect (Table 2, **3ae** and **3gi**). A similar trend was also observed with other aryl alkynes having 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-diyne containing a TMS moiety (**3ik**) is of potential for further manipulation.[8a]

Table 2 Ni–Cu catalysed synthesis of unsymmetrical conjugated diynes[a]
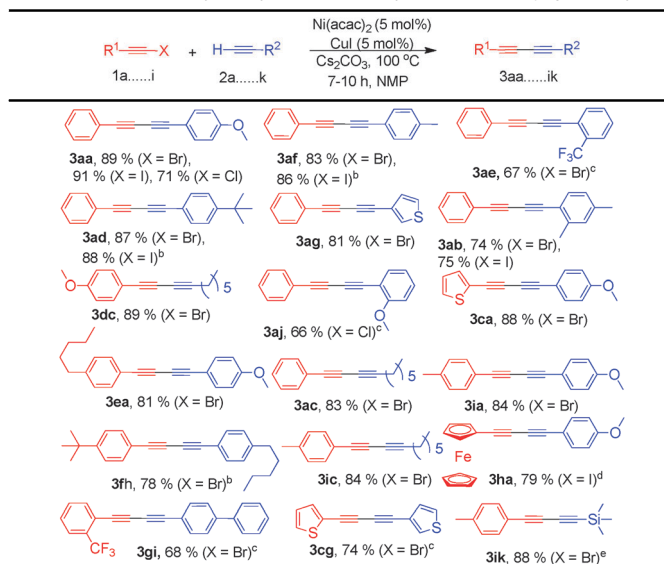
[a] General reaction conditions: alkynyl halide (1 mmol), terminal alkyne (1.2 mmol), Ni(acac)$_2$ (0.05 mmol), CuI (0.05 mmol), Cs$_2$CO$_3$ (2 equiv.), NMP (3 mL), 100 °C, 9 h, argon atmosphere. [b] 7 h. [c] 10 h. [d] Cs$_2$CO$_3$ (2.5 equiv.), 10 h. [e] Terminal alkyne (4 mmol), Et$_3$N (1 mL) in place of Cs$_2$CO$_3$, NMP (1 mL), 25–100 °C, 12 h, in a sealed tube.

The coupling of heterocyclic alkynes and alkynyl halides also 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 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.

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 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 led to homocoupled symmetric 1,3-diynes in place of the 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, **7aa** and **7bj**).
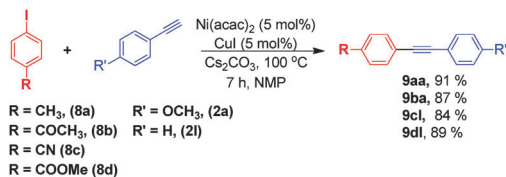
Efforts were made to apply this protocol for Sonogashira reaction. The C$_{sp^2}$–C$_{sp}$ cross-coupling of 4-ethynylanisole with diversely substituted iodo-benzenes led to the synthesis of unsymmetrical diaryl-acetylenes (Scheme 3, **9aa**, **9ba**, **9cl** and **9dl**). Several functionilities such as COMe, CO$_2$Me, CN are compatible with the reaction conditions. However, aryl iodides containing OH and NH$_2$ underwent O- and N-arylations without providing any expected coupled product. This is not unusual as the Ni–Cu system is known to catalyse such reactions.[10]

In general, the reactions are clean and high yielding. However, during alkyne–alkynyl halide cross-coupling reactions 2–5% of

Table 3 Ni–Cu catalysed synthesis of *trans*-enynes[a]

4a, 4b, 4c + H━━━R² → R¹⌒⌒━━━R²
R¹ = vinyl. styryl, cinnamyl
R² = aryl, alkyl, heteroaryl
Ni(acac)₂ (5 mol%)
CuI (5 mol%)
Cs₂CO₃, 100 °C
8-10 h, NMP
5ac.....5ca

5ac, 88 % (X = Br)   **5aa**, 84 % (X = Br)   **5ag**, 87 % (X = Br)

5bd, 79 % (X = Br)   **5ca**, 84 % (X = Br)[b]

[a] Reaction conditions: styrenyl, vinyl or 1,3-dienyl halide (1 mmol), terminal alkyne (1 mmol), Ni(acac)₂ (0.05 mmol), CuI (0.05 mmol), Cs₂CO₃ (2 equiv.), NMP (3 mL), 100 °C, 8 h, argon atmosphere. [b] 10 h.
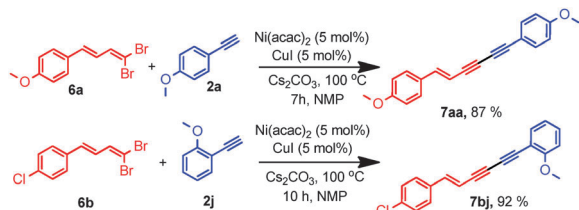
Scheme 2 Ni–Cu catalysed cross-coupling of 1,3-di-enyl-*gem*-dibromides with terminal alkynes.

R = CH₃, (**8a**)   R' = OCH₃, (**2a**)   **9aa**, 91 %
R = COCH₃, (**8b**)   R' = H, (**2l**)   **9ba**, 87 %
R = CN (**8c**)   **9cl**, 84 %
R = COOMe (**8d**)   **9dl**, 89 %

Scheme 3 Ni–Cu catalysed C_{sp²}–C_{sp} cross-coupling.

homocoupled products are formed. The reaction conditions are compatible with several functionalities and heteroaryl-, ferrocene-substituted alkynes. Many of these compounds are new and reported for the first time with full characterization data (ESI†).

To ascertain the role of the catalyst and the reaction pathway, a few experiments were performed. The reaction was carried out in the presence of nitroarene (electron acceptor), THF (electron 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 4-ethynylanisole (**2a**) indicating a non-radical pathway. Moreover, the high stereoselectivity in en-yne formation achieved in this process does not also support the radical mechanism as the vinyl radical undergoes rapid inversion of configuration.[13] Thus the possibility of a radical pathway is unlikely. On the other hand, the decrease of the reaction rate with increasing steric hindrance in aryl alkynes suggests that the reaction is more likely to follow an 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 a co-operative Ni–Cu catalytic system seems likely. As the redox potential of the Cu^I–Cu^{III}
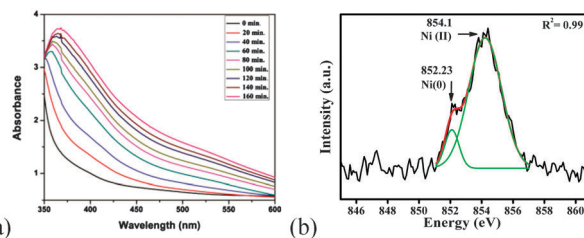

**Fig. 1** (a) UV spectra of Ni(0). (b) XPS pattern of Ni(0) and Ni(II).

system is very high under ligand free conditions the involvement of Cu in the oxidative addition step is a difficult proposition.[14] Usually, in the presence of a ligand the co-ordination of the nitrogen/phosphorus with the Cu^I center leads to a 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 considered. To monitor the change of the oxidation state of Ni(II) during the reaction an UV study of the C_{sp}–C_{sp} cross-coupling reaction was undertaken. Immediately after initiation of the reaction a peak appears in the range of 358–365 nm (Fig. 1(a)) which indicates the generation of Ni(0) species.[16] The formation of Ni(0) was also confirmed by the XPS data (Fig. 1(b)) which clearly suggest 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 (Fig. S2(a), see ESI†) of a sample of the reaction mixture also shows the presence of Ni(0) nanoparticles and it was supported by the lattice fringe calculation from the HRTEM image (Fig. S2(b), see ESI†). The distance between two (011) planes of the Ni(0) nano-particles 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 particle size diameter of the nanoparticles to be 3.7 (±0.7) nm (Fig. S3, see ESI†).

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 the presence of nickel chloride as the catalyst only a trace amount 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 agent[19] under identical conditions increased the yield of the product substantially (79%). These experimental observations 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) nanoparticles from Ni(acac)₂ in the presence of Cs₂CO₃, which then undergoes oxidative addition with alkynyl bromide to form **A**. In another cycle Cu^I interacts with alkyne to form Cu-acetylide **B** 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 an increase in the concentration of the product was observed with time (see ESI†).

Communication
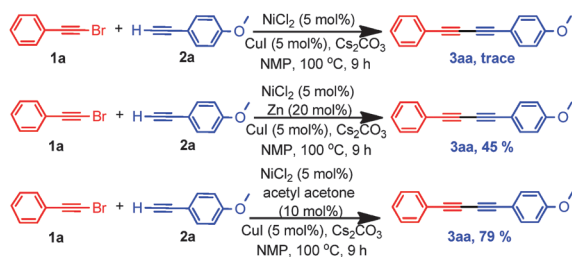
Scheme 4 Control experiments.
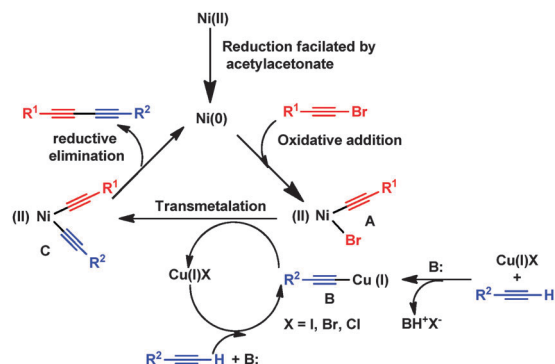
Scheme 5 Plausible reaction pathway for co-operative Ni–Cu catalysed cross-coupling of alkynyl bromide and terminal alkyne.

In conclusion, we have developed an efficient protocol for C_{sp}–C_{sp} and C_{sp}–C_{sp^2} cross-coupling of alkynes with alkynyl/alkenyl halides catalysed by a Ni–Cu co-operative system in the absence of any ligand leading to the synthesis of a series of unsymmetrical 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 wherein a Ni–Cu catalytic system in the absence of a ligand has been employed for a Cadiot–Chodkiewiez coupling reaction overcoming its associated limitations. Our catalytic system offers a great improvement to the known Pd/Cu[8]- or Cu[9] (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 protocol for the synthesis of bioactive molecules bearing di-yne and en-yne units constitutes our next goal.

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