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Highly efficient synthesis of unsymmetrical 1,3-diynes from organoalane reagents and alkynyl bromides mediated by a nickel catalyst†

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Highly efficient and simple cross-coupling reactions of alkynylbromides with organoalane reagents for the synthesis of unsymmetrical 1,3-diynes derivatives using $\text{Ni}(\text{OAc})_2$ (2–5 mol%)/ $(o\text{-furyl})_3\text{P}$ (4–10 mol%) as a catalyst are reported. Excellent yields (up to 94%) were obtained for a wide range of substrates at rt or 60 °C for 2–3 h in Et_2O or toluene.

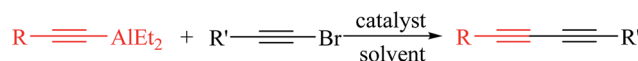
Diynes have been widely used in organic synthesis due to their significance as building blocks.¹ Amongst them, conjugated 1,3-diynes have significant applications in the preparation of natural products,² pharmaceuticals,³ π -conjugated acetylenic polymers,⁴ advanced materials⁵ and heterocyclic compounds,⁶ as well as in electronic and optical materials,⁷ and elsewhere.⁸ In addition, 1,3-diynes are common structural motifs found in pharmaceutically and biologically active compounds, which are known to have antifungal,⁹ antibacterial,¹⁰ anti-inflammatory,¹¹ anti-HIV,¹² and anticancer properties.¹³ Thus, their synthesis and applications has attracted a great amount of attention over the past few decades. Since the discovery of the Glaser homo-coupling reaction of terminal alkynes in 1869,¹⁴ a great amount of attention has been given to the development of new and efficient procedures for the synthesis of conjugated 1,3-diyne derivatives. Recently, a variety of processes have been developed for the preparation of conjugated 1,3-diynes, typical synthetic protocols including the cross-coupling reactions of 1-haloalkynes with terminal alkynes,¹⁵ cross-coupling reactions of terminal alkynes,¹⁶ cross-coupling reaction of terminal alkynes with 1,2-dihaloalkenes,¹⁷ cross-coupling of alkynylsilanes with haloalkynes,¹⁸ conjugated diynones decarbonylation reaction,¹⁹ cross-coupling reactions of aryl iodides and alkynyl acid,²⁰ oxidative coupling of alkynyl Grignard reagents,²¹ oxidative decarboxylative homo-coupling of alkynyl acids,²² oxidative homo-coupling reactions of terminal alkynes with the oxidants,²³ homo-coupling of alkynyltellurides,²⁴ haloalkynes,²⁵ and alkynylsilanes.²⁶

Despite that, these efforts have provided alternative methods for the synthesis of conjugated 1,3-diynes. However, these reactions still suffer from excess oxidants, excess bases,

cocatalysts, high temperature, relatively long reaction times, and the special reaction medium. The development of more efficient and atom economical approaches for the synthesis of conjugated 1,3-diynes remains as desirable work. In addition to the above reagents, alkynylaluminum reagents have been extensively used as nucleophiles for organic reactions.²⁷

In recent times, metal-catalyzed cross-coupling reactions of electrophiles with alkynylmetallic reagents have provided an alternative route for the preparation of alkyne compounds.²⁸ Previous studies show that organoalanes reagents are a highly efficient nucleophiles for cross-coupling reactions with aromatic halides²⁹ or benzylic halides,³⁰ and investigations have demonstrated that nickel is a good catalytic metal.³¹ To continue our efforts in developing coupling reactions using reactive organometallic reagents,^{29,30,32} we report a novel nickel(II)-catalyzed cross-coupling of alkynylhalides with alkynylaluminum reagents at ambient temperature or 60 °C in a short time with good isolated yield for the synthesis of unsymmetrical conjugated 1,3-diynes (Scheme 1).

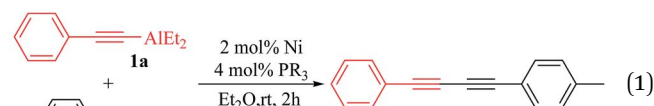
In order to optimize the reaction conditions, effects of phosphine ligand, nickel source, reaction time, solvent, the amount of organoalanes reagents, and the molar ratio of metal to ligand on the cross-coupling reaction were investigated using alkynylaluminum and alkynyl bromide as a model system. The reaction of diethyl(2-phenylethynyl)aluminum ($\text{C}_6\text{H}_5\text{C}\equiv\text{CAlEt}_2$) (**1a**) with 1-(2-bromo-ethynyl)-4-methylbenzene ($p\text{-MeC}_6\text{H}_4\text{C}\equiv\text{CBr}$) (**2a**) using a nickel catalyst of phosphine (eqn (1)) was first examined. Under the optimized conditions of 2 mol% $\text{Ni}(\text{OAc})_2$ and 4 mol% $\text{P}(o\text{-furyl})_3$ conducting in diethyl ether at room temperature over 2 h, producing **3aa** in 87% isolated yield (ESI: Tables S1 and S2†).



Scheme 1 Metal-catalyzed coupling reactions of 1-haloalkynes derivatives with organoalanes nucleophiles.

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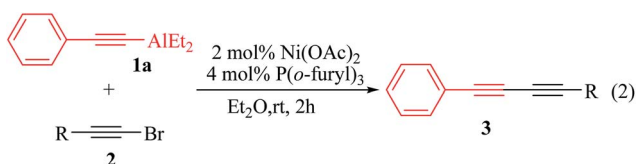
Generalities of the catalytic system were examined with various 1-bromoalkynes derivatives (eqn (2)), and the results were summarized in Table 1. As shown in Table 1, various 1-bromoalkynes derivatives bearing electron-withdrawing or electron-donating substituents were smoothly coupled to give the corresponding unsymmetrical conjugated 1,3-diynes **3** in 64–94% isolated yield (Table 1, entries 1–14). The cross-coupling reaction with 1-bromoalkynes bearing an electron-withdrawing group, such as fluoro, chloro, bromo and trifluoromethyl groups, or electron-donating group, such as methyl, ethyl, propyl and *tert*butyl groups, produced the conjugated products 1,3-diyne in good to excellent yield (Table 1, entries 1–12). In particular, the cross-coupling of 1-bromo-4-(2-bromoethynyl) benzene (**2g**) with diethyl(2-phenylethynyl) aluminum (**1a**) could also be selectively obtained the unsymmetrical conjugated 1,3-diynes **3ag** in 74% isolated yield (Table 1, entry 7). However, the cross-coupling reaction of diethyl(2-phenylethynyl)aluminum (**1a**) with 1-(2-bromoethynyl)-4-methoxybenzene (4-MeOC₆H₅C≡CBr) (**2f**) only gave products of unsymmetrical conjugated 1,3-diyne **3af** in 64% isolated yield (Table 1, entry 6) potentially due to the 1-(2-bromoethynyl)-4-

methoxybenzene was being decreased by methoxyl group. More importantly, 2-(2-bromoethynyl)pyridine and 2-(2-bromoethynyl)thiophene reagents were also effective substrates for this reaction, giving the corresponding coupling products of unsymmetrical conjugated 1,3-diynes **3am** and **3an** in 83% and 94% isolated yield, respectively (Table 1, entries 13 and 14). Unfortunately, cross-coupling reaction of 4-(2-bromoethynyl)benzonitrile (**2o**) (*p*-CNC₆H₅C≡CBr) and diethyl(2-phenylethynyl)-aluminum (**1a**) (C₆H₅C≡CAIEt₂) only gave products of unsymmetrical conjugated 1,3-diyne **3ao** in 5% yield (Table 1, entries 15). While, coupling of methyl 4-(2-bromoethynyl)benzoate (**2p**) (*p*-CH₃OOCC₆H₅C≡CBr) could not produce the target compound (Table 1, entries 16).

We subsequently investigated cross-coupling reactions of substituted aryl alkynylaluminum reagents with various 1-bromoalkynes. However, the cross-coupling reaction of diethyl(2-(4-methoxy phenyl)-ethynyl)aluminum (4-MeOC≡CAIEt₂) (**1b**) with 1-(2-bromo-ethynyl)-benzene (**2o**) employing the catalyst of 2 mol% Ni(OAc)₂ and 4 mol% P(*o*-furyl)₃ yielded coupling products of unsymmetrical conjugated 1,3-diyne **3bo** with only a 62% isolated yield. Therefore, the reaction conditions were re-tuned, and the best performed catalyst was found to be 5 mol% Ni(OAc)₂ and 10 mol% P(*o*-furyl)₃ while the reaction was conducting in toluene at 60 °C for 3 h (ESI Table S3[†]), furnishing **3bo** with 75% isolated yield.

The reaction scope was further explored on substrates of R'C≡CAIEt₂ (R' = 4-MeOPh (**1b**) or 4-FPh (**1c**), 4-MePh (**1d**)) and various 1-bromoalkynes using 5 mol% Ni(OAc)₂ and 10 mol% P(*o*-furyl)₃ conducting in toluene at 60 °C for 3 h (eqn (3)), and results are summarized in Table 2. Satisfactory application scope was demonstrated by this section of experiment. The cross-coupling reaction can be applied to C(sp)–C(sp) bond formations, affording the coupling products unsymmetrical conjugated 1,3-diynes in 51–80% isolated yield (Table 2, 1–15). Cross-coupling reactions of substituted aryl alkynylaluminum reagents **1b** or **1c** or **1d** with 1-bromoalkyne reagents containing different functional groups such as alkyl, halides (**2a**, **2g**, **2h**, **2i**, **2j**, **2k**, **2l**) could potentially couple, giving the corresponding unsymmetrical conjugated 1,3-diynes moderate to good isolated yields (Table 2, entries 1–4, 7, 8, 10–14). Furthermore, 2-(2-bromoethynyl)thiophene (**2n**) reacted successfully with diethyl(2-(4-methoxyphenyl)ethynyl)aluminum (4-MeOPhC≡C–AlEt₂) (**1b**) to provide unsymmetrical conjugated 1,3-diyne **3bn** with 74% isolated yield (Table 2, entry 5). The 2-(4-*p*-tolylbuta-1,3-diynyl)pyridine (**3dm**) resulting from 2-(2-bromo-ethynyl)pyridine (**2m**) and diethyl(2-*p*-tolyl-ethynyl) aluminum (4-MePhC≡CAIEt₂) (**1d**) was obtained with 72% isolated yield (Table 2, entry 15). While, the cross-coupling reaction of diethyl(2-(4-fluorophenyl)-ethynyl) aluminium (4-FPhC≡CAIEt₂) (**1c**) with 1-bromo-hept-1-yne (**2p**) gave the corresponding unsymmetrical conjugated 1,3-diyne **3cp** with a 51% isolated yield (Table 2, entry 9). Unfortunately, cross-coupling of 1-(2-bromoethynyl)-4-methylbenzene (**2a**) (*p*-CH₃-C₆H₅C≡CBr) and diethyl(2-(4-methylbenzoate)ethynyl) aluminium (4-MeOOCPhC≡CAIEt₂) (**1e**) could not produce the coupling product (Table 2, entries 16).

Table 1 Nickel-catalyzed cross-coupling reactions of C₆H₅C≡CAIEt₂ (**1a**) with various 1-bromoalkynes (**2**)^a



Entry	1-Bromoalkynes 2	Product 3	Yield ^b (%)
1	4-Me-Ph (2a)	3aa	87
2	4-Et-Ph (2b)	3ab	85
3	4-Propyl-Ph (2c)	3ac	86
4	4- ^t Bu-Ph (2d)	3ad	84
5	3-Me-Ph (2e)	3ae	81
6	4-MeO-Ph (2f)	3af	64
7	4-Br-Ph (2g)	3ag	74
8	4-Cl-Ph (2h)	3ah	82
9	4-F-Ph (2i)	3ai	90
10	3-F-Ph (2j)	3aj	93
11	2-F-Ph (2k)	3ak	86
12	4-CF ₃ -Ph (2l)	3al	92
13	2-Pyridinyl (2m)	3am	94
14	2-Thienyl (2n)	3an	83
15	4-CN-Ph (2o)	3ao	<5%
16	4-CH ₃ OOC-Ph (2p)	3ap	0

^a **1a**/**2** = 1.0/0.5 mmol; 2 mL Et₂O; room temperature; 2 h. ^b Isolated yield.



Table 2 Cross-coupling reactions of substituted aryl organoalanes reagents $\text{ArC}\equiv\text{CAIEt}_2$ (**1**) with various 1-bromoalkynes (**2**)^a

$\text{R}'-\text{C}\equiv\text{C}-\text{AlEt}_2 \quad \text{1} \quad + \quad \text{R}-\text{C}\equiv\text{C}-\text{Br} \quad \text{2} \xrightarrow[\text{toluene, 60}^\circ\text{C, 3h}]{5 \text{ mol\% Ni(OAc)}_2, 10 \text{ mol\% P}(o\text{-furyl})_3} \text{R}'-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{R} \quad \text{3} \quad (3)$				
Entry	1 R'	2 R	Product	Yield ^b (%)
1	4-MeOPh (1b)	4-MePh (2a)	3ba	62
2	4-MeOPh (1b)	4-ClPh (2h)	3bh	72
3	4-MeOPh (1b)	4-FPh (2i)	3bi	71
4	4-MeOPh (1b)	3-FPh (2j)	3bj	72
5	4-MeOPh (1b)	2-Thienyl (2n)	3bn	74
6	4-MeOPh (1b)	Ph (2o)	3bo	75
7	4-FPh (1c)	3-FPh (2j)	3cj	55
8	4-FPh (1c)	2-FPh (2k)	3ck	53
9	4-FPh (1c)	<i>n</i> -Pentyl (2p)	3cp	51
10	4-MePh (1d)	4-BrPh (2g)	3dg	68
11	4-MePh (1d)	4-FPh (2i)	3di	62
12	4-MePh (1d)	3-FPh (2j)	3dj	73
13	4-MePh (1d)	2-FPh (2k)	3dk	80
14	4-MePh (1d)	4-CF ₃ Ph (2l)	3dl	75
15	4-MePh (1d)	2-Pyridinyl (2m)	3dm	72
16	4-MeOOCPh (1e)	4-MePh (2a)	3af	0

^a **1/2** = 1.0/0.5 mmol; 2 mL toluene; 60 °C; 3 h. ^b Isolated yield.

The cross-coupling reactions of aliphatic alkynylaluminum reagents with various 1-bromoalkynes was also investigated under the same catalytic system. The unsymmetrical conjugated 1,3-diyne **3fo** was obtained with 52% isolated yield when 1-(2-bromoethynyl)-benzene (**2o**) coupled with the $\text{TMSC}\equiv\text{CAIEt}_2$ (**1f**) nucleophile. However, the cross-coupling reaction of 1-(2-bromoethynyl)-benzene (**2o**) coupled with the $\text{TMSC}\equiv\text{CAIEt}_2$ (**1f**) favoured a formation of the unsymmetrical conjugated 1,3-diyne **3fo** with 80% isolated yield in DME at room temperature for 3 h (ESI Table S4†). So, the reaction scope was further explored on substrates of $\text{TMSC}\equiv\text{CAIEt}_2$ (**1f**) and various 1-bromoalkynes using 5 mol% $\text{Ni}(\text{OAc})_2$ and 10 mol% $\text{P}(o\text{-furyl})_3$ conducting in DME at room temperature for 3 h (eqn (4)), and results are summarized in Table 3. As shown in Table 3, various 1-bromoalkynes derivatives bearing electron-withdrawing or electron-donating substituents were smoothly coupled to give the corresponding unsymmetrical conjugated 1,3-diyne **3** in 67–80% isolated yield (Table 3, entries 1–6). The cross-coupling reaction with 1-bromoalkynes bearing an electron-withdrawing group, such as fluoro and trifluoromethyl groups, or electron-donating group, such as methoxyl and *tert*-butyl groups, produced the conjugated products 1,3-diyne in good isolated yield (Table 3, entries 2–5). In particular, the cross-coupling of 2-(2-bromoethynyl)naphthalene (**2q**) with $\text{TMSC}\equiv\text{CAIEt}_2$ (**1f**) could also be obtained the conjugated 1,3-diyne **3fq** in 74% isolated yield (Table 3, entry 6).

The effect of the alkylhalides and dummy ligand of organoalane reagents on the reaction were investigated, and the results were summarized in Table 4. As shown in Table 4, cross-

Table 3 Cross-coupling reactions of organoalanes reagents $\text{TMSC}\equiv\text{CAIEt}_2$ (**1f**) with various 1-bromoalkynes (**2**)^a

$\text{TMS}-\text{C}\equiv\text{C}-\text{AlEt}_2 \quad \text{1f} \quad + \quad \text{R}-\text{C}\equiv\text{C}-\text{Br} \quad \text{2} \xrightarrow[\text{DME, rt, 3h}]{5 \text{ mol\% Ni(OAc)}_2, 10 \text{ mol\% P}(o\text{-furyl})_3} \text{TMS}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{R} \quad \text{3} \quad (4)$			
Entry	2 R	Product	Yield ^b (%)
1	Ph (2o)	3fo	80
2	4- ^t Bu-Ph (2d)	3fd	74
3	4-MeOPh (2f)	3ff	76
4	4-FPh (2i)	3fi	72
5	4-CF ₃ Ph (2l)	3fl	67
6	2-Naphthyl (2q)	3fq	74

^a **1/2** = 1.0/0.5 mmol; 2 mL DME; room temperature; 3 h. ^b Isolated yield.

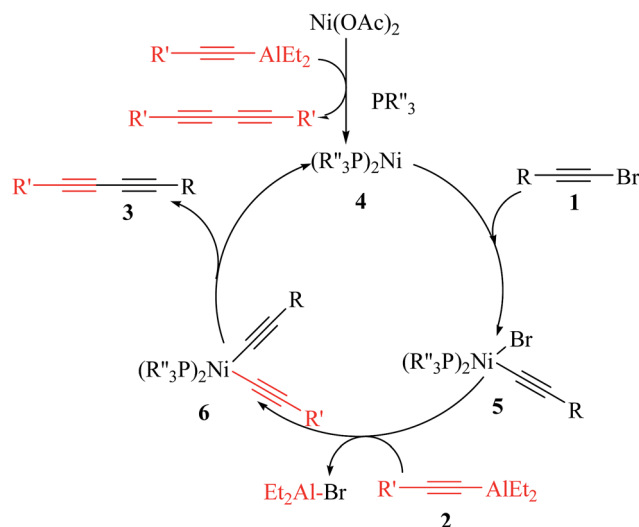
coupling reaction of dimethyl-(2-phenylethynyl)-aluminum (**1g**) ($\text{C}_6\text{H}_5\text{C}\equiv\text{CAlMe}_2$) with *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{C}\equiv\text{CBr}$ (**2a**) gave product of unsymmetrical conjugated 1,3-diyne **3aa** in 68% isolated yield (Table 4, entry 1). The coupling reaction of propargyl iodide (**2q**) with diethyl-(2-phenylethynyl)-aluminum (**1a**) ($\text{C}_6\text{H}_5\text{C}\equiv\text{CAlEt}_2$) gave product of unsymmetrical conjugated 1,3-diyne **3aa** in a 75% isolated yield (Table 4, entry 2). While, coupling of propargyl chloride (**2r**) gave coupling product **3aa** in only 48% isolated yield (Table 4, entry 3). Gratifyingly, 70% isolated yield of product **3aa** was obtained using tri(2-phenylethynyl)-aluminum (**1h**) as nucleophiles (Table 4, entry 4). The results showed that the different alkylhalides and dummy ligand of organoalane reagents are compatible with this procedure.

While a precise understanding of the reaction mechanism awaits further study, a plausible catalytic pathway is proposed in Scheme 2. The first step is the oxidative addition of 1-bromoalkyne (**1**) to $\text{Ni}(0)$ phosphine complex (**4**) (which in turn from $\text{Ni}(\text{OAc})_2$ and $\text{R}'\text{C}\equiv\text{CAIEt}_2$ (**2**) reagents) that forms the

Table 4 The effect of the alkylhalides and dummy ligand of organoalane reagents on the reaction^a

$\text{R}-\text{C}\equiv\text{C}-\text{AlR}_2 \quad \text{1} \quad + \quad \text{X}-\text{C}\equiv\text{C}-\text{R}' \quad \text{2} \xrightarrow[\text{Et}_2\text{O, rt, 3h, additive}]{5 \text{ mol\% Ni(OAc)}_2, 10 \text{ mol\% P}(o\text{-furyl})_3} \text{R}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{R}' \quad \text{3aa} \quad (5)$				
Entry	R (1)	X (2)	Product	Yield ^b (%)
1	Me (1g)	Br (2a)	3aa	68
2	Et (1a)	I (2q)	3aa	75
3	Et (1a)	Cl (2r)	3aa	48
4	PhC≡C- (1h)	Br (2a)	3aa	70

^a **1/2** = 1.0/0.5 mmol; 2 mL Et₂O; room temperature; 3 h. ^b Isolated yield.



Scheme 2 The proposed catalytic cycle for the formation of unsymmetrical conjugated 1,3-diyne 3.

organonickel(II) bromide intermediate (5). Transmetalation of $R'C\equiv CAI\text{Et}_2$ (2) with 5 gives alkyne-alkynenickelium(II) intermediate (6) and Et_2AlBr . Finally, complex 6 undergoes reductive elimination to afford the desired cross-coupling product 3 and regenerate the active $\text{Ni}(0)$ species for the next catalytic cycle.

Conclusions

In conclusion, a novel nickel-catalyzed cross-coupling reaction of 1-bromoalkynes with alkynylaluminum reagents is reported. A variety of 1-bromoalkynes with aryl, heterocycloyl, or alkyl group can be efficiently coupled to give the corresponding coupling products unsymmetrical conjugated 1,3-diyne in good yield and with good functional group compatibility. Moreover, the ready availability of the starting materials, the mild reaction conditions, and the simplicity of the operations involved are additional features making the methodology could therefore serve as a complementary option in the field of conjugated 1,3-diyne synthesis. A possible catalytic cycle was proposed to explain the formation of the products conjugated 1,3-diyne. Further application of these conjugated 1,3-diyne in organic synthesis are underway.

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