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Direct Synthesis of 1-Arylprop-1-ynes with Calcium Carbide as an Acetylene Source

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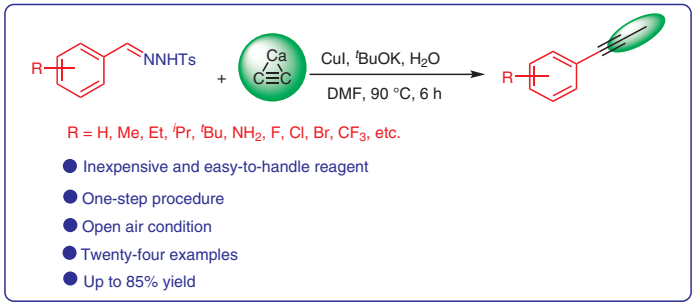

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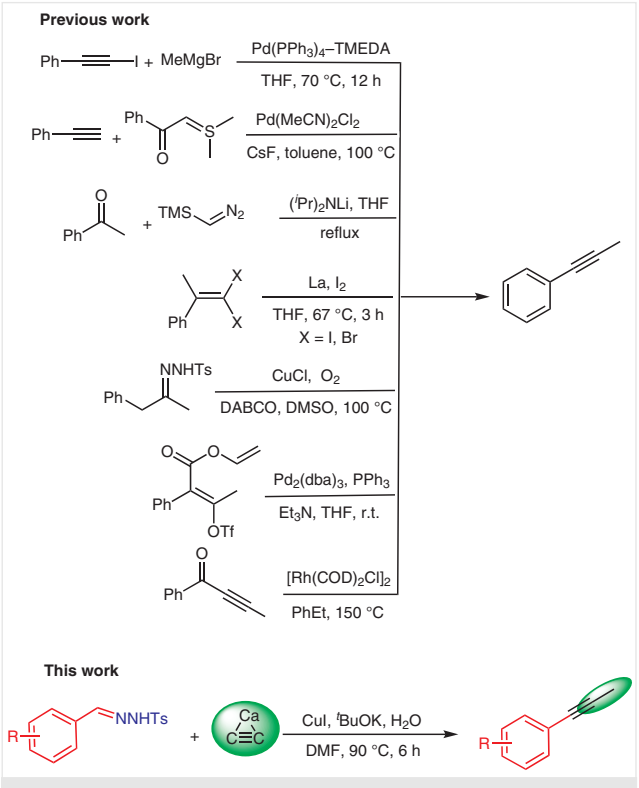
Abstract A simple method is described for the synthesis of 1-arylprop-1-ynes directly from aromatic aldehyde *p*-tosylhydrazones by using calcium carbide as an acetylene source. The salient features of this protocol are its use of a readily available and easily handled source of acetylene, its operational simplicity, its high yield, and its broad substrate scope.

Key words arylpropynes, calcium carbide, tosylhydrazones, aralkynes

Alkynes are important synthons for syntheses of pharmaceuticals and agrochemicals,[1] and are also used in the materials industry.[2] As typical examples, 1-arylprop-1-ynes are fine organic synthetic intermediates with high application value and high reactivity that have been widely used in the synthesis of polysubstituted alkenes by addition or alkenylation,[3] multifunctional heterocycles by cycloaddition,[4] arylallylic heterocycles by allylation,[5] 1,2-diketones by oxidation,[6] persubstituted benzenes by cyclotrimerization,[7] and chiral alcohols by hydration and hydrogenation.[8]

Various synthetically viable procedures have been used for the construction of 1-arylprop-1-ynes.[9] Some recently reported methods include: (i) the palladium-catalyzed Kumada cross-coupling of phenylethynyl iodide with methyl Grignard reagent,[10] (ii) the palladium-catalyzed methylation of the phenylethyne C(sp)–H bond with dimethyl sulfonium ylides,[11] (iii) the Colvin rearrangement of acetophenone by reaction with (trimethylsilyl)diazomethane,[12] (iv) the Fritsch–Buttenberg–Wiechell rearrangement of 2-phenyl-1,1-dihaloprop-1-enes by using lanthanum metal and a catalytic amount of iodine,[13] (v) the copper-catalyzed oxidative transformation of propiophenone *N*-tosylhydrazones;[14] (vi) the palladium-catalyzed tandem decarboxylation/elimination of (*E*)-enol triflates;[15] and (vii) the rhodium-catalyzed decarbonylation of conjugated ynones through carbon–alkyne bond activation[16] (Scheme 1).



Scheme 1 Syntheses of 1-arylprop-1-ynes

However, existing synthetic methods have several drawbacks; these include low yields and the use of valuable transition metals, difficult-to-obtain substrates, or mois-

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ture-sensitive reagents, and the need for harsh reaction conditions or complex procedures.

In recent years, in comparison with acetylene gas, calcium carbide has been shown to provide surprising and satisfactory performance in organic syntheses. Its most striking advantages over acetylene gas are its freedom from the risk of explosion, and the lack of a requirement for complex equipment; moreover, it is commercially available, easy to handle, and environmentally benign. There are several reports in the literature on the use of calcium carbide as an inexpensive and easily available source of acetylene.[17] Our group has recently made great efforts to investigate the direct use of calcium carbide in organic synthesis, and has reported syntheses of triarylacrylonitriles,[18] diarylethynes,[19] 2-methylbenzofurans,[20] *N*-propargyl *tert*-amines,[21] and 1,3,5-triaroylcyclohexanes.[22]

Here, we report a novel method for the direct synthesis of 1-arylprop-1-ynes by using cheap calcium carbide, as a source of acetylene, together with commercially available or readily prepared aromatic aldehyde *p*-tosylhydrazones as substrates.

We started our investigations by studying the reaction of benzaldehyde *p*-tosylhydrazone (**1a**) with calcium carbide in DMF in the presence of ^{t}BuOK as a base at 90 °C (Table 1). The reaction did not give any product in the absence of a mediator (Table 1, entry 1). When $CuCl_2$ was used as a mediator, only a trace of product was obtained (entry 2). To our delight, however, various amounts of CuCl (0.12–2.0 equiv) as a mediator gave the desired prop-1-yn-1-ylbenzene (**2a**) in yields of 16–65% (entries 3–6). The reaction worked better with CuBr and CuI as mediators (entries 7 and 8), and the best result (72% yield) was obtained with the CuI-mediated reaction (entry 8). In addition, ^{t}BuOK, KOH, K_2CO_3, Cs_2CO_3, KOAc, DMAP, and Et_3N as bases were also tested (entries 8–14), and it was found that ^{t}BuOK was the most efficient base (entry 8). The solvent also plays an important role in the reaction. Owing to the poor solubility of calcium carbide in CCl_4, EtOH, THF, or toluene, **2a** was not obtained in these media (entries 15–18). In comparison, DMF, DMSO, and MeCN were suitable solvents, and gave various amounts of **2a** (entries 8, 19, and 20), with DMF giving the highest yield (entry 8). The reaction temperature also affected the reaction (entries 8, 21–23), and 90 °C was found to be optimal. In addition, the addition of four equivalents of water based on **1a** was found to be the appropriate amount for the reaction (entry 8). Larger or smaller amounts of water both produced a drop in the yield (entries 24 and 25).

By using these optimized conditions, a range of 1-arylprop-1-ynes were prepared by the reaction of various aromatic aldehyde *p*-tosylhydrazones with calcium carbide at 90 °C in undried DMF with CuI as a mediator and ^{t}BuOK as a base (Scheme 2).[23] The reactions worked well for a wide range of substrates bearing both electron-donating groups

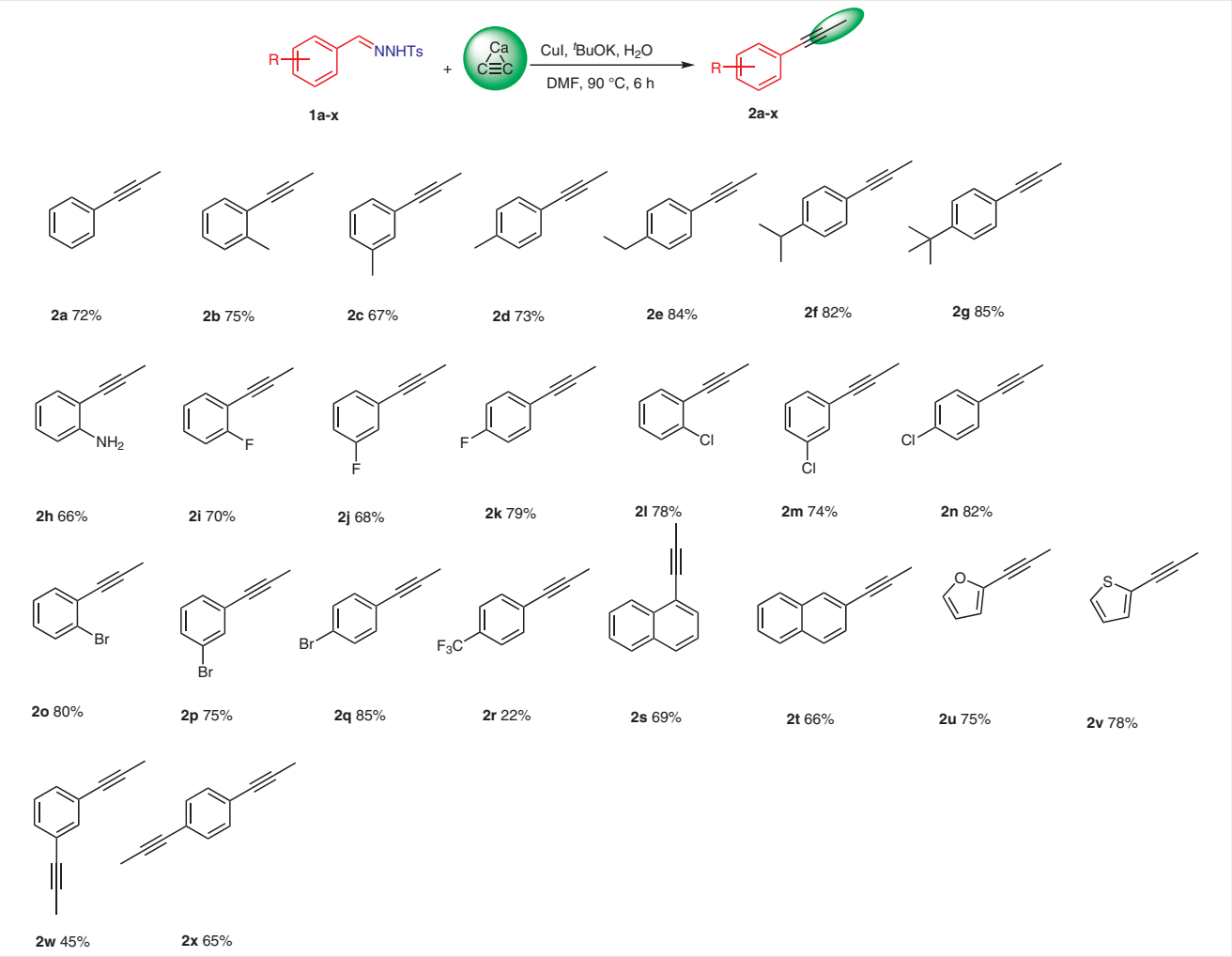
Table 1 Optimization of the Reaction Conditions[a]

1a **2a**

Entry	Mediator (equiv)	Base	Solvent	Temp (°C)	Yield[b] (%)
1	–	^{t}BuOK	DMF	90	0
2	$CuCl_2$ (1.2)	^{t}BuOK	DMF	90	trace
3	CuCl (0.12)	^{t}BuOK	DMF	90	16
4	CuCl (0.5)	^{t}BuOK	DMF	90	35
5	CuCl (1.2)	^{t}BuOK	DMF	90	65
6	CuCl (2)	^{t}BuOK	DMF	90	62
7	CuBr (1.2)	^{t}BuOK	DMF	90	67
8	CuI (1.2)	^{t}BuOK	DMF	90	72
9	CuI (1.2)	KOH	DMF	90	0
10	CuI (1.2)	K_2CO_3	DMF	90	0
11	CuI (1.2)	Cs_2CO_3	DMF	90	33
12	CuI (1.2)	KOAc	DMF	90	trace
13	CuI (1.2)	DMAP	DMF	90	trace
14	CuI (1.2)	Et_3N	DMF	90	trace
15	CuI (1.2)	^{t}BuOK	CCl_4	90	trace
16	CuI (1.2)	^{t}BuOK	EtOH	90	0
17	CuI (1.2)	^{t}BuOK	THF	90	trace
18	CuI (1.2)	^{t}BuOK	toluene	90	0
19	CuI (1.2)	^{t}BuOK	MeCN	90	15
20	CuI (1.2)	^{t}BuOK	DMSO	90	53
21	CuI (1.2)	^{t}BuOK	DMF	70	45
22	CuI (1.2)	^{t}BuOK	DMF	80	65
23	CuI (1.2)	^{t}BuOK	DMF	100	68
24	CuI (1.2)	^{t}BuOK	DMF	90	51[c]
25	CuI (1.2)	^{t}BuOK	DMF	90	45[d]

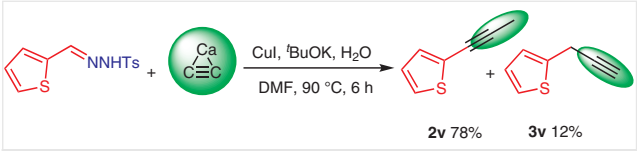
[a] Reaction conditions: **1a** (1 mmol), calcium carbide (3 mmol), H_2O (4 mmol), mediator, base (2 mmol), undried solvent (4 mL), 6 h.
[b] Isolated yield.
[c] H_2O (2 mmol).
[d] H_2O (8 mmol).

(Me, Et, ^{i}Pr, ^{t}Bu, NH_2) or electron-withdrawing groups (F, Cl, Br) on the aromatic ring, and the desired products **2a–q** were obtained in satisfactory yields with no obvious electronic effects (Scheme 2). In particular, the reaction tolerated an NH_2 group (**2h**). Exceptionally, a substrate with a strongly electron-withdrawing CF_3 group on the aromatic ring gave a low yield of **2r**. In addition, the reaction was also suitable for substrates bearing polycyclic and heterocyclic aromatic rings, and afforded the desired products **2s–v** in good yields. The di(prop-1-yn-yl)benzenes **2w** and **2x** were also obtained in moderate to good yields by a similar reaction.



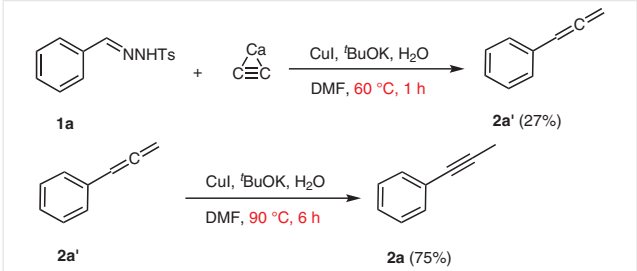
Scheme 2 Synthesis of 1-arylprop-1-ynes. *Reaction conditions*: **1a–x** (1 mmol), CaC_2 (3 mmol), H_2O (4 mmol), CuI (1.2 mmol), ^tBuOK (2 mmol), undried DMF (4 mL), 90 °C, 6 h.

Note that in the synthesis of 2-prop-1-yn-1-ylthiophene (**2v**), 3-prop-1-yn-1-ylthiophene (**3v**), an isomer of **2v**, was also isolated as a minor product in 12% yield (**2v**/**3v** = 13:2) (Scheme 3).



Scheme 3 Synthesis of isomers **2v** and **3v**

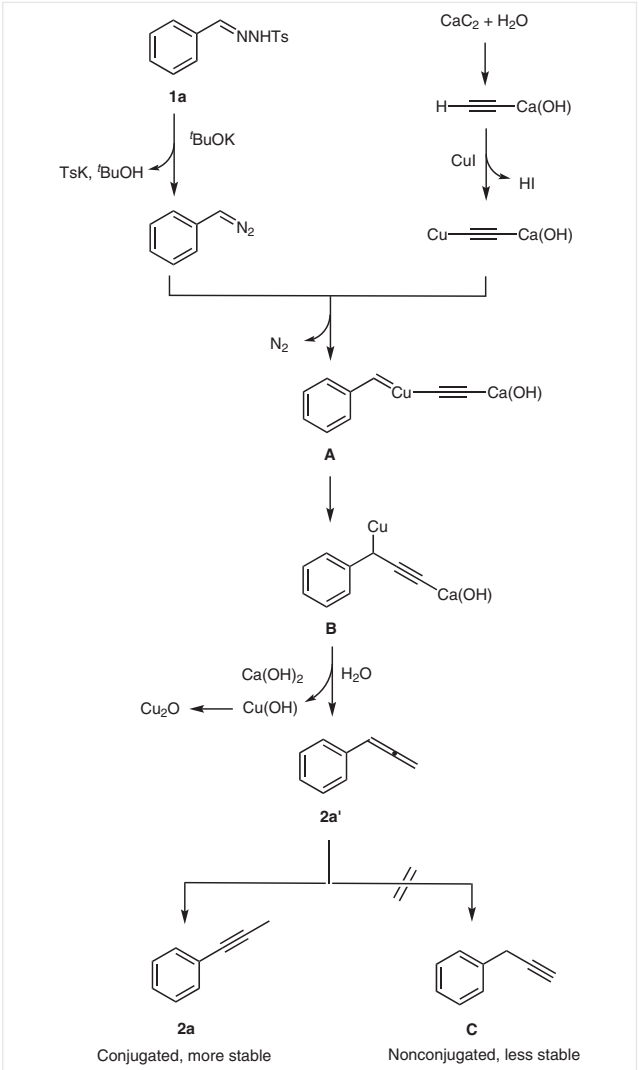
To gain insight into the reaction mechanism, control experiments were conducted (Scheme 4). When the reaction of **1a** with calcium carbide was carried out at lower temperature (60 °C) for a short time (1 h), propa-1,2-dien-1-ylbenzene (**2a′**) was isolated in low yield (27%). Diene **2a′** was subsequently converted into **2a** in 75% yield under the standard conditions. This result implies that **2a′** is an intermediate for the formation of **2a**.



Scheme 4 Control experiments

On the basis of above results and our experimental observations, a plausible mechanism is proposed for the synthesis of **2a** (Scheme 5). Initially, 2-(diazomethyl)benzene is

formed in situ by the reaction of **1a** with ^{t}BuOK (the Bamford–Stevens reaction).[24] Simultaneously, calcium carbide reacts with water to form calcium acetylide hydroxide,[17f,17g] which then transformed into copper calcium acetylide in the presence of cuprous iodide.[25] This acetylide then reacts with 2-(diazomethyl)benzene to form the copper carbene species **A**.[14b,26] A reductive elimination reaction of **A** gives intermediate **B**,[25] which abstracts a hydrogen ion from water present in the reaction system to afford propa-1,2-dien-1-ylbenzene (**2′**) with loss of copper(I) and calcium hydroxide. Diene **2a′** undergoes hydrogen rearrangement to give the conjugated product **2a**, which is more stable than the nonconjugated isomer prop-2-yn-1-ylbenzene (**C**).



Scheme 5 Proposed mechanism for the synthesis of **2a**

In conclusion, we have developed a safe, efficient, and simple method for the synthesis of 1-arylpropa-1-ynes by using calcium carbide as an inexpensive and readily obtainable source of acetylene. The synthetic method tolerates a wide range of substrates and provides a good alternative for the synthesis of internal alkynes.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610718.

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(23) **1-Arylprop-1-ynes (2a–x); General Procedure**
A mixture of the appropriate aromatic aldehyde *p*-tosylhydrazone (1 mmol), calcium carbide (3 mmol, 0.20 g for 98% purity), ^{t}BuOK (2 mmol, 0.22 g), CuI (1.2 mmol, 0.23 g), and H_2O (4 mmol, 0.07 mL) in DMF (4 mL) was stirred at 90 °C for 6 h. When the reaction was complete, the mixture was filtered to remove solids and the liquor was extracted with EtOAc (3 × 10 mL) then washed with sat. brine (3 × 10 mL). The resulting organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, PE).

1-Phenylprop-1-yne (2a)
Colorless liquid; yield: 83.6 mg (72%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.39 (dd, *J* = 7.7, 2.0 Hz, 2 H), 7.30–7.24 (m, 3 H), 2.05 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 131.46, 128.17, 127.48, 124.01, 85.76, 79.71, 4.29. HRMS: *m/z* $[M + H]^+$ calcd for C_9H_9: 117.0699; found: 117.0698.

(2-Prop-1-yn-1-ylphenyl)amine (2h)
Brown liquid; yield: 87.1 mg (66%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 7.8 Hz, 1 H), 7.10–7.06 (m, 1 H), 6.75 (d, *J* = 8.1 Hz, 1 H), 6.70 (t, *J* = 7.5 Hz, 1 H), 2.11 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 146.97, 132.01, 128.77, 118.29, 114.52, 109.40, 91.18, 76.06, 4.53. HRMS: *m/z* $[M + H]^+$ calcd for $C_9H_{10}N$: 132.0808; found: 132.0808.

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