

# One-Pot Synthesis of Conjugated (*E*)-Enynones via Two Types of Cross-Coupling Reaction

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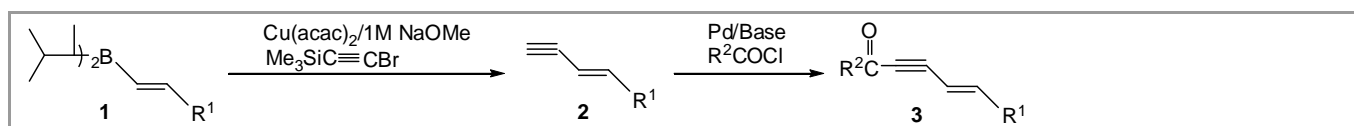
**Abstract:** (Trimethylsilyl)ethynyl bromide can be easily transformed into conjugated (*E*)-enynones, whose skeleton consists of consecutive carbonyl, ethynyl, and (*E*)-ethenyl units, via a one-pot multicomponent Suzuki-type reaction/Sonogashira reaction sequence. Thus, a three-component coupling of (trimethylsilyl)ethynyl bromide, (*E*)-alk-1-enyldisiamylborane and acid chloride is achieved in a two-step, one-pot procedure, in which (*E*)-alk-1-enyl group is installed as nucleophile in the sp carbon atom attached to bromine atom and acyl group is installed as electrophile in the other sp carbon atom.

**Key words:** (trimethylsilyl)ethynyl bromide, conjugated enynone, cross-coupling, alkenylborane, acid chloride

Conjugated enynones have found a wide range of applications as intermediates in the synthesis of natural products<sup>1</sup> and heterocycles<sup>2</sup>, as well as substrates in organic synthesis through organometallic compounds.<sup>3</sup> A great number of methods have been reported for their preparation, and the methodology can be divided into three categories: (1) the palladium and/or copper-catalyzed cross-coupling reaction of terminal alkynes with acid chlorides (Sonogashira reaction)<sup>4</sup>, (2) the cross-coupling reaction between alkynyl organometallic reagents and acid chlorides,<sup>5-15</sup> and (3) the palladium and/or copper-catalyzed carbonylative cross-coupling reaction of terminal alkynes with aryl halides (carbonylative Sonogashira reaction).<sup>16</sup> Each of them has a characteristic feature. The cross-coupling reaction using alkynyl organometallic reagents

can proceed well without employing any base which may give rise to undesired side reaction with acid chloride. Carbonylative Sonogashira coupling reaction can be performed even in protic solvent or ionic liquid. Thus it is possible to make a choice among many methods according to circumstances.

On the other hand, conjugated enynones, in which the sp carbon atom of conjugated enynone connects with an alkenyl carbon atom, also play key roles in the synthesis of natural products<sup>17</sup> and [2 + 2]-photocycloadducts.<sup>18</sup> However, the method for preparing such conjugated enynones is rare,<sup>19</sup> and there are no reports, to our knowledge, on synthesizing conjugated enynones with definite geometry. As part of our ongoing research aimed at assembling  $\pi$ -extended conjugation,<sup>20</sup> we herein report one-pot synthesis of conjugated (*E*)-enynones, (*E*)-1-arylalk-4-en-2-yn-1-ones **3**, under mild reaction conditions. Based on the copper-catalyzed cross-coupling reaction of (*E*)-alk-1-enyldisiamylboranes **1** with (trimethylsilyl)ethynyl bromide leading to the formation of terminal conjugated (*E*)-enynes **2** (Suzuki-type reaction),<sup>21</sup> we envisioned that the desired compounds **3** could be obtained by reaction of compounds **2** with acyl chlorides (Sonogashira reaction) in a two-step, one-pot manner as illustrated in Scheme 1. Therefore, the main challenge in this one-pot reaction was to investigate the reaction conditions for the Sonogashira reaction.



**Scheme 1** The proposed two-step, three-component coupling process

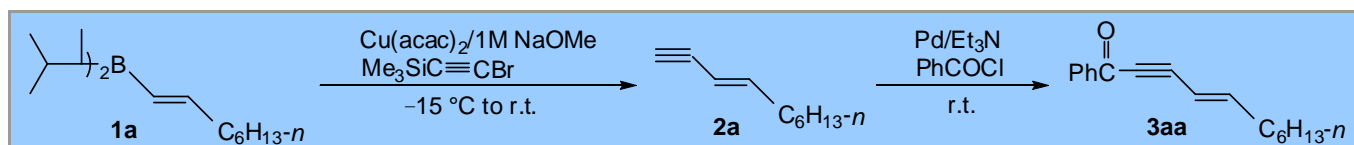
Optimization of the reaction conditions was explored using (*E*)-dec-3-en-1-yne (**2a**) and benzoyl chloride as model substrates. Thus, the cross-coupling reaction of (*E*)-oct-1-enyldisiamylborane (**1a**) (1 mmol) with (trimethylsilyl)ethynyl bromide (0.67 mmol) was carried out in the presence of Cu(acac)<sub>2</sub> (0.05 mmol) and 1 M NaOMe (0.75 mmol) at  $-15\text{ }^{\circ}\text{C}$  to room temperature overnight to generate compound **2a** (ca. 0.5 mmol).<sup>22</sup> After removal of methanol under reduced pressure, the reaction with benzoyl chloride (1 mmol)<sup>23</sup> was conducted in the presence of palladium source, ligand, and Et<sub>3</sub>N (1 mmol)<sup>24</sup> in anhydrous THF at room temperature for 2 h. Addition of CuI was unnecessary because Cu(acac)<sub>2</sub> had already been used for the cross-coupling reaction of **1a** with (trimethylsilyl)ethynyl bromide. The

results are summarized in Table 1. Use of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (2 mol% relative to compound **2a**) as a palladium source gave the desired product, (*E*)-1-phenylundec-4-en-2-yn-1-one (**3aa**), albeit in moderate yield (Table 1, entry 1). When Pd(PPh<sub>3</sub>)<sub>4</sub> (2 mol%) was used in place of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, the yield of product **3aa** improved considerably (Table 1, entry 2). Ligand-free palladium sources, such as PdCl<sub>2</sub>, Pd(OAc)<sub>2</sub>, and Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>, did not lead to any desired product at all (Table 1, entries 3-5). But, by contrast, palladium source in combination of PPh<sub>3</sub> (4 mol%) led to high yields of product **3aa** (Table 1, entries 6-8), indicating that phosphine ligand is crucial to the success of this coupling reaction. For our further studies, Pd(OAc)<sub>2</sub> is preferable to PdCl<sub>2</sub> and Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> in terms of the yield and cost.

Among phosphine ligands screened, PPh<sub>3</sub> proved to be the best ligand (Table 1, entry 8).<sup>25</sup> Reducing the load-

ing of Pd(OAc)<sub>2</sub>/PPh<sub>3</sub> showed a decreasing tendency in the yield of product **3aa** (Table 1, entry 11).

Table 1 Effect of Pd sources and ligands on the cross-coupling with benzoyl chloride<sup>a</sup>



Entry	Pd source	(mmol)	Ligand	(mmol)	Yield of <b>3aa</b> (%) <sup>b</sup>
1	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	0.01	—	—	47
2	Pd(PPh <sub>3</sub> ) <sub>4</sub>	0.01	—	—	70
3	PdCl <sub>2</sub>	0.01	—	—	0
4	Pd <sub>2</sub> (dba) <sub>3</sub> ·CHCl <sub>3</sub>	0.005	—	—	0
5	Pd(OAc) <sub>2</sub>	0.01	—	—	0
6	PdCl <sub>2</sub>	0.01	PPh <sub>3</sub>	0.02	80
7	Pd <sub>2</sub> (dba) <sub>3</sub> ·CHCl <sub>3</sub>	0.005	PPh <sub>3</sub>	0.02	86
8	Pd(OAc) <sub>2</sub>	0.01	PPh <sub>3</sub>	0.02	86
9	Pd(OAc) <sub>2</sub>	0.01	(2-furyl) <sub>3</sub> P	0.02	82
10	Pd(OAc) <sub>2</sub>	0.01	(4-MeOPh) <sub>3</sub> P	0.02	78
11	Pd(OAc) <sub>2</sub>	0.005	PPh <sub>3</sub>	0.01	84

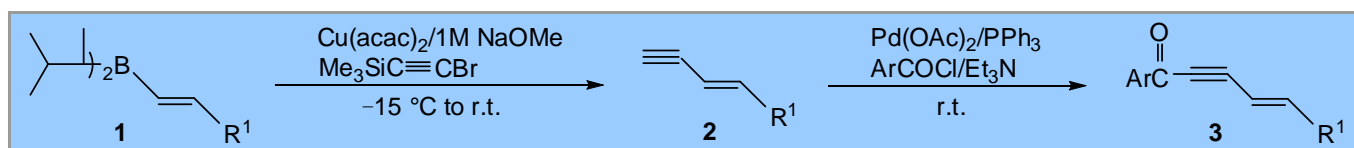
<sup>a</sup> Reagents and conditions: (1) **1a** (1 mmol), Me<sub>3</sub>SiC≡CBr (0.67 mmol), Cu(acac)<sub>2</sub> (0.05 mmol), 1M NaOMe (0.75 mmol), -15 °C to r.t., overnight; (2) C<sub>6</sub>H<sub>5</sub>COCl (1 mmol), Pd source, ligand, Et<sub>3</sub>N (1 mmol), r.t., 2 h.

<sup>b</sup> Isolated yields based on the amount of **2a** (0.5 mmol) formed.

Having established our optimized conditions for the sequential coupling reaction, we examined the scope of the one-pot synthesis of (*E*)-1-arylalk-4-en-2-yn-1-ones **3**. The results are shown in Table 2. Different types of compounds **2** underwent smooth cross-coupling with a variety of aryl chlorides to afford products **3** in good to high yields. This coupling reaction was successfully applied to compound **2** with a structurally and electronically diverse substituent (R<sup>1</sup>) (Table 2, entries 1-4). The cross-coupling reaction with various aryl chlorides was carried out using both (*E*)-dec-3-en-1-yne (**2a**) and (*E*)-

4-phenylbut-3-en-1-yne (**2b**). It is noteworthy that the use of compound **2b** provides  $\pi$ -conjugated molecules (Table 2, entries 2, 6, 8, 10, 12, 14, and 16). Electron-donating as well as electron-withdrawing aryl chloride could be used as coupling partners (Table 2, entries 5-10). Using condensed aryl chloride such as 2-naphthoyl chloride, the cross-coupling reaction could also proceed smoothly (Table 2, entries 11 and 12). In addition, heteroaryl chlorides such as 2-furoyl and 2-thiophenecarbonyl chlorides were good substrates for this coupling reaction (Table 2, entries 13-16).

Table 2 Synthesis of (*E*)-1-arylalk-4-en-2-yn-1-ones<sup>a</sup>



Entry	R <sup>1</sup>	Ar	Product	Yield <sup>b</sup> (%)
1	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	Ph	<b>3aa</b>	86
2	Ph	Ph	<b>3ba</b>	90
3	Cyclohex-1-enyl	Ph	<b>3ca</b>	92
4	Cl(CH <sub>2</sub> ) <sub>3</sub>	Ph	<b>3da</b>	88
5	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	2-Tol	<b>3ab</b>	90
6	Ph	2-Tol	<b>3bb</b>	85
7	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	4-Tol	<b>3ac</b>	79
8	Ph	4-Tol	<b>3bc</b>	77
9	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	4-ClC <sub>6</sub> H <sub>5</sub>	<b>3ad</b>	78
10	Ph	4-ClC <sub>6</sub> H <sub>5</sub>	<b>3bd</b>	82
11	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	2-naphthyl	<b>3ae</b>	87
12	Ph	2-naphthyl	<b>3be</b>	77
13	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	2-furyl	<b>3af</b>	76
14	Ph	2-furyl	<b>3bf</b>	86
15	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	2-thienyl	<b>3ag</b>	79
16	Ph	2-thienyl	<b>3bg</b>	79

<sup>a</sup> Reagents and conditions: (1) **1** (1 mmol), Me<sub>3</sub>SiC≡CBr (0.67 mmol), Cu(acac)<sub>2</sub> (0.05 mmol), 1M NaOMe (0.75 mmol), -15 °C to r.t., overnight; (2) ArCOCl (1 mmol), Pd(OAc)<sub>2</sub> (0.01 mmol), PPh<sub>3</sub> (0.02 mmol), Et<sub>3</sub>N (1 mmol), r.t., 2 h.

<sup>b</sup> Isolated yields based on the amount of **2** (0.5 mmol) formed.<sup>26</sup>

In summary, we have developed a two-step, one-pot, three-component synthesis of (*E*)-1-arylalk-4-en-2-yn-1-ones **3** using a Suzuki-type reaction/Sonogashira reaction sequence. This protocol is the first method for preparing compounds **3** in good to high yields. The extended scope of this transformation will be reported in due course.

## References and Notes

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- (22) Compound **2a** was formed in about 75% GC yield based on Me<sub>3</sub>SiC≡CBr employed; see ref. 21.
- (23) Considering that acid chloride would be consumed by reaction with residual both NaOMe and methanol, an excess amount of benzoyl chloride was employed in this one-pot reaction. Indeed, using a stoichiometric amount of benzoyl chloride (0.5 mmol), a decrease in the yield of product **3aa** was observed.
- (24) Among amine bases including *i*-Pr<sub>2</sub>NEt, Et<sub>3</sub>N was the base of choice for the cross-coupling reaction with benzoyl chloride.
- (25) To a solution of BH<sub>3</sub> (1 mmol) in THF (3 mL) was added 2-methylbut-2-ene (0.14 g, 2 mmol) dropwise at -15 °C under argon, and the mixture was stirred for 2 h at 0 °C to form a solution of disiamylborane in THF. To this solution was added oct-1-yne (0.11 g, 1 mmol) dropwise at -15 °C

and the mixture was stirred for 2 h at 0 °C. A solution of (*E*)-oct-1-enyldisiamylborane (**1a**) (1 mmol) in THF, thus prepared, was cooled to -15 °C, and Cu(acac)<sub>2</sub> (0.013 g, 0.05 mmol) was added to the solution under a flow of argon, followed by dropwise addition of (trimethylsilyl)ethynyl bromide (0.119 g, 0.67 mmol) and NaOMe (1M; 0.75 mL, 0.75 mmol). The resulting mixture was allowed to warm gradually to r.t. and stirred overnight. Methanol resulting from 1M NaOMe was removed under reduced pressure, accompanied by the solvent. After addition of THF (3 mL) to the residue under argon, the resulting mixture including (*E*)-dec-3-en-1-yne (**2a**) was cooled to 0 °C, and Pd(OAc)<sub>2</sub> (0.002 g, 0.01 mmol) and PPh<sub>3</sub> (0.005 g, 0.02 mmol) were added successively under a flow of argon, followed by dropwise addition of benzoyl chloride (0.141 g, 1 mmol) and Et<sub>3</sub>N (0.101 g, 1 mmol). The resultant mixture was stirred for 2 h at r.t. and then oxidized by the successive addition of 3M NaOH (1 mL) and 30% H<sub>2</sub>O<sub>2</sub> (0.5 mL) at 0 °C. After being stirred for 1 h at this temperature, the mixture was extracted three times with Et<sub>2</sub>O. The combined extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was purified by flash chromatography on silica gel, with hexane-CH<sub>2</sub>Cl<sub>2</sub> (1 : 1) as eluent, to give (*E*)-1-phenylundec-4-en-2-yn-1-one (**3aa**, 0.103 g, 86%). Compound **3aa**: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.89 (t, *J* = 7.1 Hz, 3H), 1.25–1.35 (m, 6H), 1.42–1.49 (m, 2H), 2.21–2.26 (m, 2H), 5.74 (dt, *J* = 16.1, 1.5 Hz, 1H), 6.63 (dt, *J* = 16.1, 7.1 Hz, 1H), 7.46–7.50 (m, 2H), 7.58–7.62 (m, 1H), 8.13–8.16 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 14.06 (CH<sub>3</sub>), 22.56 (CH<sub>2</sub>), 28.22 (CH<sub>2</sub>), 28.78 (CH<sub>2</sub>), 31.59 (CH<sub>2</sub>), 33.64 (CH<sub>2</sub>), 86.05 (≡C), 92.85 (≡C), 107.65 (=CH), 128.50 (2 × =CH), 129.50 (2 × =CH), 133.90 (=CH), 136.92 (=C), 153.10 (=CH), 178.11 (C=O); IR (neat): 2954, 2927, 2856, 2183, 1641, 1620, 1596, 1579, 1448, 1313, 1265, 1174, 956, 937, 700 cm<sup>-1</sup>; HRMS (EI): *m/z* calcd for C<sub>17</sub>H<sub>20</sub>O: 240.1514; found: 240.1508.

(26) Compounds **2b-d** were formed in 72–74% GC yields based on Me<sub>3</sub>SiC≡CBr employed; unpublished results.