



# Coupling of 3,8-Dibromo-1,10-Phenanthroline With 3,5-Diethynylheptyloxybenzene: A Suzuki/Miyaura Versus a Sonogashira Perspective

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# COUPLING OF 3,8-DIBROMO-1,10-PHENANTHROLINE WITH 3,5-DIETHYNYLHEPTYLOXYBENZENE: A SUZUKI/MIYAUURA VERSUS A SONOGASHIRA PERSPECTIVE

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## ABSTRACT

We report a new application of the Suzuki-Miyaura reaction whereas two bifunctional reactants, 3,8-dibromo-1,10-phenanthroline and 3,5-diethynylheptyloxybenzene (9), yield 3,8-bis(3-ethynyl-5-heptyloxyphenylethynyl)-1,10-phenanthroline (2) efficiently (74% yield) without polymerization. This was achieved by reacting a stoichiometric amount of 9 and  $(\text{Me}_3\text{Si})_2\text{NLi}$  to obtain quantitatively the monoacetylide anion of 9 (10). The latter was activated with B-methoxy-9-BBN and reacted in analogy to the alkynyl copper complex of a Sonogashira route. However, in the Sonogashira reaction, the alkynyl copper complex is present in small equilibrium concentrations and polymerization takes place even when reagents are mixed slowly. Actually the Sonogashira route gave no desired product 2, as the latter polymerizes easily via homo-coupling in the presence of air and Cu(I).

Sonogashira coupling involves the palladium(0) catalyzed reaction of terminal alkynes with vinyl or aryl halides in the presence of CuI or CuBr and an amine such as triethyl or diisopropyl amine.<sup>1</sup> Mechanistically, oxidative addition of the organic halide gives a Pd(II) intermediate, which undergoes transmetalation with the alkynyl copper (generated in small equilibrium quantities from the terminal alkyne, base, and copper iodide). Reductive elimination with coupling of the two organic ligands gives the product and regenerates the Pd(0) catalyst. For convenience, oftentimes the palladium catalyst is introduced as a stable, soluble Pd(II) derivative such as  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ . This complex is rapidly reduced by the terminal alkyne *in situ* to give the catalytic Pd(0) species. Due to the mild conditions usually employed (e.g. reaction at room temperature) and the use of inexpensive reagents, the Sonogashira coupling reaction has been a very convenient synthetic method for the preparation of aromatic alkynes.

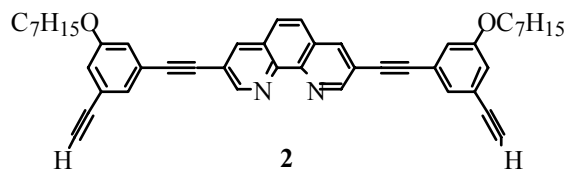
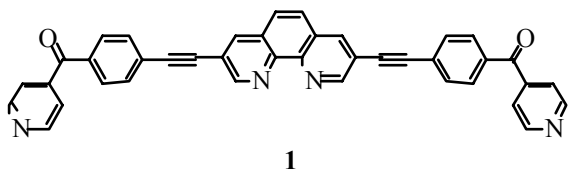
Despite its convenience, the Sonogashira reaction cannot be used for coupling of dialkynes with dibromoaromatic compounds. First, bifunctionality on both reactants generally leads to

polymerization. Furthermore, even though it might be considered that slow syringe-pump addition of the dialkyne might lead to the desirable product, unfortunately during work-up, the bisacetylenic product itself tends to undergo oxidative coupling in the presence of air and Cu(I), known as homocoupling,<sup>2</sup> leading again to polymerization.

In brief, the main causes of polymerization during the Sonogashira coupling reaction are: (a) the generation of only a small equilibrium amount of the alkynyl anion, and (b) the presence of catalytic amounts of copper (related to homocoupling). It seems that if the alkynyl anion could be generated quantitatively and activated by means other than copper, polymerization would be avoided.

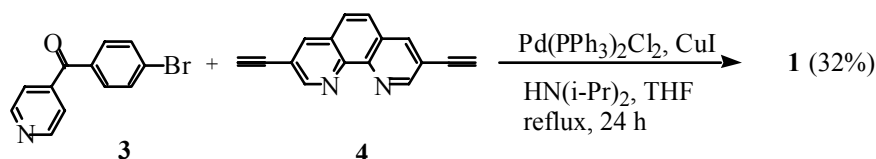
An alternative procedure that also leads to aryl alkynes is the Suzuki/Miyaura coupling reaction.<sup>3</sup> According to that procedure, the alkynyl anion is formed quantitatively by the reaction of a terminal alkyne with a stoichiometric amount of a strong base (e.g.,  $(\text{Me}_3\text{Si})_2\text{NLi}$ ). Subsequently, the alkynyl anion is activated via reaction with B-methoxy-9-borabicyclo[3.3.1]nonane (B-methoxy-9-BBN) to form a stable methoxy(alkynyl)borate complex, which subsequently reacts with an aryl bromide in the presence of Pd(0) to yield identical products with the corresponding Sonogashira coupling reaction that involves the same alkyne and aryl bromide starting materials. The Suzuki/Miyaura route uses harsher conditions (strong base) and a more expensive reagent (B-methoxy-9-BBN). However, it involves quantitative formation of the alkynyl anion and it does not use copper salts, so polymerization with bifunctional terminal halide and dibromoaromatic compounds should not be an issue.

These inferences were confirmed by comparing the synthesis of 3,8-bis(4-isonicotinoylphenylethynyl)-1,10-phenanthroline (1) with the synthesis of 3,8-bis(3-ethynyl-5-heptyloxyphenylethynyl)-1,10-phenanthroline (2). Compound 1 was designed as a ligand for intramolecular electron transfer quenching, while metal complexes of compound 2 were designed as building blocks of larger conjugated systems.



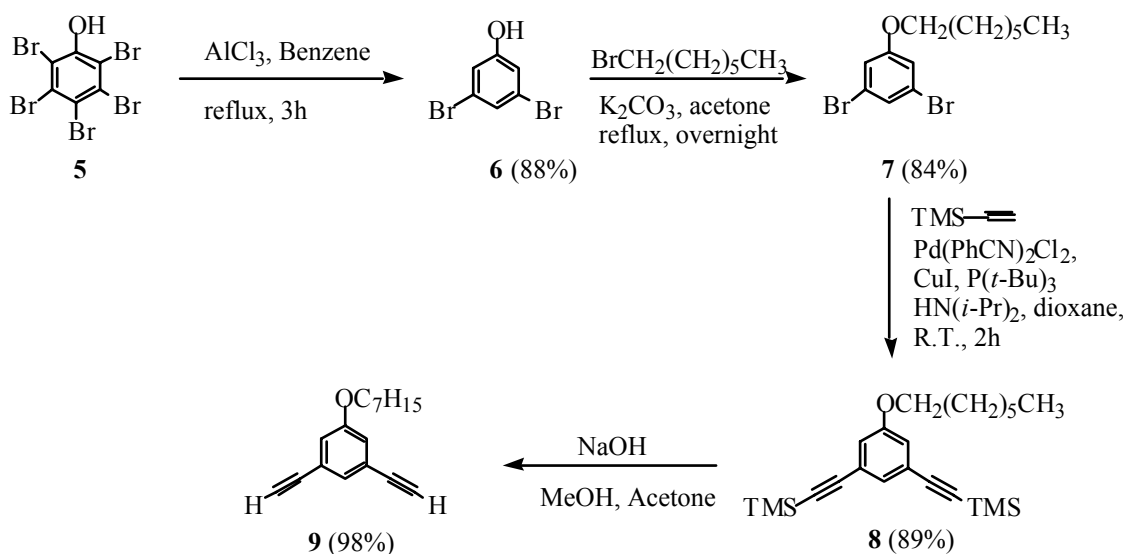
Sonogashira coupling of 4-(*p*-bromobenzoyl)pyridine (3) with 3,8-bisethynyl-1,10-phenanthroline (4, prepared also via Sonogashira coupling of TMS-protected acetylene and 3,8-dibromo-1,10-phenanthroline) proceeds uneventfully giving 1 in 32% yield (Scheme 1).<sup>4</sup> On the other hand, direct Sonogashira coupling of 3,8-dibromo-1,10-phenanthroline with 3,5-diethynylheptyloxybenzene (9) under the same conditions led to an intractable polymer.

### Scheme 1



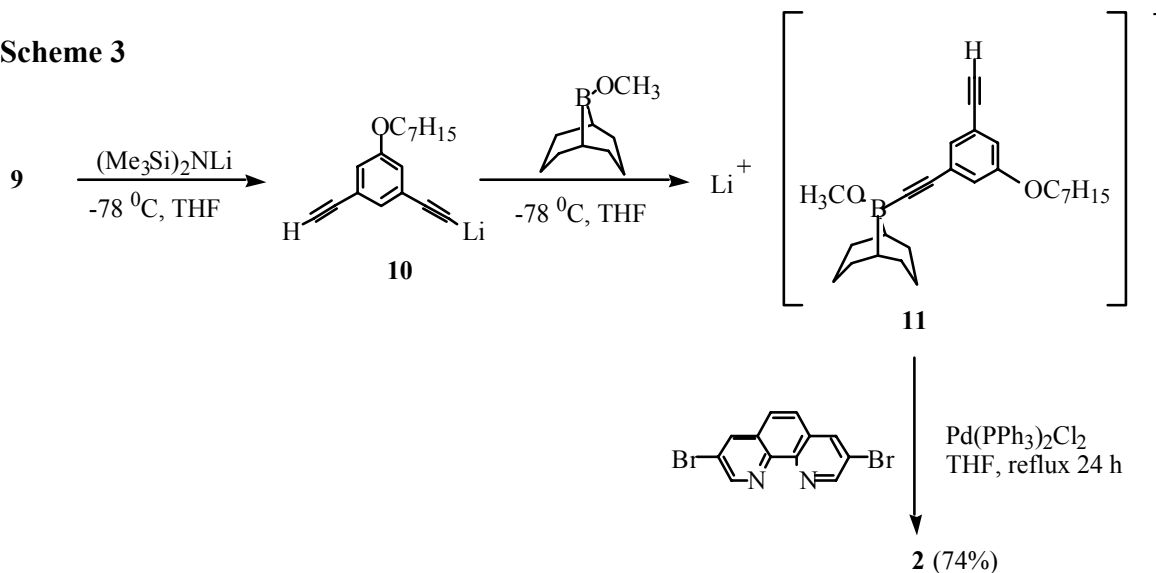
Compound 9 was synthesized according to Scheme 2. Pentabromophenol (5) was dehalogenated in benzene by  $\text{AlCl}_3$  to give 3,5-dibromophenol (6),<sup>6</sup> which then reacted with 1-bromoheptane to yield 3,5-dibromoheptyloxybenzene (7). A direct Sonogashira coupling of 7 with trimethylsilylacetylene catalyzed by  $\text{Pd}(\text{PhCN})_2\text{Cl}_2$  with  $\text{P}(t\text{-Bu})_3$  in the presence of  $\text{CuI}$  and diisopropylamine at room temperature gave compound 8, which was subsequently deprotected in the presence of  $\text{NaOH}$  in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  to give compound 9 in 65% overall yield from 5.

### Scheme 2



Of course, protection of one of the acetylenic groups of 9 could be a viable route for the synthesis of 2 via the Sonogashira reaction, however protection would introduce two more steps and would most certainly compromise the overall yield. Interestingly, both the first step of a possible protection route for the synthesis of 2, and the first step of the Suzuki/Miyaura route (Scheme 3) involve quantitative formation of the monoacetylide 10 by using a stoichiometric amount of a strong base. In the Suzuki/Miyaura route, 10 is activated with B-methoxy-9-BBN to form a stable methoxy(alkynyl)borate complex 11, which is then added to a solution of 3,8-dibromo-1,10-phenanthroline and a catalytic amount of  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  in THF. Intermediate 11 reacts in analogy to the alkynyl copper complex of the Sonogashira route yielding 2 in very good yield (74%).

**Scheme 3**



In conclusion, we have shown that coupling via the Suzuki/Miyaura route of two bifunctional reagents, namely 3,8-dibromophenanthroline and 3,5-diethynylheptyloxybenzene (**9**) gives compound **2** efficiently without polymerization.

## Experimental

**General.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian INOVA 400 NMR spectrometer and are reported as parts per million (ppm) from TMS ( $\delta$ ). Melting points were uncorrected. The Electrospray Mass Spectrometry (ESI) was conducted using a TSQ7000 (ThermoFinnigan) with an API2 source and the "performance pack" (wider aperture on the skimmer and extra turbo pump on the source). The electrospray source is equipped with a stainless steel needle; the voltage was 4.5kV. Sample solutions were injected using a 500 $\mu\text{L}$  Gastight syringe (Hamilton) in a Pump 11 syringe pump (Harvard Apparatus).

**Materials.** All starting materials, reagents and solvents were from Aldrich or Acros and used as received, unless noted otherwise.  $\text{P}(\text{t-Bu})_3$  was purchased from Strem Chemicals. For coupling reactions, all the solvents were anhydrous and were obtained directly from Aldrich or Acros.

3,8-Bis(4-isonicotinoylphenylethynyl)-1,10-phenanthroline (**1**). 4-bromobenzoylpyridine<sup>7</sup> (**3**, 0.68 g, 2.6 mmol), 3,8-diethynyl-1,10-phenanthroline<sup>8</sup> (**4**, 0.2 g, 0.88 mmol),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (60 mg, 0.085 mmol) and  $\text{CuI}$  (64 mg, 0.34 mmol) were added to anhydrous diisopropylamine (8 ml) and anhydrous DMF (40 ml) under nitrogen and the reaction mixture was refluxed for 24 h. After evaporation of the solvent under vacuum, the residue was diluted with  $\text{CH}_2\text{Cl}_2$ , washed with 5% aqueous KCN solution (3 x 20 ml), water (5 x 100 ml), and saturated aq. NaCl (100 ml). The organic phase was dried over anhydrous sodium sulfate, concentrated *in vacuo* followed by the addition of diethyl ether. The solid thus obtained was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{THF}$  to give the product (0.17 g, 32%). M.p.  $266\text{ }^\circ\text{C}$  (dec.);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 9.32 (d,  $J = 1.83\text{ Hz}$ , 2H), 8.85 (d,  $J = 5.68\text{ Hz}$ , 4H), 8.45 (d,  $J = 1.83\text{ Hz}$ , 2H), 7.89 (s, 2H), 7.86 (d,  $J = 5.49\text{ Hz}$ , 4H), 7.76



(d,  $J = 8.06$  Hz, 4H), 7.60 (d,  $J = 5.68$  Hz, 4H); MS (ESI+) 591.1816 ( $M+H$ )<sup>+</sup>, (theoretical ionic mass: 590.1743).

3,5-dibromophenol (6).<sup>6</sup> Aluminum chloride (2.67 g, 0.02 mol) was added to a solution of pentabromophenol (5, 5.0 g, 0.01 mol) in anhydrous benzene (20 ml) and the reaction mixture was heated to reflux for 3 h under nitrogen. After cooling to room temperature, the reaction mixture was poured into a mixture of HCl and ice water. The organic layer was separated and the water layer was extracted with diethyl ether (3 x 20 ml). The combined organic layers were extracted with 10% aqueous NaOH (3 x 20 ml). The combined aqueous layers were made strongly acidic with HCl. The product was then extracted with methylene chloride (3 x 20 ml) and the combined organic layers were washed with water until the aq. layer was neutral and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent *in vacuo*, gave the crude product which was recrystallized from hexane to give off-white needles (2.3 g, yield: 88%). Mp 81-82 °C (lit.<sup>6a</sup> mp 80 °C, lit.<sup>6b</sup> mp 76-79 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 4.85 (s, 1H), 6.95 (d,  $J = 1.65$  Hz, 2H), 7.25 (t,  $J = 1.65$  Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 156.4, 126.8, 123.1, 117.8.

3,5-dibromoheptyloxybenzene (7). A mixture of 3,5-dibromophenol (6, 5.0 g, 0.02 mol), potassium carbonate (2.76 g, 0.02 mol), and 1-bromoheptane (3.1 ml, 0.02 mol) in acetone (50 ml) was stirred at reflux overnight. After cooling to room temperature, water (50 ml) was added and the reaction mixture was extracted with diethyl ether (3 x 20 ml). The combined organic layers were washed first with aqueous 10% NaOH, followed by water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness under vacuum. The oil thus obtained was distilled under vacuum to give a colorless liquid (5.4 g, 84%); bp 145 °C / 0.5 torr; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 0.89 (t,  $J = 6.96$  Hz, 3H), 1.29-1.46 (m, 8H), 1.72-1.79 (m, 2H), 3.90 (t,  $J = 6.50$  Hz, 2H), 6.97 (d,  $J = 1.65$  Hz, 2H), 7.22 (t,  $J = 1.65$  Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 160.6, 126.3, 123.3, 117.1, 68.8, 32.1, 29.3, 26.2, 22.9, 14.4.

3,5-bis(trimethylsilylethynyl)heptyloxybenzene (8). Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> (46 mg, 0.12 mmol) and CuI (15.2 mg, 0.08 mmol) were added to a dry, septum-capped round bottom flask, purged with nitrogen. Anhydrous dioxane (2 ml), P(*t*-Bu)<sub>3</sub> (0.5 ml, 0.25 M solution in dioxane), HN(*i*-Pr)<sub>2</sub> (0.68 ml, 4.8 mmol), 7 (0.7 g, 2 mmol) in 0.5 ml dioxane were then added via syringe to the stirred reaction mixture. Finally, trimethylsilylacetylene (0.66 ml, 4.6 mmol) was added to the flask. In a few minutes, a precipitate was formed. After stirring the reaction mixture at room temperature for 2 h, the solvent was evaporated to dryness and the crude product was purified on a silica gel column using 2% CH<sub>2</sub>Cl<sub>2</sub> in hexane as eluent. The product was further purified by recrystallization from methanol to give a yellow solid (0.68 g, yield 89%). Mp 47 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 7.16 (t,  $J = 1.47$  Hz, 1H), 6.94 (d,  $J = 1.28$  Hz, 2H), 3.91 (t,  $J = 6.50$  Hz, 2H), 1.71-1.79 (m, 2H), 1.28-1.46 (m, 8H), 0.89 (t,  $J = 5.78$  Hz, 3H), 0.22 (s, 18H).

3,5-Bis(ethynyl)heptyloxybenzene (9). 8 (3.35 g, 8.7 mmol), acetone (30 ml), methanol (60 ml), and NaOH (0.12 g, 3 mmol) were mixed together and stir at room temperature for 2 h. Water (100 ml) was then added, followed by extraction with diethyl ether (3 x 50 ml). The combined ether extracts were washed with water until the aqueous layer was neutral, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness *in vacuo* to give a yellow solid (2.05 g, 98%). Mp 32 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 7.20 (t,  $J = 1.28$  Hz, 1H), 6.99 (d,  $J = 1.28$  Hz, 2H), 3.93 (t,  $J = 6.59$  Hz, 2H), 3.05 (s, 2H), 1.72-1.80 (m, 2H), 1.28-1.46 (m, 8H), 0.89 (t,  $J = 6.95$  Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 158.6, 128.0, 123.2, 118.8, 82.6, 77.5, 68.2, 31.7, 29.1, 29.0, 25.9, 22.6, 14.1; MS (ESI+) 241.1587 ( $M+H$ )<sup>+</sup>, (theoretical ionic mass: 240.1514).

3,8-bis(3-ethynyl-5-heptyloxyphenylethynyl)-1,10-phenanthroline (2). Lithium bis(trimethylsilyl)amide (2.25 mmol, 2.25 ml of 1 M solution in THF) was added under nitrogen to

a well stirred solution of 9 (0.86 g, 2.25 mmol) in anhydrous THF (10 ml) at  $-78^{\circ}\text{C}$ . After 30 min, B-methoxy-9-BBN (2.25 mmol, 2.25 ml of 1M solution in hexane) was added to the reaction mixture via a septum with a syringe. After stirring for 2 h at  $-78^{\circ}\text{C}$ , the solution was transferred via a cannula to a second flask containing  $\text{Pd}(\text{PPh}_3)_4$  (60 mg, 0.052 mmol) and 3,8-dibromo-1,10-phenanthroline (0.25 g, 0.75 mmol) in dry THF (30 ml) under nitrogen. The reaction mixture was then heated to reflux for 24 h and cooled to room temperature. Methylene chloride (50 ml) was added and the organic layer was washed with water ( $20 \times 100$  ml) dried with anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated to dryness. The crude product thus obtained was purified on silica gel column. Initial elution with  $\text{CH}_2\text{Cl}_2$  gave unreacted starting material. Subsequent elution with diethyl ether gave the product. After removal of the solvent *in vacuo* a light yellow solid was obtained (0.36 g, 74 %). Mp  $85\text{--}86^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 9.25 (d,  $J = 2.01$  Hz, 2H), 8.34 (d,  $J = 2.01$  Hz, 2H), 7.78 (s, 2H), 7.33 (t,  $J = 1.28$  Hz, 2H), 7.12 (t,  $J = 1.46$  Hz, 2H), 7.05 (t,  $J = 1.28$  Hz, 2H), 3.98 (t,  $J = 6.5$  Hz, 4H), 3.10 (s, 2H), 1.78–1.82 (m, 4H), 1.48 (m, 8H), 1.28–1.46 (m, 8H), 0.91 (t,  $J = 6.87$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) 158.6, 152.1, 144.2, 137.9, 127.8, 127.5, 126.7, 123.4, 123.3, 119.2, 118.9, 118.0, 92.9, 86.4, 82.5, 77.6, 68.2, 31.7, 29.0, 28.9, 25.8, 22.5, 14.0; MS (ESI+) 657.3476 (M+H) $^+$  (theoretical ionic mass: 656.3403).

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4. According to the literature, direct Sonogashira couplings on 3,8-dibromo-1,10-phenanthroline are complicated by complexation of the Cu(I) catalyst with the phenanthroline's nitrogens.<sup>5a</sup> In that respect, Sonogashira coupling of Ru(II)-coordinated 3,8-dibromo-1,10-phenanthroline works exceptionally well.<sup>5b</sup>
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13. ABSTRACT (Maximum 200 words)  We report a new application of the Suzuki-Miyaura reaction whereas two bifunctional reactants, 3,8-dibromo-1,10-phenanthroline and 3,5-diethynylheptyloxybenzene ( <b>9</b> ), yield 3,8-bis(3-ethynyl-5-heptyloxyphenylethynyl)-1,10-phenanthroline ( <b>2</b> ) efficiently (74 percent yield) without polymerization. This was achieved by reacting a stoichiometric amount of <b>9</b> and (Me <sub>3</sub> Si) <sub>2</sub> NLi to obtain quantitatively the monoacetylide anion of <b>9</b> ( <b>10</b> ). The latter was activated with B-methoxy-9-BBN and reacted in analogy to the alkynyl copper complex of a Sonogashira route. However, in the Sonogashira reaction, the alkynyl copper complex is present in small equilibrium concentrations and polymerization takes place even when reagents are mixed slowly. Actually the Sonogashira route gave no desired product <b>2</b> , as the latter polymerizes easily via homo-coupling in the presence of air and Cu(I).				
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