

# Synthesis of symmetric and unsymmetric 1,4-bis(*p*-R-phenylethynyl)benzenes via palladium/copper catalyzed cross-coupling and comments on the coupling of aryl halides with terminal alkynes

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(Received January 5, 1994)

## Abstract

A series of symmetric 1,4-bis(*p*-R-phenylethynyl)benzenes (**6a–h**) have been prepared via Pd<sup>II</sup>/Cu<sup>I</sup> catalyzed cross-coupling of 1,4-diiodobenzene (**5**) and *p*-substituted phenylethyne (**4a–h**). Similarly, the unsymmetric analogues (**9a–c**) were obtained from 1-iodo-4-(*p*-nitrophenylethynyl)benzene (**8**) and *p*-substituted phenylethyne (**4c**, **4d**, **4g**). Quantitative analysis of 1,4-(trimethylsilyl)butadiyne (**10**), produced in the catalytic coupling of ethynyltrimethylsilane with aryl halides using PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>/CuI in an amine solvent, confirmed that catalyst initiation proceeds via reduction of Pd<sup>II</sup> to Pd<sup>0</sup> with concomitant oxidative homo-coupling of two ethynyltrimethylsilane molecules producing exactly one equivalent of **10** based on Pd<sup>II</sup>. If air is present, the PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>/CuI/amine mixture provides a very effective system for catalytic oxidative homo-coupling of terminal alkynes to diynes and thus air must be rigorously excluded from the cross-coupling reactions. Hydrodehalogenation can compete effectively with the cross-coupling reaction for highly fluorinated aryl halides. Under certain conditions, the fluorinated aryl bromide or iodide can serve as the oxidant for the alkyne to diyne oxidative homo-coupling reaction. This can be avoided by appropriate choice of reaction conditions and reagents. These competing pathways have significant implications for the cross-coupling of aryl halides with terminal alkynes and are discussed herein.

**Key words:** Cross-coupling reaction; Aryl halide; Alkyne; Palladium complexes; Copper complexes; Non-linear optics; Liquid crystal; Hydrodehalogenation

## Introduction

During the last decade, the palladium/copper catalyzed cross-coupling of terminal alkynes with aryl halides has become one of the most powerful synthetic methods to prepare ethynylarenes [1, 2] and their derivatives [3]. This method has also been used in the syntheses of pharmaceutical [4] and other biologically active agents [5]. Recently, a series of cross-coupling reactions has been performed in aqueous media, a methodology with significant implications for biological systems [6]. There are extensive applications of this coupling reaction in the preparation of functional organics and polymers in order to meet the challenge for a new generation of materials [7].

Part of our efforts have been focussed on the preparation of highly  $\pi$ -conjugated organic and organo-metallic complexes with interesting physical and non-linear optical properties [8]. Recently, we have extended

this coupling methodology to prepare a variety of long-chain alkynylarenes which were used in subsequent reactions to obtain Pt-containing acetylide polymers [9]. In conjunction with the organic analogues i.e. poly(phenyleneethynylene)s (PPE), these materials are of significant current interest due to their unique properties including heat stability [10], one-dimensional electron conductivity [11], third-order non-linear optical properties [12], as well as liquid crystal behaviour [7d, 13]. To probe the complexity of liquid crystal and non-linear optical behaviours of the polymers, a thorough understanding at the molecular level is crucial. Experimental [7b,c, 14a,b] as well as theoretical [14c] studies on second-order non-linear optical properties of various tolans have been conducted recently to correlate structure–properties relationships. Likewise, several theoretical models have been put forth to describe the nematic behaviour of rod-like molecules [15], but their applicabilities have been limited due to the lack of truly linear compounds.

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In this work, we report a convenient route to a series of linear symmetric 1,4-bis(*p*-R-phenylethynyl)benzenes (R = H (**6a**) [7d], Me (**6b**), OMe (**6c**), SMe (**6d**), CN (**6e**), NO<sub>2</sub> (**6f**), NMe<sub>2</sub> (**6g**), CF<sub>3</sub> (**6h**) and their unsymmetric analogues via Pd/Cu catalyzed coupling of 1,4-diiodobenzene (**5**) and *p*-R-phenylethyne (**4a–h**). We have also synthesized 1,4-bis(4-pyridylethynyl)benzene via coupling of **5** and 4-ethynylpyridine. More importantly, we have carried out a number of control experiments to investigate the catalyst initiation process, the Pd-assisted homo-coupling of terminal alkynes, and the competing hydrodehalogenation of highly fluorinated aryl halides. Taken together, these results have significant implications for the cross-coupling reactions of aryl halides and terminal alkynes.

## Results and discussion

### Synthesis

Both electron-donating and accepting *para*-substituted phenylethyne (**4a–f**) were prepared via coupling of *p*-R-C<sub>6</sub>H<sub>4</sub>-I (**1a–h**) and 2-methyl-3-butyn-2-ol (**2**) in the presence of catalytic amounts of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and CuI in an amine solvent, followed by treatment of **3a–f** with NaOH in refluxing toluene. A typical procedure for the coupling reaction is illustrated in Scheme 1. All attempts to deprotect **3g** and **3h** resulted in decomposition of the desired products. Compounds **4g** and **4h** were obtained in a similar fashion using ethynyltrimethylsilane instead of **2**, as the trimethylsilyl protecting group can be removed readily under much milder conditions (NaOH/methanol/room temperature).

In subsequent reactions, 1,4-diiodobenzene (**5**) was allowed to couple with **4a–h** to afford a series of symmetric 1,4-bis(*p*-R-phenylethynyl)benzenes (R = H (**6a**), Me (**6b**), OMe (**6c**), SMe (**6d**), CN (**6e**), NMe<sub>2</sub> (**6g**), CF<sub>3</sub> (**6h**)) (Scheme 2). Similarly, the pyridyl derivative **7** was obtained from the coupling reaction of 4-ethynylpyridine and **5** (Scheme 3).

All reactions were carried out at room temperature followed by a brief period at reflux, and 1,4-diiodobenzene was chosen because of its higher reactivity than 1,4-dibromobenzene. Such mild coupling condi-

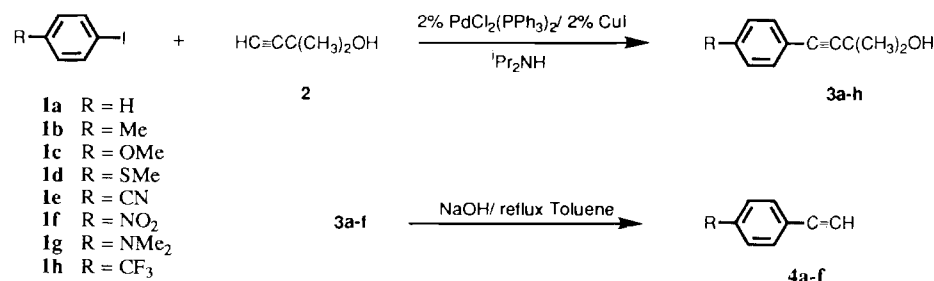
tions are highly desirable as terminal alkynes tend to undergo decomposition at high temperature. The unsymmetric derivatives (**9a–c**), on the other hand, were prepared in a controlled stepwise manner via the intermediate 1-iodo-4-(*p*-nitrophenylethynyl)benzene (**8**) (Schemes 4 and 5).

### UV-Vis studies

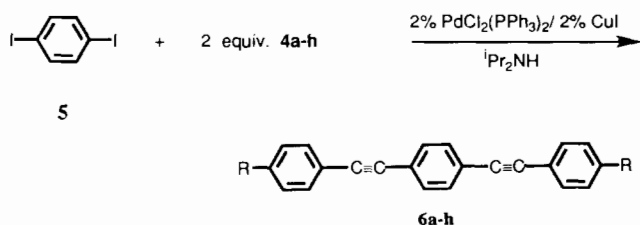
Compounds **6a–h** and **9a–c** have strong absorptions in the near UV (322–390 nm) and emission in the near UV-Vis (340–523 nm, purple to yellow) regions. Absorption and emission spectroscopic data for the symmetric and the unsymmetric bis(phenylethynyl)benzenes are summarized in Tables 1 and 2, respectively. For the symmetric compounds, it is apparent that both electron-donating and electron-withdrawing groups in the *para* position affect the absorption, as well as the emission bathochromically. The same effect was also observed for the styrylstilbenes and distyrylanthracenes [16]. Essentially, linear relationships were established between the longest wavelengths ( $\lambda_{\text{max}}$ ) and the Hammett constants ( $\sigma_p$ ) for both absorption and emission data as shown in Fig. 1 for the former case. Similarly, the effect of the substituents on the optical properties was also observed for the unsymmetric compounds, with the largest shift being for the NMe<sub>2</sub> derivative.

### Catalyst initiation and homo-coupling processes

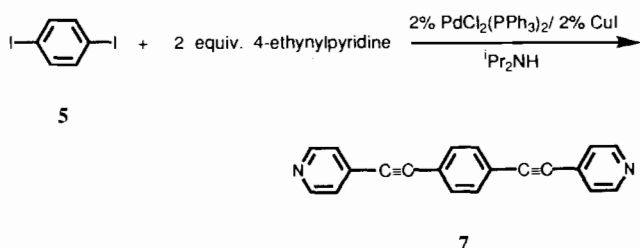
A generally accepted mechanism for the cross-coupling reaction was proposed initially by Hagihara and co-workers [17] (Scheme 6), in which PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> is the catalyst precursor. The whole process can be divided into two parts: (i) catalyst initiation; (ii) the catalytic cycle. Small amounts of diyne observed in the reaction might be the by-product resulting from the initial formation of bis(triphenylphosphine)bis(trimethylsilyl-ethynyl)palladium(II) when PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> reacts with an alkynyl copper ate complex in the presence of a base. Reductive elimination of bis(trimethylsilyl)butadiyne (**10**) would give 'Pd(PPh<sub>3</sub>)<sub>2</sub>'. Thus, reduction of Pd<sup>II</sup> to Pd<sup>0</sup> is accomplished via the oxidative coupling of two equivalents of Me<sub>3</sub>SiC≡CH. 'Pd(PPh<sub>3</sub>)<sub>2</sub>' undergoes oxidative addition of aryl halide to form Pd(PPh<sub>3</sub>)<sub>2</sub>(Ar)(X), *trans*-metallation gives Pd(PPh<sub>3</sub>)<sub>2</sub>-



Scheme 1.



Scheme 2.



Scheme 3.

(Ar)(C≡CR), followed by reductive elimination giving ethynylarenes and regenerating 'Pd(PPh<sub>3</sub>)<sub>2</sub>'. We put 'Pd(PPh<sub>3</sub>)<sub>2</sub>' in quotes, as the exact nature of this species is still not clear. Several reports [18] indicate that halide anions remain associated with the (PPh<sub>3</sub>)<sub>2</sub>Pd<sup>0</sup> centre.

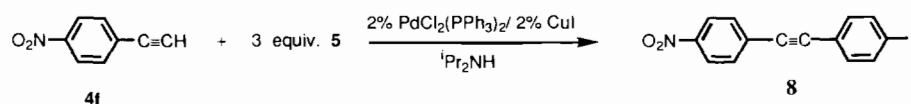
Although the formation of the diene in the coupling reactions has been reported by several research groups [2, 5c, 17], accurate quantitative confirmation of its amount has not been reported. Claims from different groups on the amount of diene appearing in the coupling reaction (ranging from 1 to more than 4 equiv.) are rather confusing [2i,j, 5c, 17]. Adventitious oxygen may be responsible for some spurious results as terminal alkynes undergo facile catalytic oxidative homo-coupling in the presence of copper and oxygen (*vide infra*). In order to examine the reduction process leading to the formation of the Pd<sup>0</sup> catalytic species, we designed a series of control experiments, which are depicted in Scheme 7. The quantitative experiments were carried out via careful GC analysis using internal standards. Products were confirmed by GC-MS analysis.

In exp. i, compound **10** was not formed when a catalytic amount of CuI (0.02 mmol) was added to an Et<sub>2</sub>NH solution (8 ml) of HC≡CSiMe<sub>3</sub> (1.0 mmol) under a high purity nitrogen atmosphere. Exp. ii was conducted under the same conditions as exp. i, except that 0.01 mmol of Pd(PPh<sub>3</sub>)<sub>4</sub> was added. In this case, only a trace amount of **10** (<10<sup>-4</sup> mmol) was observed

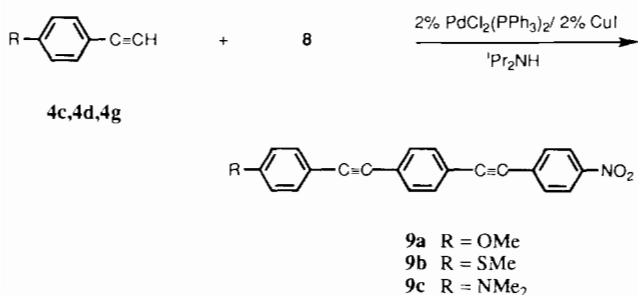
when the reaction was monitored over a period of 24 h. Repeating this experiment with 10 times as much Pd(PPh<sub>3</sub>)<sub>4</sub> gave the same result. In exp. iii, 0.02 mmol of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, and 0.02 mmol of CuI in 8 ml of Et<sub>2</sub>NH under N<sub>2</sub> produced 0.02 mmol of **10** within 5 min. The second trial was run with 0.01 mmol of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and exactly 0.10 mmol of the diyne was observed within 10 min. The colour of the solution changed from colourless to yellow, to yellow-brown and finally to dark brown. Aliquots taken from the above two experiments between 10 min and 24 h contained identical amounts of **10**, i.e. exactly 1.00 ± 0.03 equiv. based on PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. It was found that once **10** was formed in exp. iii, its amount did not change upon addition of aryl halides. Thus, when 1 mmol of 4-NCC<sub>6</sub>H<sub>4</sub>Br was added to the second trial, the diyne concentration remained at the original level for 12 h while [4-NCC<sub>6</sub>H<sub>4</sub>Br] decreased and [4-NCC<sub>6</sub>H<sub>4</sub>C≡C-SiMe<sub>3</sub>] increased, as monitored by GC. No other significant products were observed. In exp. iv, an Et<sub>2</sub>NH solution of 1.0 mmol of HC≡CSiMe<sub>3</sub> with 0.02 mmol of CuI present was exposed to air for 2 min and then recapped (maximum amount of oxygen in the system was *c.* 0.2–0.3 mmol). After 1 h, 0.044 mmol of **10** was observed, and after 4 h, the amount of **10** increased to 0.15 mmol (yield 30% based on HC≡CSiMe<sub>3</sub>). In exp. v, the same conditions as in exp. iv were employed, but with 0.05 mmol of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> added; 0.28 mmol (yield 56% based on HC≡CSiMe<sub>3</sub>) of **10** was formed within 2 h. Similar results were obtained for phenylacetylene in diisopropylamine, although the coupling proceeded much slower. Again, a significant enhancement in the 'Cu-promoted' oxidative coupling was observed upon addition of a catalytic amount of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> to the reaction. Oxidative coupling of ethynyl compounds in the presence of Cu<sup>I</sup>, O<sub>2</sub> and nitrogen donor ligands is well known [19]. However, the CuI/R<sub>2</sub>NH system is not very effective. The above results demonstrate that Pd can assist Cu in the oxidative homo-coupling of alkynes in the presence of O<sub>2</sub>. Thus, as the PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>/CuI/R<sub>2</sub>NH system is a rather efficient one for oxidative homo-coupling of terminal alkynes, care must be taken to avoid oxygen when carrying out cross-couplings involving terminal alkynes.

#### Hydrodehalogenation

We were intrigued with the report by Neenan and Whitesides [2f] on the Pd-catalyzed cross-coupling of



Scheme 4.



Scheme 5.

TABLE 1. Absorption and emission data for *p*-R-C<sub>6</sub>H<sub>4</sub>-C≡C-C<sub>6</sub>H<sub>4</sub>-C≡C-C<sub>6</sub>H<sub>4</sub>-*p*-R (**6a-h**)

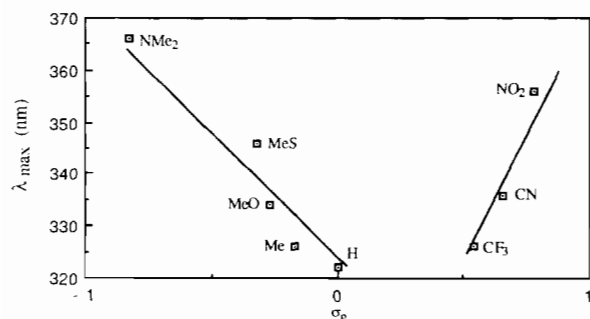
R	Absorption <sup>a</sup> λ (nm) (log ε)	Emission <sup>a</sup> λ (nm) (λ <sub>excitation</sub> (nm))
H ( <b>6a</b> )	322 (4.79), 342 (4.56)	351, 365 (322)
Me ( <b>6b</b> )	326 (4.77), 348 (4.52)	354, 369 (326)
MeO ( <b>6c</b> )	334 (4.77), 354 (4.56)	365, 380 (334)
MeS ( <b>6d</b> )	346 (4.84), 366 (4.64)	382, 399 (346)
CN ( <b>6e</b> )	336 (4.75), 358 (4.56)	364, 385 (336)
NO <sub>2</sub> ( <b>6f</b> )	356 (4.63), 380 (4.48)	406, 426 (356)
NMe <sub>2</sub> ( <b>6g</b> )	366 (4.76), 390 (4.60)	410, 430 (366)
CF <sub>3</sub> ( <b>6h</b> )	326 (4.76), 346 (4.54)	356, 370 (326)

<sup>a</sup>Absorption and emission spectra were recorded in toluene.

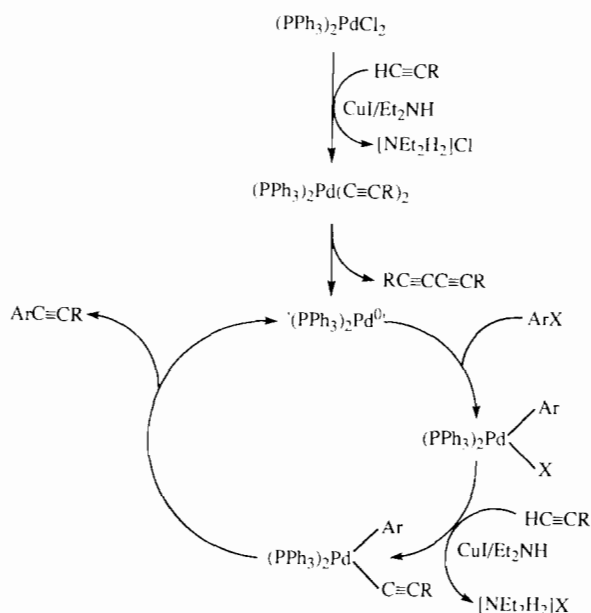
TABLE 2. Absorption and emission data for *p*-O<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-C≡C-C<sub>6</sub>H<sub>4</sub>-C≡C-C<sub>6</sub>H<sub>4</sub>-*p*-R (**9a-c**)

R	Absorption <sup>a</sup> λ (nm) (log ε)	Emission <sup>a</sup> λ (nm) (λ <sub>excitation</sub> (nm))
MeO ( <b>9a</b> )	294 (4.51), 356 (4.57)	364, 398 (356)
MeS ( <b>9b</b> )	294 (4.53), 356 (4.62)	382, 408 (356)
NMe <sub>2</sub> ( <b>9c</b> )	320 (4.45), 382 (4.42)	523 (382)

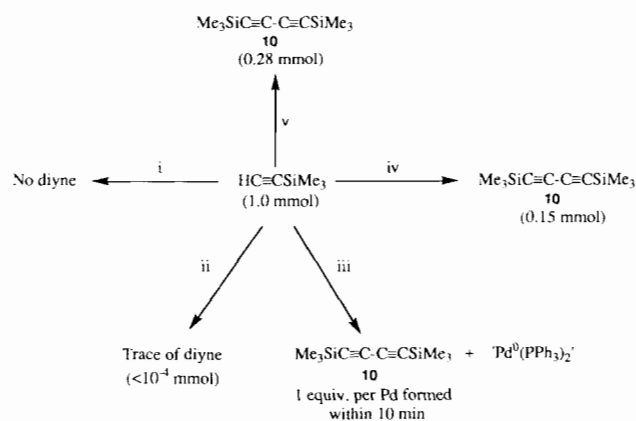
<sup>a</sup>Absorption and emission spectra were recorded in toluene.

Fig. 1. Correlation between λ<sub>max</sub> (absorption) and Hammett constants (σ<sub>p</sub>).

various aryl halides and ethynyltrimethylsilane. Although the reported isolated yields were very good for most of the aryl halides, the yield using bromopentafluorobenzene was remarkably low (20%). It appeared to us that there might be a competing process



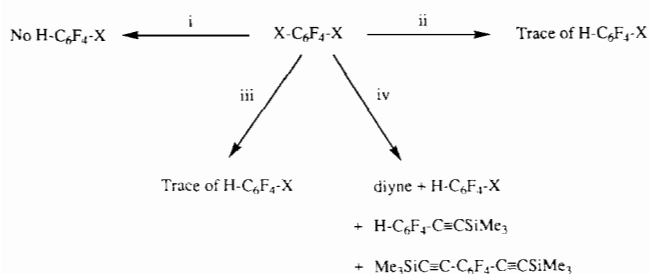
Scheme 6.



Scheme 7.

i: 0.02 mmol CuI, 8 ml Et<sub>2</sub>NH, N<sub>2</sub>; ii: 0.01 or 0.10 mmol Pd(PPh<sub>3</sub>)<sub>4</sub>, 0.02 mmol CuI, 8 ml Et<sub>2</sub>NH, N<sub>2</sub>; iii: 0.02 or 0.10 mmol PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 0.02 mmol CuI, 8 ml Et<sub>2</sub>NH, N<sub>2</sub>, 24 h; iv: 0.02 mmol CuI, 8 ml Et<sub>2</sub>NH, exposed to air for 2 min, 4 h; v: 0.05 or 0.10 mmol PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 0.02 mmol CuI, 8 ml Et<sub>2</sub>NH, exposed to air for 2 min, N<sub>2</sub>, 2 h.

in the coupling reaction leading to a low yield in this case. Indeed, a search in the literature revealed that aryl halides have been used effectively as oxidizing agents in the oxidation of primary and secondary alcohols to aldehydes and ketones respectively [20]. These transformations were carried out in the presence of base and are catalyzed by Pd [20] or Ru [21] catalysts. It seemed quite possible that a similar process was occurring in the cross-coupling reactions involving a rather highly activated fluorinated aryl halide and a potential hydrogen-donor terminal alkyne. In order to investigate this process in detail, we conducted the series of control experiments shown in Scheme 8.



$\text{X-C}_6\text{F}_4\text{-X}$ ;  $\text{X}=\text{I, Br, Cl}$

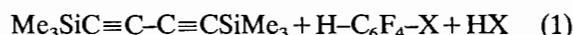
Scheme 8.

i:  $\text{Et}_2\text{NH}$ ; ii:  $\text{Et}_2\text{NH}$ , 5%  $\text{CuI}$ ; iii:  $\text{Et}_2\text{NH}$ , 5%  $\text{PdCl}_2(\text{PPh}_3)_2$ ; iv:  $\text{Et}_2\text{NH}$ , 2.2 equiv.  $\text{HC}\equiv\text{CSiMe}_3$ , 5%  $\text{PdCl}_2(\text{PPh}_3)_2$ , 5%  $\text{CuI}$ .

All experiments were performed under a high purity nitrogen atmosphere, at room temperature for a period of 5 days. In exp. i, a 0.15 M solution of  $\text{X-C}_6\text{F}_4\text{-X}$  ( $\text{X}=\text{I, Br, Cl}$ ) in  $\text{Et}_2\text{NH}$  remained unchanged. Exp. ii was conducted under the same conditions as exp. i, except that 5 mol%  $\text{CuI}$  was added. In this case, only a trace amount of  $\text{H-C}_6\text{F}_4\text{-X}$  was detected for  $\text{X}=\text{Br}$  by GC-MS analysis. However, in exp. iii, in the presence of 5 mol%  $\text{PdCl}_2(\text{PPh}_3)_2$ , trace amounts of  $\text{H-C}_6\text{F}_4\text{-X}$  were observed for both  $\text{X}=\text{Br}$  and  $\text{I}$ . For  $\text{X}=\text{Cl}$ , no exchange of halide was detected in any case. In exp. iv, when 2.2 equiv. of  $\text{HC}\equiv\text{CSiMe}_3$  were added to the  $\text{Et}_2\text{NH}$  solution of  $\text{X-C}_6\text{F}_4\text{-X}$  ( $\text{X}=\text{Br, I}$ ) along with 5 mol% of both  $\text{CuI}$  and  $\text{PdCl}_2(\text{PPh}_3)_2$ , several products were observed arising from the cross-coupling and the hydrodehalogenation processes. The reactions were monitored at approximately 3 h intervals. It was established that the amount of  $\text{H-C}_6\text{F}_4\text{-X}$  increases concomitant with the formation of diyne **10**. The reaction was essentially complete after 2 days at room temperature for the iodo derivative, while only 98% conversion was achieved for the bromo analogue after 8 days. The final product mixture was analyzed by GC-MS and found to contain  $\text{H-C}_6\text{F}_4\text{-I}$ ,  $\text{HC}_6\text{F}_4\text{C}\equiv\text{CSiMe}_3$ ,  $\text{Me}_3\text{SiC}\equiv\text{C-C}_6\text{F}_4\text{-C}\equiv\text{CSiMe}_3$  and **10**. On the other hand, only  $\text{H-C}_6\text{F}_4\text{-Br}$  and **10** were detected for the bromo case. These findings suggest strongly that the hydrodehalogenation process competes effectively with the cross-coupling pathway in these reactions, particularly for the fluorinated aryl bromide where only hydrodebromination is operable. If, however, the reaction was carried out at reflux conditions, up to 97% of the cross-coupled product ( $\text{Me}_3\text{SiC}\equiv\text{C-C}_6\text{F}_4\text{-C}\equiv\text{CSiMe}_3$ ) was obtained in either case.

We have also investigated the reactivity of the monohalide analogues, i.e. bromopentafluorobenzene ( $\text{C}_6\text{F}_5\text{Br}$ ) and iodopentafluorobenzene ( $\text{C}_6\text{F}_5\text{I}$ ) in less detail. The reaction of  $\text{C}_6\text{F}_5\text{I}$  and  $\text{HC}\equiv\text{CSiMe}_3$  was complete in less than 7 h at room temperature, whereas reaction with the bromo derivative was incomplete after 24 h. Analysis via GC-MS showed the coupled products

$\text{C}_6\text{F}_5\text{-C}\equiv\text{CSiMe}_3$  and **10** for both cases. The amount of the homo-coupled product **10** was consistently more than twice that of the cross-coupled product ( $\text{C}_6\text{F}_5\text{C}\equiv\text{CSiMe}_3$ ). Thus, hydrodehalogenation is clearly the predominant process for the pentafluorinated aryl halides at room temperature. Based on the above findings, a stoichiometric equation (eqn. (1)) can be written in which aryl halide (an oxidant) oxidizes terminal alkyne to diyne in the presence of a Pd/Cu catalyst system.



## Conclusions

We have demonstrated the utility of the Pd-catalyzed cross-coupling methodology for the synthesis of symmetric and unsymmetric 1,4-bis(*p*-R-phenylethynyl)benzenes (**6a-h**, **9a-c**). The cross-coupling reaction can be conducted in a stepwise fashion leading to the isolation of the intermediate **8** and eventually to **9a-c**. Based on the results obtained from the control experiments, we suggest strongly that the cross-coupling reaction should be performed in a rigorously oxygen free atmosphere. The reason is that terminal alkyne is prone to homo-coupling in the presence of oxygen. This process is catalyzed by  $\text{Cu}^{\text{I}}$ , and even more effectively when both  $\text{Pd}^{\text{II}}/\text{Cu}^{\text{I}}$  catalysts are present in solution. For the fluorinated aryl halides, the hydrodehalogenation process competes and can even dominate over the cross-coupling process, especially for the pentafluorinated compounds. It is thus best to conduct these cross-couplings at high temperature throughout the course of the reaction to avoid hydrogen-halide exchange.

## Experimental

### General

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk or glove box techniques. Diethylamine and diisopropylamine were distilled from  $\text{CaH}_2$  under  $\text{N}_2$ .

Nuclear magnetic resonance experiments were performed on a Bruker AC200 spectrometer at the following frequencies:  $^1\text{H}$ , 200 MHz;  $^{13}\text{C}\{^1\text{H}\}$ , 50 MHz.  $^1\text{H}$  chemical shifts were referenced to the internal standard tetramethylsilane (TMS) and  $^{13}\text{C}$  chemical shifts were referenced to the solvent resonances and are relative to the external standard TMS. All spectra were recorded in  $\text{CDCl}_3$  unless otherwise stated. FT-IR spectra were

recorded as KBr disks on a Bomem Michelson MB Series FT-IR spectrophotometer. Absorption spectra were recorded on a Hewlett-Packard 8452A Diode Array UV-Vis spectrophotometer. Emission spectra were recorded on a Perkin-Elmer MPF-2A spectrophotometer. Elemental analyses were obtained from M-H-W Laboratories, Phoenix, AZ. The terminal alkynes, 4-nitro-, 4-cyano-, 4-methoxy-, 4-methylthiophenylethyne and 4-ethynylpyridine were prepared via literature procedures using 2-methyl-3-butyne-2-ol as the protected terminal alkyne. In this work, a similar method was employed using ethynyltrimethylsilane, to synthesize 4-(dimethylamino)phenylethyne and 4-(trifluoromethyl)phenylethyne. Bromopentafluorobenzene, 1,4-bromo-, 1,4-diiodo-, 1,4-dichlorobenzenes, ethynylbenzene and 4-ethynyltoluene were purchased from Aldrich and checked for purity by GC-MS prior to use.

GC-MS analyses were performed on a Hewlett-Packard 5890 Series II/5971A MSD instrument equipped with an HP 7673A autosampler and a fused silica column (30 m × 0.25 mm × 0.25 μm, cross-linked 5% phenylmethyl silicone). The following operating conditions were used: injector, 260 °C; detector, 280 °C; oven temperature was ramped from 70 to 260 °C at the rate of 20 °C/min. UHP grade helium was used as the carrier gas. For the catalyst initiation experiments, gas chromatographic analyses were performed on a Hewlett-Packard 5890A instrument equipped with a flame ionization detector (FID). Toluene (BDH, 99.7%) was used as an internal integration standard. For quantitative studies of catalyst initiation, additional calibration was obtained by adding known concentrations of Me<sub>3</sub>SiC≡C-C≡CSiMe<sub>3</sub> to each sample prior to GC analysis.

#### General synthesis of symmetric 1,4-bis(*p*-*R*-phenylethynyl)benzenes (6a-h)

##### Synthesis of 1,4-bis(phenylethynyl)benzene (6a)

A solution of phenylethyne (1.349 g, 13.13 mmol) in diisopropylamine (20 ml) was added to a suspension containing 1,4-diiodobenzene (1.877 g, 5.69 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.16 g, 0.22 mmol) and CuI (0.044 g, 0.22 mmol) under nitrogen. The reaction mixture was allowed to stir at room temperature for 2 h and then heated to reflux for an additional 10 min. The solvent was removed *in vacuo*, and the crude product was extracted into hot toluene and filtered through a 1 cm pad of silica gel (70–230 mesh). Compound **6a** (white powder) was obtained in 3 crops by cooling the hot toluene solution. The yield was 1.259 g (79%); m.p. 180–181 °C. <sup>1</sup>H (200 MHz): δ 7.32–7.37 (phenyl H, 8H, m), 7.50–7.55 (phenyl H, 6H, m). IR (KBr), ν (cm<sup>-1</sup>): 2185 (C≡C). MS (EI), *m/z* (rel.): 278 (*M*<sup>+</sup>, 100), 250 (3), 237 (1), 224 (2), 174 (1), 139 (11), 125 (2),

113 (2). *Anal.* Calc. for C<sub>22</sub>H<sub>14</sub>: C, 94.93; H, 5.07. Found: C, 94.99; H, 5.24%.

*1,4-Bis(p-tolylethynyl)benzene (6b)*: white powder (yield 75%); m.p. 219–221 °C. <sup>1</sup>H: δ 2.35 (Me, 6H, s), 7.12–7.16 (terminal phenyl H, 4H, m), 7.39–7.47 (terminal + central phenyl H, 8H, overlapped m). IR (KBr), ν (cm<sup>-1</sup>): 2211 (C≡C). MS (EI), *m/z* (rel.): 306 (*M*<sup>+</sup>, 100), 289 (11), 276 (3), 263 (2), 213 (2), 189 (3), 153 (8), 138 (3). *Anal.* Calc. for C<sub>24</sub>H<sub>18</sub>: C, 94.08; H, 5.92. Found: C, 94.09; H, 6.11%.

*1,4-Bis(p-methoxyphenylethynyl)benzene (6c)*: white plates (yield 89%); m.p. 215–216 °C. <sup>1</sup>H: δ 3.82 (OMe, 6H, s), 6.84–6.90 (terminal phenyl H, 4H, m), 7.43–7.47 (terminal + central phenyl H, 8H, overlapped m). <sup>13</sup>C{<sup>1</sup>H} (50 MHz): 55.4, 88.2, 91.3, 114.1, 115.3, 123.2, 131.4, 133.2, 159.8. IR (KBr), ν (cm<sup>-1</sup>): 2215 (C≡C). MS (EI), *m/z* (rel.): 338 (*M*<sup>+</sup>, 100), 323 (33), 308 (5), 295 (4), 280 (6), 252 (9), 250 (7), 224 (7), 213 (3), 169 (20), 148 (9), 126 (13), 113 (9). *Anal.* Calc. for C<sub>24</sub>H<sub>18</sub>O<sub>2</sub>: C, 85.18; H, 5.36. Found: C, 84.96; H, 5.53%.

*1,4-Bis(p-methylthiophenylethynyl)benzene (6d)*: yellow plates (yield 74%); m.p. 247–248 °C. <sup>1</sup>H: δ 2.49 (SMe, 6H, s), 7.17–7.24 (terminal phenyl H, 4H, m), 7.40–7.47 (terminal + central phenyl H, 8H, overlapped m). IR (KBr), ν (cm<sup>-1</sup>): 2213 (C≡C). MS (EI), *m/z* (rel.): 370 (*M*<sup>+</sup>, 100), 355 (28), 340 (15), 308 (2), 295 (6), 276 (2), 263 (4), 185 (22), 178 (7), 169 (4), 154 (4), 147 (7), 126 (3), 113 (2). *Anal.* Calc. for C<sub>24</sub>H<sub>18</sub>S<sub>2</sub>: C, 77.79; H, 4.90. Found: C, 77.60; H, 5.01%.

*1,4-Bis(p-cyanophenylethynyl)benzene (6e)*: yellow plates (yield 38%); m.p. 278–280 °C. <sup>1</sup>H: 7.53 (central phenyl H, 4H, s), 7.57–7.67 (terminal phenyl H, 8H, m). IR (KBr), ν (cm<sup>-1</sup>): 2228 (overlapped, C≡C and C≡N). MS (EI), *m/z* (rel.): 328 (*M*<sup>+</sup>, 100), 300 (3), 249 (1), 175 (1), 164 (15), 150 (3), 137 (3), 136 (3), 124 (2). *Anal.* Calc. for C<sub>24</sub>H<sub>12</sub>N<sub>2</sub>: C, 87.79; H, 3.68. Found: C, 87.58; H, 3.54%.

*1,4-Bis(p-nitrophenylethynyl)benzene (6f)*: orange crystals (yield 58%); m.p. 253–254 °C. <sup>1</sup>H: δ 7.56 (central phenyl H, 4H, s), 7.60–7.70 (terminal phenyl H, 4H, m), 8.19–8.23 (terminal phenyl H, 4H, m). IR (KBr), ν (cm<sup>-1</sup>): 2211 (C≡C). MS (EI), *m/z* (rel.): 368 (*M*<sup>+</sup>, 100), 338 (18), 322 (7), 292 (6), 276 (20), 275 (18), 274 (49), 263 (17), 248 (9), 224 (8), 137 (8), 132 (7), 125 (7), 124 (7), 112 (7). *Anal.* Calc. for C<sub>22</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>: C, 71.74; H, 3.28. Found: C, 71.49; H, 3.40%.

*1,4-Bis(p-dimethylaminophenylethynyl)benzene (6g)*: the isolation of this product was similar to that for **6a** except that neutral alumina was used instead of silica gel; orange solid (yield 68%); m.p. 297–300 °C (dec.). <sup>1</sup>H: δ 2.98 (NMe<sub>2</sub>, 12H, s), 7.62–7.67 (terminal phenyl H, 4H, m), 7.36–7.42 (terminal + central phenyl H, 8H, overlapped m). IR (KBr), ν (cm<sup>-1</sup>): 2204 (C≡C). MS (EI), *m/z* (rel.): 364 (*M*<sup>+</sup>, 100), 349 (6), 348 (13), 333 (3), 332 (4), 276 (5), 182 (35), 181 (29), 173 (10), 166

(2), 160 (4), 152 (3), 138 (9), 137 (3), 125 (3), 121 (3). *Anal.* Calc. for  $C_{26}H_{24}N_2$ : C, 85.68; H, 6.64. Found: C, 85.43; H, 6.71%.

*1,4-Bis(p-trifluoromethylphenylethynyl)benzene (6h)*: white plates (yield 67%); m.p. 220–222 °C.  $^1H$ :  $\delta$  7.53 (terminal phenyl H, 4H, broad s), 7.61 (terminal+central phenyl H, 8H, broad s). IR (KBr),  $\nu$  ( $cm^{-1}$ ): 2216 ( $C\equiv C$ ). MS (EI),  $m/z$  (rel.): 414 ( $M^+$ , 100), 396 (2), 395 (6), 344 (3), 343 (2), 325 (1), 323 (1), 294 (2), 276 (2), 274 (2), 198(2), 182 (3), 173 (2), 157 (2). *Anal.* Calc. for  $C_{24}H_{12}F_6$ : C, 69.57; H, 2.92. Found: C, 69.31; H, 2.71%.

#### *Synthesis of 1,4-bis(4-pyridylethynyl)benzene (7)*

A mixture containing 4-ethynylpyridine (0.187 g, 1.81 mmol), 1,4-diiodobenzene (0.251 g, 0.76 mmol),  $PdCl_2(PPh_3)_2$  (0.02 g, 0.03 mmol) and CuI (0.006 g, 0.03 mmol) under nitrogen was charged with diisopropylamine (20 ml). The reaction mixture was allowed to stir at room temperature for 2 h and then heated at reflux for an additional 10 min. The work up procedure was similar to that of **6a** using neutral alumina instead of silica gel. Compound **7** was obtained as an orange powder (0.170 g, 80%); m.p. 100 °C (dec.).  $^1H$ :  $\delta$  7.34–7.37 (pyridine H, 4H, m), 7.53 (phenyl H, 4H, s), 8.58–8.61 (pyridine H, 4H, m). IR (KBr),  $\nu$  ( $cm^{-1}$ ): 2219 ( $C\equiv C$ ). MS (EI),  $m/z$  (rel.): 280 ( $M^+$ , 100), 251 (6), 240 (2), 224 (4), 200 (2), 174 (2), 150 (2), 140 (7), 126 (2), 113 (3), 100 (6), 87 (5), 74 (3), 63 (1). *Anal.* Calc. for  $C_{20}H_{12}N_2$ : C, 69.57; H, 2.92. Found: C, 69.31; H, 2.71%.

#### *Synthesis of 1-iodo-4-(p-nitrophenylethynyl)benzene (8)*

A solution of *p*-nitrophenylethyne (0.792 g, 5.39 mmol) in degassed diisopropylamine (60 ml) was added dropwise to a suspension containing 1,4-diiodobenzene (5.314 g, 16.10 mmol),  $PdCl_2(PPh_3)_2$  (0.226 g, 0.32 mmol), and CuI (0.061 g, 0.32 mmol) in 20 ml of diisopropylamine over a period of 20 h. At the end of the reaction, the mixture was filtered to remove the diisopropylammonium iodide salt and the excess solvent was then removed *in vacuo*. The crude product was dissolved in hot toluene and purified via column chromatography on silica gel (70–230 mesh) with toluene as the eluant. Compound **8** (orange flakes) was obtained in several crops by cooling the hot toluene solution. Yield 1.460 g (78%); m.p. 222–224 °C.  $^1H$ :  $\delta$  7.24–7.27 (phenyl H, 2H, m), 7.62–7.74 (phenyl H, 4H, overlapped m), 8.18–8.23 (phenyl H, 2H, m). IR (KBr),  $\nu$  ( $cm^{-1}$ ): 2211 ( $C\equiv C$ ). MS (EI),  $m/z$  (rel.): 349 ( $M^+$ , 100), 319 (6), 240 (12), 303 (6), 291 (5), 176 (36), 163 (7), 150 (10), 126 (3), 111 (2), 99 (3), 88 (5), 75 (5), 63 (2). *Anal.* Calc. for  $C_{14}H_8NIO_2$ : C, 48.16; H, 2.31. Found: C, 48.42; H, 2.27%.

#### *General synthesis of unsymmetric 1,4-bis(p-R-p-R'-phenylethynyl)benzenes (9a-c)*

##### *Synthesis of 1-(p-methoxyphenylethynyl)-4-(p-nitrophenylethynyl)benzene (9a)*

A solution of *p*-methoxyphenylethyne (0.159 g, 1.14 mmol) in diisopropylamine (15 ml) was added dropwise to a suspension containing **8** (0.246 g, 0.70 mmol),  $PdCl_2(PPh_3)_2$  (0.010 g, 0.01 mmol) and CuI (0.003 g, 0.01 mmol) in diisopropylamine (20 ml) under  $N_2$ . After stirring at room temperature for 1 h, the reaction mixture was heated to reflux for an additional 10 min. The work up was identical to that for **6a**. Compound **9a** was obtained as orange crystals (0.190 g, 76%); m.p. 280 °C (sublimed).  $^1H$ :  $\delta$  3.82 (OMe, 3H, s), 6.84–6.91 (terminal phenyl H, 2H, m), 7.42–7.48 (terminal phenyl H, 2H, m), 7.50 (central phenyl H, 4H, s), 7.62–7.68 (terminal phenyl H, 2H, m), 8.25–8.28 (terminal phenyl H, 2H, m). IR (KBr),  $\nu$  ( $cm^{-1}$ ): 2205 ( $C\equiv C$ ). MS (EI),  $m/z$  (rel.): 353 ( $M^+$ , 100), 338 (14), 323 (9), 307 (6), 292 (6), 263 (34), 237 (6), 213 (3), 177 (4), 148 (4), 132 (17), 119 (10), 106 (3). *Anal.* Calc. for  $C_{23}H_{15}NO_3$ : C, 78.18; H, 4.28. Found: C, 78.17; H, 4.19%.

*1-(p-methylthiophenylethynyl)-4-(p-nitrophenylethynyl)benzene (9b)*: yellow plates (yield 84%); m.p. 227–228 °C.  $^1H$ :  $\delta$  2.50 (SMe, 3H, s), 7.14–7.22 (terminal phenyl H, 2H, m), 7.41–7.45 (terminal phenyl H, 2H, m), 7.51 (central phenyl H, 4H, s), 7.63–7.67 (terminal phenyl H, 2H, m), 8.19–8.24 (terminal phenyl H, 2H, m). IR (KBr),  $\nu$  ( $cm^{-1}$ ): 2207 ( $C\equiv C$ ). MS (EI),  $m/z$  (rel.): 369 ( $M^+$ , 100), 354 (10), 339 (10), 323 (7), 306 (11), 277 (4), 274 (10), 263 (11), 250 (3), 237 (3), 224 (3), 185 (5), 170 (3), 156 (4), 153 (4), 138 (6), 132 (6), 119 (4). *Anal.* Calc. for  $C_{23}H_{15}NO_2S$ : C, 74.78; H, 4.09. Found: C, 74.76; H, 4.27%.

*1-(p-dimethylaminophenylethynyl)-4-(p-nitrophenylethynyl)benzene (9c)*: the work up procedure was similar to that for **6a** except that neutral alumina was used instead of silica gel; orange plates (yield 67%); m.p. 210–212 °C.  $^1H$ :  $\delta$  2.99 (NMe<sub>2</sub>, 6H, s), 6.62–6.67 (terminal phenyl H, 2H, m), 7.37–7.42 (terminal phenyl H, 2H, m), 7.48 (central phenyl H, 4H, s), 7.62–7.66 (terminal phenyl H, 2H, m), 8.19–8.23 (terminal phenyl H, 2H, m). IR (KBr),  $\nu$  ( $cm^{-1}$ ): 2205 ( $C\equiv C$ ). MS (EI),  $m/z$  (rel.): 366 ( $M^+$ , 100), 336 (16), 320 (23), 276 (18), 274 (11), 183 (8), 168 (7), 163 (11), 160 (7), 154 (10), 138 (15), 125 (7). *Anal.* Calc. for  $C_{24}H_{18}N_2O_2$ : C, 78.67; H, 4.95. Found: C, 77.53; H, 5.23%.

#### Acknowledgements

We thank the Natural Science and Engineering Research Council of Canada (T.B.M., grant support; P.N., postgraduate scholarship) and Johnson Matthey Ltd. for a loan of  $PdCl_2$ .

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