Synthesis of ethynylated biaryls and asymmetric diethynylated benzene *via* sequential Sonogashira and Suzuki couplings in water

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Abstract
Two 1-bromo-4-ethynylbenzene candidates were synthesized from 1-bromo-4-iodobenzene *via* Sonogashira coupling then sequentially employed in Suzuki coupling with arylboronic acids in water to give ethynylated biaryl derivatives. Optimization of the reaction condition was done using two different palladium sources and various bases/solvents systems. Further sequential Sonogashira coupling of 1-bromo-4-ethynylbenzene candidates, in aqueous medium, afforded asymmetric diethynylated benzene derivatives.

Keywords: arylacetylenes, cross-coupling, catalysis, palladium, aqueous medium

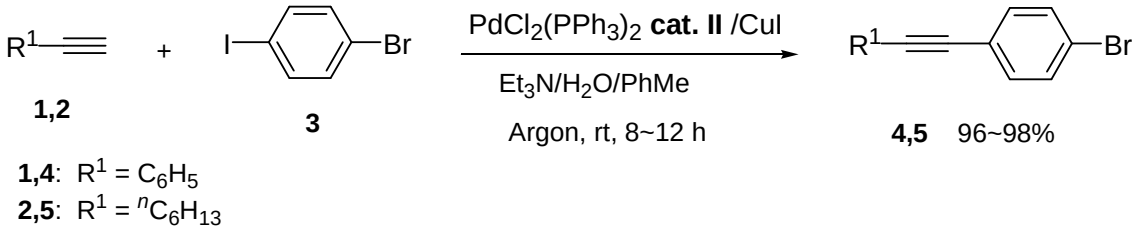
Introduction

Palladium-catalyzed Sonogashira cross-coupling reaction of aryl halides with terminal alkynes is one of the most important reactions for synthesis of disubstituted alkynes.[1,2] Unsymmetrical diarylethynes, as structural motifs with carbon–carbon triple bonds, have been developed in many synthetic transformations, pharmaceutical chemistry, natural products, and organic functional materials.[3-8] In addition, Suzuki-Miyaura cross-coupling reaction is one of the most versatile and utilized reactions for carbon-carbon bond formation in the synthesis of natural products and pharmaceuticals.[9-13] Water as an available, cheap, renewable, safe and green solvent and allows easy work up and separation, has been exploited in several catalytic C–C bond formation reactions and was reported as an important partner in improving the catalyst activity.[14-18] In continuation of our research work on C-C cross-coupling reactions catalyzed by Pd(II)-complexes in water,[19-29] we envisioned here that the 1-bromo-4-iodobenzene represents a suitable candidate for sequential Sonogashira and Suzuki cross-coupling for synthesis of new

ethynylated biaryls and asymmetric diethynylated benzene derivatives using either the benzothiazole-oxime Pd(II)-complex **I** or the commercially available $PdCl_2(PPh_3)_2$ **II** in aqueous medium.

Results and Discussion

The first task was to synthesize 1-bromo-4-(2-phenylethynyl)benzene (**4**) and 1-bromo-4-(1-octynyl)benzene (**5**)**,** via Sonogashira coupling of 1-bromo-4-iodobenzene (**3**) with phenylacetylene (**1**) or 1-octyne (**2**), to serve as substrates for achieving the objectives. The coupling was conducted in aqueous conditions at room temperature following a recently reported procedure for analogous examples.[29] Thus, reaction of equimolar amounts of 1-bromo-4-iodobenzene (**3**) with phenylacetylene (**1**) or 1-octyne (**2**) at room temperature using $PdCl_2(PPh_3)_2$ (cat. **II**) (1 mol%) and CuI (2 mol%) in toluene/water mixed solvent (1/1, v/v) in the presence of triethylamine under argon furnished the corresponding 1-bromo-4-ethynylbenzene derivatives **4** and **5** in 98% and 96% isolated yields, respectively (Scheme 1).

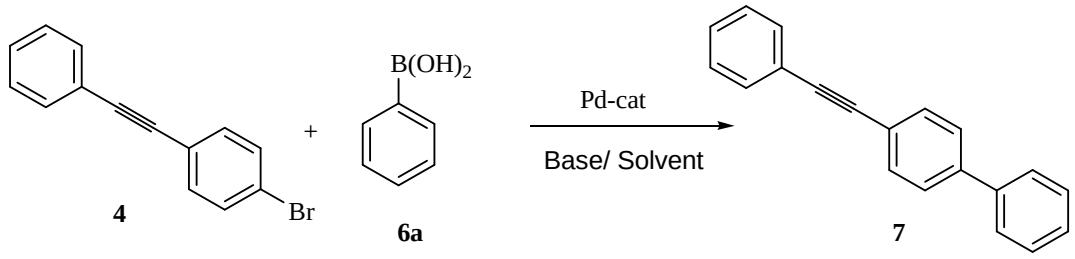


Scheme 1. Synthesis of 1-bromo-4-ethynylbenzene derivatives **4** and **5**

From a survey of the literature, it was found that very few examples of Suzuki cross-coupling of 1-bromo-4-ethynylbenzene derivatives **4** and **5** were reported.[30-32] Therefore, we first concerned on evaluation of the catalytic activity of the Pd-precatalysts **I** and **II** in the Suzuki-Miyaura cross-coupling reaction of 1-bromo-4-(2-phenylethynyl)benzene (**4**) with phenylboronic acid (**6a**) under different catalytic conditions (*e.g.* concentration of catalyst, bases and solvents). At first, the reaction was carried out using Pd-oxime-complex (cat. **I**) in different solvents (water and toluene) at reflux temperature using a variety of bases and the results are outlined in Table 1. Tetrabutylammonium bromide (TBAB) was used in 0.6 equiv for water solvent. Using NaOH/TBAB/water as catalytic system in the presence of 1 mol% Pd-cat **I** at reflux temperature for 8 hr gave only 50% yield and the starting material did not completely consume (Table 1, run 1). Repeating the same conditions using 2 mol% of the Pd-cat **I** resulted in full conversion into the cross-coupled product 1-phenyl-2-(4-biphenylyl)acetylene (**7**) in 85% isolated yield (Table 1, run 2). Under the typical conditions above, when water was replaced with toluene at reflux for 4 hr, the product **6** was obtained in 73% yield (Table 1, run 3). Using K_2CO_3/TBAB/water and 2 mol% Pd-cat **I** at reflux yielded 88% yield of **7** (Table 1, run 4).

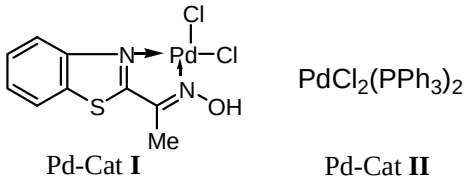
Next, the coupling reaction was carried out using bis(triphenylphosphine)palladium(II) dichloride; $PdCl_2(PPh_3)_2$ (cat **II**) in water or toluene at 60 °C using K_2CO_3 or Et_3N as bases and as shown in Table 1, runs 5-8. Conducting Suzuki coupling using Et_3N/H_2O/TBAB system in the presence of 1 mol% of cat **II** gave better result (93% yield) of **7** if compared with the catalytic system K_2CO_3/H_2O/TBAB (70% yield) under the same conditions (Table 1, runs 5, 7). Toluene was not suitable solvent either in the presence of Et_3N or K_2CO_3 where the products yields were 20% and 30%, respectively (Table 1, runs 6 and 8). The obtained product was identical with that reported from Sonogashira coupling of phenylacetylene with 4-bromobiphenyl.[33]

Table 1. Suzuki coupling of 1-bromo-4-(2-phenylethynyl)benzene (**4**) with phenylboronic acid (**6a**)



Run	Pd-cat. (mol%)	Base	Solvent	Temp. °C	Time hr	Yield %[a]
1	Pd-cat **I** (1)	NaOH	H_2O	100	8	50
2	Pd-cat **I** (2)	NaOH	H_2O	100	4	85
3	Pd-cat **I** (2)	NaOH	Toluene	100	4	73
4	Pd-cat **I** (2)	K_2CO_3	H_2O	100	4	88
5	Pd-cat **II** (1)	Et_3N	H_2O	60	2	93
6	Pd-cat **II** (1)	Et_3N	Toluene	60	2	20
7	Pd-cat **II** (1)	K_2CO_3	H_2O	60	2	72
8	Pd-cat **II** (1)	K_2CO_3	Toluene	60	2	30

[a]*Conditions*: Bromide **4**/Boronic acid **6a**/Base/TBAB/Solvent (ml): 1:1.5:2:0.6:2, thermal heating.



Pd-Cat **I** Pd-Cat **II**

When Suzuki coupling of the 1-bromo-4-(2-phenylethynyl)benzene (**4**) with 3-chlorophenylboronic acid (**6b**) was similarly carried out in H_2O/K_2CO_3/TBAB reaction system under thermal heating at 100 °C using 1 mol% Pd-cat. **I** (Table 2, run 1) or at 60 °C using 1

mol% Pd-cat **II** (Table 2, run 2)**,** it resulted in the formation of 1-(3-chlorophenyl)-2-(4-biphenylyl)acetylene (**8**) in excellent isolated yields.

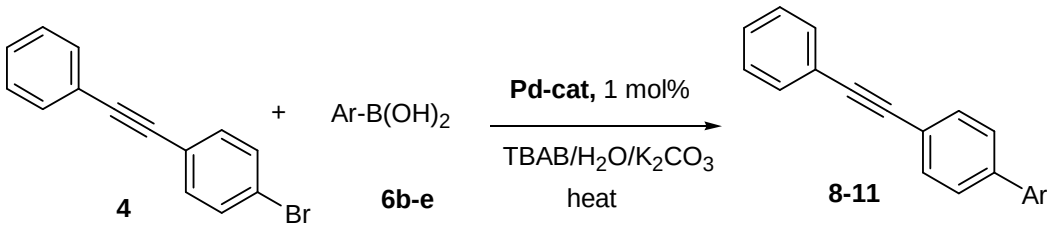
Likewise, 2-(4-biphenylyl)-1-(4-tolyl)acetylene (**9**) was synthesized *via* Suzuki coupling of 1-bromo-4-(2-phenylethynyl)benzene **4** with 4-tolylboronic acid **6c** in H_2O/K_2CO_3/TBAB using 1 mol% of Pd-catalysts **I** and **II** as described in Table 2, runs 3,4. 2-(4-Biphenylyl)-1-(4-tolyl)acetylene (**9**) was obtained in 60% yield after 24 hours at reflux (using Pd-cat **I)** and in 92% yield after 2 hr at 60 °C (using Pd-cat **II**), respectively. Product **9** was alternatively synthesized in literature by Sonogashira coupling of 4-bromophenyltrifluoroborate with phenylacetylene using $Pd(PPh_3)_4$/CuI catalyst in DMSO-d_6 followed by Suzuki coupling of the product with 4-bromotoluene.[34]

Pd-catalyst **I** was found to be less efficient (Table 2, run 5) in water/TBAB/K_2CO_3 after heating the coupling partners **4** and **6d** for 24 hr at reflux, where 2-(4-biphenylyl)-1-(3-anisyl)acetylene (**10**) was obtained in 70% yield and the starting material did not completely consume as detected by TLC. In contrast, when $PdCl_2(PPh_3)_2$ **II** was employed at 60 ^oC, the cross-coupling partners **4** and **6d** were completely consumed after 2 hr with full conversion into the coupling product **10** and 95% isolated yield (Table 2, run 6). Structure of 2-(4-biphenylyl)-1-(3-anisyl)acetylene (**10**) was elucidated by ^1H and ^{13}C NMR and IR spectroscopy. The ^1H NMR spectrum of **10** revealed characteristic singlet signal at δ 3.87 due to methoxy protons in addition to the aromatic protons and its ^{13}C NMR spectrum showed 17 carbon signals and the IR spectrum showed a peak at 2206 cm^{-1} corresponding to the acetylene moiety.

The Suzuki coupling reaction of 1-bromo-4-(2-phenylethynyl)benzene (**4**) with 3-thienylboronic acid (**6e**) was similarly carried out under thermal heating in water as shown in Table 2, runs 7, 8. Using 1 mol% Pd-complex **I** in water/TBAB/K_2CO_3**,** a poor yield (35%) of 2-(4-biphenylyl)-1-(3-thienyl)acetylene (**11**) was obtained after 24 hr of reflux. The use of $PdCl_2(PPh_3)_2$ (cat. **II**) (1 mol%) at 60 °C for 24 hours gave 89% yield of the coupled product **11** (Table 2, run 8).

The alkyne moiety is a π-electron donating group and consequently the aryl bromide **4** is considered as deactivated bromide. This may be a reason for, in some cases, the low conversion yields when our previously reported[22] Pd-catalyst **I** was employed in the catalytic system comparing to the more reactive catalyst $PdCl_2(PPh_3)_2$.

Table 2. Suzuki coupling of 1-bromo-4-(2-phenylethynyl)benzene **4** with arylboronic acids **6b-e**



4 **6b-e** **8-11**

Run	$ArB(OH)_2$	Ar	Product	Pd catalyst	Temp. °C	Time hr	Yield %[a]
1	**6b**	Cl	**8**	cat. **I**	100	3	96
2	**6b**	Cl	**8**	cat. **II**	60	5	93
3	**6c**	Me	**9**	cat. **I**	100	24	61
4	**6c**	Me	**9**	cat. **II**	60	2	92
5	**6d**	OMe	**10**	cat. **I**	100	24	70
6	**6d**	OMe	**10**	cat. **II**	60	2	95
7	**6e**	S	**11**	cat. **I**	100	24	35
8	**6e**	S	**11**	cat. **II**	60	24	89

[a]*Conditions*: Bromide/Boronic acid/Base/TBAB/water (ml): 1:1.5:2:0.6 :2, thermal heating.

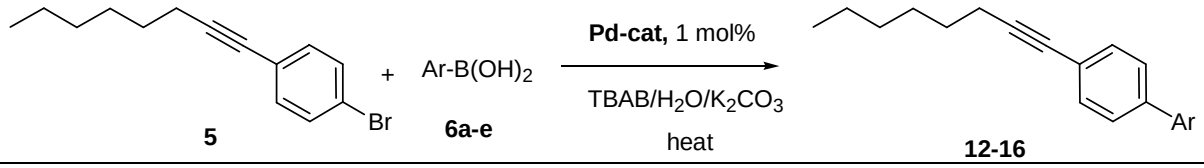
Next, Suzuki coupling reaction of 1-bromo-4-(1-octynyl)benzene (**5**) with phenylboronic acid (**6a**) was conducted in water as green solvent in the presence of 1 mol% of the Pd-precatalysts **I** or **II** to afford 1-(4-biphenylyl)-1-octyne **12** as outlined in Table 3. The cross-coupling reactions using Pd-catalyst **I** (at 100 °C) or Pd-catalyst **II** (at 60 °C) in water/TBAB/K_2CO_3 led to the formation of **12** in 92% and 95% isolated yields, respectively (Table 3, runs 1,2). Alternatively, Zhao and his group[35] synthesized compound **12** by Sonogashira coupling of 4-iodobiphenyl with 1-octyne **2** in neat diethylamine using $PdCl_2(PPh_3)_2$ (cat. **II**) and CuI at room temperature.

Further, Suzuki coupling of 1-bromo-4-(1-octynyl)-benzene (**5**) and 3-chlorophenylboronic acid (**6b**) was similarly carried out in H_2O/TBAB/K_2CO_3 using 1 mol% of Pd-catalyst **I** (at 100 °C for 4 hr) and Pd-catalyst **II** (at 60 °C for 2 hr) gave 1-(3´-chloro-4-biphenylyl)-1-octyne (**13**) in 91% and 94% isolated yields, respectively (Table 3, runs 3, 4). In the same manner, Suzuki cross-coupling reactions of 1-bromo-4-(1-octynyl)benzene (**5**) with 4-tolylboronic acid (**6c**) and 4-anisylboronic acid (**6d**) were conducted in the catalytic system; H_2O/TBAB/K_2CO_3 in the presence of 1 mol% Pd-catalyst **I** at 100 °C for 24 hours and the starting material were not completely consumed, as tested by TLC, and the cross-coupled products **14** and **15** were obtained in 40% and 50% yields, respectively (Table 3, runs 5, 7). When Suzuki coupling reactions of 1-bromo-4-(1-octynyl)benzene (**5**) with 4-tolylboronic acid (**6c**) and 4-anisylboronic acid (**6d**) were repeated in the presence of 1 mol% Pd-catalyst **II** at 60 °C, the cross-coupled products 1-(4-(4´-tolyl)phenyl)-1-octyne (**14**) and 1-(4-(4´-anisyl)phenyl)-1-octyne (**15**) were obtained in 87% and 90% yields, respectively (Table 3, run 6, 8).

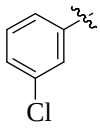
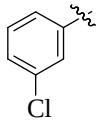
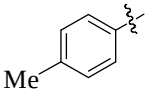
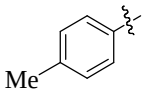
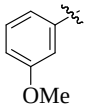
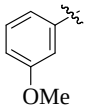
Pd-complex **I** was found to be a poor catalyst for coupling of 1-bromo-4-(1-octynyl)benzene (**5**) with 3-thienylboronic acid (**6e**) in water/TBAB/K_2CO_3 where the reaction did not complete even after 24 hr heating at 100 °C (Table 3, run 9) and the cross-coupled product 1-(4-(3-thienyl)phenyl)-1-octyne (**16**) was isolated in only 40% yield. The use of 1 mol% of $PdCl_2(PPh_3)_2$ (cat. **II**) at 60 °C for 15 hr, however, resulted in full conversion of the starting bromide **5** into the cross-coupled product **16** in 90% isolated yield (Table 3, run 10).

By controlling the reaction conditions, it was easy to introduce two different ethynyl groups into benzene ring starting with 1-bromo-4-iodobenzene (**3**). The 4-bromo-1-(oct-1-ynyl)benzene (**5**) was used further in a sequential Sonogashira cross-coupling with phenylacetylene **1** using $PdCl_2(PPh_3)_2$ (cat **II**) (1 mol%) in the presence of CuI (2 mol%) and triethylamine (2 equiv) in water/toluene mixed solvent (1 : 1, v : v) under argon atmosphere at 60°C for 24 h, to give the new 1-(oct-1-ynyl)-4-(2-phenylethynyl)benzene (**19**) in 65% isolated yield as shown in Scheme 2. Pd-complex (cat **II**) was found to be not appropriate catalyst for Sonogashira coupling of 4-bromo-1-(oct-1-ynyl)benzene (**5**) with phenylacetylene **1**, where conducting the reaction using 1 mol% of cat **II** in toluene/H_2O/Et_3N without CuI under argon atmosphere at 60°C for 24 h gave only 19% yield of compound **19**.

Table 3. Suzuki coupling of 1-bromo-4-(1-octynyl)benzene (**5**) with arylboronic acid **6a-e**

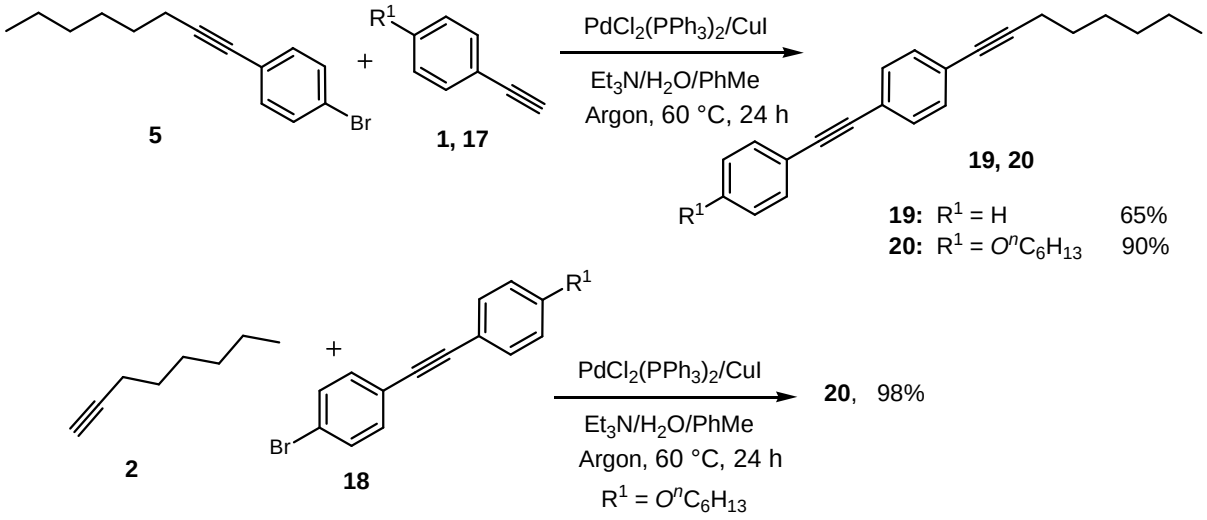


5 **6a-e** **12-16**

Run	$ArB(OH)_2$	Ar	Product	Pd catalyst	Temp. °C	Time hr	Yield %[a]
1	**6a**		**12**	cat. **I**	100	2	92
2	**6a**		**12**	cat. **II**	60	2	95
3	**6b**		**13**	cat. **I**	100	4	91
4	**6b**		**13**	cat. **II**	60	2	94
5	**6c**		**14**	cat. **I**	100	24	40
6	**6c**		**14**	cat. **II**	60	3	87
7	**6d**		**15**	cat. **I**	100	24	50
8	**6d**		**15**	cat. **II**	60	3	90
9	**6e**		**16**	cat. **I**	100	24	40
10	**6e**		**16**	cat. **II**	60	15	90

[a]*Conditions*: Bromide/Boronic acid/Base/TBAB/water (ml): 1:1.5:2:0.6:2, thermal heating.

By the same strategy, the asymmetric diethynylated benzene derivative; 1-(4-hexyloxyphenylethynyl)-4-(1-octynyl)benzene (**20**) could be synthesized. Thus, cross-coupling reaction of 4-bromo-1-(oct-1-ynyl)benzene (**5**) with 4-hexyloxyphenylacetylene (**17**) using $PdCl_2(PPh_3)_2$ (cat **II**) (1 mol%) in the presence of CuI (2 mol%) in toluene/H_2O/Et_3N under argon atmosphere at 60°C for 24 h yielded **20** in 90% isolated yield. It is worthy to note that, the asymmetric diethynylbenzene derivative **20** could be synthesized alternatively in excellent yield (98%) through coupling of 1-octyne **2** with 4-bromo-1-(4-hexyloxyphenylethynyl)benzene (**18**) using $PdCl_2(PPh_3)_2$ in the presence of CuI in toluene/water mixed solvent and triethylamine as a base under argon atmosphere at 60°C for 24 h (Scheme 2). The reaction molar ratios were typically; 1 mmol alkyne **2**, 1 mmol bromide **18**, 2 mmoles Et_3N, 1 mol% $PdCl_2(PPh_3)_2$ and 2 mol% CuI in water/toluene (2 ml, 1:1 v/v).



Scheme 2. Synthesis of asymmetric diethynylated benzene derivatives **19** and **20**

Conclusions

We have developed an effective and convenient protocol for the palladium(II)-catalyzed ligand-free synthesis of 4-ethynylated biaryl derivatives via sequential Sonogashira then Suzuki cross-coupling reaction in water in the presence of K_2CO_3 in open air. Also, sequential Sonogashira cross-coupling 1-bromo-4-iodobenzene different ethynylated benzene derivatives using ligand-free Pd(II)-catalyst, in aqueous medium under argon atmosphere, led to the formation of the asymmetric 1,4-diethynylated benzene derivatives.

Experimental section

General: Melting points were measured in open glass capillaries with a Gallenkamp apparatus. The infrared spectra were recorded in potassium bromide disks on a Pye Unicam SP 3-300 and Shimaduz FTIR 8101 PC infrared spectrophotometer. NMR spectra were recorded with a Varian Mercury VXR-300 NMR spectrometer at 300 MHz (^{1}H NMR) and at 75 MHz (^{13}C NMR) at Cairo University or on a Jeol LA 400 MHz (400 MHz for ^{1}H, 100 MHz for the ^{13}C) at Assiut University, using $CDCl_3$ as solvent and internal standard (δ 7.27 and 77.36 ppm, for ^{1}H NMR and ^{13}C NMR, respectively). Chemical shifts (δ) and *J* values are reported in ppm and Hz, respectively. Electrospray ionization mass spectrometry (EI-MS) analyses were obtained at 70 eV with a type Shimadzu GCMQP 1000 EX spectrometer. Analytical thin-layer chromatography (TLC) was conducted using pre-coated silica gel 60778 plates (Fluka), and the spots were visualized with UV light at 254 nm. Fluka silica gel 60741 (70-230 mesh) was used for flash column chromatography. For the elimination of atmospheric oxygen from the reaction medium, the aqueous solvent was firstly deoxygenated with a stream of argon for 30 min before use. Synthesis of the Pd(II)-complex (Pd-cat **I**)[22] and 4-hexyloxyphenylacetylene **17**[29,36] were prepared following the procedures reported in literature.

Preparation of 1-bromo-4-ethynylbenzene derivatives 4 and 5

To $PdCl_2(PPh_3)_2$ **II** (7 mg, 0.01 mmol), CuI (3.8 mg, 0.02 mmol), and 1-bromo-4-iodobenzene **3** (283 mg, 1 mmol) in toluene (1 mL) and Et_3N (280 μL, 2 mmoles) in water (1 mL), was added phenylacetylene **1** or 1-octyne **2** (1 mmol) under an argon atmosphere, and stirring was continued at room temperature for 18 hr. Then the mixture was diluted with 20 mL of diethyl ether and then passed through a Celite pad to remove any insoluble solid residue, which was washed with 20 mL of diethyl ether. The combined filtrate was evaporated under reduced pressure to leave a crude product, which was subjected to flash column chromatography on silica gel (hexane-ethyl acetate) (100:1) to furnish of the cross-coupled products **4** and **5**, respectively.

1-Bromo-4-(2-phenylethynyl)benzene (**4**)**:**[37] White powder, yield 98%; mp. 80-81 ºC; ^{1}H NMR ($CDCl_3$) δ 7.35-7.42 (m, 5H, ArH), 7.48-7.56 (m, 4H, ArH).

4-Bromo-1-(oct-1-ynyl)benzene (**5**)**:**[38] Yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 3H, *J* = 6.6 Hz), 1.28-1.63 (m, 8H), 2.39 (t, 2H, *J* = 7.2 Hz), 7.25 (d, 2H, *J* = 8.7 Hz), 7.42 (d, 2H, *J* = 8.7 Hz).

Effect of base and solvent on Suzuki coupling of 1-bromo-4-(phenylethynyl)benzene (4) with phenylboronic acid 6a using palladium catalyst I

A mixture of 1-bromo-4-(2-phenylethynyl)benzene (**4**) (257 mg, 1 mmol), phenylboronic acid **6a** (183 mg, 1.5 mmol), TBAB (194 mg, 0.6 mmol), palladium catalyst **I** (7.4 mg, 2 mol%) and the appropriate base (2 mmol) in water or toluene (2 mL) was heated at 100 °C with stirring under open air. The cross-coupled product, in each time, was then extracted with diethyl ether (3x30 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ then filtered and the

solvent was evaporated under reduced pressure. The residue was then purified *via* column chromatography with hexane-ethyl acetate as an eluent to give the cross-coupled product **7**.

Effect of base and solvent on Suzuki coupling of 1-bromo-4-(phenylethynyl)benzene (4) with phenylboronic acid 6a using palladium catalyst II

A mixture of 1-bromo-4-(2-phenylethynyl)benzene (**4**) (257 mg, 1 mmol), phenylboronic acid **6a** (183 mg, 1.5 mmol), TBAB (194 mg, 0.6 mmol), palladium catalyst **II** (7 mg, 1 mol%) and the appropriate base (2 mmol) in degassed solvent: water or toluene (2 mL) was heated at 60 °C with stirring under argon atmosphere. The cross-coupled product, in each time, was then extracted with diethyl ether (3x30 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ then filtered and the solvent was evaporated under reduced pressure. The residue was then purified *via* column chromatography with hexane-ethyl acetate as an eluent to give the cross-coupled product **7**.

Suzuki cross-coupling of 1-bromo-4-ethynylbenzene derivatives 4 and 5 with arylboronic acids 6a-e using Pd-catalyst I. *General procedure*

A mixture of 1-bromo-4-(phenylethynyl)benzene (**4**) or 1-bromo-4-(oct-1-ynyl)benzene (**5**) (1 mmol), and the appropriate arylboronic acid **6a-e** (1.5 mmol), TBAB (194 mg, 0.6 mmol), palladium catalyst **I** (7.4 mg, 2 mol%), K_2CO_3 (276 mg, 2 mmol), and water (2 mL) was shaken at 100 °C under open air. After the reaction was almost complete (monitored by TLC), the reaction mixture was left to cool to room temperature. The products were then extracted three times with diethyl ether (3x30 ml) and then the organic fractions were combined together, dried over $MgSO_4$, filtered, and then the solvent was removed under vacuum. The residue was then purified *via* column chromatography with hexane-ethyl acetate as an eluent to give the corresponding cross-coupled products **7-11** and **12-16**, respectively.

Suzuki cross-coupling of 1-bromo-4-ethynylbenzene derivatives 4 and 5 with arylboronic acids 6a-e using $PdCl_2(PPh_3)_2$ II. *General procedure*

To a mixture 1-bromo-4-(phenylethynyl)benzene (**4**) or 1-bromo-4-(oct-1-ynyl)benzene (**5**) (1 mmol) and $PdCl_2(PPh_3)_2$ (cat. **II**) (7 mg, 0.01 mmol) in degassed water (2 mL), was added the appropriate arylboronic acid **6a-e** (1.5 mmol) with stirring under an argon atmosphere. After that, K_2CO_3 (276 mg, 2 mmol) was added and the mixture was left to stir at 60 ^oC till the reaction was almost complete (monitored by TLC). After cooling, the resulting mixture was extracted with diethyl ether (3x30 mL). The organic fractions were combined together, dried over $MgSO_4$, filtered, and then the solvent was removed under vacuum to leave a crude solid, which was purified by chromatography on silica gel with hexane-ethyl acetate to furnish the corresponding coupling products **7-11** and **12-16**, respectively.

4-(2-Phenylethynyl)biphenyl (7): Off-white solid, mp 160-161 ºC (Lit.[33] mp. 162-163 ºC); IR (ν_{max}, cm^{-1}): 3034, 2219, 1482. ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.31-7.38 ($4H_{arom}$, m, 4CH),

7.43-7.47 (2H$_{arom}$, m, 2CH), 7.51-7.62 (8H$_{arom}$, m, 8CH); MS (EI, 70 eV): *m/z* (%) = 254 (M^+, 100), 250 (7.2), 127 (17.6), 113 (8.3), 80 (14.9), 64 (8.7).

3'-Chloro-4-(phenylethynyl)biphenyl (8): Off-white solid, mp 117-118 ºC; IR (ν_{max}, cm^{-1}): 3057, 2325, 1468. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.32-7.38 (5H$_{arom}$, m, 5CH), 7.47 (1H$_{arom}$, d, $^3J_{HH}$ 8.7 Hz, 1H), 7.50-7.65 (7H$_{arom}$, m, 7CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 89.0, 90.4, 122.8, 123.1, 125.1, 126.9, 127.1, 127.6, 128.4, 130.1, 131.6, 132.1, 134.7, 139.4, 142.1; MS (EI, 70 eV): *m/z* (%) = 290 (M^++2, 35), 289 (M^++1, 22.7), 288 (M^+, 100), 252 (27.9), 250 (15.7), 144 (14.8), 126 (21.3), 113 (16.9), 100 (6.9), 80 (15.9), 64 (9.7). Anal. Calcd for $C_{20}H_{13}Cl$ (288.77): C, 83.19; H, 4.54%. Found: C, 83.55; H, 4.61%.

4'-Methyl-4-(phenylethynyl)biphenyl (9): Off-white solid, mp 155-156 ºC (Lit.[34] mp. 155 ºC); IR (ν_{max}, cm^{-1}): 3025, 2915, 2208, 1492. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 2.39 (3H, s, CH_3), 7.24 (2H$_{arom}$, d, $^3J_{HH}$ 8.0 Hz, 2CH), 7.33-7.37 (3H$_{arom}$, m, 3CH), 7.50 (2H$_{arom}$, d, $^3J_{HH}$ 8.0 Hz, 2CH), 7.54-7.60 (6H$_{arom}$, m, 6CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 21.1, 89.4, 89.9, 121.8, 123.3, 126.5, 126.8, 128.3, 129.6, 131.6, 131.9, 132.3, 137.4, 137.5, 140.9; MS (EI, 70 eV): *m/z* (%) = 269 (M^++1, 37.5), 268 (M^+, 100), 251 (10.2), 189 (15.6), 150 (5.4), 115 (11.1), 106 (9.3), 91 (5.6), 77 (6.9), 63 (13.6), 51 (17.9).

3'-Methoxy-4-(phenylethynyl)biphenyl (10): White crystals, mp 106 ºC; IR (ν_{max}, cm^{-1}): 3012, 2926, 2206, 1591. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.87 (3H, s, CH_3), 6.90-6.92 (1H$_{arom}$, m, 1CH), 7.13-7.39 (5H$_{arom}$, m, 5CH), 7.54-7.62 (7H$_{arom}$, m, 7CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 55.3, 89.2, 90.1, 112.7, 113.0, 119.5, 122.3, 123.2, 127.0, 128.2, 128.3, 129.9, 131.6, 131.9, 140.8, 141.8, 159.9; MS (EI, 70 eV): *m/z* (%) = 284 (100) [M^+], 254 (7.5), 241 (20.5), 215 (4.5), 142 (6.3), 126 (5.5), 108 (6.8). Anal. Calcd for $C_{21}H_{16}O$ (284.35): C, 88.70; H, 5.67%. Found: C, 88.98; H, 5.47%.

3-(4-(Phenylethynyl)phenyl)thiophene (**11**): Off-white solid, mp 175-176 ºC; IR (ν_{max}, cm^{-1}): 3096, 2213, 1589, 1435. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.20 (1H$_{thiophene}$, s, 1CH), 7.34-7.41 (5H$_{arom}$, m, 5CH), 7.49-7.60 (6H$_{arom}$, m, 6CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 89.3, 89.9, 120.8, 121.8, 123.2, 126.1, 126.3, 126.5, 128.2, 128.4, 131.6, 132.1, 135.5, 141.6; MS (EI, 70 eV): *m/z* (%) = 260 (3.1) [M^+], 230 (53.7), 215 (89.7), 201 (16.7), 165 (16.5), 152 (64.9), 125 (20.4), 80 (85.4), 64 (100), 55 (55.6). Anal. Calcd for $C_{18}H_{12}S$ (260.35): C, 83.04; H, 4.65; S, 12.32%. Found: C, 82.76; H, 4.55; S, 12.28%.

4-(1-Octynyl)biphenyl (12):[35] Yellow oil; IR (ν_{max}, cm^{-1}): 3058, 2926, 2219, 1479. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 0.90 (3H$_{aliph}$, t, $^3J_{HH}$ 5.7 Hz, CH_3), 1.25-1.64 (8H$_{aliph}$, m, 4CH_2), 2.41 (2H$_{aliph}$, t, $^3J_{HH}$ 7.2 Hz, CH_2), 7.31-7.55 (9H$_{arom}$, m, 9CH); MS (EI, 70 eV): *m/z* (%) = 262 (M^+, 72.4), 240 (68.9), 231 (74.7), 215 (94.3), 191 (100), 180 (37.9), 137 (42.5), 121 (42.5), 98 (68.9), 86 (40.2), 62 (85.1), 52 (36.8).

4-(1-Octynyl)-3'-chloro-1,1'-biphenyl (13): Colorless oil; IR (ν_{max}, cm^{-1}): 3027, 2925, 2222, 1644, 1494. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 0.91 (3H$_{aliph}$, t, $^3J_{HH}$ 7.0 Hz, CH_3), 1.23-1.65 (8H$_{aliph}$, m, 4CH_2), 2.42 (2H$_{aliph}$, t, $^3J_{HH}$ 7.2 Hz, CH_2), 7.29-7.55 (8H$_{arom}$, m, 8CH), 7.62 (1H$_{arom}$, d, $^4J_{HH}$ 8.4 Hz, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.1, 19.5, 22.6, 28.6, 28.7, 31.3, 80.2, 91.7, 123.7, 125.1, 127.1, 127.3, 127.5, 129.9, 132.0, 134.7, 138.6, 142.3; MS (EI, 70 eV): *m/z*

(%) = 299 (M^++2, 52.1), 297 (M^+, 100), 288 (52.4), 267 (14.5), 253 39.9), 230 (89.2), 215 (76.8), 202 (38.8), 189 (72.9), 152 (76.5), 113 (43.9), 101 (19.1), 80 (27.3), 64 (21.2). Anal. Calcd for $C_{20}H_{21}Cl$ (296.83): C, 80.93; H, 7.13%. Found: C, 80.78; H, 7.20%.

4-(1-Octynyl)-4'-methyl-1,1'-biphenyl (14): Off-white solid, mp 36-37 ºC; IR (ν_{max}, cm^{-1}): 3026, 2924, 2223, 1494. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 0.91 ($3H_{aliph}$, t, $^3J_{HH}$ 7.0 Hz, CH_3), 1.25-1.65 ($8H_{aliph}$, m, $4CH_2$), 2.38 ($3H_{aliph}$, s, CH_3), 2.42 ($2H_{aliph}$, t, $^3J_{HH}$ 7.2 Hz, CH_2), 7.23-7.25 ($2H_{arom}$, d, $^3J_{HH}$ 8.4 Hz, 2CH), 7.43-7.64 ($6H_{arom}$, m, 6CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.1, 19.5, 21.1, 22.6, 28.6, 28.7, 31.4, 80.4, 91.0, 122.7, 126.6, 126.8, 129.5, 131.9, 137.3, 137.6, 140.1; MS (EI, 70 eV): *m/z* (%) = 277 (M^++1, 23.6), 276 (M^+, 100), 247 (12.6), 233 (28.9), 219 (27.9), 205 (81.3), 192 (42.3), 179 (21.9), 165 (16.9), 115 (17.6), 105 (25.9), 91 (20.4), 79 (15.1), 57 (24.3), 55 (30.0). Anal. Calcd for $C_{21}H_{24}$ (276.41): C, 91.25; H, 8.75%. Found: C, 91.11; H, 8.64%.

4-(1-Octynyl)-3'-methoxy-1,1'-biphenyl (15): Colorless oil; IR (ν_{max}, cm^{-1}): 3037, 2926, 2224, 1459. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.91 ($3H_{aliph}$, t, $^3J_{HH}$ 7.2 Hz, CH_3), 1.15-1.34 ($4H_{aliph}$, m, $2CH_2$), 1.42-1.49 ($2H_{aliph}$, m, CH_2), 1.57-1.64 ($2H_{aliph}$, m, CH_2), 2.41 (2H, t, $^3J_{HH}$ 7.2 Hz, CH_2), 3.83 ($3H_{aliph}$, s, OCH_3), 6.86-6.88 ($1H_{arom}$, m, CH), 7.09-9.21 ($2H_{arom}$, m, 2CH), 7.31-7.34 ($1H_{arom}$, m, CH), 7.44 ($2H_{arom}$, d, $^3J_{HH}$ 8.4 Hz, 2CH), 7.50 ($2H_{arom}$, d, $^3J_{HH}$ 8.4 Hz, 2CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.1, 19.5, 22.6, 28.7, 29.7, 31.4, 55.2, 80.3, 91.2, 112.8, 119.4, 123.2, 126.9, 127.1, 129.7, 131.9, 139.9, 141.9, 159.9; MS (EI, 70 eV): *m/z* (%) = 292 (M^+, 20.6), 291 (31.1), 270 (29.7), 255 (46.9), 248 (31.6), 220 (27.3), 207 (33.5), 190 (30.1), 145 (35.4), 138 (100), 102 (12.9), 90 (16.7), 76 (17.7), 63 (18.7). Anal. Calcd for $C_{21}H_{24}O$ (292.41): C, 86.26; H, 8.27%. Found: C, 86.49; H, 8.24%.

3-(4-(1-Octynyl)phenyl)thiophene (16): Off-white solid, mp 35 ºC; IR (ν_{max}, cm^{-1}): 3100, 2925, 2225, 1458. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.91 ($3H_{aliph}$, t, $^3J_{HH}$ 7.2 Hz, CH_3), 1.25-1.34 ($4H_{aliph}$, m, $2CH_2$), 1.42-1.49 ($2H_{aliph}$, m, CH_2), 1.55-1.64 ($2H_{aliph}$, m, CH_2), 2.41 ($2H_{aliph}$, t, $^3J_{HH}$ 7.4 Hz, CH_2), 6.31-7.52 ($7H_{arom+thiophene}$, m, 7CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.1, 19.5, 22.6, 28.6, 28.7, 31.4, 80.4, 91.1, 120.5, 122.7, 126.1, 126.3, 126.8, 131.9, 134.7, 141.7; MS (EI, 70 eV): *m/z* (%) = 269 (M^++1, 22.1), 268 (M^+, 100), 239 (15.4), 225 (42.8), 211 (32.7), 197 (81.4), 184 (21.3), 165 (45.4), 152 (25.5), 139 (12.6), 115 (19.3), 97 (11.7), 79 (7.6), 63 (11.2). Anal. Calcd for $C_{18}H_{20}S$ (268.41): C, 80.54; H, 7.51; S, 11.95%. Found: C, 80.27; H, 7.33; S, 11.82%.

Preparation of 4-bromo-1-(4-hexyloxyphenylethynyl)benzene (18):[39]

To a stirred mixture of $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol), CuI (3.8 mg, 0.02 mmol) and 1-bromo-4-iodobenzene **3** (283 mg, 1 mmol) in toluene (1 mL) and Et_3N (280 μL, 2 mmoles) in water (1 mL), was added 4-hexyloxyphenylacetylene **17** (242 mg, 1.2 mmol) under an argon atmosphere. The stirring was continued at room temperature for 10 h. The two phases of the resulting mixture were separated and the aqueous layer was extracted with diethyl ether. The combined organic layer was concentrated under reduced pressure to leave a crude solid, which was purified by flash column chromatography on silica gel using hexane/ethyl acetate (15:1) to give 0.32 g

compound **18** (90% yield) as white crystals. Mp. 108-109 °C; IR (ν_{max}, cm^{-1}): 3050, 2925, 2855, 2206, 1598, 1507. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 0.93 ($3H_{aliph}$, t, $^3J_{HH}$ 6.9 Hz, CH_3), 1.34-1.54 ($6H_{aliph}$, m, $3CH_2$), 1.78-1.83 ($2H_{aliph}$, m, CH_2), 3.98 ($2H_{aliph}$, t, $^3J_{HH}$ 6.6 Hz, OCH_2), 6.88 ($2H_{arom}$, d, $^3J_{HH}$ 8.7 Hz, 2CH), 7.37 ($2H_{arom}$, d, $^3J_{HH}$ 8.7 Hz, 2CH), 7.43-7.49 ($4H_{arom}$, m, 4CH); MS (EI, 70 eV): *m/z* (%) = 358 (M^++2, 48.7), 357 (M^++1, 13.5), 356 (M^+, 49.5), 274 (98.2), 272 (100), 205 (25.7), 163 (27.7), 121 (28.3), 55 (10.4).

Synthesis of asymmetric 1,4-diethynylbenzene derivatives 19 and 20

To a stirred mixture of $PdCl_2(PPh_3)_2$ (3.5 mg, 0.005 mmol), CuI (1.9 mg, 0.01 mmol) and 4-bromo-1-(oct-1-ynyl)benzene **5** (132 mg, 0.5 mmol) in toluene (1 mL) and Et_3N (280 μL, 2 mmol) in water (1 mL), was added phenylacetylene **1** or 4-hexyloxyphenylacetylene **17** (0.6 mmol) dropwise under an argon atmosphere. The stirring was continued for 24 h at 60 °C. The two phases of the resulting mixture were separated and the aqueous layer was extracted with diethyl ether. The combined organic layer was concentrated under reduced pressure to leave a crude solid, which was purified by flash column chromatography on silica gel using hexane/ethyl acetate (10:1) to give the corresponding coupling products **19** and **20**, respectively.

1-(1-Octynyl)-4-(2-phenylethynyl)benzene (19): Off-white solid, mp. 60-61 °C; IR (ν_{max}, cm^{-1}): 3009, 2927, 2858, 2214, 1601, 1513. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 0.94 ($3H_{aliph}$, t, $^3J_{HH}$ 6.9 Hz, CH_3), 1.29-1.36 ($4H_{aliph}$, m, $2CH_2$), 1.43-1.53 ($2H_{aliph}$, m, CH_2), 1.59-1.66 ($2H_{aliph}$, m, CH_2), 2.44 ($2H_{aliph}$, t, $^3J_{HH}$ 6.9 Hz, CH_2), 7.35-7.45 ($3H_{arom}$, m, 3CH), 7.48-7.56 ($6H_{arom}$, m, 6CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 13.9, 19.4, 22.5, 25.6, 28.6, 31.3, 80.3, 87.7, 90.8, 92.2, 114.5, 114.9, 122.6, 123.4, 123.6, 131.1, 131.3, 132.9; MS (EI, 70 eV): *m/z* (%) = 287 (M^+, 3.5), 231 (6.8), 205 (58.6), 121 (46.6), 80 (100), 64 (59.6), 55 (14.8). Anal. Calcd for $C_{22}H_{22}$ (286.41): C, 92.26; H, 7.74%. Found: C, 92.45; H, 7.87%.

1-(4-Hexyloxyphenylethynyl)-4-(1-octynyl)benzene (20): Off-white solid, mp. 73-74 °C; IR (ν_{max}, cm^{-1}): 3040, 2925, 2853, 2214, 1601, 1511. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 0.91-0.96 ($6H_{aliph}$, m, $2CH_3$), 1.29-1.51 ($16H_{aliph}$, m, $8CH_2$), 2.44 ($2H_{aliph}$, t, $^3J_{HH}$ 6.9 Hz, CH_2), 3.98 ($2H_{aliph}$, t, $^3J_{HH}$ 6.9 Hz, OCH_2), 6.86 ($2H_{arom}$, d, $^3J_{HH}$ 8.4 Hz, 2CH), 7.38-7.47 ($6H_{arom}$, m, 6CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 13.00, 13.02, 18.36, 21.42, 21.45, 24.56, 27.45, 27.53, 28.02, 30.20, 30.43, 66.97, 79.28, 86.72, 90.04, 91.52, 113.59, 121.51, 122.63, 130.08, 130.37, 131.65, 131.90, 158.30. Anal. Calcd for $C_{28}H_{34}O$ (386.57): C, 87.00; H, 8.87%. Found: C, 86.83; H, 8.96%.

Alternative synthesis of 1-(4-hexyloxyphenylethynyl)-4-(1-octynyl)benzene (20)

To a mixture of $PdCl_2(PPh_3)_2$ (3.5 mg, 0.005 mmol), CuI (1.9 mg, 0.01 mmol), and 4-bromo-1-(4-hexyloxyphenylethynyl)benzene **18** (178 mg, 0.5 mmol) in toluene (1 mL) and Et_3N (140 μL, 1 mmol) in water (1 mL), was added 1-octyne **2** (90 μL, 0.6 mmol) dropwise under an argon atmosphere. The crude product was purified as shown above to give 0.19 g (98% yield) of **20**.

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