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Efficient synthesis of 3,3′,5,5′-tetra(*p*-X-phenylethynyl)biphenyl (X: NMe_2; OMe) by homocoupling of 1-bromo-3,5-di(*p*-X-phenylethynyl) benzene or by heterocoupling of 3,3′,5,5′-tetraethynylbiphenyl with *p*-X-phenylbromobenzene with nickel or palladium complexes, respectively

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ABSTRACT

The conjugated 3,3′,5,5′-tetra(*p*-X-phenylethynyl)biphenyl derivatives were efficiently obtained by homocoupling of 1-bromo-3,5-di(*p*-X-phenylethynyl)benzene mediated by zero-valent nickel complexes. The 1-bromo-3,5-di(*p*-X-phenylethynyl)benzene was previously prepared by heterocoupling between 1-bromo-3,5-di(ethynyl)benzene and *p*-X-iodobenzene (X: NMe_2; OMe) catalysed by the palladium/copper system in good yield. The necessary 1-bromo-3,5-di(ethynyl)benzene was obtained by heterocoupling between 1,3,5-tribromobenzene and 2-methyl-3-butyn-2-ol catalysed by palladium and successive treatment with sodium hydroxide in dry toluene, in good yield.

The same 3,3′,5,5′-tetra(*p*-X-phenylethynyl)biphenyl (X: NMe_2; OMe) derivatives were alternatively synthesised in highest yield by heterocoupling between 3,3′,5,5′-tetra(ethynyl)biphenyl and *p*-X-bromobenzene (X: NMe_2; OMe) catalysed by palladium in excellent yields. Previously, 3,3′,5,5′-tetra(ethynyl)biphenyl was obtained in practically quantitative yield by homocoupling of 1-bromo-3,5-di-[4-(2-methyl-3-butyn-2-ol)] benzene mediated by the zero-valent nickel complex to the 3,3′,5,5′-tetra{di[4-(2-methyl-3-butyn-2-ol)]}biphenyl followed the treatment with sodium hydroxide.

1. Introduction

Symmetric biaryls were usually prepared by the Ullman reaction, which requires an aryl halide in equimolar amount with copper powder and temperatures up to 200 °C.[1] Methods for the synthesis of biaryl or oligoaryl compounds with different properties were reported.[2] Actually, the coupling reaction of organic halides can be catalysed by transition organometallic nucleophiles in moderated temperatures and is an attractive method for the synthesis of σ C–C bonds.[3]

Synthesis of conjugated *p*-(ethynylphenylethynyl)$_n$benzene derivatives was recently reported, showing fluorescence emission properties.[4]

The 3,3′,5,5′-tetra(*p*-X-phenylethynyl)biphenyls (X: NMe_2; OMe) of controlled structure and dimension were synthesised by two successive catalysed methods: (i) homocoupling of the appropriate halophenyl derivative mediated by in situ recently prepared zero-valent nickel complexes;[5] and (ii) Sonogashira palladium/copper catalyst heterocoupling between the corresponding ethynylbenzene and the appropriate halophenyl derivative.[6]

Thus, the homocoupling of haloaryl derivatives mediated by the zero-valent nickel complex affords efficiently the corresponding biaryl under mild conditions. Semmelhack et al.[7] use stoichiometric amounts of bis-(1,5-dichlorooctadiene)nickel(0) in *N*,*N*-dimethylformamide. In general, the zero-valent nickel complexes were prepared in situ by reduction of Ni[$(PPh_3)_2$]Cl_2 with Zn in presence of tetrabutylammonium iodide in tetrahydrofuran.[8,9]

In the same way, the homocoupling of a conveniently substituted halobenzene to biphenyls was selectivity achieved by a palladium catalyst, sodium carbonate and TBAB, all supported on activated carbon.[10]

We have analysed different zero-valent nickel complexes for the homocoupling of haloarenes.[8] Thus, the zero-valent tetrakis-(triphenylphosphine)nickel was used in the intramolecular cyclisation between an aryl halide and an exocyclic double bond. On the basis of the secondary products' identification, a mechanism of reaction has been proposed.[8] The first step is the oxidative addition of the aryl halide to the zero-valent nickel complex as L_3Ni–ArX π complex, followed by the metathesis to the L_2XNi–Ar σ complex and the σ-nickel coordination to the double bond giving the effective cyclisation and hydride nickel halide species in solution of THF ($HNiClL_2$).

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The reductive elimination of the formed species of arylnickel(II) affords the biaryl compound and regenerates the nickel(0) species.[10]

Tsou and Kochi[11] proposed a radical mechanism, which implies the oxidative addition of the haloarene ArX to the Ni(I)X intermediate giving the $ArNi(II)X_2$ complex.

We now report the synthesis of conjugated 3,3′,5,5′-tetra(*p*-X-phenylethynyl)biphenyls (X: NMe_2; OMe) by homocoupling reaction of conjugated halophenyl derivatives mediated by zero-valent nickel and palladium complexes.

2. Results and discussion

The synthesis of the 3,3′,5,5′-(tetraethynyl-*p*-X-phenyl)biphenyl compounds has been undertaken as partially conjugated dendron structures by combining the catalysed homo and heterocoupling reactions.

2.1. Synthesis of 3,3′,5,5′-tetra(*p*-*N*,*N*-dimethylamino)(phenylethynyl)biphenyl (5)

Compound **3** was prepared by heterocoupling reaction between 2-methyl-3-butyn-2-ol and 1,3,5-tribromobenzene (2.4 molar ratio, respectively) in triethylamine, in the presence of dichloro bis(triphenyl)phosphine palladium and cuprous iodide, at room temperature. After chromatography, 1-bromo-3,5-di[4-(2-methyl-3-butyn-2-ol)]benzene (**1**) was isolated as yellow solid, mp 95–97 °C, in moderated yield (56%),[12] Scheme 1.

Compound **1** was treated with catalytic amount of anhydrous powder of sodium hydroxide in dry toluene at the reflux temperature to give 1-bromo-3,5-di(ethynyl)benzene (**2**) as a pale-yellow solid, mp 102–105 °C, in practically quantitative yield, Scheme 1.

The biphenyl **5** was prepared by homocoupling of 1-bromo-3,5-di(*p*-*N*,*N*-dimethylaminophenylethynyl)benzene (**3**) catalysed by the zero-valent nickel complex in stoichiometric amount, Scheme 2.

Now, 1-bromo-3,5-di(*p*-*N*,*N*-dimethylaminophenylethynyl)-benzene (**3**) was prepared by heterocoupling between 1-bromo-3,5-diethynylbenzene (**2**) and *p*-(*N*,*N*-dimethylamino)-iodobenzene in presence of dichloro bis(triphenylphosphine) palladium (5 mol %) and cuprous iodide (2 mol %) in triethylamine at 60 °C. Compound **3** was isolated as a brown solid, mp >300 °C, in good yield (67%), Scheme 2.

Finally, the homocoupling of 1-bromo-3,5-(*p*-*N*,*N*-dimethylaminophenylethynyl)benzene (**3**) was catalysed by zero-valent nickel complex in THF at room temperature giving **5** as a yellow oil, with good yield (65%).

The zero-valent nickel complex catalyst was always used in stoichiometric molar ratio with the bromo derivative and was prepared in situ by reaction between dichloro bis(triphenylphosphine) nickel with powder of zinc as the reductive agent and tetrabutylammonium iodide as a phase transfer agent, in tetrahydrofuran as solvent.

2.2. Synthesis of 3,3′,5,5′-tetra(*p*-methoxy)(phenylethynyl)-biphenyl (6)

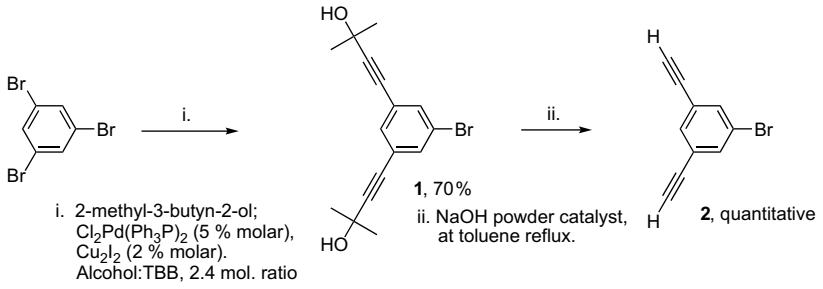
Compound **6** was obtained by the homocoupling reaction of 1-bromo-3,5-(*p*-methoxyphenylethynyl)benzene (**4**) catalysed by zero-valent nickel complex in THF, at room temperature, as a yellow oil in good yield (61%).

Compound **4** was obtained by heterocoupling between 1-bromo-3,5-diethynylbenzene and *p*-(dimethoxy)-iodobenzene in presence of the palladium–copper system in triethylamine at 40 °C as a brown solid, mp >300 °C, in good yield (87%).

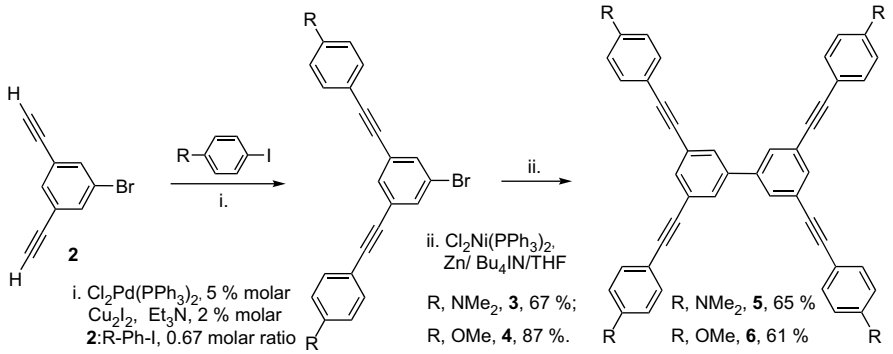
Alternatively the yield in the synthesis of the 3,3′,5,5′-tetra-(substituted)biphenyl (**5**, **6**) was improved by heterocoupling reaction between 3,3′5,5′-tetra(ethynyl)biphenyl (**8**) and *p*-(X)-iodobenzene catalysed by dichloro bis(triphenylphosphine) palladium and cuprous iodide system in diethylamine.

2.3. Synthesis of 3,3′,5,5′-tetra(ethynyl)biphenyl (8)

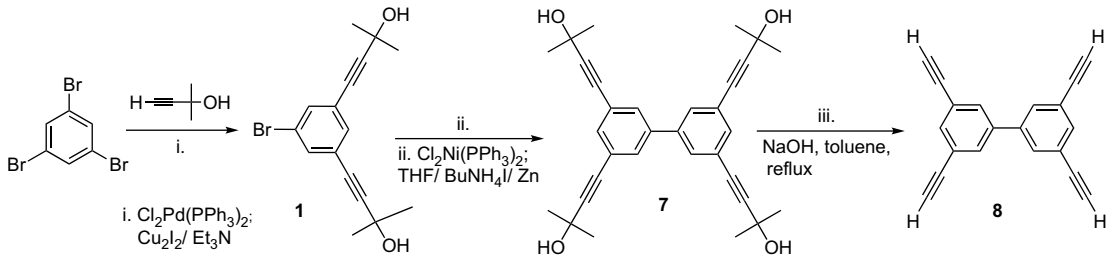
In this way, compound **1** was obtained by heterocoupling between 1,3,5-tribromobenzene and 2-methyl-3-butyn-2-ol, in



Scheme 1.



Scheme 2.



Scheme 3.

0.43 molar ratio, respectively, catalysed by dichloro bis(triphenylphosphine) palladium and cuprous iodide in triethylamine.[12] The monobromo derivative **1** was isolated as a white solid, mp 52–54 °C, in good yield (70%), Scheme 3.

The homocoupling reaction of the monobromo derivative **1** in presence of the zero-valent nickel complex in THF, at room temperature, affords the biphenyl derivative **7** as a white solid, mp 191–193 °C, in excellent yield (95%), Scheme 3.

Now, 3,3′,5,5′-tetra(ethynyl)biphenyl was obtained by treatment of the tetrasubstituted biphenyl **7** with catalytic anhydrous powdered sodium hydroxide, in dry toluene at the reflux temperature, as a yellow solid, which was crystallised in hexane, mp 189–191 °C, in good yield (87%).

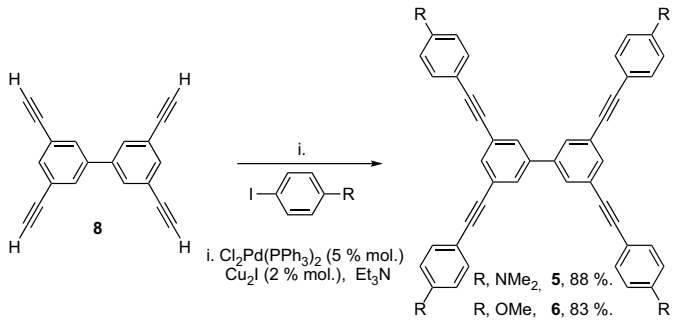
Compound **8** serves to prepare the 3,3′,5,5′-tetra(*p*-X-phenyl)-biphenyl by heterocoupling with the appropriate *p*-X-iodobenzene catalysed by the palladium/copper system.

2.4. Synthesis of 3,3′,5,5′-Tetra[*p*-(*N*,*N*-dimethylamino-phenyl)biphenyl (5) from 8

Thus, compound **5** was obtained by heterocoupling between 3,3′,5,5′-tetra(ethynyl)biphenyl (**8**) and *p*-(*N*,*N*-dimethylamino)-iodobenzene, in triethylamine, catalysed by dichloro bis(triphenylphosphine) palladium and cuprous iodide. Compound **5** was isolated as yellow oil, in excellent yield (93%). The analytical and spectral data coincide with the same compound obtained by homocoupling of **3** with the zero-valent nickel complex. Hence, highest yield was obtained for the heterocoupling catalysed reaction.

2.5. Synthesis of 3,3′,5,5′-tetra(*p*-methoxyphenyl-ethynyl)biphenyl (6) from 8

Compound **6** was obtained by heterocoupling of 3,3′,5,5′-tetra-(ethynyl)biphenyl (**8**) with *p*-iodoanisole, in triethylamine, catalysed by dichloro bis(triphenylphosphine) palladium and cuprous iodide, as yellow oil, in good yield (83%), Scheme 4.



Scheme 4.

3. Conclusions

The homocoupling of 1-bromo-3,5-di(*p*-X-phenylethynyl)-benzene derivatives to the corresponding biphenyl derivatives can be carried out in good yield with stoichiometric catalytic amounts of the nickel zero-valent complex. The presence of the catalyst in lowest amounts gives minor yield in the homocoupled product and hence the zero-valent nickel catalyst complex was not regenerated during the reaction.

Alternatively, highest yield for the same 3,5,3′,5′-tetra(*p*-X-phenylethynyl)biphenyl derivatives can be obtained by heterocoupling between 3,5,3′,5′-tetra(ethynyl)biphenyl and *p*-X-iodobenzene in presence of palladium catalyst (5 mol %) and cuprous iodide (2 mol %) in excellent yields. Previously, the 3,5,3′,5′-tetra(ethynyl)biphenyl intermediate (**8**) was obtained by homocoupling of 1-bromo-3,5-di(2-methyl-3-butyn-2-ol)benzene to the biphenyl intermediate **7** in excellent yield, and successive careful treatment with sodium hydroxide in toluene, at the reflux temperature, in practically quantitative yield.

4. Experimental

4.1. General

Melting points were determined in open capillaries using a Reichert hot-stage microscope and are uncorrected. IR spectra of solids were recorded as KBr pellets and IR spectra of oils were recorded as thin films on NaCl plates with a Bruker Vector 22 spectrophotometer, and the wave numbers are given in cm^{-1}. ^1H and ^{13}C NMR spectra were recorded at 200 and 75 MHz, respectively, on a Bruker Aspect spectrometer, chemical shifts are given in δ, using TMS as an internal reference and constant *J* values are given in hertz, the solvent is $CDCl_3$. Mass spectra were recorded on a VG Autospec spectrometer at 70 eV. Elemental analyses were performed with a LECO CHN-900. Yields are given after silica gel column chromatography separation.

4.2. Synthesis of 3,3′,5,5′-tetra(*p*-*N*,*N*-dimethylamino-phenylethynyl)biphenyl (5)

*4.2.1. 3,5-Bis(3-methyl-1-butyn-3-ol)-1-bromobenzene (**1**)*

A mixture of 2-methyl-3-butyn-2-ol (64.5 mg, 0.77 mmol), tribromobenzene (100 mg, 0.32 mmol), $Pd[(PPh_3)_2]Cl_2$ (5 mol %) and Cu_2I_2 (2% mol) in toluene (20 mL) was stirred at room temperature for 12 h (monitored by TLC). Then, a saturated aqueous solution of ammonium chloride (30 ml) and a little amount of KCN (5 mg) were added, and the organic layer was separated and dried on sodium sulfate. Finally solvent was removed and compound **1** was isolated as a white solid, mp 52–54 °C (401.2 mg, 70%).[12]

^1H NMR ($CDCl_3$): 7.44 (d, 2H, *J*=1.62 Hz, H-2, H-6), 7.34 (t, 1H, *J*=1.62 Hz, H-4), 2.89 (br s, 2H, 2-OH), 1.57 (s, 12H, 4-Me).

*4.2.2. 1-Bromo-3,5-di(ethynyl)benzene (**2**)*

Compound **1** (100 mg, 0.5 mmol) was treated with a catalytic amount of powder sodium hydroxide in dry toluene at reflux temperature for 2 h giving **2** as a pale-yellow solid, mp 102–105 °C, in practically quantitative yield.

IR (KBr): 3345 (≡CH), 3029 (ArC–H), 2248 (C≡C), 1268 (C═C), 825 and 715 (1,3,5-trisubst.), 686 (C–Br). ^{1}H NMR ($CDCl_3$): 7.60 (s, 2H, H-2, H-6), 7.52 (s, 1H, H-4), 3.13 (s, 2H, ≡C–H). ^{13}C NMR ($CDCl_3$): 135.1 (C-2, C-6), 134.2 (C-1), 124.2 (C-3, C-5), 121.8 (C-4), 81.1 (≡C–Ph), 79.3 (≡C–H). Anal. Calcd for $C_{10}H_5Br$ (205.05): C, 58.58; H, 2.46. Found: C, 58.65; H, 2.52.

*4.2.3. 1-Bromo-3,5-di(p-N,N-dimethylamino-phenylethynyl)benzene (**3**)*

To a mixture of **2** (41.01 mg, 0.20 mmol) and dichloro bis-(triphenylphospine) palladium (15 mg, 0.061 mmol, 5 mol %) and cuprous iodide (2 mol %) was added a solution of *p-N,N*-dimethyl-amino-iodobenzene (61.5 mg, 0.30 mmol) in freshly distilled tri-ethylamine and stirred at 60 °C for 24 h. The mixture was treated with a saturated aqueous solution of ammonium chloride (20 ml) and a little amount of potassium cyanide (5 mg) and extracted with dichloromethane. After solvent was removed the residual solid obtained was purified by silica gel column chromatography (hexane/dichloromethane, 2:1) giving **3** (55.66 mg, 67%) as a brown solid mp >300 °C.

IR (KBr): 3062 (ArC–H), 2975 (C–H), 2236 (C≡C), 1654 (C═C), 1445 (CH3), 1352 (C–N), 820 (*p*-subst.), 810 and 698 (1,3,5-trisubst.), 664 (C–Br). ^{1}H NMR ($CDCl_3$): 7.53 (t, 3H, *J*=1.21 Hz, H-2, H-4, H-6), 7.39 (d, 4H, *J*=8.9 Hz, H-2′, H-6′), 6.66 (d, 4H, *J*=8.9 Hz, H-3′, H-5′), 3.00 (s, 12H, 2N–Me_2). ^{13}C NMR ($CDCl_3$): 150.3 (C-4′), 132.9 (C-1), 132.6 (C-3′, C-5′), 132.4 (C-2′, C-6′), 126.1 (C-2, C-6), 121.70 (C-3, C-5), 111.8 (C-4), 109.2 (C-1′), 92.4 (C≡*C*–Ph–Br), 85.59 (Me_2N–Ph–*C*≡C–), 40.2 (N–Me_2). Anal. Calcd for $C_{26}H_{73}N_2Br$ (447.37): C, 69.81; H, 5.18; N, 7.15. Found: C, 69.44; H, 5.12; N, 7.08.

*4.2.4. 3,3′,5,5′-Tetra(p-N,N-dimethylaminophenylethynyl)-biphenyl (**5**)*

A solution of Ni[$(PPh_3)_2$]Cl_2 (92.12 mg, 0.14 mmol), Bu_4NI (51.7 mg, 0.14 mmol), powder of Zn (14 mg, 0.21 mmol) in dry THF was stirred for 30 min and then was added **3** (60 mg, 0.14 mmol) and stirred for 12 h at room temperature. Solvent was removed and the residual brown oil was purified by silica gel column chromatography giving **5** (66 mg, 65%) as a yellow oil.

IR (KBr): 3012 (ArC–H), 2988 (C–H), 2210 (C≡C), 1670 (C═C, conj.), 1486 (CH_3), 1342 (C–N), 730 (Ph-subst.). ^{1}H NMR ($CDCl_3$): 7.90 (t, 2H, *J*=7.5 Hz, H-4, H-4′), 7.67 (d, 8H, *J*=7.0 Hz, H-2″, H-6″), 7.62 (d, 8H, *J*=7.00 Hz, H-3″, H-5″), 7.53 (dd, 4H, *J*=7.5, 1.6 Hz, H-2, H-6, H-2′, H-6′), 2.97 (s, 24H, 8NMe_2). ^{13}C NMR ($CDCl_3$): 144.3 (C-4″), 135.9 (C-1, C1′), 134.7 (C-4, C-4′), 133.8 (C-2″, C-6″), 122.08 (C-3″, C-5″), 111.70 (C-3″, C-5″), 111.03 (C-1″), 97.64 (≡*C*–BiPh), 85.45 (–C≡*C*–Ph–NMe_2), 42.16 (N–Me_2). Anal. Calcd for $C_{52}H_{46}N_4$ (726.97): C, 85.91; H, 6.38; N, 7.71. Found: C, 85.57; H, 6.18; N, 7.54.

4.3. Synthesis of 3,3′,5,5′-tetra(*p*-methoxy)(phenylethynyl)-biphenyl (6)

*4.3.1. 1-Bromo-3,5-di(p-methoxyethynyl)benzene (**4**)*

To a mixture of **2** (38.33 mg, 0.20 mmol), dichloro bis(triphenylphospine) palladium (15 mg, 0.061 mmol, 5 mol %) and cuprous iodide (2 mol %) was added a solution of *p*-methoxy-iodobenzene (57.48 mg, 0.30 mmol) in freshly distilled triethylamine and stirred at 60 °C for 24 h. The mixture was treated with a saturated aqueous solution of ammonium chloride (20 ml) and a little amount of potassium cyanide (5 mg) and extracted with dichloromethane (10 ml). After solvent was removed the residual solid obtained was purified by silica gel column chromatography (hexane/dichloromethane, 2:1) giving **4** (68.48 mg, 87%) as a brown solid mp >300 °C.

*4.3.2. 3,3′,5,5′-Tetra(p-methoxyphenylethynyl)biphenyl (**6**)*

A solution of $Cl_2Ni(PPh_3)_2$ (92.12 mg, 0.14 mmol), Bu_4NI (51.7 mg, 0.14 mmol), powder of Zn (14 mg, 0.21 mmol) in dry THF was stirred for 30 min and then was added **4** (56.08 mg, 0.14 mmol) and stirred for 12 h at room temperature. Solvent was removed and the residual brown oil was purified by silica gel column chromatography giving **6** (61.7 mg, 61%) as a yellow oil.

Anal. Calcd for $C_{48}H_{34}O_4$ (674.79): C, 85.44; H, 5.08. Found: C, 85.27; H, 5.18.

4.4. Synthesis of 3,5,3′,5′-tetra(ethynyl)biphenyl (8)

*4.4.1. 3,3′5,5′-Tetra(3-methyl-1-butyn-3-ol)biphenyl (**7**)*

A mixture of $Cl_2Ni(PPh_3)_2$ (480 mg, 0.72 mmol), tetrabutyl-ammonium iodide (267 mg, 0.72 mmol) and powder of Zn (68.8 mg, 1.1 mmol), was stirred at room temperature for 30 min. Then, a solution of 1-bromo-3,5-di(3-methyl-1-butyn-3-ol)benzene (**4**) (240 mg, 0.72 mmol) in dry THF (20 mL) was added and stirred for 6 h. Finally, the solvent was removed and the brown solid was purified by silica gel column chromatography (3:1 hexane/dichloromethane) giving biphenyl **7** as a white solid, mp 191–193 °C (167 mg, 95%).

IR (KBr): 3345 (O–H), 2983, 2228 (C≡C), 1587, 1556 (C═C), 1165, 949, 866 (1,3,5-trisubst.). ^{1}H NMR ($CDCl_3$): 7.45 (d, 4H, *J*=1.21 Hz, H-2, H-6, H-2′, H-6′), 7.36 (t, 2H, *J*=1.21 Hz, *J*=1.21 Hz, H-4, H-4′), 2.64 (s, 4H, OH), 1.58 (s, 24H, Me). ^{13}C NMR ($CDCl_3$): 133.9 (C-4, C-4′), 133.2 (C-2, C-6, C-2′, C-6′), 132.9 (C-1, C-1′), 124.6 (C-3, C5, C-3′, C-5′), 95.6 (≡C–C–OH), 79.9 (≡C–Ph), 65.5 (C–OH), 31.2 (Me). Anal. Calcd for $C_{32}H_{34}O_4$ (482.62): C, 79.64; H, 7.10. Found: C, 79.74; H, 5.18.

*4.4.2. 3,3′5,5′-Tetra(ethynyl)biphenyl (**8**)*

A solution of 3,5,3′,5′-tetra(3-methyl-1-butyn-3-ol)biphenyl (150 mg, 0.31 mmol) in dry toluene was treated with a catalytic amount of anhydrous powder of NaOH and warmed at reflux temperature for 5 h. After the solvent was removed giving **8** as a solid, it was crystallised in hexane as a yellow solid, mp 189–191 °C, in excellent yield (75 mg, 98%).

IR (KBr): 3055 (C≡H), 1422, 1266, 896, 741 and 706 (1,3,5-trisubst.). ^{1}H NMR ($CDCl_3$): 7.60 (d, 4H, *J*=1.2 Hz, H-5), 7.52 (t, 2H, *J*=1.2, 1.2 Hz), 3.13 (s, 4H). ^{13}C NMR ($CDCl_3$): 135.1 (C-1), 134.2 (C-6), 132.3 (C-5), 121.8 (C-4), 81.1 (C-3), 79.3 (C-2). Anal. Calcd for $C_{20}H_{10}$ (250.3): C, 95.97; H, 4.03. Found: C, 95.77; H, 3.88.

4.5. Synthesis of 3,5,3′,5′-tetra(*p-N,N*-dimethylamino) (phenylethynyl)biphenyl (5) from 3,5,3′,5′-tetra (ethynyl)biphenyl (5)

A mixture of *p*-(*N,N*-dimethylamino)-iodobenzene (494 mg, 2.0 mmol), dichloro bis(triphenylphosphine) palladium (31 mg, 0.04 mmol), cuprous iodide (0.01 mmol) and a solution of 3,5,3′,5′-tetra(ethynyl)biphenyl (100 mg, 0.44 mmol) in triethylamine was stirred at 40 °C for 8 h, and then hydrolysed with a saturated aqueous solution of ammonium chloride (30 ml) and a little amount of potassium cyanide (10 mg) and extracted with dichloromethane (20 ml). After solvent was removed, the residual oil was purified by chromatography on silica gel column (10:1, hexane/dichloromethane) giving the biphenyl **5** as a yellow oil (281.5 mg, 88%).

^{1}H NMR ($CDCl_3$): 7.67 (d, 8H, *J*=6.99 Hz, H-11, H-4), 7.62 (d, 8H, *J*=6.99 Hz, H-3), 7.53 (dd, 4H, *J*=7.53, 1.6 Hz, H-9), 7.9 (t, 2H,

J=7.53 Hz, H-11), 2.97 (s, 24H, H-1). ^{13}C NMR ($CDCl_3$): 144.3 (C-2), 135.9 (C-10), 134.7 (C-11), 133.8 (C-4), 122.08 (C-8), 111.70 (C-3), 111.03 (C-5), 97.64 (C-7), 85.45 (C-6), 42.16 (N–Me_2). IR (KBr): 3012 (ArC–H), 2988 (C–H), 2210 (C≡C), 1670 (C=C), 1486 (CH_3), 1342 (C–N), 730 (1,3,5-trisubst.). Anal. Calcd for $C_{52}H_{46}N_4$ (726.97): C, 85.91; H, 6.38; N, 7.71. Found: C, 85.66; H, 6.25; N, 7.43.

4.6. Synthesis of 3,5,3′,5′-tetra(*p*-methoxyphenylethynyl)-biphenyl (6) from 3,5,3′,5′-tetra(ethynyl)biphenyl (6)

A mixture of *p*-iodoanisole (490 mg, 2.08 mmol), dichloro bis (triphenylphosphine) palladium (31 mg, 0.04 mmol), cuprous iodide (0.01 mmol) and a solution of 3,5,3′,5′-tetra(ethynyl)biphenyl (100 mg, 0.44 mmol) in triethylamine was stirred at 60 °C (external bath) for 12 h. After was hydrolysed with a saturated aqueous solution of ammonium chloride (20 ml) and potassium cyanide (5 mg), and extracted with dichloromethane (10 ml). After solvent was removed, the residual oil was purified by silica gel column chromatography (10:1, hexane/dichloromethane) giving the biphenyl **6** as a yellow oil (398 mg, 83%).

IR (KBr): 2976 (C–H), 2862 (O–Me), 2360 and 2340 (C≡C), 1535, 1267 (ArC–O–Me), 841 (1,3,5-trisubst.). ^{1}H NMR ($CDCl_3$): 7.58 (d, 4H, J=1.2 Hz, H-2, H-6, H-2′, H-6′), 7.46 (d, 8H, J=8.9 Hz, H-2″, H-6″), 7.31 (t, 2H, J=1.2 Hz, H-4, H-4′), 6.89 (d, 8H, J=8.9 Hz, H-3″, H-5″), 3.83 (s, 12H, Me). ^{13}C NMR ($CDCl_3$): 160.0 (C-4″), 133.3 (C-4, C-4′), 133.3 (C-2, C-6, C-2′, C-6′), 132.75 (C-1, C-1′), 125.6 (C-2, C-6, C-2′, C-6′), 123.4 (C-3, C-5, C-3′, C-5′), 114.1 (C-3″, C-5″), 114.0 (C-1″), 91.2 (≡C–BiPh), 86.0 (≡C–Ph–OMe), 55.3 (Me). Anal. Calcd for $C_{48}H_{34}O_4$ (674.79): C, 85.44; H, 5.08. Found: C, 85.13; H, 5.22.

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