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Selective and Efficient Access to *Ortho*, *Meta* and *Para* Ring-substituted Phenylacetylene Derivatives $R\text{-}[C{\equiv}C\text{-}C_6H_4]_x\text{-}Y$ (Y : H, NO_2, CN, I, NH_2)

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ABSTRACT : *ortho*, *meta* and *para* isomers of iodo and amino ring-substituted phenylacetylene as well as rod-like arylacetylene derivatives were prepared by a simple synthetic route involving three consecutive reactions : the palladium-catalysed carbon-carbon bond formation, the Sandmeyer reaction and the desilylation of the protected trimethylsilylalkynes. © 1997 Elsevier Science Ltd.

INTRODUCTION

Alkynes are at the cross-road of several fields of chemistry. They are involved in material science as components of molecular-scale wires[1-3] or as precursors for two or three dimensional carbon networks.[4] They constitute, in polymer science, key-monomers for the synthesis of the polyacetylenes[5-7] and organometallic poly-ynes[8-11]. They are also key starting products in organic catalysis for the selective transformation of low-cost molecules in value-added products[12-15]. New substituted alkynes and selective, high yield synthesis are in great demand for these various fields of research.

In the phenylacetylene series, amino and iodo ring substituants are key intermediate groups as they can be easily transformed in a variety of functional groups. Amino groups lead access to amide, imine or urethane functionality. Aryl iodide are involved in classical organic chemistry to give corresponding alcohol, ether, nitrile or ester *via* nucleophilic substitution reactions, as well as in metal mediated organic chemistry[16,17].

We have recently reported[18] the synthesis of new *p*-phenylacetylene derivatives $H\text{-}(C{\equiv}C\text{-}C_6H_4)_x\text{-}C{\equiv}C\text{-}Si^iPr_3$ with different lengths (x = 1 to 4) of the π-conjugated system. We now report a general strategy for the design of the selected *ortho*, *meta* or *para* -iodo and -amino phenylacetylene

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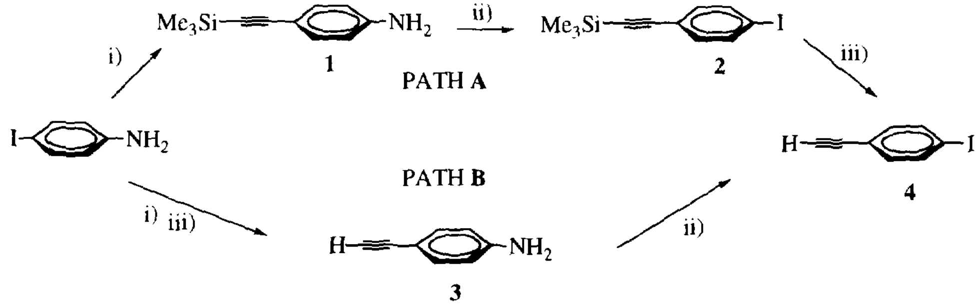
isomers $R\text{-}C{\equiv}C\text{-}C_6H_4\text{-}Y$ (Y : I, NH_2 ; R : H, $SiMe_3$) and of several substituted rod-like arylacetylene derivatives $R\text{-}[C{\equiv}C\text{-}C_6H_4]_x\text{-}Y$ (R : H, $SiMe_3$; x : 1, 2 ; Y : H, NO_2, CN, NH_2). This functional alkyne synthesis involved consecutively i) a palladium-catalyzed carbon-carbon bond formation, ii) the transformation of an amino group in an iodo group using the Sandmeyer reaction and iii) a desilylation reaction of silylalkynes to generate terminal alkynes.

DISCUSSION

Ortho, meta, para -iodo and -amino phenylacetylene isomers

The synthesis of 4-ethynyl iodobenzene **4** was first achieved in three steps following the route A[18] (Scheme1). Using the straightforward catalytic method reported by S. Takahashi et al.[19], the Pd/Cu catalyzed carbon-carbon coupling of 4-iodoaniline and trimethylsilylacetylene gave the derivative 4-trimethylsilylethynyl aniline **1**. The transformation of **1** into the corresponding iodo derivative **2** *via* a Sandmeyer reaction, followed by a desilylation of the trimethylsilyl group led to the 4-ethynyl iodobenzene **4** in good yield[18]. As the 4-ethynylaniline **3** could be directly prepared from the 4-iodoaniline,[19] we have considered the more direct way **B** to obtain the target product **4**. The reaction of the amino compound **3** in concentrated hydrochloric acid with sodium nitrite at 0 °C, followed by reaction with KI indeed led us to obtain the iodo product **4** in good yield (73 %).

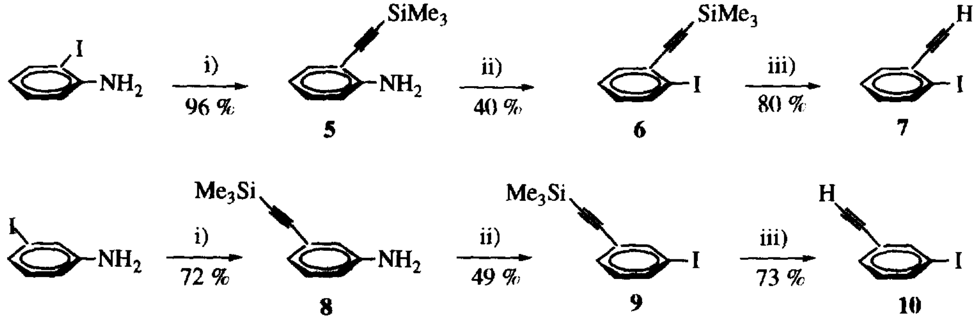


Legend : i) $Me_3SiC{\equiv}C\text{-}H$, $PdCl_2(PPh_3)_2$ (1 mol %), CuI (1 mol %), NEt_3 (solvent), r.t.
ii) HCl 12N, $NaNO_2$; 0°C, KI.
iii) EtOH, NaOH in THF, 30 min.

Scheme 1

The overall yield for the 4-ethynyl iodobenzene **4** from the starting product 4-iodoaniline was better according to the path B (58 %) than the path A (48 %). However the high stability of the silylated compounds **1** and **2** in comparison with the product **3**, which was rapidly transformed in a brown product (even stored at low temperature), led us to prefer the path **A** as a competitive approach. Thus, the synthesis of *ortho* and *meta* derivatives of the phenylacetylene were attempted following the strategy **A**.

The Pd/Cu catalyzed cross-coupling of trimethylsilylacetylene with the commercial 2-iodoaniline and 3-iodoaniline led to their corresponding trimethylsilylethynylaniline derivatives **5** (96 %) and **8** (72 %) respectively (Scheme 2). Their respective Infrared spectra clearly showed the presence of the strong symmetric and antisymmetric stretching band absorptions, characteristic of the amino group and of the C≡C-Si function (**5** : 2147 cm^{-1} ; **8** : 2156 cm^{-1}). These amino products were precursors of a large panel of phenylacetylene derivatives by modification of the amino function. Thus, we considered their transformation into iodo derivatives *via* the Sandmeyer reaction (Scheme 2).



Legend : i) $Me_3SiC{\equiv}C\text{-}H$, $PdCl_2(PPh_3)_2$ (1 mol %), CuI (1 mol %), NEt_3 (solvent), r.t.
ii) HCl 12N, $NaNO_2$; 0°C, KI.
iii) EtOH, NaOH in THF, 30 min.

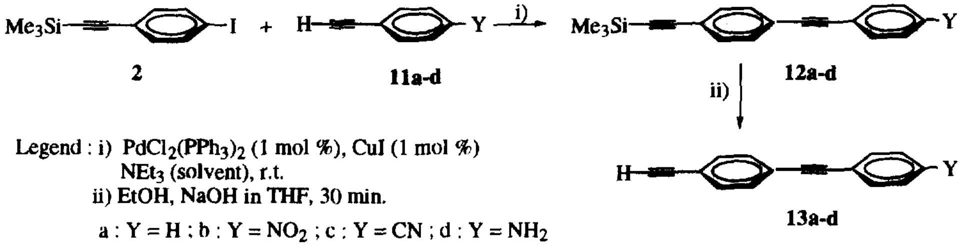
Scheme 2

The reaction between amino compounds **5** and **8** and sodium nitrite at 0 °C in a concentrated hydrochloric medium led to their non isolated corresponding diazoic salts, which were *in situ* treated with KI to give the products 2-trimethylsilylethynyl iodobenzene **6** (40 %) and 3-trimethylsilylethynyl iodobenzene **9** (49 %) respectively. The IR spectroscopy indicated the complete desappearance of the NH_2 absorption bands and the presence of the unaffected silylated alkyne moiety absorption. These protected alkynes were reacted with sodium hydroxide in ethanol/THF mixture, at room temperature, to give by desilylation the terminal alkynes 2-ethynyl iodobenzene **7** (80 %) and 3-ethynyl iodobenzene **10** (73 %) in good yields (Scheme 2). The appearance of the strong ≡C-H band vibration and the complete desappearance of the C≡C-Si vibration in Infrared spectroscopy as well as the ^{1}H and ^{13}C NMR spectroscopies confirmed the quantitative deprotection of the silylated alkynes. The structure of the 1-2 disubstituted phenylacetylene derivatives **5**, **6** and **7** and of the 1-3 disubsituted products **8**, **9** and **10** were clearly confirmed by ^{1}H and ^{13}C NMR specstroscopies.

The synthesis of the *ortho* - iodophenylacetylene **7** was already reported in three steps via the dimetallation of phenylacetylene followed by the addition of iodine.[20-22] The *ortho* - directing and -activating effect of the C≡CLi group induced only an *ortho* substitution, thus the *meta* and *para* derivatives **4** and **10** were not accessible by this way.

Substituted rod-like aryldiynes derivatives R-[C≡C-C_6H_4]$_2$-Y

By modification of the iodo or of the protected acetylenic functions, the trimethylsilylethynyl iodobenzene isomers **2**, **6** and **9** could be useful for the synthesis of more elaborate molecules. The *para* derivative **2** was successively used as building block to increase step by step the length of the *p*-phenylacetylene derivatives H-(C≡C-C_6H_4)$_x$-C≡C-Si^{i}Pr$_3$ (x = 1 to 4)[18]. Thus we have considered a more general application of this precursor **2** towards the synthesis of several functionalized alkynes containing neutral (Y : H), electron - attracting (Y : NO_2, CN) or -donating (Y : NH_2) groups. The Pd/Cu catalysed carbon-carbon coupling of the trimethylsilylethynyl *para* -iodobenzene **2** and the phenylacetylene **11a** or their *para*-nitro **11b**, *para*-cyano **11c** and *para*-amino **11d** derivatives gave the corresponding rod-like compounds **12a-d** in good yields (scheme 3). Their Infrared spectrum indicated the deseapparance of the strong ≡C-H vibration of the compounds **11** and the presence of two C≡C absorption bands, at 2150 cm^{-1} for the C≡CSi and 2110 cm^{-1} for the internal triple bond respectively. The ^{13}C NMR spectra of the products **12** showed particularly signals corresponding to the silylated triple bond (near 96 and 104 ppm) and to the internal triple bond (near 88 and 93 ppm). The deprotection of these compounds **12** gave the corresponding terminal alkynes **13a-d** in good yields (scheme 3). The ^1H and ^{13}C NMR as well as infrared spectroscopies clearly indicated that the desilylation reaction was selective and did not affect the internal triple bond or the Y fonction.



Legend : i) $PdCl_2(PPh_3)_2$ (1 mol %), CuI (1 mol %)
NEt_3 (solvent), r.t.
ii) EtOH, NaOH in THF, 30 min.
a : Y = H ; b : Y = NO_2 ; c : Y = CN ; d : Y = NH_2

Scheme 3

CONCLUSION

A synthetic strategy is described that provides an efficient access to each *ortho, meta, para* isomers of the iodo and amino ring-substituted phenylacetylene derivatives **1** - **10** from the commercial iodoaniline isomers. These bifunctional products show synthetic potential for the formation of C-C bonds *via* catalysis by activation of the acetylenic or the iodo function. Morever, due to the well-established chemistry of aryl amine and aryl iodide these compounds are key synthetic intermediates to open the access to new functional arylacetylenes. Diynes **12** and **13**, due to the extension of the delocalized π-system as well as the presence of the functional group Y, are precursors of new ligands in organometallic chemistry, monomers for the synthesis of polyphenylacetylene derivatives as well as starting products in catalysis.

ACKNOWLEDGEMENTS

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EXPERIMENTAL

General data. Solvents were dried by standard methods and all reactions involving palladium complexes were conducted under nitrogen by standard Schlenk tube techniques. Elemental analyses were performed by the CNRS analysis laboratory, Vernaison (France). NMR spectra were recorded on a Bruker AM 300 P operating at 300.131 MHz for ^1H, 75.469 MHz for ^{13}C. High resolution mass spectra were obtained on a Varian Mat 311 spectrometer (Electronic ionisation mode). Compounds **1-3** and **11b-d** were prepared by previously described procedures.[18,19] Trimethylsilylacetylene, phenylacetylene, 2-iodoaniline and 3-iodoaniline were purchased from ACROS.

Synthesis of aromatic acetylenic compounds by catalytic C-C bond formation

A slight excess of the terminal alkyne was added to a solution of the iodoarene derivative in deoxygenated diethylamine with 1 mol% of $PdCl_2(PPh_3)_2$ and 1 mol% of CuI. After stirring for 20 h at room temperature, the solvent was evaporated and the brown residue was extracted with diethylether. After evaporation, the crude product was purified by column chromatography on alumina with pentane as eluent.

5 (1-amino, 2-trimethylsilylethynylbenzene) pale yellow oil ; 96 % yield from 2.19 g (10 mmol) of 2-iodoaniline, 1.55 mL (11 mmol) of trimethylsilylacetylene, 0.070 g (0.1 mmol) of $PdCl_2(PPh_3)_2$ and 0.019 g (0.1 mmol) of CuI ; IR (neat) ν/cm^{-1} 3475 and 3384 (m, NH_2), 2147 (m, C≡C) ; ^1H NMR δ (300.133 MHz, $CDCl_3$, 297 K) 7.28 (d, 1H, H_3 or H_6, C_6H_4, $^3J_{HH}$ = 8 Hz), 7.10 (d, 1H, H_3 or H_6, C_6H_4, $^3J_{HH}$ = 8 Hz), 6.65 (m, 2H, H_4 or H_5, C_6H_4), 4.21 (s broad, 2H, NH_2), 0.25 (s, 9H, CH_3) ; ^{13}C {^1H} NMR δ (75.469 MHz, $CDCl_3$, 297 K) 148.26 (C-NH_2), 132.28, 129.92, 117.79 and 114.20 (CH of C_6H_4), 107.81, 101.79 and 99.78 (*C*-*C*≡*C*), 0.19 (CH_3) ; Elemental analysis calcd. for $C_{11}H_{15}NSi$ (Found) C : 69.81 (70.17) ; H : 7.99 (7.92).

8 (1-amino, 3-trimethylsilylethynylbenzene) yellow oil ; 72 % yield from 2.81 g (12.8 mmol) of 3-iodoaniline, 1.75 mL (13 mmol) of trimethylsilylacetylene, 0.194 g (0.27 mmol) of $PdCl_2(PPh_3)_2$ and 0.067 g (0.35 mmol) of CuI ; IR (neat) ν/cm^{-1} 3465 and 3374 (m, NH_2), 2156 (m, C≡C) ; ^1H NMR δ (300.133 MHz, $CDCl_3$, 297 K) 7.65 (t, 1H, H_5, $^3J_{HH}$ = 8 Hz), 6.86 (dm, 1H, H_4 or H_6, $^3J_{HH}$ = 8 Hz), 6.78 (s, 1H, H_2), 6.63 (dm, 1H, H_4 or H_6, $^3J_{HH}$ = 8 Hz), 3.52 (s broad, 2H, NH_2), 0.22 (s, 9H, CH_3) ; ^{13}C {^1H} NMR δ (75.469 MHz, $CDCl_3$, 297 K) 146.14 (C-NH_2), 129.91, 122.47, 118.24 and 115.63 (CH of C_6H_4), 123.78 (*C*-C≡C), 105.38 (*C*≡C-Si), 93.47 (C≡*C*-Si), 0.04 (CH_3) ; Elemental analysis calcd. for $C_{11}H_{15}NSi$ (Found) C : 69.81 (69.48) ; H : 7.99 (7.99).

12a 1-trimethylsilylethynyl-4-(phenylethynyl)benzene white powder ; 55 % yield from 2.655 g (8.84 mmol) of p-trimethylsilyl ethynyl 4-iodobenzene **4**, 0.988 ml (9 mmol) of phenylacetylene **11a**, 0.077 g (0.109 mmol) of $PdCl_2(PPh_3)_2$ and 0.037 g (0.194 mmol) of CuI ; IR (KBr), ν/cm^{-1} 2200 (w, C≡C), 2153 (s, C≡CSi) ; ^1H NMR δ (200.13 MHz, $CDCl_3$, 297 K) 7.48 (m, 2H, Ph), 7.43 (s, 4H, Ph), 7.32 (m, 3H, Ph), 0.24 (s, 9H, CH_3) ; ^{13}C {^1H} NMR δ (50.33 MHz, $CDCl_3$, 297 K) 131.94, 131.67, 131.43, 128.53 and 128.44 (CH of Ph), 123.39, 123.05 and 122.94 (*C*-C≡), 104.69, 96.29 (*C*≡*C*-Si), 91.33 and 89.07 (*C*≡*C*), -0.027 (CH_3). HRMS m/z calcd for $C_{19}H_{18}Si$ (found) M^+ : 274.1179 (274.118)

12b 1-trimethylsilylethynyl-4-((4-nitrophenyl)-ethynyl)benzene white solid ; 22 % yield from 0.442 g (3 mmol) of p-nitrophenylacetylene **11b**, 0.892 g (2.97 mmol) of p-trimethylsilyl ethynyl 4-iodo benzene, 0.028 g (4.10^{-2} mmol) of $PdCl_2(PPh_3)_2$ and 0.008 g (4, 2.10^{-2} mmol) of CuI ; IR (KBr), ν/cm^{-1} 2214 (w, C≡C), 2152 (m, C≡CSi), 1350 (s, NO_2) ; ^{1}H NMR δ (200.13 MHz, $CDCl_3$, 297 K) 8.20 (d, 2H, $^3J_{HH}$ = 9 Hz, C_6H_4), 7.63 (d, 2H, $^3J_{HH}$ = 9 Hz, C_6H_4), 7.45 (s, 4H, C_6H_4), 0.23 (s, 9H, CH_3) ; ^{13}C {^{1}H} NMR δ (50.33 MHz, $CDCl_3$, 297 K) 148.54 (C-NO_2), 133.74, 133.49, 133.09 and 125.14 (CH of C_6H_4), 131.40, 125.49 and 123.47 (*C*-C≡), 105.73, 98.58 (C≡C-Si), 95.65 and 90.72 (C≡C), 1.33 (CH_3). HRMS m/z calcd for $C_{19}H_{17}NO_2Si$ (found) M$^+$: 319.1029 (319.102). Elemental analysis calcd. for $C_{19}H_{17}NO_2Si$ (Found) C : 71.44 (71.14) ; H : 5.36 (5.79).

12c 1-trimethylsilylethynyl-4-((4-cyanophenyl)-ethynyl)benzene pale yellow powder ; 98 % yield from 0.698 g (5.49 mmol) of p-cyanophenylacetylene **11c**, 1.66 g (5.53 mmol) of p-trimethylsilyl ethynyl 4-iodobenzene, 0.039 g (0.055 mmol) of $PdCl_2(PPh_3)_2$ and 0.013 g (0.068 mmol) of CuI ; IR (KBr), ν/cm^{-1} 2228 (m, CN), 2214 (m, C≡C), 2150 (m, C≡CSi) ; ^{1}H NMR δ (200.13 MHz, $CDCl_3$, 297 K) 7.58 (m, 4H, C_6H_4), 7.43 (s, 4H, C_6H_4), 0.23 (s, 9H, CH_3) ; ^{13}C {^{1}H} NMR δ (50.33 MHz, $CDCl_3$, 297 K) 132.12, 132.05 and 131.63 (CH of C_6H_4), 127.98, 123.92, 122.2 (*C*-C≡), 118.51 (CN), 111.72 (*C*-CN), 104.36, 97.05 (C≡C-Si), 93.35 and 89.51 (C≡C), -0.07 (CH_3). HRMS m/z calcd for $C_{20}H_{17}NSi$ (found) M$^+$: 299.1130 (299.113).

12d 1-trimethylsilylethynyl-4-((4-aminophenyl)-ethynyl)benzene pale yellow powder ; 97 % yield from 1.14 g (9.7 mmol) of p-aminophenylacetylene **11d**, 2.92 g (9.7 mmol) of p-trimethylsilyl ethynyl iodobenzene, 0.068 g (0.097 mmol) of $PdCl_2(PPh_3)_2$ and 0.013 g (0.097 mmol) of CuI ; IR (KBr), ν/cm^{-1} 3465, 3375 (s, NH_2), 2209 (m, C≡C), 2153 (m, C≡CSi) ; ^{1}H NMR δ (300.133 MHz, $CDCl_3$, 297 K) 7.41 (s, 4H, C_6H_4), 7.32 (d, 2H, $^3J_{HH}$ = 7 Hz, C_6H_4), 6.6 (d, 2H, $^3J_{HH}$ = 7 Hz, C_6H_4), 3.82 (broad, 2H, NH_2), 0.25 (s, 9H, CH_3) ; ^{13}C {^{1}H} NMR δ (75.469 MHz, $CDCl_3$, 297 K) 133.09, 131.89, 131.15 and 114.79 (CH of C_6H_4), 124.13, 122.92, 112.33 (*C*-C≡), 146.92 (*C*-NH), 104.91, 95.90 (C≡C-Si), 92.30 and 87.18 (C≡C), 0.01 (CH_3). HRMS m/z calcd for $C_{19}H_{19}NSi$ (found) M$^+$: 289.1287 (289.1283). Elemental analysis calcd. for $C_{19}H_{19}NSi$ (Found) C : 78.86 (78.56) ; H : 6.62 (6.48).

Synthesis of iodoarene derivatives by the Sandmeyer reaction

A slight excess of sodium nitrite dissolved in water was added to a slurry of the amino arene compound in concentrated hydrochloric acid at 0 °C. After 50 min, the reaction mixture was added dropwise into a solution of potassium iodide in water at 0 °C. The reaction mixture was allowed to reach the room temperature and stirred overnight. The aqueous layer was extracted twice with diethylether. After evaporation of the solvent, the brown crude product was purified by column chromatography on alumina with pentane as eluent.

4 (1-iodo,4-ethynylbenzene) white solid ; 73 % yield from 0.73 g (6.24 mmol) of **3**, 0.443 g (6.42 mmol) of $NaNO_2$ and 1.356 g (8.12 mmol) of KI ; **IR** (KBr), ν/cm^{-1} 3264 (s, ≡C-H), 2101 (w, C≡C) : ^1H NMR δ (300.133 MHz, $CDCl_3$, 297 K) 7.54 (d, 2H, C_6H_4, $^3J_{HH}$ = 8 Hz), 7.12 (d, 2H, C_6H_4, $^3J_{HH}$ = 8 Hz), 3.01 (s, 1H, C≡C-H) ; ^{13}C {^1H} NMR δ (75.469 MHz, $CDCl_3$, 297 K) 137.53, 133.62 (CH of C_6H_4), 121.64 (*C*-C≡), 94.49.55 (C-I), 82.72 (*C*≡C-H), 78.61 (C≡*C*-H). Elemental analysis calcd. for C_8H_5I (Found) C : 42.12 (42.79) ; H : 2.21 (2.26).

6 (1-iodo,2-trimethylsilylethynylbenzene) yellow oil : 40 % yield from 1.83 g (9.7 mmol) of **5**, 0.73 g (10.6 mmol) of $NaNO_2$ and 2.08 g (12.6 mmol) of KI : IR (neat), ν/cm^{-1} 2162 (s, C≡C) : ^1H NMR δ (300.133 MHz, $CDCl_3$, 297 K) 7.64 (dd, 1H, H_3 or H_6, C_6H_4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.27 (dd, 1H, H_3 or H_6, C_6H_4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.09 (dt, 1H, H_4 or H_5, C_6H_4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 6.79 (dt, 1H, H_4 or H_5, C_6H_4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 0.08 (s, 9H, CH_3) ; ^{13}C {^1H} NMR δ (75.469 MHz, $CDCl_3$, 297 K) 138.72, 132.76, 129.58 and 127.73 (CH of C_6H_4), 128.23 (*C*-C≡), 106.55 (C-I), 106.00 (*C*≡C-Si), 101.30 (C≡*C*-Si), -0.15 (CH_3).

9 (1-iodo,3-trimethylsilylethynylbenzene) pale yellow oil ; 49 % yield from 1.73 g (9.2 mmol) of **8**, 0.63 g (9.2 mmol) of $NaNO_2$ and 1.56 g (9.4 mmol) of KI ; IR (neat), ν/cm^{-1} 2162 (s, C≡C) : ^1H NMR δ (300.133 MHz, $CDCl_3$, 297 K) 7.81 (t, 1H, H_2, $^4J_{HH}$ = 2 Hz), 7.63 (dm, 1H, H_4 or H_6, $^3J_{HH}$ = 8 Hz), 7.41 (dm, 1H, H_4 or H_6, $^3J_{HH}$ = 8 Hz), 7.02 (t, 1H, H_5, $^3J_{HH}$ = 8 Hz), 0.23 (s, 9H, CH_3) ; ^{13}C {^1H} NMR δ (75.469 MHz, $CDCl_3$, 297 K) 140.54, 137.50, 131.03 and 129.74 (CH of C_6H_4), 125.19 (*C*-C≡C), 103.16 (*C*≡C-Si), 95.92 (C≡*C*-Si), 93.62 (C-I), -0.12 (CH_3) ; Elemental analysis calcd. for $C_{11}H_{13}ISi$ (Found) C : 44.01 (44.74) ; H : 4.36 (4.44).

Synthesis of substituted phenylacetylene derivatives

An equimolar amount of aqueous sodium hydroxyde (1 M) is added to a stirred solution of the silylated product dissolved in a 1/1 ethanol/THF mixture. After 30 min the solvents are removed under reduced pressure (10 mm Hg). The residue is extracted with diethyl ether. After drying of the organic layer with magnesium sulfate and evaporation of the solvent, the crude product was purified by column chromatography on alumina with pentane as eluent.

7 (2-iodo phenylacetylene) yellow oil ; 80 % yield from 1.14 g (3.8 mmol) of **6** ; IR (neat), ν/cm^{-1} 3290 (s, H-C≡), 2104 (w, C≡C) ; ^1H NMR δ (300.133 MHz, $CDCl_3$, 297 K) 7.84 (dd, 1H, H_3 or H_6, C_6H_4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.50 (dd, 1H, H_3 or H_6, C_6H_4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.5 Hz), 7.30 (dt, 1H, H_4 or H_5, C_6H_4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.03 (dt, 1H, H_4 or H_5, C_6H_4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.5 Hz), 3.33 (s, 1H, ≡CH) ; ^{13}C {^1H} NMR δ (75.469 MHz, $CDCl_3$, 297 K) 138.83, 133.48, 130.01 and 127.83 (CH of C_6H_4), 128.76 (*C*-C≡C), 100.50 (C-I), 85.17 (*C*≡CH), 81.04 (C≡*C*H). Elemental analysis calcd. for C_8H_5I (Found) C : 42.14 (42.95) ; H : 2.25 (2.40).

10 (3-iodo phenylacetylene) pale yellow oil ; 73 % yield from 0.945 g (3.2 mmol) of **9** ; IR (neat), ν/cm^{-1} 3289 (s, H-C≡), 2108 (w, C≡C) ; ^{1}H NMR δ (300.133 MHz, $CDCl_3$, 297 K) 7.72 (t, 1H, H_2, $^{4}J_{HH}$ = 2 Hz), 7.55 (dt, 1H, H_4 or H_6, $^{3}J_{HH}$ = 8 Hz, $^{4}J_{HH}$ = 1 Hz), 7.32 (dt, 1H, H_4 or H_6, $^{3}J_{HH}$ = 8 Hz, $^{4}J_{HH}$ = 2 Hz), 6.92 (t, 1H, H_5, $^{3}J_{HH}$ = 8 Hz), 2.99 (s, 1H, ≡CH) ; $^{13}C\{^{1}H\}$ NMR δ (75.469 MHz, $CDCl_3$, 297 K) 140.72, 137.91 and 131.29 (CH of C_6H_4), 129.87 (IC-*C*-C-C≡), 124.19 (*C*-C≡C-), 81.93 (*C*≡CH), 78.63 (C≡*C*H) ; ^{13}C NMR (75.499 MHz, $CDCl_3$, 297 K) 140.72 (dt, CH of C_6H_4, $^{1}J_{CH}$ = 169 Hz, $^{2}J_{CH}$ = 6 Hz), 137.91 (dt, CH of C_6H_4, $^{1}J_{CH}$ = 168 Hz, $^{2}J_{CH}$ = 7 Hz), 131.29 (dt, CH of C_6H_4, $^{1}J_{CH}$ = 164 Hz, $^{2}J_{CH}$ = 7 Hz), 129.87 (d, IC-*C*-C-C≡, $^{1}J_{CH}$ = 162 Hz), 124.19 (s, *C*-C≡C), 81.93 (d, *C*≡CH, $^{2}J_{CH}$ = 50 Hz), 78.63 (d, C≡*C*H, $^{1}J_{CH}$ = 252 Hz) ; Elemental analysis calcd. for C_8H_5I (Found) C : 42.14 (42.68) ; H : 2.21 (2.35).

13a 1-ethynyl-4-(phenylethynyl)benzene white powder ; 80 % yield from 1.342 g (4.89 mmol) of **12a** ; IR (KBr), ν/cm^{-1} 3282 (s, ≡C-H), 2210 (w, C≡C), 2108 (w, C≡CH) ; ^{1}H NMR δ (200.13 MHz, $CDCl_3$, 297 K) 7.53 (m, 2H, Ph), 7.46 (s, 4H, Ph), 7.34 (m, 3H, Ph), 3.15 (s, 1H, ≡C-H) ; $^{13}C\{^{1}H\}$ NMR (50.33 MHz, $CDCl_3$, 297 K) 132.12, 131.70, 131.53, 128.59 and 128.46 (CH of Ph), 123.83, 122.98 and 121.91 (*C*-C≡), 91.43, 88.89 (C≡C), 83.34 (*C*≡C-H), 78.95 (C≡*C*-H). HRMS m/z calcd for $C_{16}H_{10}$ (found) M^{+} : 202.0782 (202.0789).

13b 1-trimethylsilylethynyl-4-((4-nitrophenyl)-ethynyl)benzene pale yellow powder ; 78 % yield from 0.179 g (0.55 mmol) of **12b** ; IR (KBr), ν/cm^{-1} 3259 (s, ≡CH), 2214 (m, C≡C), 2101 (m, C≡CH), 1342 (s, NO_2) ; ^{1}H NMR δ (200.13 MHz, $CDCl_3$, 297 K) 8.20 (d, 2H, C_6H_4), 7.63 (d, 2H, C_6H_4), 7.48 (s, 4H, C_6H_4), 3.18 (s, 1H, ≡C-H) ; $^{13}C\{^{1}H\}$ NMR δ (50.33 MHz, $CDCl_3$, 297 K) 146.87 (C-NO_2), 132.37, 132.26, 131.76 and 123.73 (CH of C_6H_4), 129.90, 123.05 and 122.52 (*C*-C≡), 101.29 and 93.97 (C≡C), 83.02 (*C*≡C-H), 79.60 (C≡*C*-H). HRMS m/z calcd for $C_{16}H_9NO_2$ (found) M^{+} : 247.0633 (247.0629).

13c 1-trimethylsilylethynyl-4-((4-cyanophenyl)-ethynyl)benzene pale yellow powder ; 68 % yield from 1.553 g (5.186 mmol) of **12c** ; IR (KBr), ν/cm^{-1} 3237 (s, H-C≡), 2229 (m, CN), 2214 (m, C≡C), 2101 (w, C≡CH) ; ^{1}H NMR δ (200.13 MHz, $CDCl_3$, 297 K) 7.6 (m, 4H, C_6H_4), 7.46 (s, 4H, C_6H_4), 3.18 (s, H, ≡C-H) ; $^{13}C\{^{1}H\}$ NMR δ (50.33 MHz, $CDCl_3$, 297 K) 132.24, 132.15 and 131.71 (CH of C_6H_4), 127.90, 122.86 and 122.66 (*C*-C≡), 118.48 (CN), 93.10 and 89.55 (C≡C), 83.05 (*C*≡C-H), 79.52 (C≡*C*-H). HRMS m/z calcd for $C_{17}H_9N$ (found) M^{+} : 227.0735 (227.0731).

13d 1-ethynyl-4-((4-aminophenyl)-ethynyl)benzene pale yellow powder ; 94 % yield from 2.31 g (7.99 mmol) of **12d** ; IR (KBr), ν/cm^{-1} 3465, 3375 (s, NH_2), 3272 (s, ≡C-H), 2207 (m, C≡C), 2163 (m, C≡CH) ; ^{1}H NMR δ (300.133 MHz, $CDCl_3$, 297 K) 7.43 (s, 4H, C_6H_4), 7.32 (m, 2H, C_6H_4), 6.6 (m, 2H, C_6H_4), 3.76 (broad, 2H, NH_2), 3.08 (s, 1H, ≡C-H) ; $^{13}C\{^{1}H\}$ NMR δ (75.469 MHz, $CDCl_3$, 297 K) 146.92 (*C*-NH), 133.08, 132.04, 131.20 and 112.21 (CH of C_6H_4), 124.52, 121.13 and 114.77 (*C*-C≡), 92.36, 86.99 (C≡C), 83.49 (*C*≡C-H), 78.73 (C≡*C*-H). Elemental analysis calcd. for $C_{16}H_{11}N$(Found) C : 88.44 (88.74) ; H : 5.11 (5.40).

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