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Regioselective Electrophilic Alkylation of Anilines with Phenylacetylene in the Presence of Montmorillonite KSF.

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Abstract: Substituted anilines react with phenylacetylene in the presence of montmorillonite KSF affording 1,1-diarylethylenes 3 in good yields and excellent selectivities. In the presence of an excess of phenylacetylene, *para*-toluidine and *para*-anisidine give the corresponding 2,6-bis(1-phenyl-vinyl)anilines. © 1997 Published by Elsevier Science Ltd. All rights reserved.

Introduction

The electrophilic *C*-alkylation of aromatic amines with reagents containing carbon-carbon multiple bonds represents an important and a not easily accessible process. Indeed, the normal activating effect of the amino group is often reversed by complex formation with the acid catalyst. Thus, these compounds cannot generally be *C*-alkylated under normal Friedel-Crafts conditions[1] and some special methodologies were needed to perform the reaction. For example, Kolka early reported the direct *ortho*-alkylation of aromatic amines with alkenes in the presence of aluminium anilides.[2] Some few other catalysts were also described as effective promoters of the reaction. These include activated clays, silica-alumina, zeolites and $CoCl_2$ or $CdCl_2$ salts of anilines.[3]

Moreover, *ortho*-allylarylamines were synthesised *via* amino-Claisen rearrangement of aromatic *N*-allylamines.[4]

To the best of our knowledge, no *C*-alkylation of aromatic amines with alkynes has been described. The literature reports only few examples of the synthesis of enamines by *N*-alkylation of anilines with phenylacetylene.[5]

In conjunction with our research program concerning the use of solid acids in fine chemicals preparation,[6] we were intrigued with the possibility of obtaining direct *C*-alkylation of aromatic amines with alkynes over commercially available heterogeneous catalysts.

In fact in the last five years the use of heterogeneous catalysts in different areas of the organic synthesis has reach a great development, not only for the possibility to perform environmentally benign synthesis, but also for the good yields frequently accompanied by excellent selectivities that can be achieved.[7]

Results and Discussion

Here we report the *ortho*-regioselective synthesis of 1,1-diarylethylenes **3** by direct, liquid phase *C*-alkylation of anilines with phenylacetylene over montmorillonite KSF.

Compounds **3** are of considerable interest due to their use as synthetic intermediates to prepare indoles[8] and quinolines.[9]

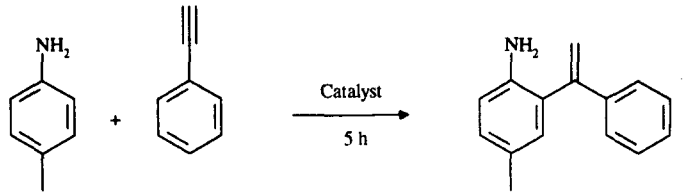
In trying to establish the best conditions to perform the reaction, a first series of experiments were made with phenylacetylene and *para*-toluidine in the presence of various heterogeneous promoters. All catalysts utilised were of commercial quality or easily preparable and were used without any previous chemical modification. Reactions were carried out as follows: 1.0 g of the heterogeneous catalyst was added to a solution of phenylacetylene **2** (1.0 g, 10 mmol) and *para*-toluidine **1a** (1.1 g, 10 mmol) in the selected solvent (10 ml). The mixture was heated at the selected temperature under stirring for 5 hours. After cooling to room temperature, filtration, washing with diethylether and distillation of the solvents, conversions and yields were determined by gas chromatographic analysis (see Experimental).

Results obtained with zeolites suggest that yields did not relate to the acidity of the different catalysts tested (Table 1, entries a and b). This was probably attributable to the fact that the temperature programmed desorption of ammonia gas (NH_3-TPD) may not accurately represent the active acid sites accessible to this alkylation process for all zeolitic catalysts. The extremely low yield (4%) observed with the zeolite ZSM-5 (acidity 0.57 meq H^+/g) in comparison with that obtained with zeolite HSZ-360 (yield 55%; acidity 0.30 meq H^+/g) would probably be attributable to the different pore dimension (ZSM-5 ~5Å[10]; HSZ-360 ~8Å[11]). Thus HSZ-360 would accommodate into the pores both reagents easier than ZSM-5 affording product **3a** in better yield.

Moreover it is worth of note that an amorphous silica-alumina[12] with lower surface area and stronger acidity (Table 1, entry c) than zeolite HSZ-360 behaves as a less effective promoter, in agreement with previously reported studies indicating that zeolites show higher catalytic activity than amorphous silica-alumina with similar SiO_2/Al_2O_3 molar ratio.[13]

In the presence of montmorillonites K10 and KSF the system was more reactive affording **3a** in 65% and 75% yield respectively and similar high selectivity (98% and 96%) (Table 1, emtries d and e). Moreover, these results are well related to the acidity of the catalysts whose structures are quite similar.[14] The use of xylene as non chlorurated aromatic solvent resulted in good yield, but some by-products were recovered due to the competitive reaction of **2** with the solvent (Table 1, entry f). The best result was obtained by carrying out the reaction without any solvent at 140°C under efficient stirring (Table 1, entry g).

Table 1. Reaction of *para*-toluidine and phenylacetylene under different experimental conditions.



1a **2** **3a**

Entry	Catalyst (Supplier)	Acidity* (meq H^+/g)	Surface Area§ (m^2/g)	Temp. (°C)	Solvent	Yield$ (%)	Selectivity# (%)
a	Zeolite HSZ-360 (Tosoh)	0.30	500 ± 10	160	1,2-diClC_6H_4	55	96
b	Zeolite ZSM-5 (BDH)	0.57	250 ± 10	160	1,2-diClC_6H_4	4	97
c	Amorphous Si-Al (See ref. 12)	0.50	190 ± 10	160	1,2-diClC_6H_4	8	92
d	Montmorillonite K10 (Fluka)	0.70	200 ± 10	160	1,2-diClC_6H_4	65	98
e	Montmorillonite KSF (Fluka)	0.85	15 ± 10	160	1,2-diClC_6H_4	75	96
f	Montmorillonite KSF (Fluka)	"	"	140	Xylene	65	91
g	Montmorillonite KSF (Fluka)	"	"	140	–	90	97

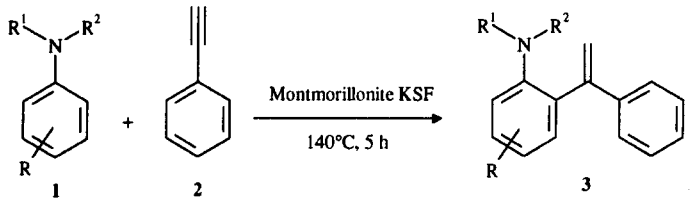
* Determined in our laboratory by temperature programmed desorption of ammonia gas (NH_3-TPD): Berteau, P.; Delmon, B. *Catal. Today*, **1989**, *5*, 121.
§ Determined in our laboratory by B.E.T. method: Brunauer, S.; Emmett, P.H.; Teller, E. *J. Am. Chem. Soc.*, **1938**, *60*, 309.
$ Determined by g.l.c. analysis.
# Calculated with respect to **1a**.

For comparison, the reaction with some classical Lewis acids such as $AlCl_3$, $SnCl_4$ and $TiCl_4$ was also done under similar conditions. Series of vigorous reactions occurred to afford mixtures of tar materials accompanied by some unreacted starting *para*-toluidine.

The reaction was then applied to various substituted anilines; as reported in Table 2, the yields and selectivities of products **3** are satisfactory or excellent and complete *ortho*-regioselective control was observed in all cases. It is remarkable that the *meta*-toluidine gave an equimolecular mixture of the two *ortho*-alkylated products despite the steric hindrance of the inner *ortho* isomer **3e int** (Table 2, entry e).

Inspection of the data presented in Table 2 reveals that the reaction represents a typical electrophilic substitution (Table 2, entries a, b, d, i and j). Moreover the *ortho*-substituted anilines show lower yields with respect to the corresponding *para*-isomers probably due to some steric hindrance troubling the interaction with the catalyst surface (Table 2, entries a, b, f and g).

Table 2. Reaction of variously substituted anilines and phenylacetylene in the presence of montmorillonite KSF.



Entry	R	R^1	R^2	Product	Yield (%) $	Selectivity (%) #
a	4-CH_3	H	H	**3a**	87	97
b	4-OCH_3	H	H	**3b**	93	95
c	4-$(CH_3)_3C$	H	H	**3c**	50	88
d	4-Cl	H	H	**3d**	62	94
e	3-CH_3	H	H	**3e ext + 3e int**	43 + 40	96
f	2-CH_3	H	H	**3f**	65	91
g	2-OCH_3	H	H	**3g**	50	95
h	3,4 	H	H	**3h**	32	97
i	4-Br	H	H	**3i**	50*	92
j	4-NO_2	H	H	**3j**	12	95
k	H	H	H	**3k**	65	94
l	H	CH_3	H	**3l**	42	96
m	H	C_2H_5	C_2H_5	**3m**	0	-

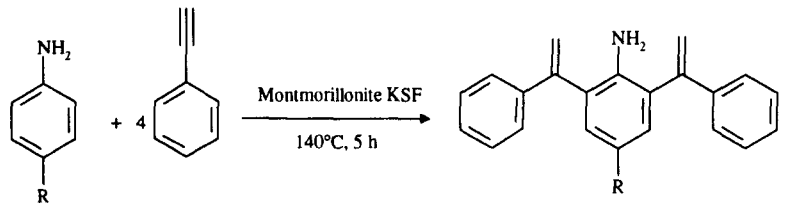
$ Isolated yields.
# Calculated with respect to **1**.
* Reaction time: 1 hour.

Finally the substitution on the nitrogen atom has an important effect in the present reaction; in fact, whereas aniline **1k** gave the product **3k** with 65% yield, *N*-methylaniline **1l** afforded compound **3l** in 42% yield and *N,N*-diethylaniline **1m** was completely recovered unchanged (entries k-m).

Since in a previous study we have found that dihydroquinolines were obtained by reacting aromatic amines with an excess of phenylacetylene under metal-template catalysis,[15] we analysed the reaction of substrates **1a**, **1b**, **1d** and **1f** with an excess of phenylacetylene under KSF catalysis (Table 3).

A consecutive reaction of **3a** and **3b** with phenylacetylene and formation of the1:2 products **4a** and **4b** took place under these conditions. On the contrary the 1:1 product **3d** was obtained with *para*-chloroaniline and a complex mixture of compounds was produced with *ortho*-toluidine **1f**.

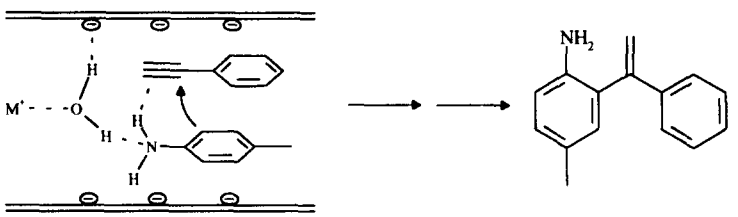
Table 3. Reaction of anilines **1** with an excess of phenylacetylene **2**.



1 2 4

Entry	R	Product	Yield (%)	Selectivity (%)
a	CH_3	**4a**	80	95
b	OCH_3	**4b**	82	92

Concerning the role of the catalyst, it is known that activity of montmorillonites is mainly due to its high surface acidity. Isomorphous substitution of Si(IV) by Al(III) in tetrahedral layers is responsible for both Lewis and Brönsted acidity. The Brönsted acidity is further increased by the presence of interlamellar cations required to maintain electroneutrality of the layers, which can polarise water molecules located between the negatively charged oxygens of the sheet and positively charged counter ions.[7b] We could suggest the above depicted mechanistic scheme to explain activation and *ortho*-regioselective control of the present reaction[16] (Figure).



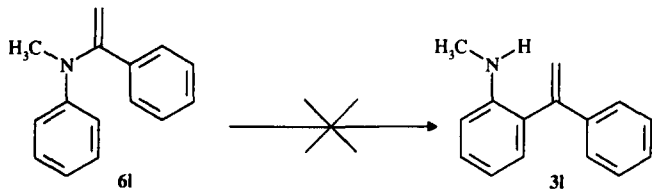
5 3a

Figure

Aromatic amines can intercalate into the layered structure of the catalyst by a variety of host-guest interactions.[17] We therefore considered that accommodation of aniline into interlayer area of the catalyst could result from H-bonding with the water polarised molecule. This interaction enhances the acidity of the N-H

proton which can undergo further H-bond with phenylacetylene producing the reactive complex **5** with a geometry suitable for a six-membered ring concerted mechanism in agreement with the early reported *ortho*-regioselective alkylation of phenols and aromatic amines with alkenes under homogeneous catalysis.[2,18]

An alternative mechanism would require the *N*-alkylation followed by the *N-C ortho*-regioselective rearrangement. In order to verify this alternative hypothesis the supposed intermediate enamine **6l**[5] was heated in *ortho*-dichlorobenzene at 160°C for 5 hours in the presence of montmorillonite KSF. After normal work-up compound **6l** was completely recovered unchanged (Scheme).



Scheme

This result rules out the rearrangement and support the proposed direct *C*-alkylation process even if the real mechanism can be more complicated due to the complexity of the reactive system.

In summary, we report our studies on the use of montmorillonite KSF as a very efficient catalyst for alkylation of *C*-substituted and *N*-monosubstituted anilines with phenylacetylene. This study is currently under progress to extend the reaction to aliphatic alkynes and to obtain substituted indoles and quinolines after a cyclization-oxidation process.

Experimental

Melting and boiling points were obtained on an Electrothermal melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet PC5 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AC300 at 300 MHz. Chemical shifts are expressed in ppm relative to TMS as internal standard. Mass spectra were obtained on a Hewlett-Packard HP-5971 A instrument. Gas chromatographic analyses were performed on a Dani 8221-a instrument [SPB-1 Supelco column, 30 m, 40°C (4), 10°C/min, 200°C] connected with a Hewlett-Packard HP 3396A integrator. Microanalyses were carried out by Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica dell'Università di Parma. TLC analyses were performed on Stratocrom SIF silica gel plates (Carlo Erba) developed with hexane-ethyl acetate mixtures. All reagents were of commercial quality from freshly opened containers.

Synthesis of substituted 1,1-diarylethylenes 3. General Procedure A. The selected aniline (10 mmol), phenylacetylene (1.0 g, 10 mmol) and montmorillonite KSF (1 g) are introduced in a round bottomed flask equipped with magnetic stirrer and a reflux condenser. The reaction mixture is heated at 140°C for 5 hours and

then cooled to rt. After filtration, the catalyst is washed with diethylether (100 ml); the solvent is distilled off under reduced pressure and the crude is chromatographed on silica gel column with hexane : ethyl acetate 95 : 5 as eluant to give the products.

1-Phenyl-1-(2-amino-5-methylphenyl)ethylene (3a).[19] Pale yellow oil, b.p. 143-145°C/0.05 mmHg (Found: C, 85.9; H, 7.4; N, 6.5. $C_{15}H_{15}N$ requires C, 86.1; H, 7.2; N, 6.7%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 2.23 (s, 3 H, CH_3), 3.3 (br s, 2 H, NH_2), 5.31 (d, 1 H, ½ CH_2, J=1.4 Hz), 5.75 (d, 1 H, ½ CH_2, J=1.4 Hz), 6.57 (d, 1H, H-3, J=7.9 Hz), 6.91 (s, 1 H, H-6), 6.94 (d, 1 H, H-4, J=7.9 Hz), 7.2-7.4 (m, 5 H, H-arom); IR (NaCl) 3463 (NH), 3374 (NH); MS (EI) m/e 209 (M^+, 65%), 208 (100), 194 (38).

1-Phenyl-1-(2-amino-5-methoxyphenyl)ethylene (3b). Pale brown oil, b.p. 152-154°C/0.01 mm Hg (b.p. lit[20] 157°C/0.01 mm Hg) (Found: C, 80.3; H, 6.6; N, 6.0. $C_{15}H_{15}NO$ requires C, 80.0; H, 6.7; N, 6.2%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 3.0 (br s, 2 H, NH_2), 3.75 (s, 3 H, OCH_3), 5.35 (d, 1 H, ½ CH_2, J=1.3 Hz), 5.80 (d, 1 H, ½ CH_2, J=1.3 Hz), 6.66 (d, 1H, H-3, J=8.5 Hz), 6.72 (d, 1 H, H-6, J=2.9 Hz), 6.77 (dd, 1 H, H-4, J=8.5 and 2.9 Hz), 7.2-7.4 (m, 5 H, H-arom); IR (NaCl) 3440 (NH), 3365 (NH); MS (EI) m/e 225 (M^+, 97%), 224 (100), 165 (44).

1-Phenyl-1-(2-amino-5-*tert*-butylphenyl)ethylene (3c). Pale brown oil, b.p. 196-200°C/0.05 mmHg (Found: C, 86.1; H, 8.6; N, 5.5. $C_{18}H_{21}N$ requires C, 86.0; H, 8.4; N, 5.6%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 1.29 (s, 9 H, $(CH_3)_3C$), 3.4 (br s, 2 H, NH_2), 5.35 (d, 1 H, ½ CH_2, J=1.4 Hz), 5.79 (d, 1 H, ½ CH_2, J=1.4 Hz), 6.64 (d, 1H, H-3, J=8.3 Hz), 7.12 (d, 1 H, H-6, J=2.3 Hz), 7.19 (dd, 1 H, H-4, J=8.3 and 2.3 Hz), 7.2-7.4 (m, 5 H, H-arom); IR (NaCl) 3467 (NH), 3377 (NH); MS (EI) m/e 251 (M^+, 45%), 236 (100), 220 (8).

1-Phenyl-1-(2-amino-5-chlorophenyl)ethylene (3d). Pale brown oil, b.p. 140-144°C/0.1 mm Hg (b.p lit[21] 142-145°C/0.1 mm Hg) (Found: C, 73.0; H, 5.5; Cl, 15.3; N, 6.3. $C_{14}H_{12}ClN$ requires C, 73.2; H, 5.3; Cl, 15.4; N, 6.1%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 3.4 (br s, 2 H, NH_2), 5.36 (s, 1 H, ½ CH_2), 5.82 (s, 1 H, ½ CH_2), 6.62 (d, 1H, H-3, J=9.1 Hz), 7.0-7.2 (m, 2 H, H-4 and H-6), 7.3-7.4 (m, 5 H, H-arom); IR (NaCl) 3474 (NH), 3386 (NH); MS (EI) m/e 231 (M^++2, 15%), 229 (M^+, 67), 228 (100), 214 (30).

1-Phenyl-1-(2-amino-4-methylphenyl)ethylene (3e ext). Pale brown oil, b.p. 118-120°C/0.05 mmHg (Found: C, 86.3; H, 7.5; N, 6.5. $C_{15}H_{15}N$ requires C, 86.1; H, 7.2; N, 6.7%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 2.29 (s, 3 H, CH_3), 3.5 (br s, 2 H, NH_2), 5.33 (d, 1 H, ½ CH_2, J=1.4 Hz), 5.75 (d, 1 H, ½ CH_2, J=1.4 Hz), 6.53 (s, 1H, H-3), 6.61 (d, 1 H, H-5, J=7.6 Hz), 7.00 (d, 1 H, H-6, J=7.6 Hz), 7.2-7.4 (m, 5 H, H-arom); IR (NaCl) 3469 (NH), 3378 (NH); MS (EI) m/e 209 (M^+, 58%), 208 (100), 194 (49).

1-Phenyl-1-(2-amino-6-methylphenyl)ethylene (3e int). Pale brown oil, b.p. 113-114°C/0.05 mmHg (Found: C, 85.9; H, 7.4; N, 6.5. $C_{15}H_{15}N$ requires C, 86.1; H, 7.2; N, 6.7%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 2.07 (s, 3 H, CH_3), 3.6 (br s, 2 H, NH_2), 5.27 (d, 1 H, ½ CH_2, J=1.4 Hz), 6.04 (d, 1 H, ½ CH_2, J=1.4 Hz), 6.60 (d, 1H, H-3 or H-5, J=7.7 Hz), 6.66 (d, 1 H, H-5 or H-6, J=7.7 Hz), 7.05 (t, 1 H, H-4, J=7.7 Hz), 7.2-7.4 (m, 5 H, H-arom); IR (NaCl) 3469 (NH), 3379 (NH); MS (EI) m/e 209 (M^+, 86%), 208 (76), 194 (100).

1-Phenyl-1-(2-amino-3-methylphenyl)ethylene (3f). Pale brown oil, b.p. 155-158°C/0.05 mm Hg (Found: C, 86.3; H, 7.4; N, 6.8. $C_{15}H_{15}N$ requires C, 86.1; H, 7.2; N, 6.7%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 2.15 (s, 3 H, CH_3), 3.6 (br s, 2 H, NH_2), 5.18 (d, 1 H, ½ CH_2, J=1.4 Hz), 5.76 (d, 1 H, ½ CH_2, J=1.4 Hz), 6.70 (t, 1H, H-5, J=7.4 Hz), 6.97 (dd, 1 H, H-4, J=7.4 and 1.4 Hz), 7.03 (dd, 1 H, H-6, J=7.4 and 1.0 Hz), 7.2-7.4 (m, 5 H, H-arom); IR (NaCl) 3462 (NH), 3376 (NH); MS (EI) m/e 209 (M^+, 61%), 208 (100), 194 (61).

1-Phenyl-1-(2-amino-3-methoxyphenyl)ethylene (3g).[22] Pale brown oil, b.p. 149-150°C/0.05 mmHg (Found: C, 80.3; H, 6.6; N, 6.4. $C_{15}H_{15}NO$ requires C, 80.0; H, 6.7; N, 6.2%); ^{1}H NMR (C_6D_6, 300 MHz), δ (ppm) 3.34 (s, 3 H, OCH_3), 3.7 (br s, 2 H, NH_2), 5.29 (d, 1 H, ½ CH_2, J=1.4 Hz), 5.64 (d, 1 H, ½ CH_2, J=1.4 Hz), 6.55 (dd, 1H, H-4 or H-6, J=7.8 and 1.1 Hz), 6.70 (t, 1 H, H-5, J=7.8 Hz), 6.88 (dd, 1 H, H-6 or H-4, J=7.8 and 1.1 Hz), 7.0-7.4 (m, 5 H, H-arom); IR (NaCl) 3479 (NH), 3385 (NH); MS (EI) m/e 225 (M^+, 95%), 224 (100), 210 (56).

1-Phenyl-1-(2-amino-1-antryl)ethylene (3h). Pale yellow solid, m.p. 154-156°C (Found: C, 89.3; H, 6.0; N, 4.6. $C_{22}H_{17}N$ requires C, 89.5; H, 5.8; N, 4.7%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 2.8 (br s, 2 H, NH_2), 5.50 (d, 1 H, ½ CH_2, J=1.4 Hz), 6.34 (d, 1 H, ½ CH_2, J=1.4 Hz), 7.11 (d, 1H, H-3 or H-4, J=9.0 Hz), 7.2-7.5 (m, 7H, H-arom), 7.7-8.0 (m, 2H, H-arom), 7.89 (d, 1 H, H-4 or H-3, J=9.0 Hz), 8.10 (s, 1 H, H-5 or H-10), 8.31 (s, 1 H, H-10 or H-5); IR (KBr) 3473 (NH), 3379 (NH); MS (EI) m/e 295 (M^+, 100%), 205 (10).

1-Phenyl-1-(2-amino-5-bromophenyl)ethylene (3i).[23] Pale brown oil, b.p. 177-180°C/0.05 mmHg (Found: C, 61.5; H, 4.6; Br, 29.0; N, 5.5. $C_{14}H_{12}BrN$ requires C, 61.3; H, 4.4; Br, 29.1; N, 5.1%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 3.1 (br s, 2 H, NH_2), 5.35 (d, 1 H, ½ CH_2, J=1.3 Hz), 5.80 (d, 1 H, ½ CH_2, J=1.3 Hz), 6.57 (d, 1H, H-3, J=9.1 Hz), 7.2-7.4 (m, 7 H, H-4, H-6 and H-arom); IR (NaCl) 3474 (NH), 3385 (NH); MS (EI) m/e 276 (M^++3, 42%), 274 (M^++1, 85), 85 (100).

1-Phenyl-1-(2-amino-5-nitrophenyl)ethylene (3j). Pale brown oil, b.p. 175-178°C/0.05 mmHg (Found: C, 70.2; H, 4.9; N, 11.5. $C_{14}H_{12}N_2O_2$ requires C, 70.0; H, 5.0; N, 11.7%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 4.0 (br s, 2 H, NH_2), 5.44 (d, 1 H, ½ CH_2, J=0.8 Hz), 5.89 (d, 1 H, ½ CH_2, J=0.8 Hz), 6.65 (d, 1H, H-3, J=9.5 Hz), 7.3-7.4 (m, 5 H, H-arom), 8.0-8.1 (m, 2H, H-4 and H-6); IR (NaCl) 3489 (NH), 3382 (NH); MS (EI) m/e 241 (M^++1, 43%), 211 (19), 85 (100).

1-Phenyl-1-(2-aminophenyl)ethylene (3k). Pale brown solid, m.p. 77.5-78.5 °C (m.p. lit[24]: 77-77.5°C) (Found: C, 85.9; H, 6.6; N, 7.4. $C_{14}H_{13}N$ requires C, 86.1; H, 6.7; N, 7.2%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 3.5 (br s, 2 H, NH_2), 5.34 (d, 1 H, ½ CH_2, J=1.4 Hz), 5.78 (d, 1 H, ½ CH_2, J=1.4 Hz), 6.67 (d, 1H, H-3, J= 7.8 Hz), 6.77 (td, 1 H, H-5, J=7.4 and 0.8 Hz), 7.10 (dd, 1 H, H-6, J=7.4 and 1.4 Hz), 7.14 (td, 1 H, H-4, J=7.8 and 1.4 Hz), 7.2-7.4 (m, 5 H, H-arom); IR (KBr) 3476 (NH), 3382 (NH); MS (EI) m/e 195 (M^+, 52%), 194 (100), 180 (51).

1-Phenyl-1-(2-*N*-methylaminophenyl)ethylene (3l).[25] Yellow oil, b.p. 116-118°C/0.05 mm Hg.

Synthesis of substituted 2,6-bis(1-phenylvinyl)anilines 4. General Procedure B. The reactions were carried out as described in General Procedure A by using a phenylacetylene / aniline molar ratio 4 / 1.

2,6-bis(1-phenylvinyl)-4-methylaniline (4a): pale yellow solid, m.p. 91-93°C (Found: C, 88.6; H, 6.6; N, 4.7. $C_{23}H_{21}N$ requires C, 88.7; H, 6.8; N, 4.5%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 2.28 (s, 3 H, CH_3), 3.4 (br s, 2 H, NH_2), 5.36 (d, 2 H, 2 x ½ CH_2, J=1.4 Hz), 5.79 (d, 2 H, 2 x ½ CH_2, J=1.4 Hz), 6.94 (s, 2 H, H-3 and H-5), 7.2-7.4 (m, 10 H, H-arom); IR (KBr) 3464 (NH), 3381 (NH); MS (EI) m/e 311 (M^+, 100%), 296 (17).

2,6-bis(1-phenylvinyl)-4-methoxyaniline (4b): yellow oil, b.p. 147-148°C/0.05 mm Hg (Found: C, 84.2; H, 6.5; N, 4.1. $C_{23}H_{21}NO$ requires C, 84.4; H, 6.5; N, 4.3%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 3.2 (br s, 2 H, NH_2), 3.78 (s, 3 H, OCH_3), 5.38 (d, 2 H, 2 x ½ CH_2, J=1.3 Hz), 5.81 (d, 2 H, 2 x ½ CH_2, J=1.3 Hz), 6.75 (s, 2 H, H-3 and H-5), 7.2-7.5 (m, 10 H, H-arom); IR (NaCl) 3466 (NH), 3380 (NH); MS (EI) m/e 328 (M^++1, 100%), 314 (9).

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