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Stereospecific synthesis of conjugated (1*E*,3*E*)- and (1*Z*,3*Z*)-1,4-di(*n*-*N*,*N*-dimethylaminophenyl)-1,3-butadienes from 2-chloro-1-(*n*-*N*,*N*-dimethylaminophenyl)ethenes: fluorescence properties

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Abstract—The conjugated 1,4-di(*n*-*N*,*N*-dimethylaminophenyl)-1,3-butadienes (*n*=*o*-, *m*-, *p*-) were efficiently synthesised by homocoupling of the appropriate 2-chloro-1-(*n*-*N*,*N*-dimethylaminophenyl)ethene (*n*=*o*-, *m*-, *p*-) with stoichiometric amounts of zerovalent nickel complexes. The 1,3-butadienes were obtained as a mixture of stereoisomers, with independence of the starting *E* or *Z* chlorovinyl isomer. Moreover, the stereospecific (*Z*,*Z*) stereoisomer was obtained by partial hydrogenation of the corresponding 1,3-butadiyne, while the stereospecific (*E*,*E*) stereoisomer was obtained by exposure to the sunlight radiation of the (*Z*,*Z*) or the (*Z*,*E*) compound in ethanol.

1. Introduction

The synthesis of the highly conjugated polyene structures as molecular organic materials show a wide spread interest because these exhibit semiconductor and optical properties. Methods for the synthesis of 1,3-butadiene compounds have been reported.[1] An elegant and practical synthesis for 1,4-diphenyl-1,3-butadiene was the homocoupling of the (*E*)- or (*Z*)-β-bromostyrene with zerovalent nickel complexes giving the (*E*,*E*)- or (*Z*,*Z*)-1,4-diphenyl-1,3-butadiene, respectively, while the (*E*,*Z*) isomer was isolated in low yield.[2]

However, the zerovalent nickel complexes were more investigated in the homocoupling reaction of arylhalides or arylsulfonates,[3,4,5] or Grignard reagents with catalytic amounts of nickel complexes,[6,7,8] to the preparation of diaryl or diheteroaryl or polyaryl derivatives.[9] The homocoupling of organic halides or heteroarylhalides was efficiently catalysed by electroreductive nickel complexes in organic solvent or ionic liquid solvent.[10] (*Z*)-3-Halopropenoates were homocoupled using catalytic amounts of nickel chloride and zinc in the presence of water in pyridine, affording a mixture of (*Z*) and (*E*)-3-hexenedioates.[11]

In general, the active zerovalent nickel species can be prepared in situ from stoichiometric amounts of zinc powder and catalytic amounts of nickel salts or complexes.[12]

Now, we report the homocoupling of (*E*)- or (*Z*)-2-chloro-1-(*n*-*N*,*N*-dimethylaminophenyl)ethene (*n*=*o*-, *m*-, *p*-) with zerovalent nickel complexes and the stereochemistry of the reaction.

2. Results and discussions

The 2-chloro-1-(*n*-*N*,*N*-dimethylaminophenyl)ethene (*n*=*o*-, *m*- and *p*-) (**1**–**3**) were obtained by means of the Wittig reaction between the appropriate aldehyde and the chloromethylen(triphenyl)phosphonium ylide,[13,14] as yellow oils, in good yield, Scheme 1. The separation of phosphine and phosphine oxide by extraction with hexane followed by silica gel column chromatography with toluene as eluent give pure *Z*/*E* mixtures (1:1 and 4:1 for compound **3**), which were used for the homocoupling reaction. The *Z* and *E* isomers can be purely isolated using hexane–toluene (2/1) as eluent, excepting for compound **2**.

The homocoupling reaction of 2-chloro-1-arylethenes **1**–**3** was carried out with stoichiometric amounts of zerovalent nickel complexes, which were prepared in situ by reaction between dichloro bis(triphenylphosphine) nickel and powder of zinc as the reducing agent in presence of

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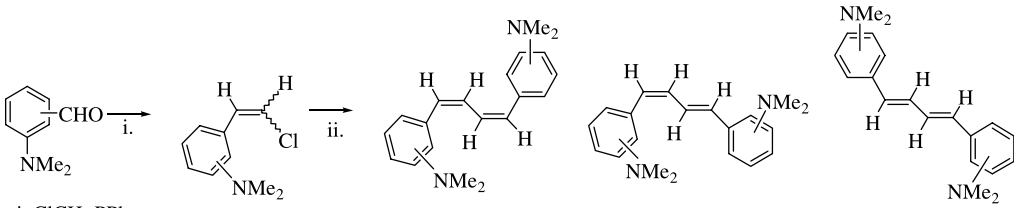


Isomer		%	Z	E			
ortho,	**1**	96	3	2	**4a**	**4b**	**4c**
meta,	**2**	82	2	3	**5a**	**5b**	**5c**
para,	**3**	80	3	2	**6a**	**6b**	**6c**

Scheme 1.

Table 1. Homocoupling of 2-chloro-1-(*n*-*N*,*N*-dimethylaminophenyl)ethenes with zerovalent nickel complexes

Compound	Isomer	1,3-Butadiene (%)[a]		
1 *o*-NMe_2	Z	**4a** (1*Z*,3*Z*), 22	**4b** (1*Z*,3*E*), 42	**4c** (1*E*,3*E*), 34
1 *o*-NMe_2	*E*	**4a** (1*Z*,3*Z*), Traces	**4b** (1*Z*,3*E*), 19	**4c** (1*E*,3*E*), 75
2 *m*-NMe_2	*Z*/*E* (2:3)	**5a**, —	**5b** (1*Z*,3*E*), 43	**5c** (1*E*,3*E*), 45
3 *p*-NMe_2	*E*	**6a**, —	**6b**, —	**6c** (1*E*,3*E*), 95
3 *p*-NMe_2	*Z*/*E* (1:1)	**6a** (1*Z*,3*Z*), 2	**6b** (1*Z*,3*E*), 77	**6c**, —
3 *p*-NMe_2	*Z*/*E* (4:1)	**6a** (1*Z*,3*Z*), 4	**6b** (1*Z*,3*E*), 79	**6c**, —

[a] Yield refers to isolated product after purification by column chromatography.

tetra-*n*-butylammonium iodide as a phase transfer component in dry THF, Scheme 1.[15] The results of the homocoupling reaction are summarised in Table 1.

In this way, the homocoupling of (*Z*)-2-chloro-1-(*o*-*N*,*N*-dimethylaminophenyl)ethene (**1**) affords to a mixture of stereoisomers characterised by IR and ^{1}H NMR spectra, in good yield (98%): (1*Z*,3*Z*)-**4a** (22%); (1*Z*,3*E*)-**4b** (42%); (1*E*,3*E*)-1,4-di(*o*-*N*,*N*-dimethylaminophenyl)-1,3-butadiene (**4c**) (34%) as yellow oils.

However, the homocoupling of the (*E*)-**1** isomer gives (1*E*,3*E*)-**4c** as the main product (75%) and (1*Z*,3*E*)-**4b** (19%). Moreover, (1*Z*,3*Z*)-**4a** isomer was detected in traces, Table 1, Scheme 1.

Compound **4c** shows fluorescence radiation emission with important quantum yield, Table 2.

Table 2. UV–vis and fluorescence spectra of 1,3-butadienes and 1,3-butadiyne **9**

Compound	UV–vis (CH_2Cl_2)[a] λ_{max} (nm)	ε (M^{-1} cm^{-1})	F (CH_2Cl_2)[a,b] λ_{em} (nm)	Φ_f[c]
4c	377	49,500	465	0.25
5c	342	42,600	477	0.29
9	378	97,600	428	8.3×10^{-4}
6a	405	82,400	438	0.32
6c	405	203,200	440	0.26

[a] At room temperature.
[b] $[c]\cong10^{-8}$ M.
[c] Fluorescence quantum yield in dichloromethane referred to quinine sulfate in H_2SO_4 (1 N) and $\lambda_{exc.}$ 365 nm.

Hence, the homocoupling reaction of the (*Z*)-**1** stereoisomer gives the (1*Z*,3*Z*)-1,3-butadiene, which retains the configuration of the starting (*Z*)-chlorovinyl derivative but as the mino product, while an important isomerization to (1*Z*,3*E*) and (1*E*,3*E*) takes place. Moreover, the homocoupling of (*E*)-**1** isomer gives the (1*E*,3*E*) stereoisomer as the main product, while the isomerized product (1*Z*,3*E*) was the minoritary one, Table 1.

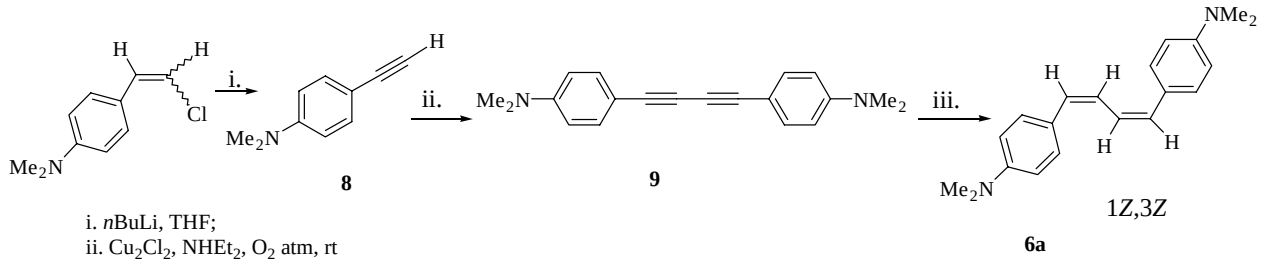
On the other hand, the (1*Z*,3*Z*)-**4a** and (1*Z*,3*E*)-**4b** 1,3-butadienes in ethanol, were completely transformed in (1*E*,3*E*)-**4c**, by exposure to the sunlight radiation, in presence of iodine crystals.[16]

The homocoupling of the (*Z*/*E*)-2-chloro-1-(*m*-*N*,*N*-dimethylaminophenyl)ethene (**2**) mixture (*Z*/*E*, 2:3), gives a practically equimolar mixture of (1*Z*,3*E*)-**5b** and (1*E*,3*E*)-1,4-di(*m*-*N*,*N*-dimethylaminophenyl)-1,3-butadiene (**5c**) in good yield (88%). The **5c** isomer shows fluorescent emission radiation in solution, Table 2.

In the same way, the homocoupling of (*E*)-2-chloro-1-(*p*-*N*,*N*-dimethylaminophenyl)ethene (**3**), gives exclusively the (1*E*,3*E*)-1,3-butadiene **6c**, in excellent yield (95%), as a white solid mp 245–246 °C. Thus, compound **6c** retains the stereochemistry of the starting chlorovinyl derivative.

However, the homocoupling of the (*Z*/*E*)-2-chloro-1-(*p*-*N*,*N*-dimethylaminophenyl)ethene mixtures (*Z*/*E*, 1:1 or 4:1), gives (1*Z*,3*E*)-**6b** (mp 255–256 °C, 77 and 79%, respectively) and (1*Z*,3*Z*)-**6a** in low yield (2 or 4%, respectively, by HPLC, mp 231.7 °C by DSC), Table 1.

On the other hand, both **6a** and **6b** stereoisomers in solution of ethanol were completely transformed in the (1*E*,3*E*) stereoisomer **6c** by sunlight exposure, in presence of iodine crystals.[16] Compounds **6a** and **6c**, in solution, show fluorescent emission radiation, Table 2.

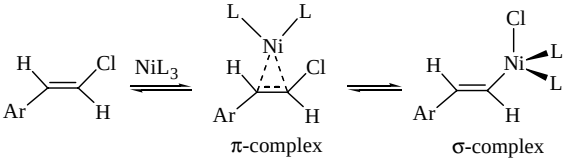


Scheme 2.

Moreover, the minoritary (1*Z*,3*Z*)-**6a** stereoisomer was purely synthesised as a reference in the analysis of the homocoupling mixture. The stereospecific synthesis was carried out by partial hydrogenation of 1,4-di(*p*-*N*,*N*-dimethylaminophenyl)-1,3-butadiyne (**9**) catalysed by palladium on barium sulfate treated with lead acetate and quinoline (Lindlar type catalyst). Compound **6a** was isolated as a yellow solid, mp 231.7 °C (DSC), in 96% yield, Scheme 2.

The synthesis of 1,3-butadiyne **9** was carried out by oxidative dimerization of the corresponding acetylene **8** under the Glaser reaction conditions, catalysed by cuprous chloride under oxygen atmosphere in dry pyridine at 40 °C, in practically quantitative yield. The terminal acetylene **8** was prepared by treatment of 2-chloro-1-(*p*-*N*,*N*-dimethylaminophenyl)ethene (**3**) with butyl lithium in good yield.[13,17]

The anomalous (*E*)→(*Z*) isomerization, observed during the homocoupling reaction, could be due to the formation of a π-nickel-double bond complex, decreasing the double bond order, which permit the rotation of the C–C bond in the complex. The formation of a π-complex was usually proposed prior to the oxidative addition to the C–halogen bond by the nickel complexes.[12,13,18] The sterical interactions on the π–σ nickel complex equilibrium, are responsible of the pathway of the homocoupling and the resulting 1,3-butadiene stereochemistry, being of minor importance the thermodynamical stability,[18,19,20] Scheme 3.



Scheme 3.

The conjugated stereoisomers of 1,4-di(*n*-*N*,*N*-dimethylaminophenyl)-1,3-butadienes, in solution of dichloromethane show fluorescence emission radiation, with important quantum yields (25–32%), which are not dependent of the stereochemistry. In contrast, the conjugated 1,3-butadiyne **9** shows fluorescence radiation emission in very low quantum yield, Table 2.

3. Conclusions

The conjugated 1,4-di(*n*-*N*,*N*-dimethylaminophenyl)-1,3-butadienes (*n*=*o*-, *m*-, *p*-) can be efficiently obtained by homocoupling of the appropriate 2-chloro-1-(*n*-*N*,*N*-dimethylaminophenyl)ethene (*n*=*o*-, *m*-, *p*-) with stoichiometric amounts of zerovalent nickel complexes prepared in situ by reduction of dichloro bis(triphenyl)phosphine nickel with powder zinc in tetrahydrofuran. The 1,3-butadienes were obtained as a mixture, which is independent of the starting *E* or *Z* chlorovinyl derivative. Moreover, stereospecific (*Z*,*Z*) stereoisomer was obtained by partial hydrogenation of the corresponding 1,4-di(*n*-*N*,*N*-dimethylaminophenyl)-1,3-butadiyne. The last can be obtained by catalytic homocoupling of the *n*-(*N*,*N*-dimethylaminophenyl)acetylene. The (*E*,*E*) stereoisomer can be stereospecifically isolated by exposure to the sunlight radiation of the (*Z*,*Z*) or (*Z*,*E*) isomers or their mixture in ethanol.

4. Experimental

4.1. General

Melting points were determined in open capillaries using a Buchi or 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}. ^{1}H and ^{13}C NMR spectra were recorded at 200 and 75 MHz, respectively, on a Bruker Aspect spectrometer. Chemical shifts are given in δ with TMS as an internal reference and constants coupling J are given in Hz, 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. The UV–vis spectra were recorded on a Hewlett Packard 8453 spectrometer, frequencies are given in nm and ε in $L\,mol^{-1}\,cm^{-1}$. All fluorescence spectra were recorded at room temperature at 10^{-8} M on a SLM Aminco Bowman series 2, the fluorescence quantum yield was determined in dichloromethane on freshly prepared samples (air-equilibrated) with absorbances at the excitation wavelength (365 nm for the standard quinine sulfate). The quinine sulfate samples in 1 N H_2SO_4 concentration were employed as a standard ($\Phi_f=0.55$) to measure the fluorescence quantum yields, which were corrected taking into account the refractive indices of the solvents used. Yields are given after silica gel column chromatography separation (silica gel 60, 200–400 mesh) using the solvents or solvent crystallization referred in the corresponding experiment.

4.2. Preparation of 2-chloro-1-(*n*-*N*,*N*-dimethylaminophenyl)ethenes (1–3). General procedure

A solution of *n*-butyllithium 1.6 M in hexane (90 mL, 144 mmol) was slowly added to a suspension of chloromethylen(triphenyl)phosphonium ylide (38 g, 109 mmol) in 210 mL of dry THF, under argon atmosphere at 0 °C. The mixture was stirred for 30 min until an intense red colour, and then *n*-*N*,*N*-dimethylaminobenzene carboxaldehyde (11 g, 73 mmol) was added with stirring at room temperature overnight. After, the solvent was evaporated to leave a brown oil, that was purified by silica gel column chromatography, to give the 2-chloroethenyl derivative.

4.2.1. 2-Chloro-1-(*o*-*N*,*N*-dimethylaminophenyl)ethene (1). Toluene was used as the eluent, giving both isomers as a yellow oil, 12.68 g (*Z*/*E*, 3:2). The *Z* and *E* isomers were isolated using hexane–toluene (2/1): (*Z*)-**1**, 7.66 g (60%) as a pale-yellow oil; (*E*)-**1**, 5.02 g (40%) as a pale-yellow oil.

Isomer (*Z*)-**1**. IR (film, cm^{-1}): 2800, 1600, 740, 660. ^1H NMR ($CDCl_3$): δ 7.84–7.80 (m, 1H), 7.24–7.13 (m, 1H), 7.06–6.90 (m, 2H), 6.85 (d, 1H, $J=7.9$ Hz), 6.28 (d, 1H, $J=7.9$ Hz, 1H), 2.70 (s, 6H). EM (70 eV): 181 (M^+, 14), 166 (2), 146 (72), 131 (100). $C_{10}H_{12}NCl$ (181.66). Anal. Calcd: C 66.12, H 6.66, N 7.71. Found: C 65.97, H 6.55, N 7.65.

Isomer (*E*)-**1**. IR (film, cm^{-1}): 2800, 1600, 960, 740. ^1H NMR ($CDCl_3$): δ 7.33–7.18 (m, 2H), 7.12 (d, 1H, $J=13.7$ Hz), 7.07–6.93 (m, 2H), 6.62 (d, 1H, $J=13.7$ Hz), 2.73 (s, 6H). EM (70 eV): 181 (M^+, 6), 166 (10), 146 (88), 131 (100). $C_{10}H_{12}NCl$ (181.66). Anal. Calcd: C 66.12, H 6.66, N 7.71. Found: C 66.06, H 6.37, N 7.54.

4.2.2. 2-Chloro-1-(*m*-*N*,*N*-dimethylaminophenyl)ethene (2). Toluene was used as the eluent, giving the mixture of both isomers as a yellow oil, 10.83 g (*Z*/*E*, 2:3, 82%).

Mixture (*Z*/*E*)-**2**. IR (film, cm^{-1}): 2790, 1590, 990, 840, 760, 710, 690. ^1H NMR ($CDCl_3$): 7.24 (dd, 1H, $J=7.8$ Hz, *Z*), 7.17 (dd, 1H, $J=7.8$ Hz, *E*), 7.09–7.07 (m, 1H, *Z*), 7.03–6.99 (m, 1H, *Z*), 6.80 (d, 1H, $J=13.6$ Hz, *E*), 6.73–6.65 (m, 4H, *Z*/*E*), 6.61 (d, 1H, $J=13.6$ Hz, 1H, *E*), 6.22 (d, 1H, $J=8.2$ Hz, *Z*), 6.22 (d, 1H, $J=8.2$ Hz, *Z*), 2.95 (s, 6H, *Z*), 2.94 (s, 6H, *E*). EM (70 eV): 181 (M^+, 72), 180 (100), 165 (8), 144 (6), 130 (6). $C_{10}H_{12}NCl$ (181.66). Anal. Calcd: C 66.12, H 6.66, N 7.71. Found: C 65.78, H 6.74, N 7.46.

4.2.3. 2-Chloro-1-(*p*-*N*,*N*-dimethylaminophenyl)ethene (3). Hexane–toluene (1/1) was used as the eluent, recovering two fractions containing the mixture of both isomers as yellow oils: (5.40 g, *Z*/*E*, 1:1, 40.9% and; 5.22 g, *Z*/*E*, 4:1, 39.5%). The *E* and *Z* isomer were isolated from the *Z*–*E* (1/1) mixture toluene as eluent, giving (*E*)-**3**, 2.70 g as a yellow oil, and (*Z*)-**3**, 2.29 g as a pale-yellow solid, mp 37–39 °C.

Isomer Z-**3**. IR (film, cm^{-1}): 2810, 1600, 1360, 830, 700. ^1H NMR ($CDCl_3$): δ 7.63–6.69 (m, 4H), 6.50 (d, 1H, $J=8.1$ Hz), 6.04 (d, 1H, $J=8.1$ Hz), 2.99 (s, 6H). EM (70 eV): 181 (M^+, 92), 180 (100), 165 (18), 144 (9), 130 (8). $C_{10}H_{12}NCl$ (181.66). Anal. Calcd: C 66.12, H 6.66, N 7.71. Found: C 66.22, H 6.57, N 7.63.

Isomer E-**3**. IR (KBr, cm^{-1}): 2810, 1600, 1360, 960, 830. ^1H NMR ($CDCl_3$): δ 7.17–6.66 (m, 4H), 6.73 (d, 1H, $J=13.7$ Hz), 6.42 (d, 1H, $J=13.7$ Hz), 2.96 (s, 6H). EM (70 eV): 181 (M^+, 75), 180 (100), 165 (25), 144 (12), 130 (4). $C_{10}H_{12}NCl$ (181.66). Anal. Calcd: C 66.12, H 6.66, N 7.71. Found: C 66.35, H 6.41, N 7.50.

4.3. Homocoupling reactions with tris(triphenylphosphine)nickel prepared from dichlorobis(triphenylphosphine)nickel. General procedure

To a suspension of dichlorobis(triphenylphosphine) nickel (719 mg, 1.1 mmol), tetrabutylammonium iodide (407 mg, 1.1 mmol) and powdered zinc (107 mg, 1.65 mmol) in 5 mL of dry THF, under argon atmosphere, was stirred for 30 min until the mixture becomes dark red. Then a solution of the chloroethenyl derivative **1**–**3** (200 mg, 1.1 mmol) in 2 mL of dry THF was added and stirred at room temperature for 24 h. Then, hexane was added to the mixture, filtered and the solvent removed. The crude product was purified by chromatography on a silica gel column, using dichloromethane as the eluent.

4.3.1. 1,4-Di(*o*-*N*,*N*-dimethylaminophenyl)-1,3-butadiene (4). Following the general method, three isomers were separated as yellow oils: (1*Z*,3*Z*)-1,4-di(*o*-*N*,*N*-dimethylaminophenyl)-1,3-butadiene (**4a**), 35 mg (22%); (1*Z*,3*E*)-1,4-di(*o*-*N*,*N*-dimethylaminophenyl)-1,3-butadiene (**4b**), 70 mg (40%); (1*E*,3*E*)-1,4-di(*o*-*N*,*N*-dimethylaminophenyl)-1,3-butadiene (**4c**), 55 mg (34%).

(1Z,3Z)-1,4-Di(o-N,N-dimethylaminophenyl)-1,3-butadiene (**4a**). IR (film, cm^{-1}): 2800, 1600, 1500, 770, 700. ^1H NMR ($CDCl_3$): δ 7.56–7.52 (m, 2H), 7.26–7.17 (m, 2H), 7.07–6.99 (m, 4H), 6.70–6.52 (m, 4H), 2.81 (s, 12H). EM (70 eV): 292 (M^+, 100), 277 (12), 248 (14), 233 (3), 172 (24), 158 (29), 145 (48). $C_{20}H_{24}N_2$ (292.42). Anal. Calcd: C 82.15, H 8.27, N 9.58. Found: C 82.01, H 8.42, N 9.62.

(1Z,3E)-1,4-Di(o-N,N-dimethylaminophenyl)-1,3-butadiene (**4b**). IR (film, cm^{-1}): 2800, 1600, 1500, 960, 770, 700. ^1H NMR ($CDCl_3$): δ 7.73–7.64 (m, 2H), 7.55–7.42 (m, 2H), 6.94–6.73 (m, 4H), 6.63–6.45 (m, 4H), 2.78 (s, 12H). EM (70 eV): 292 (M^+, 100), 277 (18), 248 (9), 233 (10), 172 (13), 158 (41), 145 (58). $C_{20}H_{24}N_2$ (292.42). Anal. Calcd: C 82.15, H 8.27, N 9.58. Found: C 82.41, H 8.30, N 9.42.

(1E,3E)-1,4-Di(o-N,N-dimethylaminophenyl)-1,3-butadiene (**4c**). UV–vis (CH_2Cl_2), λ_{max} (nm): 377 (ε, 49,500). Fluorescence (CH_2Cl_2), λ_{max} (nm): 465 ($\phi=0.25$). IR (film, cm^{-1}): 2800, 1600, 1500, 960, 770. ^1H NMR ($CDCl_3$): δ 7.49 (dd, 2H, $J=8.0$, 2.0 Hz), 7.28–7.20 (m, 2H), 7.05–6.97 (m, 4H), 6.70–6.52 (m, 4H), 2.72 (s, 12H). EM (70 eV): 292 (M^+, 100), 277 (12), 248 (15), 233 (9), 172 (25), 158 (45), 145 (41). $C_{20}H_{24}N_2$ (292.42). Anal. Calcd: C 82.15, H 8.27, N 9.58. Found: C 82.38, H 8.02, N 9.34.

4.3.2. 1,4-Di(*m*-*N*,*N*-dimethylaminophenyl)-1,3-butadiene (5). Following the general method, were separated two isomers: (1*Z*,3*E*)-1,4-di(*m*-*N*,*N*-dimethylaminophenyl)-1,3-butadiene (**5b**) as an oil 69 mg (43%); (1*E*,3*E*)-1,4-di(*m*-*N*,*N*-dimethylaminophenyl)-1,3-butadiene (**5c**), as an oil 73 mg (45%).

(1Z,3E)-1,4-Di(m-N,N-dimethylaminophenyl)-1,3-butadiene (**5b**). IR (film, cm^{-1}): 2820, 1590, 1500, 990, 840, 775, 690. ^1H NMR ($CDCl_3$): δ 7.26–7.15 (m, 2H), 6.89–6.61 (m, 6H), 6.52–6.33 (m, 4H), 2.96 (s, 12H). EM (70 eV): 292 (M^+, 100), 277 (14), 248 (10), 233 (5), 172 (19), 158 (31), 145 (53). $C_{20}H_{24}N_2$ (292.42). Anal. Calcd: C 82.15, H 8.27, N 9.58. Found: C 81.99, H 8.37, N 9.39.

(1E,3E)-1,4-Di(m-N,N-dimethylaminophenyl)-1,3-butadiene (**5c**). IR (film, cm^{-1}): 2820, 1590, 1500, 990, 840, 775. UV–vis (CH_2Cl_2), λ_{max} (nm): 283 (ε, 35,000), 316s (ε, 53,400), 327 (ε, 57,300), 342 (ε, 42,600). Fluorescence (CH_2Cl_2), λ_{max} (nm): 477 ($\phi=0.29$). ^1H NMR ($CDCl_3$): δ 7.26–7.15 (m, 2H), 6.95 (dd, 4H, $J=15.5$, -0.5 Hz), 6.89–6.61 (m, 6H), 3.00 (s, 12H). EM (70 eV): 292 (M^+, 100), 277 (10), 248 (5), 233 (8), 172 (24), 158 (39), 145 (41). $C_{20}H_{24}N_2$ (292.42). Anal. Calcd: C 82.15, H 8.27, N 9.58. Found: C 81.92, H 8.45, N 9.75.

4.3.3. 1,4-Di(*p*-*N*,*N*-dimethylaminophenyl)1,3-butadiene (6a and 6b). Following the general method to the (*Z*/*E*)-2-chloro-1-(*p*-*N*,*N*-dimethylaminophenyl)ethene mixtures (*Z*/*E*, 1:1 or 4:1), two isomers were separated: (1*Z*,3*Z*)-1,4-di(*p*-*N*,*N*-dimethylaminophenyl)-1,3-butadiene (**6a**), as a yellow solid, mp 231.7 °C by DSC, 3 mg (2%) or 6 mg (4%) (mixture 1:1 or 1:4, respectively); (1*Z*,3*E*)-1,4-di(*p*-*N*,*N*-dimethylaminophenyl)-1,3-butadiene (**6b**), yellow solid, mp 255–256 °C, 124 mg (77%) or 127 mg (79%) (mixture 1:1 or 1:4, respectively).

(1Z,3Z)-1,4-Di(p-N,N-dimethylaminophenyl)-1,3-butadiene (**6a**). UV–vis (CH_2Cl_2), λ_{max} (nm): 386 (ε, 104,200), 405 (ε, 82,400). Fluorescence (CH_2Cl_2), λ_{max} (nm): 438 ($\phi=0.32$). IR (KBr, cm^{-1}): 2910, 1605, 1510, 800, 710. ^1H NMR ($CDCl_3$): δ 7.32 (d, 4H, $J=8.3$ Hz), 6.74 (d, 4H, $J=8.3$ Hz), 6.73 (d, 2H, $J=7.5$ Hz), 6.55 (d, 2H, $J=7.5$ Hz), 2.97 (s, 12H). EM (70 eV): 292 (M^+, 100), 248 (9), 172 (23), 146 (34), 77 (3). $C_{20}H_{24}N_2$ (292.42). Anal. Calcd: C 82.15, H 8.27, N 9.58. Found: C 82.47, H 8.33, N 9.41.

(1Z,3E)-1,4-Di(p-N,N-dimethylaminophenyl)-1,3-butadiene (**6b**). IR (KBr, cm^{-1}): 2950, 1605, 1510, 800, 710. ^1H NMR ($CDCl_3$): δ 7.32 (d, 4H, $J=8.3$ Hz), 6.81 (d, 4H, $J=8.3$ Hz), 6.80 (m, 2H), 6.53 (m, 2H), 2.98 (s, 12H). EM (70 eV): 292 (M^+, 100), 248 (10), 172 (30), 146 (28), 77 (2). $C_{20}H_{24}N_2$ (292.42). Anal. Calcd: C 82.15, H 8.27, N 9.58. Found: C 82.40, H 8.39, N 9.50.

4.3.4. 1,4-Di(*p*-*N*,*N*-dimethylaminophenyl)1,3-butadiene (6c). Following the general method to (*E*)-2-chloro-1-(*p*-*N*,*N*-dimethylaminophenyl)ethene (**3**), 152 mg (95%) of the (1*E*,3*E*)-1,4-di(*p*-*N*,*N*-dimethylaminophenyl)1,3-butadiene (**6c**) was obtained as a yellow solid, mp 245–246 °C.

UV–vis (CH_2Cl_2), λ_{max} (nm): 388 (ε, 24,400), 405 (ε, 203,200). Fluorescence (CH_2Cl_2), λ_{max} (nm): 440 ($\phi=0.26$). IR (film, cm^{-1}): 2800, 1610, 1520, 990, 815. ^1H NMR ($CDCl_3$): δ 7.32 (dd, 4H, $J=8.8$, -0.1 Hz), 6.78 and 6.71 (dd, 4H, $J=15.5$, -0.1 Hz), 6.70 (dd, 4H, $J=8.8$, -0.1 Hz), 2.97 (s, 12H). EM (70 eV): 292 (M^+, 100), 277 (9), 248 (16), 202 (32), 172 (45), 158 (68), 77 (2). $C_{20}H_{24}N_2$ (292.42). Anal. Calcd: C 82.15, H 8.27, N 9.58. Found: C 82.23, H 8.19, N 9.69.

4.3.5. Stereospecific synthesis of (1*Z*,3*Z*)-1,4-di(*p*-*N*,*N*-dimethylaminophenyl)-1,3-butadiene (6a). To a solution of 1,4-di(*p*-*N*,*N*-dimethylaminophenyl)-1,3-butadiyne (**9**) (0.25 g, 0.867 mmol) in toluene (5 mL) was added deactivated palladium on barium sulfate (0.048 g) and quinoline (0.095 mL). Deactivation was carried out by previous treatment with an aqueous solution of lead acetate (7%) at 80 °C, for 45 min.

The mixture was treated with hydrogen at room pressure and temperature with stirring for 6 h. After, solvent was removed and the residual solid purified by silica gel column chromatography dichloromethane–hexane (3/2) giving the (1*Z*,3*Z*)-diene derivative **6a** (0.24 g, 96%) as a yellow solid (mp 231.7 °C, by DSC).

4.3.6. Preparation of *p*-(*N*,*N*-dimethylamino)phenylacetylene (8). To a solution of 2-chloro-1-(*p*-*N*,*N*-dimethylaminophenyl)ethene 200 mg (1.10 mmol) in dry THF (15 mL) was slowly added a solution of *n*-butyl lithium in hexane (2.0 mL, 1.6 M). The mixture was stirred for 3 h. Then, was hydrolysed with a saturated aqueous ammonium chloride solution and extracted with dichloromethane, dried with anhydrous $MgSO_4$. After, solvent was removed at reduced pressure and the residual brown solid was purified by silica gel column chromatography, using toluene as eluent. The acetylene derivative **8** was isolated as a yellow solid, mp 51–52 °C, 139 mg (86%).

IR (KBr, cm^{-1}): 3290, 2810, 2100, 1610, 1520, 1360, 820. ^1H NMR ($CDCl_3$): δ 7.37 (dd, 2H, $J=8.3$, -0.1 Hz), 6.62 (dd, 2H, $J=8.3$, -0.1 Hz), 2.97 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 150.2, 133.0 (2C), 115.5 (2C), 108.5, 84.8, 74.7, 39.9. EM (70 eV): 145 (M^+, 100), 144 (96), 129 (27), 115 (9), 101 (24), 77 (10). $C_{10}H_{11}N$ (145.20). Anal. Calcd: C 82.72, H 7.64, N 9.65. Found: C 82.63, H 7.44, N 9.73.

4.3.7. 1,4-Di(*p*-*N*,*N*-dimethylaminophenyl)-1,3-butadiyne (9) by homocoupling of compound 8. A solution of cuprous chloride (0.037 g) in pyridine and the acetylene **8** (0.53 g, 3.7 mmol), under an oxygen atmosphere. The mixture was stirred at room temperature for 1 h. After, pyridine was removed at reduced pressure and hydrolysed with an aqueous solution (50 mL) of ammonium chloride (5 g), and potassium cyanide (1.25 g), and extracted with dichloromethane. The organic layer was dried with anhydrous magnesium sulfate and after filtration, the solvent was evaporated giving 1,4-di(*p*-*N*,*N*-dimethylaminophenyl)-1,3-butadiyne (**9**), which was purified by flash silica gel column chromatography giving a brown solid 0.512 g, 96% mp 235–238 °C.

UV–vis (CH_2Cl_2), λ_{max} (nm): 351 (ε, 113,000), 378 (ε, 97,600). Fluorescence (CH_2Cl_2), λ_{max} (nm): 428 ($\phi=8.3\times10^{-4}$). IR (KBr, cm^{-1}): 2930, 2120, 1600, 1505, 1350, 810. ^1H NMR ($CDCl_3$): δ 7.40 (d, 4H, $J=8.2$ Hz), 6.63 (d, 4H, $J=8.2$ Hz), 2.98 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 150.2, 133.5 (2C), 111.6 (2C), 108.4, 82.2, 72.5, 39.9. EM (70 eV): 288 (M^+, 100), 272 (16), 144 (13). $C_{20}H_{20}N_2$ (288.39). Anal. Calcd: C 83.30, H 6.99, N 9.71. Found: C 83.09, H 6.63, N 9.66.

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