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Synthesis of conjugated (1*E*,3*E*)- and (1*Z*,3*Z*)-1,4-di(*n*-pyridyl) (or *n*-quinolyl)-1,3-butadienes from *n*-(2′-chloroethenyl)pyridine (or quinoline)

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ABSTRACT

The homocoupling reaction between the conjugated *n*-(2-chloroethenyl)pyridine; *n*, 2-, 3- and 4- (or quinoline; *n*, 2- and 4-) mediated by zero-valent nickel complexes at room temperature affords to the corresponding 1,4-diaryl-1,3-butadiene, always as the 1*E*,3*E* stereoisomer. The yield in 1,4-diaryl-1,3-butadiene increases with the nickel catalyst and hence, the active zero-valent nickel catalyst is not regenerated during the homocoupling reaction.

The stereospecific synthesis of (1*Z*,3*Z*)-1,4-di(4′-pyridyl)-1,3-butadiene stereoisomer was efficiently carried out by partial hydrogenation of the appropriate 1,4-di(4′-pyridyl)-1,3-butadiyne.

1. Introduction

The synthesis of the highly conjugated polyene structures as molecular organic materials show a wide-spread interest because these exhibit an important stability, semiconductor and optical properties.[1]

An elegant and practical synthetic method for 1,4-diphenyl-1,3-butadiene was the homocoupling of the (*E*)- or (*Z*)-β-bromostyrene with zero-valent nickel complexes giving the (*E*,*E*)- or (*Z*,*Z*)-1,4-diphenyl-1,3-butadiene, respectively, while the (*E*,*Z*) isomer was always isolated in low yield.[2]

The homocoupling reaction was also investigated with arylsulfonates,[3–5] in the presence of the nickel complexes. The Grignard reagents in catalytic amounts of nickel complexes,[6,7] have be used for the preparation of diaryl or diheteroaryl or polyaryl derivatives.[8] The homocoupling of organic halides or heteroarylhalides was efficiently catalysed by electroreductive nickel complexes in organic solvent or ionic liquids solvent.[9]

The (*Z*)-3-halopropenoates were homocoupled using catalytic amounts of nickel chloride and zinc in water with pyridine, affording a mixture of (*E*) and (*Z*)-3-hexenedioates.[10]

The homocoupling reaction of the *E*-, *Z*- isomers or *E*/*Z* mixtures of 2-chloro-1-(*p*-*N*,*N*-dimethylaminophenyl)ethene, in the presence of the zero-valent nickel complexes, was recently reported.[11a] The active zero-valent nickel species were prepared in situ from stoichiometric amounts of zinc powder and dichloro bis (triphenylphosphine)nickel complex,[11a] or catalytic nickel salts.[11b]

Now, we report the homocoupling of (*E*)- or (*Z*)-*n*-(2′-chloroethenyl)pyridine (or quinoline) containing conjugated electron withdrawing heterocycle rings, with zero-valent nickel complexes, to explore the influence of the nitrogen electron lone pair on the catalyst and the stereochemistry of the reaction.

2. Results and discussion

The homocoupling reaction of the *n*-(2′-chloroethenyl)pyridine (or quinoline), having conjugated electron withdrawing heterocycles as the susbtituent on the double bond, in the presence of zero-valent nickel complexes, was explored to prepare the conjugated 1,4-di(*n*-pyridyl) (or *n*-quinolyl)-1,3-butadienes.

In this way, *n*-(2′-chloroethenyl)pyridines (**1**–**3**) (or quinolines, **4** and **5**) were prepared by means of the Wittig reaction between the chloromethylen(triphenyl)phosphorane and *n*-pyridine (or quinoline) carboxaldehyde in toluene as yellow oils as a mixture of the *E* and *Z* isomers. For **1**, **4** and **5** both isomers were purely isolated by chromatography and used separately in the homocoupling reaction.

The phosphorane reagent was prepared in situ by reaction of chloromethyl(triphenyl)phosphonium chloride with *n*-butyllithium, [11a,12,13] Scheme 1.

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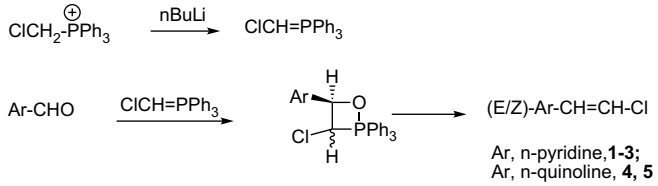
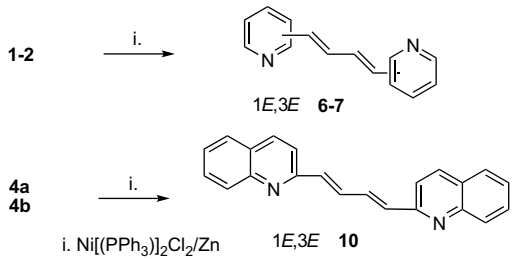


Scheme 1.

The homocoupling reaction of the *n*-(2′-chloroethenyl)pyridine (or quinoline) derivatives was carried out in the presence of the zero-valent nickel complex as catalyst, which was prepared in situ from dichloro bis(triphenylphosphine) nickel and powder of zinc as the reducing agent and tetra-*n*-butylammonium iodide as a phase transfer component in dry tetrahydrofuran, under argon atmosphere,[11] Scheme 2.



Scheme 2.

The homocoupling of (*E*)-2-(2′-chloroethenyl)pyridine (**1a**) in the presence of the zero-valent nickel complex in 3.3, 1.7 and 1, **1a**/Ni[$(PPh_3)_2$] catalyst molar ratio, gives always the (1*E*,3*E*) 1,4-di(2′-pyridyl)-1,3-butadiene (**6**) as the unique stereoisomer in 24, 63 and 92% yield, respectively.

In the same way, the homocoupling of the *Z* isomer (**1b**) with the zero-valent nickel complex in 3.3, 1.7 and 1, **1b**/Ni[$(PPh_3)_2$] catalyst molar ratio, gives also the (1*E*,3*E*) stereoisomer in 19, 58 and 89% yield, respectively. Hence, in this case, $Z \rightarrow E$ isomerisation of **1b** isomer was necessary during the homocoupling reaction.

On the other hand, 3-(2′-chloroethenyl)pyridine (**2**) was obtained by the Wittig reaction between the chloromethylen(-triphenyl)phosphorane and 3-pyridinecarboxaldehyde in toluene as yellow oil mixture of stereoisomers (**2a**/**2b**, 1:1), which was not possible to separate by chromatographic methods. The homocoupling was carried out with the stereoisomeric mixture (**2a**/**2b**, 1:1) in the presence of the zero-valent nickel complex in 3.3, 1.7 and 1, (**2a**,**2b**/Ni[$(PPh_3)_2$]) catalyst molar ratio, giving exclusively the (1*E*,3*E*)-1,4-di(3′-pyridyl)-1,3-butadiene (**7**) in 27, 58 and 87%, respectively, as a pale yellow solid mp 129–131 °C. Hence, during the homocoupling reaction with the nickel complex a partial $Z \rightarrow E$ isomerisation of (*Z*)-**2b** was necessary.

In the same way, 4-(2′-chloroethenyl)pyridine (**3**) was obtained by the Wittig reaction between the chloromethylen (triphenyl)phosphorane and 4-pyridinecarboxaldehyde in toluene, as yellow oil mixture (**3a**/**3b**, 1:1). The mixture (**3a**/**3b**) was used in the homocoupling reaction with the zero-valent nickel complex but both isomers of 4-(2′-chloroethenyl)pyridine in the presence of the catalyst decompose at room temperature to give a water soluble green solid of complicated identification.

Complementary, the stable isomer (1*Z*,3*Z*)-1,4-di(4′-pyridyl)-1,3-butadiene isomer (**8**) was stereospecifically obtained in good yield (96%), by partial catalytic hydrogenation of 1,4-di(4′-pyridyl)-1,3-butadiyne (**9**), with partially deactivated palladium catalyst, as a yellow solid (mp 88–90 °C). Compound **9** was prepared by hydrochloric acid elimination of (**3**) with potassium *tert*-butoxide at room temperature, in good yield, Scheme 3.

Compound **3** was prepared by homocoupling of 4-pyridinacetylene catalysed by cuprous chloride in pyridine with excellent yield. Compound **9** was applied as coordinative agent to prepare a copper(I) complex forming stable polycatenated molecular ladders as a new structural motif in coordination polymers,[14] Scheme 3.

The experimental results of the homocoupling reaction of *n*-(2′-chloroethenyl)pyridines (**1**–**3**) mediated by the zero-valent nickel complex are summarised in Table 1.

The electron withdrawing character of quinoline in conjugated *x*-(2′-chloroethenyl)quinolines was also analysed in the homocoupling reaction. Thus, 2-(2′-chloroethenyl)quinoline (**4a**/**4b**) was obtained by the Wittig reaction between chloromethylen-(triphenyl)phosphorane and 2-quinoline carboxaldehyde, as yellow oil mixture of *E*/*Z* (1:1) isomers, in good yield (84%), Scheme 1.

The 2-quinoline carboxaldehyde (or 4-quinoline carboxaldehyde) was obtained by oxidative treatment of 2-methylquinoline (or 4-methylquinoline) with freshly sublimated selenium dioxide, as white (or yellow) crystals in good yield.[15]

The 2-, 3- and 4-chloroquinolines and their acetylene derivatives were obtained and homocoupled to the bis(*n*-quinolines) or to the 1,4-di(*n*-quinolyl)-1,3-butadiynes by other synthetic strategy.[15]

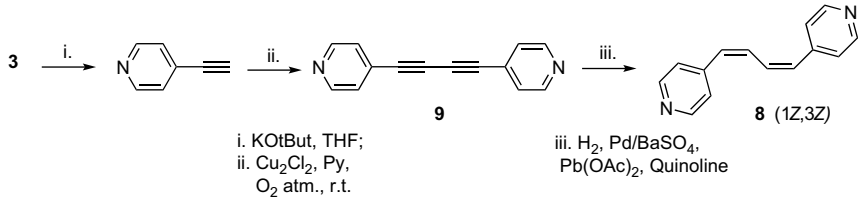
The (*E*)-2-(2′-chloroethenyl)quinoline (**4a**) isomer was homocoupled in the presence of the zero-valent nickel complex under stoichiometric catalyst at room temperature giving (1*E*,3*E*)-1,4-di(2-quinolyl)-1,3-butadiene (**10**), as the unique stereoisomer in 85% yield, Scheme 2, Table 2.

In the same way, the (*Z*)-2-(2′-chloroethenyl)quinoline (**4b**) isomer in the presence of the zero-valent nickel complex under stoichiometric catalyst at room temperature gives (1*E*,3*E*)-1,4-di(2-quinolyl)-1,3-butadiene (**10**), as the unique stereoisomer in 84% yield, Table 2. Hence, during the reaction $Z \rightarrow E$ isomerisation of **4b** takes place.

The 4-(2′-chloroethenyl)quinoline (**5**) was obtained by the Wittig reaction between the chloromethylen(triphenyl)phosphorane and 4-quinoline carboxaldehyde in hexane as a brown oil, mixture of isomers (**5a**/**5b**, 3:2). Both isomers were isolated by chromatography: (*E*)-4-(2′-chloroethenyl)quinoline (**5a**) as yellow crystals (mp 45–46 °C) and (*Z*)-4-(2′-chloroethenyl)quinoline (**5b**), as colourless oil.

Both **5a** and **5b** isomers are stable in solution of hexane under argon atmosphere but are unstable to the air and to the ambient light or in contact with the zero-valent nickel complex.

Thus, the homocoupling reaction of (*E*)-4-(2′-chloroethenyl)quinoline (**5a**) in the presence of the zero-valent nickel



Scheme 3.

Table 1
Homocoupling reaction of *x*-(2′-chloroethenyl)pyridines with zero-valent nickel complex in situ production: Ni[$(PPh_3)]_2Cl_2$

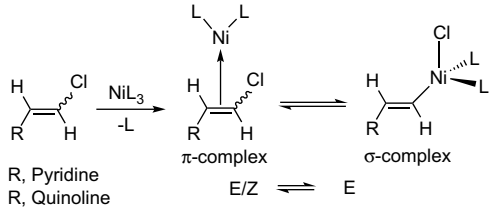
Subst/Ni, m.r.	*n*	Compound	Isomer	1,3-Butadiene	Yield (%)	Mp (°C)
3.3	2	**1a**	*E*	**6** (1*E*,3*E*)	24	115–117
1.7	2	**1a**	*E*	**6** (1*E*,3*E*)	63	115–117
1	2	**1a**	*E*	**6** (1*E*,3*E*)	92	115–117
3.3	2	**1b**	*Z*	**6** (1*E*,3*E*)	19	115–117
1.7	2	**1b**	*Z*	**6** (1*E*,3*E*)	58	115–117
1	2	**1b**	*Z*	**6** (1*E*,3*E*)	89	115–117
3.3	3	**2a**/**2b**	*E*/*Z*, 1:1	**7** (1*E*,3*E*)	27	124–126
1.7	3	**2a**/**2b**	*E*/*Z*, 1:1	**7** (1*E*,3*E*)	58	124–126
1	3	**2a**/**2b**	*E*/*Z*, 1:1	**7** (1*E*,3*E*)	87	124–126
1	4	**3a**/**3b**	*E*/*Z*, 1:1	Decomposed	—	—

Zero-valent nickel complex: Ni[$(PPh_3)]_2Cl_2$ (*n* mmol); PPh_3 (4.3 mmol); *n*-Bu_4NI (7.0 mmol); Zn powder (15 mmol); anhydrous THF; 2′-chloroethenylpyridine substrate (7.0 mmol), molar ratio substrate/Ni[$(PPh_3)_2Cl_2$ (3.3, 1.7, 1).

Table 2
Homocoupling reaction of *x*-(2′-chloroethenyl)quinoline with the zero-valent nickel complex in situ production: [$Ni(PPh_3)_2]Cl_2$

Subst/Ni, m.r.	*n*	Compound	Isomer	1,3-Butadiene	Yield (%)	Mp (°C)
1.0	2	**4a**	*E*	**10** (1*E*,3*E*)	85	197–198
1.0	2	**4b**	*Z*	**10** (1*E*,3*E*)	84	197–198
1.0	4	**5a**/**5b**	*E*/*Z*, 1:1	Decomposed	—	—

Zero-valent nickel complex: Ni[$(PPh_3)_2]Cl_2$ (7.0 mmol); PPh_3 (4.3 mmol); *n*-Bu_4NI (7.0 mmol); Zn powder (15 mmol); dry THF; *n*-(2′-chloroethenyl)quinoline substrate (7.0 mmol).

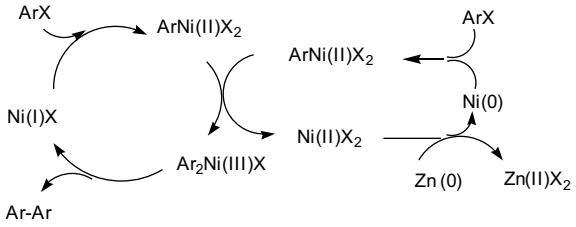


Scheme 4.

complexes, fails because **5a** decomposes. In the mixture of reaction **5a** was partially recovered but the homocoupling product was not observed.

In the same way, the homocoupling experiments carried out with (*Z*)-4-(2′-chloroethenyl)quinoline (**5b**), in the presence of the zero-valent nickel complexes, at variable temperature, decomposes and **5** was recovered as a mixture of the *E*/*Z* isomers. The homocoupling product was not observed.

The (*Z*)→(*E*) isomerisation observed during the homocoupling reaction of the 2′-chlorovinyl derivatives **1b**, **2b**, **4b** and **5b** could be due to the formation of a π-nickel-double bond complex, which decreases the double bond order allowing the rotation of the C–C bond in the π-complex. The formation of a π-complex was proposed prior to the oxidative addition to the C–halogen bond by the nickel complex.[16] The volume interactions of the substituents on



Scheme 5.

the π–σ nickel complex equilibrium, could be responsible of the pathway of the homocoupling and the reason of the 1,3-butadiene stereochemistry,[16] being of minor importance the thermodynamic stability, Scheme 4.[17]

On the basis of the electroanalysis of the Ni complex, it was proposed a mechanism for the homocoupling reaction of aryl halides through a chain reaction involving several valences of the nickel complex: Ni(0), Ni(I), Ni(II) and Ni(III) complexes, Scheme 5.[18]

The role of the nickel reagents in the activation of the carbon–halogen bond is commonly interpreted by the involvement of arylnickel(II) intermediates formed by oxidative addition of the aryl halide to in situ generated Ni(0) complex. There is general agreement on the biaryl formation by reductive elimination from a diarylnickel species.[18]

In general, the homocoupling of 2′-chloroethenylbenzene with the zero-valent nickel complex affords to a mixture of 1,3-butadiene stereoisomers.[11a] In contrast, the homocoupling of 2′-chloroethenylpyridines or quinolines with the zero-valent nickel complex gives only the 1*E*,3*E* stereoisomer. The different stereochemical behaviour for the homocoupling reaction can be due to the heterocyclic nitrogen electron lone pair as donor ligand, which can interchange the coordination ligands around the nickel complex responsible of the stereospecificity.

3. Conclusions

The stereospecific synthesis of (1*E*,3*E*)-1,4-dipyridyl (or diquinolyl)-1,3-butadiene can be carried out by the homocoupling reaction of *x*-(2′-chloroethenyl)pyridine (or quinoline) mediated by zero-valent nickel complexes in good yield.

Variable molar ratio of (2′-chloroethenyl)/nickel zero-valent complex has been employed and the highest yield in the homocoupling product was founded for stoichiometric nickel amounts. Hence, the nickel catalyst system used was not regenerated along the reaction.

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 50 MHz, respectively, on a Bruker Aspect 200 MHz spectrometer, chemical shifts are given in δ, using $CDCl_3$ as the solvent and TMS as an internal reference and constant *J* values are given in hertz. Mass spectra were recorded in 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. 2-(2′-Chloroethenyl)pyridine (1): general procedure

To a solution of chloromethylen(triphenyl)phosphonium chloride (18.7 g, 57 mmol) in dry THF (60 mL), at 0 °C was added a solution of BuLi (35.6 mL, 57 mmol, 1.6 M) in hexane, and stirred for 30 min. Then, a solution of 2-pyridincarboxaldehyde (2 g, 19 mmol) was added, stirring at room temperature for 10 h. After, solvent was removed at reduced pressure and the residual oil extracted in hexane (200 mL), dried over magnesium sulfate, filtered and solvent removed. The residual oil of 2-(2′-chloroethenyl)-pyridine (**1**) was a mixture of the *E*/*Z* isomers, which was purified by silica gel

column chromatography (ethyl acetate/hexane, 2:1) giving **1a** (*E*, 0.33 g, 12%) and **1b** (*Z*, 1.71 g, 65%) as yellow oils.

*4.2.1. (E)-2-(2′-Chloroethenyl)pyridine (**1a**)*

ν_{max}(film), cm^{-1}, 3070 (=C–H), 1620 (C=C, conj.), 1580 and 1560 (C=C and C=N) and 970 (*E*). δ_H (200 MHz; $CDCl_3$) 6.67 (1H, d, *J* 13.3 Hz, C*H*=), 7.20 (2H, m, H-3 and H-5), 7.43 (1H, d, *J* 13.3 Hz, =C*H*Cl), 7.63 (1H, m, H-4) and 8.53 (1H, br s, H-6). MS, *m*/*z* 141 (9), 139 (M^+, 27), 104 (100), 78 (25) and 51 (18).

*4.2.2. (Z)-2-(2′-Chloroethenyl)pyridine (**1b**)*

ν_{max}(film), cm^{-1}, 3055 (=C–H), 1620 (C=C, conj.), 1580 and 1560 (C=C and C=N) and 670 (*Z*). δ_H (200 MHz; $CDCl_3$) 6.49 (1H, d, *J* 8.3 Hz, C*H*=), 6.86 (1H, d, *J* 8.3 Hz, =C*H*Cl), 7.19 (1H, dd, *J* 7.9 and 6.0 Hz, H-5), 7.70 (1H, t, *J* 7.9 Hz, H-4), 8.02 (1H, d, *J* 7.9 Hz, H-3) and 8.62 (1H, d, *J* 6.0 Hz, H-6). MS, *m*/*z* 141 (9), 139 (M^+, 22), 104 (100), 84 (13), 78 (30) and 51 (27).

*4.2.3. 3-(2′-Chloroethenyl)pyridine (**2**)*

Following the general procedure, a mixture of **2a**/**2b** (1:1, by ^1H NMR) was obtained, as colourless oil (2.38 g, 90%). ν_{max}(film), cm^{-1}, 3050 (=C–H), 1610 and 1605 (C=C, conj.), 1580 and 1560 (C=C and C=N), 970 (*E*) and 730 (*Z*). δ_H (200 MHz; $CDCl_3$) 6.29 (1H, d, *J* 8.2 Hz, C*H*=, *Z*), 6.69 (1H, d, *J* 13.9 Hz, C*H*=, *E*), 6.74 (1H, d, *J* 8.2 Hz, =C*H*Cl, *Z*), 6.85 (1H, d, *J* 13.9 Hz, =C*H*Cl, *E*), 7.25 (1H, d, *J* 8.0 Hz, H-5, *E*), 7.32 (1H, dd, *J* 8.0 and 5.4 Hz, H-5, *Z*), 7.60 (1H, d, *J* 8.0 Hz, H-4, *E*), 8.13 (1H, d, *J* 8.0 Hz, H-4, *Z*), 8.49 (1H, br s, H-6, *E*), 8.52 (1H, d, *J* 5.4 Hz, H-6, *Z*), 8.53 (1H, br s, H-2, *E*) and 8.76 (1H, br ds, H-2, *Z*). MS, *m*/*z* 141 (8), 139 (M^+, 29), 104 (100), 86 (10), 77 (46) and 51 (64).

*4.2.4. 4-(2-Chloroethenyl)pyridine (**3**)*

Following the general procedure, a mixture of **3a**/**3b** (1:1, by ^1H NMR) was obtained, as colourless oil (2.22 g, 84%). ν_{max}(film), 3060 (=C–H), 1610 (C=C, conj.), 1590 and 1540 (C=C and C=N), 960 (*E*) and 720 (*Z*). δ_H (200 MHz; $CDCl_3$) 6.48 (1H, d, *J* 8.2 Hz, C*H*=, *Z*), 6.60 (1H, d, *J* 8.2 Hz, =C*H*Cl, *Z*), 6.69 (1H, d, *J* 13.8 Hz, C*H*=, *E*), 6.77 (1H, d, *J* 13.8 Hz, =C*H*Cl, *E*), 7.16 (2H, d, *J* 4.8 Hz, H-3 and H-5, *E*), 7.52 (2H, d, *J* 4.6 Hz, H-3 and H-5, *Z*), 8.56 (2H, d, *J* 4.8 Hz, H-2 and H-6, *E*) and 8.62 (2H, d, *J* 4.6 Hz, H-2 and H-6, *Z*). MS, *m*/*z* 141 (8), 139 (M^+, 29), 112 (29), 104 (38), 86 (84), 77 (36), 63 (16) and 51 (100).

*4.2.5. 2-(2′-Chloroethenyl)quinoline (**4a**/**4b**)*

Previously, 2-quinolylcarboxaldehyde was obtained by oxidative treatment of 2-methylquinoline with recently sublimed SeO_2 following a reported method, mp 69–71 °C.[17]

To a solution of chloromethylen(triphenyl)phosphonium chloride (18.7 g, 57 mmol) in dry THF (60 mL), at 0 °C was added a solution of BuLi (35.6 mL, 1.6 M, 57 mmol) in hexane, and stirred for 30 min. Then, a solution of 2-quinolylcarboxaldehyde (2.99 g, 19 mmol) in hexane (20 mL) was added and stirred at room temperature for 14 h. After, solvent was removed and the residual oil was purified by silica gel column chromatography (hexane/ethyl acetate, 1:1) giving the *E* isomer (**4a**) as yellow solid (mp 45–46 °C) (1.25 g, 43% yield), and the *Z* isomer (**4b**) as colourless oil (1.03 g, 35%).

*4.2.5.1. Compound **4a**.* IR (KBr), 3060 (=C–H), 1610 (C=C, conj.), 1590 and 1540 (C=C and C=N), 925 (CH=CHCl, *E*), 800, 780, 760, 740 (C–H ring). δ_H 8.19 (d, *J* 8.54 Hz, H-8), 8.11 (d, *J* 8.30 Hz, H-5), 7.85 (dd, *J* 10.31 and 1.24 Hz, H-4), 7.59 (m, H-6), 7.44 (d, *J* 10.30 Hz, H-3), 7.42 (d, *J* 11.45 Hz, =CHCl), 7.16 (d, *J* 11.45 Hz, *Z*, CH=). MS, *m*/*z* 189 (M^+, 20), 191 (M^++2, 8), 154 (100), 128 (M^+, 29), 101 (16), 77 (16), 63 (9).

*4.2.5.2. Compound **4b**.* IR (film), 3060 (=C–H), 1610 (C=C, conj.), 1590 and 1540 (C=C and C=N), and 720 (CH=CHCl, *Z*), and 830, 800, 750, 730 (C–H ring). δ_H 8.20 (d, *J* 8.78 Hz, H-3), 8.13 (d, *J* 6.52 Hz, H-8), 8.08 (d, *J* 8.78 Hz, H-4), 7.82 (dd, *J* 6.43, 1.55 Hz, H-5), 7.74 (m, H-7), 7.57 (m, H-6), 7.06 (d, *J* 7.88 Hz, =CHCl), 6.62 (d, *J* 7.88 Hz, CH=). MS, *m*/*z* 189 (M^+, 22), 191 (M^++2, 7), 154 (100), 128 (29), 101 (10), 77 (18), 63 (11).

*4.2.6. 4-(2′-Chloroethenyl)quinoline (**5a**/**5b**)*

Previously, 4-quinolylcarboxaldehyde was obtained by oxidative treatment of 4-methylquinoline with recently sublimed SeO_2 following a reported method, mp 49–51 °C.

Following the general procedure was obtained a mixture of **5a**/**5b** (1:1) as a yellow oil, which was isolated by silica gel column chromatography (ethyl acetate/hexane, 1:1), giving **5a** (1.17 g, 40%) yellow solid (dec), and **5b** colourless oil (1.11 g, 38%).

*4.2.6.1. Compound **5a**, E isomer.* IR (KBr), 3060 (=C–H), 1620 (C=C, conj.), 1590 and 1510 (C=C and C=N), and 950 (CH=CHCl, *Z*), and 820, 760, 720 (C–H ring). δ_H 8.90 (d, *J* 4.30 Hz, H-2), 8.15 (dd, *J* 8.66 and 1.00 Hz, H-8), 8.05 (dd, *J* 8.69 and 1.6 Hz, H-5), 7.77 (m, H-7), 7.60 (m, H-6), 7.35 (d, *J* 4.30 Hz, H-3), 6.88 (d, *J* 12.90 Hz, =CHCl), 7.55 (d, *J* 12.90 Hz, CH=). MS, *m*/*z* 189 (M^+, 23), 191 (M^++2, 7), 154 (100), 127 (29), 101 (7), 77 (17) and 63 (18).

*4.2.6.2. Compound **5b**, Z isomer.* IR (film), 3060 (=C–H), 1620 (C=C, conj.), 1590 and 1510 (C=C and C=N), 730 (=CHCl, *Z*), and 810, 770, 720 (C–H ring). δ_H 8.85 (d, *J* 8.51 Hz, H-2), 8.05 (d, *J* 8.20 Hz, H-8), 7.83 (dd, *J* 8.20, 1.60 Hz, H-5), 7.65 (m, H-7), 7.55 (d, *J* 8.51 Hz, H-3), 7.45 (m, H-6), 6.61 (d, *J* 8.17 Hz, =CHCl), 7.13 (d, *J* 8.17 Hz, CH=). MS, *m*/*z* 189 (M^+, 28), 191 (M^++2, 9), 154 (100), 127 (37), 101 (8), 77 (19) and 63 (22).

4.3. Homocoupling reaction catalysed by dichloro bis(triphenylphosphine) nickel/Zn system: general procedure

A suspension of dichloro bis(triphenylphosphine) nickel(II) (719 mg, 1.1 mmol), tetrabutylammonium iodide (407 mg, 1.1 mmol) and powder of zinc (107 mg, 1.65 mmol) in 5 mL of dry THF under argon atmosphere, was stirred until the mixture becames dark-red, then it was left to stand for 30 min and a solution of the *n*-(2′-chloroethenyl)pyridine (or quinoline) (1.1 mmol) in dry THF (2 mL) was added and stirred at room temperature overnight. Then, hexane was added to the mixture, filtered and the solvent removed. The crude product was purified by silica gel column chromatography.

*4.3.1. Homocoupling of **1a** in variable **1a**/Ni[(PPh$_3$)]$_2$Cl$_2$ molar ratio*

Following the general procedure but in variable 2′-chloroethenyl derivative/Ni[$(PPh_3)]_2Cl_2$ molar ratio of 0.3, 0.6 1.0, was always isolated (1*E*,3*E*)-1,4-di-(2-pyridyl)-1,3-butadiene (**6**) as the unique stereoisomer, in 24, 63 and 92% yield, respectively, as yellow solid, mp 115–117 °C.

IR (KBr): 1610 (C=C, conj.), 1575 and 1560 (C=C and C=N), 970 (CH=CH, *E*). δ_H 8.59 (d, 2H, *J* 4.9 Hz, H-6), 7.65 (t, 2H, *J* 7.7 Hz, H-4), 7.34 (d, 2H, *J* 7.7 Hz, H-3), 7.14 (dd, 2H, *J* 7.7 and 4.9 Hz, H-5), H_A=7.49 and H_x=6.84 (AA′XX′, 4H, J_{Ax}=15.2 Hz, $J_{Ax'}$=−0.7 Hz, CH=CH). δ_C 155.1 (C-2), 149.5 (C-6), 136.4 (C-4), 134.1 (Py–C=*C*), 132.3 (C-3), 122.3 and 122.1 (4C, Py–*C*=C and C-5). MS, *m*/*z* 208 (M^+, 5), 207 (M^+−1, 4), 130 (100), 103 (10), 89 (8), 78 (46), 63 (21) and 51 (68). Anal. calcd for $C_{14}H_{12}N_2$: C, 80.70; H, 5.85; N, 13.44. Found: C, 80.45; H, 5.88; N, 13.27%.

*4.3.2. Homocoupling of **1b** in variable **1b**/Ni[(PPh$_3$)]$_2$Cl$_2$ molar ratio*

Following the general procedure for the homocoupling reaction of **1b** in variable 2-chloroethenyl/Ni[$(PPh_3)]_2Cl_2$ molar ratio of 0.3, 0.6 and 1.0, was always isolated (1*E*,3*E*)-1,4-di(2-pyridyl)-1,3-

butadiene (**6**) as the only stereoisomer in 19, 58 and 89% yield, respectively, as yellow solid, mp 115–117 °C.

*4.3.3. Homocoupling of (**2a**/**2b**, 1:1) in variable (**2a**/**2b**)/ Ni[(PPh$_3$)]$_2$Cl$_2$ molar ratio*

Following the general procedure for the homocoupling of **2** in variable 2′-chloroethenyl (**2a**/**2b**, 1:1)/Ni[(PPh$_3$)]$_2$Cl$_2$ molar ratio of 0.3, 0.6 and 1.0, was always isolated (1*E*,3*E*)-1,4-di-(3-pyridyl)-1,3-butadiene (**7**) as the only stereoisomer in 27, 52 and 87% yield, respectively, as yellow solid, mp 124–126 °C.

*4.3.3.1. Compound **7**.* IR (KBr): 1615 (C=C, conj.), 1580 and 1560 (C=C and C=N), 960 and 950 (CH=CH, *E*). δ_H 8.60 (d, 2H, *J* 2.0 Hz, H-2 and H-2′), 8.47 (dd, 2H, *J* 4.7 and 2.0 Hz, H-6 and H-6′), 7.60 (td, 2H, *J* 8.0 and 2.0 Hz, H-4 and H-4′), 7.26 (dd, 2H, *J* 8.0 and 4.7 Hz, H-5 and H-5′), H_A=7.01 and H_x=6.68 (AA′XX′, 4H, J_{Ax}=16.3 Hz, $J_{Ax'}$=−0.8 Hz, CH=CH). δ_C 148.3 (C-2), 148.1 (C-6), 132.2 (4C, Py–C=*C* and C-4), 130.1 (Py–*C*=C), 129.7 (C-3), 123.2 (C-5). MS, *m*/*z* 208 (M$^+$, 100), 207 (M$^+$−1, 93), 181 (42), 130 (54), 103 (19), 77 (31), 63 (26) and 51 (34). Anal. calcd for $C_{14}H_{12}N_2$: C, 80.70; H, 5.85; N, 13.44. Found: C, 80.39; H, 5.65; N, 13.15%.

*4.3.4. 1,4-Di(4′-pyridyl)-1,3-diacetylene (**9**)*

4.3.4.1. 4-Ethynylpyridine. To a solution of **3** (*E*/*Z* mixture, 1:1) (3.2 g, 0.023 mol) in dry THF (48 mL) at 0 °C, was added potassium *tert*-butoxide (6.4 g, 0.057 mol) in THF (64 mL) and stirred at room temperature for 30 min. The mixture was poured on ice-water and neutralised with a solution of ammonium chloride (20%) and extracted with dichloromethane. The organic layer was dried over magnesium sulfate, filtered and solvent removed and purified by silica gel column chromatography (ethyl acetate:hexane, 2:1), giving a white solid mp 62–63 °C.

IR (KBr): 3270, 2100 (C≡C). δ_H 8.61 (br d, *J* 6.80 Hz, 2H, H-2 and H-6), 7.40 (br d, *J* 6.8 Hz, 2H, H-3 and H-5), 3.40 (s, 1H). MS, *m*/*z* 103 (M$^+$, 100), 76 (52), 63 (7).

*4.3.4.2. 1,4-Di(4′-pyridyl)-1,3-diacetylene (**9**).* To a solution of cuprous chloride (37 mg) in pyridine (2.2 mL) and under oxygen atmosphere was added 4-ethynylpyridine (0.73 g, 3.7 mmol) with stirring at 40–45 °C for 1 h. Then, the pyridine was removed at reduced pressure and the residual solid was washed with a solution of ammonium chloride in water (50 mL, 10%) and extracted with dichloromethane. The organic layer was newly washed with a saturated aqueous solution of ammonium chloride, dried over magnesium sulfate, filtered and the solvent removed at reduced pressure giving 1,4-di-(4′-pyridyl)-1,3-diacetylene (**9**) as yellow solid, which was crystallised from ethanol/water to give a pale yellow solid mp 199–201 °C, (0.69 g, 95%).

*4.3.4.3. Compound **9**.* IR (KBr): 1590 and 1538 (C=C and C=N). δ_H 7.39 (d, *J* 6.08 Hz, 4H, two H-3 and two H-5), 8.63 (d, *J* 6.08 Hz, 4H, two H-2 and two H-6). MS, *m*/*z* 204 (M$^+$, 100), 177 (9), 151 (11), 102 (19) and 78 (10).

*4.3.5. (1Z,3Z)-1,4-Di(4′pyridyl)-1,3-butadiene (**8**) by partial hydrogenation*

In a hydrogenator apparatus were introduced the diacetylene (**9**) (0.19 g, 0.95 mmol) and the deactivated palladium on barium sulfate (0.048 mg, 10% Pd). The deactivated palladium catalyst on barium sulfate was obtained by treatment with an aqueous solution of Pb(OAc)$_2$ (0.1 mL, 8%) at 80 °C stirring for 5 min and with a solution of quinoline (0.1 mL) in toluene (5 mL). Hydrogen was introduced at the atmospheric pressure and room temperature. The mixture was stirred for 4 h and then, the solvent was removed at reduced pressure giving a residual solid that was extracted with methanol and purified by silica gel column chromatography (ethyl acetate/hexane, 2:1). (1Z,3Z)-1,4-Di(4′-pyridyl)-1,3-butadiene as colourless solid mp 88–90 °C (0.188 g, 96%).

*4.3.5.1. Compound **8**.* IR (KBr), 1590 (C=C), 1580 and 1550 (C=C and C=N), 700 (=C–H, *Z* isomer). δ_H 6.51 (AA′XX′ system, *J* 7.70 Hz, 2H, H-2′ and H-3′), 6.71 (AA′XX′ system, *J* 7.70 Hz, 2H, H-1′ and H-4′), 7.20 (d, *J* 5.00 Hz, 4H, H-3 and H-5), 8.58 (d, *J* 5.00 Hz, 4H, H-2 and H-6). MS, *m*/*z* 208 (34), 207 (M$^+$−1, 100), 130 (24), 104 (3), 77 (13). Anal. calcd for $C_{14}H_{12}N_2$: C, 80.70; H, 5.85; N, 13.44. Found: C, 80.54; H, 5.68; N, 13.33%.

*4.3.6. Homocoupling of (E)-2-(2′-chloroethenyl)quinoline (**4a**)*

Following the general procedure for the homocoupling of **4a** in **4a**/Ni stoichiometric molar ratio catalyst was separated (1*E*,3*E*)-1,4-di-(2-quinolyl)-1,3-butadiene (**10**) as the only stereoisomer in 85% yield, as yellow solid, mp 197–198 °C.

*4.3.6.1. Compound **10**.* IR (KBr): 1610 (C=C, conj.), 1595, 1540 (C=C and C=N), 950 (CH=CH, *E*), 810, 780, 750 and 740. δ_H 8.15 (d, 2H, *J* 7.72 Hz, H-8), 8.08 (d, 2H, *J* 7.65 Hz, H-5), 7.79 (d, 2H, *J* 7.78 Hz, H-4), 7.71 (m, 2H, H-7), 7.65 (d, 2H, *J* 7.78 Hz, H-3), 7.51 (m,2H, H-6), 7.08–7.32 (m, 4H). MS, *m*/*z* 308 (M$^+$, 48), 180 (100), 128 (43), 73 (52), 69 (85) and 57 (69). Anal. calcd for $C_{22}H_{16}N_2$: C, 85.68; H, 5.23; N, 9.08. Found: C, 85.42; H, 5.09; N, 8.78%.

*4.3.7. Homocoupling of (Z)-2-(2′-chloroethenyl)-quinoline (**4b**)*

Following the general procedure for the homocoupling of **4b**/Ni in stoichiometric molar ratio catalyst of 1.0 was separated (1*E*,3*E*)-1,4-di(2-quinolyl)-1,3-butadiene (**10**) as the only stereoisomer in 84% yield, as a yellow solid, mp 197–198 °C.

*4.3.8. Homocoupling of (E)- and (Z)-4-(2′-chloroethenyl)-quinoline (**5a** and **5b**)*

Following the general procedure for the homocoupling of **5a** (or **5b**), in stoichiometric molar ratio catalyst, giving a complex mixture. By silica gel column chromatography (hexane/ethyl acetate, 2:1) was isolated **5a** (or **5a**/**5b**) as the main component, but the homocoupling product was never detected.

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