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Alternative approaches to (*Z*)-1,2-bis(2-bromopyridin-3-yl)ethenes, key intermediates in the synthesis of the 1,10-phenanthroline core

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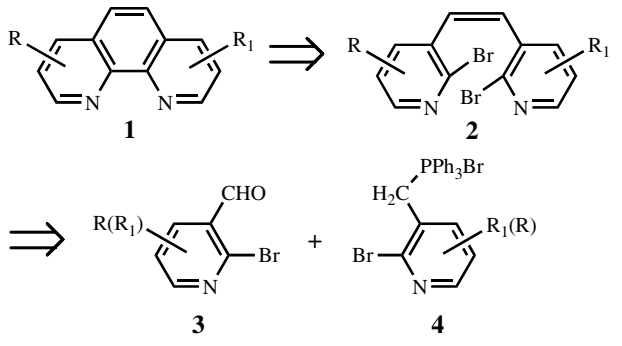
Abstract

A study on the synthesis of (*Z*)-1,2-bis(2-bromopyridin-3-yl)ethenes, key intermediates in the preparation of 1,10-phenanthrolines, based on selective Sonogashira and Suzuki–Miyaura cross-coupling reactions has been carried out.

Keywords: (*Z*)-Alkenes; Alkynes; Nitrogen heterocycles; Sonogashira reaction; Suzuki–Miyaura reaction; Palladium catalysts

We have recently reported a new protocol for the synthesis of substituted 1,10-phenanthrolines **1**, which serve as essentially universal ligands for metals,[1] by the de novo construction of the phenanthroline core (Scheme 1).[2] The approach is hinged upon the Ullmann intramolecular coupling of *cis*-1,2-bis(2-bromopyridin-3-yl)ethenes **2** that are in turn obtained by Wittig reaction of 2-bromonicotinaldehydes **3** with phosphonium salts **4** prepared from 2-bromo-3-(bromomethyl)pyridines.



Scheme 1.

Since the crucial point of this approach is the obtainment of **2**, we decided to explore alternative routes to the Wittig reaction that affords **2** in high yields, but in several cases fails to give good cis/trans stereoselectivity. Moreover, the phosphonium salts **4** are not easily available. Besides the Wittig and related reactions,[3] the main routes to the preparation of (*Z*)-alkenes are the cis-hydrogenation of alkynes[4] and the metal-catalyzed cross-coupling reactions of stereodefined substituted alkenes.[5] Based on this background, we herein report the results obtained in the synthesis of **2** tackling the last two approaches by selective Sonogashira and Suzuki–Miyaura cross-coupling reactions.

In order to prepare **2** via semihydrogenation of alkynes, a valuable method to obtain dipyridylethynes was required. Among the several approaches to obtain internal alkynes[6] we devoted our attention to Sonogashira palladium-catalyzed cross-coupling reaction,[7] taking into account that the reactivity of halogens toward coupling reactions is known to be I > Br ≫ Cl and that the positions *ortho* or *para* to the nitrogen of pyridine are usually reactive enough with chlorine to give acceptable yields of coupled products,

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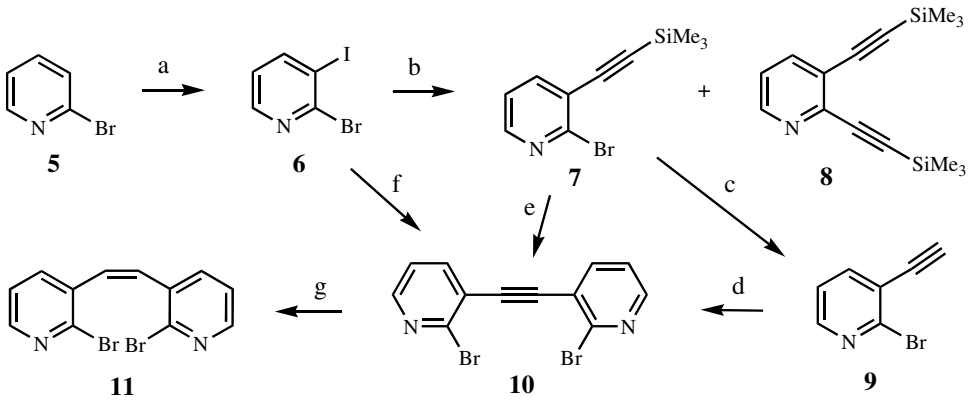


Scheme 2. Reagents and conditions: (a) LDA, THF, −95 °C, then I_2–THF, 82%; (b) $Pd(PPh_3)_2Cl_2$, TMS–acetylene, CuI, Et_3N, 1.5 h, 85%; (c) KOH, MeOH, 1.5 h, 83%; (d) **6**, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, rt, 2.5 h, 46%; (e) **6**, $Pd(PPh_3)_2Cl_2$, CuI, DBU, H_2O, benzene, 7 h, 70%; (f) $Pd(PPh_3)_2Cl_2$, CuI, DBU, H_2O, benzene, 7 h, 65%; (g) H_2 (4 atm), 5% Pd on $BaSO_4$, benzene, 24 h, 51%.

whereas meta positions require bromine, iodine, or triflates for sufficient reactivity.[8]

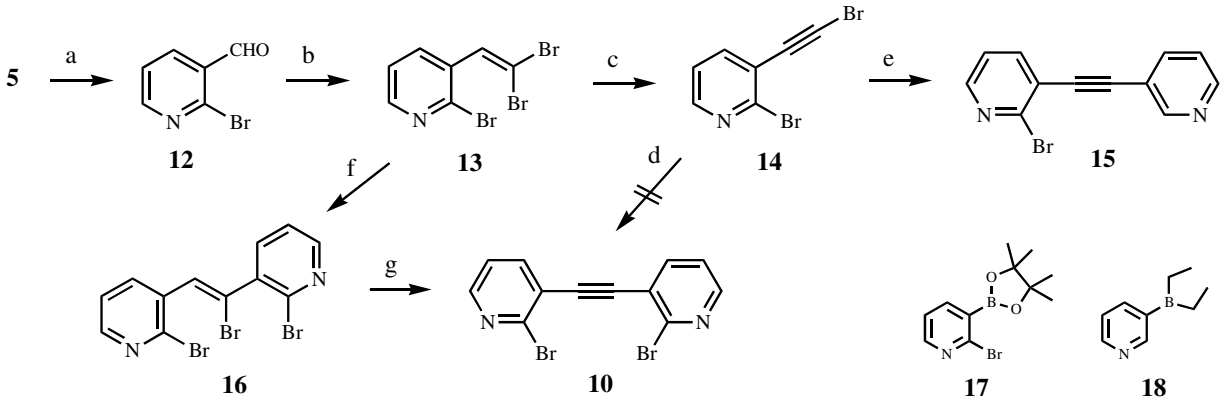
On this basis we examined the Sonogashira reaction of 2-bromo-3-iodopyridine **6**[9] with an excess of TMS–acetylene under Sogonashira conditions (Scheme 2). The reaction [$Pd(PPh_3)_2Cl_2$, CuI, Et_3N, 25 °C] after 18 h afforded only the diacetylene adduct **8**[10] in 65% yield, but when the reaction was stopped after 1.5 h the desired monoacetylene product **7** was isolated in 85% yield. After TMS deprotection with methanolic KOH (MeOH, 1.5 h, 83%), the resulting 2-bromo-3-ethynylpyridine **9** was coupled in the usual way (2.5 h) with **6** to give dipyridylethyne **10** in 46% yield. In order to avoid the silane deprotection step, the direct conversion of **7** to **10** was then examined. Treatment of **7** with **6** under modified Sonogashira conditions[11] [$Pd(PPh_3)_2Cl_2$, CuI, DBU–H_2O, benzene, rt, 7 h] afforded **10** in 70% yield. This satisfactory result encouraged us to carry out two sequential cross-coupling reactions starting from **6** in one-pot. Thus, the treatment of **6** with TMS–acetylene in the presence of DBU [$Pd(PPh_3)_2Cl_2$, CuI, DBU–H_2O, benzene, rt, 7 h] afforded **10** in 65% yield.[12]

The semihydrogenation of **10** was initially pursued using Lindlar's catalyst at atmospheric pressure, but although a variety of conditions (substrate/catalyst = 1/0.1 to 1/1; MeOH or benzene; 25–50 °C) were examined, no reaction was observed. The hydrogenation was then performed using 5% palladium on Ba_2SO_4 at atmospheric pressure. With MeOH as the solvent complete hydrogenation to 1,2-bis(2-bromopyridin-3-yl)ethane occurred after 3.5 h, and without it was possible to detect the formation of the intermediate semihydrogenation alkene **11**. On the other hand, the formation of **11** took place using benzene as the solvent, though the reaction was very slow and a large amount of the catalyst was required. Therefore, the reaction was performed in a Parr apparatus under pressure. The best conditions to obtain **11** were found by carrying out the hydrogenation in benzene for 24 h at 4 atm and using a w/w ratio of substrate/catalyst = 1/2 (51% yield).

We next went on to carry out the preparation of **10** following a different coupling reaction that considers the cross-coupling of a 1-haloalkyne with a pyridyl metal reagent. Among the possible 3-metalated 2-bromopyridines we decided to exploit organoboron derivatives because boronated pyridines have been profitably used for Suzuki–Miyaura cross-coupling reactions.[13] Moreover, 2-bromopyridin-3-yl-boronic acid or esters are now easily available via halogen–metal exchange or directed *ortho*-metalation.[14]

The first step in this direction was the preparation of 2-bromo-3-(2-bromoethynyl)pyridine **14** by dehydrobromination of 1,1-dibromoalkene **13** (*t*-BuOK, THF, 0 °C to rt, 3 h, 95%) that was in turn obtained from 2-bromonicotinaldehyde **12**[15] according to Corey and Fuchs procedure[16] (CBr_4, PPh_3, CH_2Cl_2, 0 °C to rt, 1 h, 85%) (Scheme 3). With 1-bromoalkyne **14** in hand its coupling with pyridylborate ester **17** was examined under a variety of palladium-catalyzed cross-coupling conditions. Initially, carrying out the coupling of **14** with **17** [$Pd(PPh_3)_4$, KOH, Bu_4NBr, THF, reflux, 6 h], the disappearance of the starting material was observed, but no dipyridylalkyne derivative **10** was detected. Disappointing results were also obtained by changing the base and the solvent [$Pd(PPh_3)_4$, K_2CO_3, THF–H_2O (or 1,4-dioxane–H_2O), reflux, up to 72 h]. In order to determine if the results were imputable to bromoalkyne **14** or to **17**, the cross-coupling of **14** with 3-(diethylboryl)pyridine **18** was inspected.[17] Under the usual conditions the reaction failed to give alkyne **15** that on the contrary was obtained in 17% yield when Cs_2CO_3 was used as the base [$Pd(PPh_3)_4$, Cs_2CO_3, 1,4-dioxane–H_2O, 65 °C, 72 h]. Similar results (20% yield) were obtained when catalytic Bu_4NBr was employed.

These disappointing results prompted us to examine an alternative procedure that starting from **13** inverts the dehydrobromination-coupling steps (Scheme 3). Thus, **13** was cross-coupled with **17** in the presence of Pd_2dba_3 and TFP[18] to give the expected monoarylated compound **16** in 90% yield[19] and then dehydrobrominated with DBU[20]

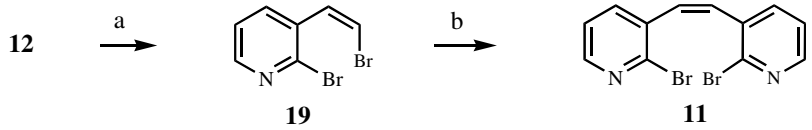


Scheme 3. Reagents and conditions: (a) LDA, THF, −78 °C, 3 h then Me_2NCHO, 1 h, 80–85%; (b) CBr_4, PPh_3, CH_2Cl_2, 0 °C to rt, 85%; (c) *t*-BuOK, THF, 0 °C to rt, 3 h, 95%; (d) **17**, $Pd(PPh_3)_4$, KOH, Bu_4NBr, THF, reflux, 6 h or 17, $Pd(PPh_3)_4$, K_2CO_3, H_2O, THF (or 1,4-dioxane), reflux, 72 h; (e) **18**, $Pd(PPh_3)_4$, Cs_2CO_3, H_2O, THF, 65 °C, 6 h, 21%; (f) Pd_2dba_3 (2.5%), TFP (15%), 1,4-dioxane, Cs_2CO_3 (2.0 equiv), H_2O, 65 °C, 4 h, 90%; (g) DBU (2.0 equiv), THF–DMSO, rt, 1 h, 95%.

[DBU (2.0 equiv), THF–DMSO, rt, 1 h] to provide the corresponding ethynyl derivative **10** in >95% yield (86% yield from **15**).

Next, the possibility to obtain **11** by the cross-coupling reaction of stereodefined 1-haloalkenes was examined by Suzuki–Miyaura cross-coupling reactions (Scheme 4). Thus, (*Z*)-1-bromoalkene **19**, prepared in 72% yield by Wittig reaction of aldehyde **12** with the phosphonium salt $Br^{-+}PPh_3CH_2Br$,[21] was coupled with **17** under a variety of conditions (Table 1). Partial conversion of the starting material was generally observed even in a longer reaction period. On the other hand, the reduction of the yield was detected by extending the reaction time. The best yield of **11** (51%) was obtained by using *trans*-$PdCl_2(PPh_3)_2$ as the catalyst (Table 1, entry 6).

In conclusion, we have demonstrated that *cis*-1,2-bis(2-bromo-3-pyridyl)ethenes can be profitably prepared by Sonogashira and Suzuki–Miyaura cross-coupling reactions.[22] Both cross-coupling processes show high selectivity in the substitution of the halide leaving groups, because the palladium insertion occurs on the iodo-carbon bond in the 3-position of the pyridine ring (Sonogashira) and



Scheme 4. Reagents and conditions: (a) $Br^{-+}PPh_3CH_2Br$, *t*-BuOK (1 equiv), THF, −78 °C, 72%; (b) **17**, *trans*-$PdCl_2(PPh_3)_2$, Cs_2CO_3, toluene/H_2O, 90 °C, 60 h, 51%.

Table 1
Coupling of **19** with **17**

Entry	Reagent	Procedure[a]	Solvent	Temperature (°C)	Reaction time (h)	Conversion[b] (%)	Yield[c] (%)
1	$Pd(PPh_3)_4$, K_2CO_3	A	1,4-Dioxane	80	60	73	40
2	$Pd(PPh_3)_4$, K_2CO_3	A	1,4-Dioxane	80	100	84	36
3	$Pd(PPh_3)_4$, K_2CO_3	A	Toluene–EtOH	100	84	100	24
4	Pd_2dba_3/TFP, Na_2CO_3	B	1,4-Dioxane–H_2O	65	36	50	37
5	Pd(dppf), Cs_2CO_3	C	Toluene–H_2O	90	48	81	22
6	$PdCl_2(PPh_3)_2$, Cs_2CO_3	C	Toluene–H_2O	90	48	70	51
7	$Pd(OAc)_2$, Cs_2CO_3	D	DMF	25	5	100	17

[a] Procedure A: A mixture of **19** (1.0 mmol), **17** (1.05 mmol), and K_2CO_3 (3.0 mmol) in 1,4-dioxane (5 mL) or toluene–EtOH (7 mL + 0.7 mL) was degassed by bubbling nitrogen for few minutes; then, $Pd(PPh_3)_4$ (0.05 mmol) was added and the resulting mixture was heated at the proper temperature under nitrogen. Procedure B: A mixture of **19** (1.0 mmol), **17** (1.05 mmol), tris(2-furyl)phosphine (TFP, 0.15 mol), and Na_2CO_3 (2.0 mmol) in 1,4-dioxane–H_2O (5 mL + 2 mL) was degassed by bubbling nitrogen for few minutes; then, Pd_2dba_3 (0.05 mmol) was added and the resulting mixture was heated at 65 °C under nitrogen. Procedure C: A mixture of **19** (1.0 mmol), **17** (1.05 mmol) and Cs_2CO_3 (3.0 mmol) in toluene-H_2O (3 mL + 1 mL) was degassed by bubbling nitrogen for few minutes; then, Pd(dppf) (0.05 mmol) or *trans*-$PdCl_2(PPh_3)_2$ (0.05 mmol) was added and the resulting mixture was heated at 90 °C under nitrogen. Procedure D: A mixture of **19** (1.0 mmol), **17** (1.1 mmol), Cs_2CO_3 (2.0 mmol), and $Pd(OAc)_2$ (0.025 mmol) in DMF (1 mL) was stirred at rt for 5 h under nitrogen.

[b] Determined by ^1H NMR.

[c] Yield based on the converted starting material and flash chromatography (petroleum ether/EtOAc = 7:3).

on the bromo-carbon bond in the alkene moiety (Suzuki–Miyaura), notwithstanding the high electrophilicity of the bromo-carbon bond in the 2-position of the pyridine ring. Both protocols allow to obtain the key intermediate **10** from the same starting material **5** in similar overall yields (50–60%), but the first one requires less steps (2 vs 3) and moreover appears to be cheaper. Although the presented procedures have been developed to obtain **11**, the simplest exponent of alkenes of type **2**, they can be likely extended to more complex *cis*-1,2-dipyridylethene derivatives. In this case, the choice of the method is however dictated by either the availability of the starting points, namely the iodo- or formylpyridine derivative, or the symmetry of the target compound. In general, availability of starting material being equal, the Sonogashira protocol appears to be preferable if the dipyridylalkyne to be synthesized is symmetrically substituted, whereas the Suzuki–Miyaura protocol comes out if the target is a dipyridylalkyne substituted on only one heterocycle ring. Therefore, the methods are complementary and can be chosen according to the desired dipyridylalkyne. Further studies on this subject are currently in progress.

Acknowledgments

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12. *2-Bromo-3-(2-(2-bromopyridin-3-yl)ethynyl)pyridine* (**10**): A 25 mL round-bottom flask with teflon-coated magnetic stir bar was fitted with a rubber septum and flame-dried under vacuum. The flask was purged with dry argon, and charged with $PdCl_2(PPh_3)_2$ (16.8 mg, 6 mol %), CuI (15.2 mg, 10 mol %) and 2-bromo-3-iodopyridine (0.228 g, 0.80 mmol). Septum was parafilmed after solids were added. While stirring, dry benzene (4.0 mL, starting material is 0.20 M in dry benzene) sparged with dry argon was added by syringe. Argon-sparged DBU (718 μL, 6 equiv) was then added by syringe, followed by a purge of the reaction flask with argon. Ice-chilled trimethylsilylethynylene (57 μL, 0.50 equiv) was then added by syringe, followed immediately by distilled water (5.8 μL, 40 mol %). The reaction flask was covered with aluminum foil and left stirring at a high speed for 7 h, at the end of which the reaction mixture was partitioned in ethyl ether and distilled water (50 mL each). The organic layer was washed with saturated aqueous NaCl (1 × 75 mL), dried over $MgSO_4$, gravity-filtered and the solvent was removed in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 8:2 to 1:1) to give **10**: mp 195–197 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 8.40 (m, 2H), 7.92–7.84 (m, 2H), 7.36–7.28 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 149.3, 144.4, 141.2, 122.8, 122.2, 92.3.
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(300 MHz, $CDCl_3$): δ 8.34 (dd, 1 H, $J = 4.8$, 1.8 Hz), 7.79 (dd, 1H, $J = 7.8$, 1.8 Hz), 7.26 (dd, 1H, $J = 7.8$, 4.8 Hz), 3.52 (s, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 149.1, 144.5, 141.8, 122.5, 122.1, 84.7, 79.8. *2-Bromo-3-(2-bromoethynyl)pyridine* (**14**): mp 138 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 8.32 (dd, 1H, $J = 4.8$, 1.8 Hz), 7.75 (dd, 1H, $J = 7.8$, 1.8 Hz), 7.25 (dd, 1H, $J = 7.8$, 4.8 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 148.8, 144.4, 141.5, 123.1, 122.1, 71.6, 58.3. *2-Bromo-3-(2-(pyridin-3-yl)ethynyl)pyridine* (**15**): mp 54–56 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 8.82 (d, 1H, $J = 1.8$ Hz), 8.61 (dd, 1H, $J = 4.8$, 1.8 Hz), 8.35 (dd, 1H, $J = 4.8$, 1.8 Hz), 7.89 (td, 1H, $J = 7.8$, 1.8 Hz), 7.84 (dd, 1H, $J = 7.8$, 1.8 Hz), 7.41–7.25 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 152.0, 149.2, 149.0, 144.5, 140.9, 138.7, 123.2, 122.9, 122.2, 119.6, 92.8, 88.9. *(Z)-2-Bromo-3-(2-bromovinyl)pyridine* (**19**): low melting solid; ^1H NMR (300 MHz, $CDCl_3$): δ 8.25 (dd, 1H, $J = 4.8$, 1.8 Hz), 8.03 (dd, 1H, $J = 7.8$, 1.8 Hz), 7.24 (dd, 1H, $J = 7.8$, 4.8 Hz), 7.09 (d, 1H, $J = 7.8$ Hz), 6.63 (dd, 1H, $J = 7.8$ Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 149.2, 143.0, 138.5, 132.5, 130.2, 122.2, 111.2.