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**Full Paper**

# Novel and Simple Synthesis of Brominated 1,10-Phenanthrolines

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A novel, simple, and reasonably efficient synthesis of 3,8-dibromo-1,10-phenanthroline, 3,6-dibromo-1,10-phenanthroline, 3,5,8-tribromo-1,10-phenanthroline, and 3,5,6,8-tetrabromo-1,10-phenanthroline is presented herein. The crucial role of a new catalyst (sulfur dichloride – $SCl_2$) for the bromination of 1,10-phenanthroline is reported. The bromination of 1,10-phenanthroline monohydrate in the presence of $SCl_2$ and pyridine yielded the brominated compounds, previously only possible through the complicated multi-step and tedious Skraup synthesis method. The application of the bromination catalyst $SCl_2$ as a medium-strength Lewis acid is demonstrated for the first time, and the results are compared with the behaviours of known weak (sulfur chloride – $S_2Cl_2$) and strong (thionyl chloride – $SOCl_2$) bromination catalysts. A reaction mechanism was proposed.

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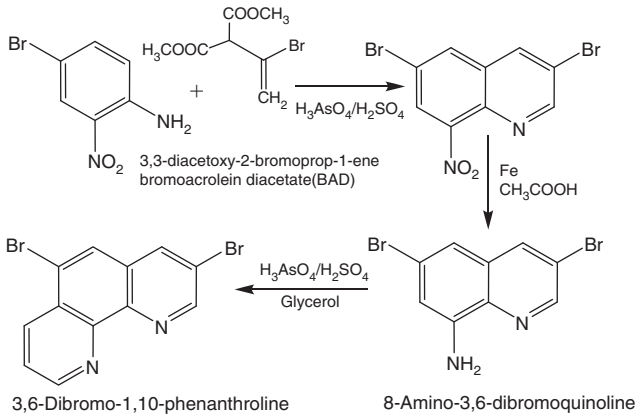
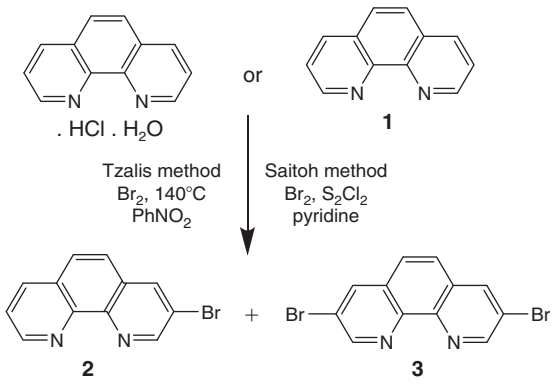
## Introduction

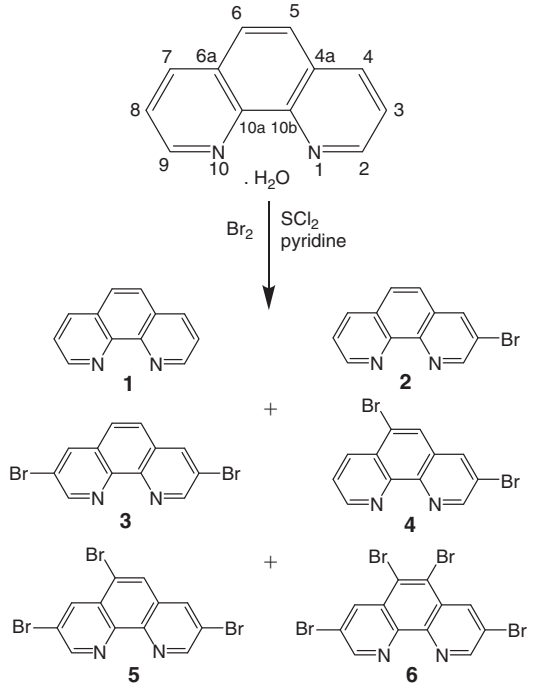
1,10-Phenanthroline (**1**) is an important ligand in the chemistry of both transition and lanthanide metals, as these complexes often show attractive chemical and physical properties.[1–4] Simple bromination of 1,10-phenanthroline is difficult and non-selective, which is typical of π-deficient aromatic compounds.[5] Generally, aromatic compounds functionalised with electron-withdrawing imine nitrogen (C=N–) are π-deficient in nature, and their electrophilic substitution with halogens ($Br_2$) usually requires harsh reaction conditions.[6] The bromo derivatives of **1** (such as 3- or 4-bromo; 3,5-, 3,6-, 3,8-, 4,7-, and 5,6-dibromo; 3,5,6-tribromo; and 3,5,6,8-tetrabromo) can be obtained through the Skraup synthesis route.[7,8] However, this multi-step procedure generates low yields, requires the use of carcinogens, such as 3,3-diacetoxy-2-bromoprop-1-ene (i.e. bromoacrolein diacetate), and produces toxic arsenic waste. An example of this reaction for the synthesis of 3,6-dibromo-1,10-phenanthroline is shown in Scheme 1. To our knowledge, this literature study[7] is the only report that describes the double Skraup synthesis of brominated 1,10-phenanthrolines; however, the products are only characterised by elemental analysis and melting point assessments. The preparation of π-conjugated polymers containing **1**, such as poly(1,10-phenanthroline-3,8-diyl) and its co-polymers,[9] requires the synthesis of 3,8-dibromo-1,10-phenanthroline as a monomer or co-monomer for coupling polymerisation processes. For this reason, a direct and relatively simple electrophilic bromination of **1** was investigated and developed. Tzalis and co-workers[10] reported that the bromination of 1,10-phenanthroline monohydrochloride monohydrate in nitrobenzene at 140°C gave 3-bromo-1,10-phenanthroline (**2**, 33 % yield) and 3,8-dibromo-1,10-phenanthroline (**3**, 17 % yield). They suggested that an HCl salt activates the phenanthroline ring for substitution. Saitoh et al.[11] reported that the bromination of **1** in 1-chlorobutane (reflux) in the presence of sulfur chloride ($S_2Cl_2$) and pyridine gave the desired product **3** in 34 % yield (Scheme 2). The Saitoh method gradually became a widely used synthetic procedure for the preparation of 3,8-dibromo-1,10-phenanthroline.[12–15] Although both methods provide facile routes to the preparation of **3**, little is known about the bromination mechanism. The authors generally used **3** as a monomer for the synthesis of conjugated polymers or as an important ligand in transition metal complexes, but no detailed studies on the bromination reaction have been conducted. The yields were given mostly for the crude material prior to purification, and the reaction mixtures were not analysed. Thomas[16]




**Scheme 1.** Skraup synthesis route of 3,6-dibromo-1,10-phenanthroline.




**Scheme 2.** Bromination of 1,10-phenanthroline monohydrochloride monohydrate (Tzalis method[10]) and 1,10-phenanthroline (**1**) (Saitoh method[11]), yielding 3-bromo-1,10-phenanthroline (**2**) and 3,8-dibromo-1, 10-phenanthroline (**3**).




**Scheme 3.** Bromination of 1,10-phenanthroline monohydrate to products **1**–**6** in the presence of sulfur dichloride ($SCl_2$) and the numbering scheme used for NMR signal assignment.

compared these methods and provided a critical and detailed discussion in which he suggested a bromination mechanism.In this study, the reaction mixtures were separated by flash chromatography, and all the reaction products were purified and characterised. Along with **3**, the major by-product **2** and starting material **1** were isolated from the reaction mixture. The yields of other minor by-products were negligible. As concluded, both the Tzalis and Saitoh methods are only convenient for the synthesis of bromo derivatives **2** and **3**.

Replacing sulfur chloride ($S_2Cl_2$) with sulfur dichloride ($SCl_2$) and using 1,10-phenanthroline monohydrate instead of **1** allowed for a much more efficient bromination of **1**. With these modifications, we were able to synthesise 3,8-dibromo-1, 10-phenanthroline (**3**), 3,6-dibromo-1,10-phenanthroline (**4**), 3,5, 8-tribromo-1,10-phenanthroline (**5**), and 3,5,6,8-tetrabromo-1, 10-phenanthroline (**6**) in reasonable yields (Scheme 3, Table 1). However, 3-bromo-1,10-phenanthroline (**2**) was only isolated as a minor product. In this paper, we report a novel electrophilic aromatic substitution of 1,10-phenanthroline monohydrate, yielding highly brominated derivatives of **1**. This represents a significant simplification of the Skraup synthesis method[7] for the formation of compounds **3**, **4**, **5**, and **6**.

## Results and Discussion

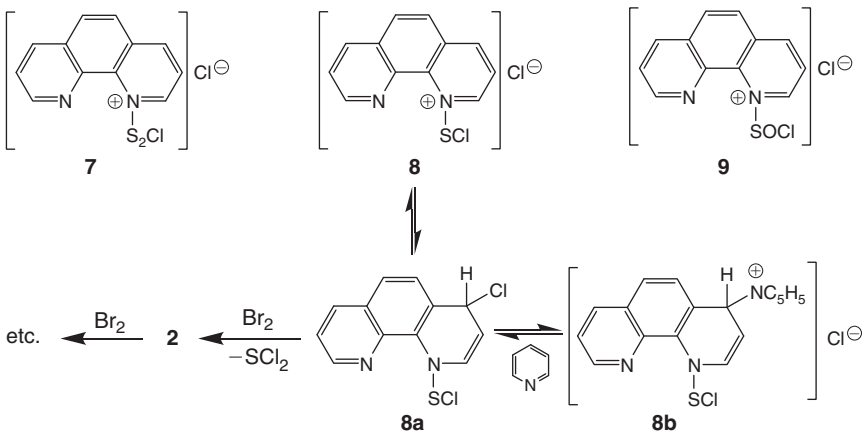
### *Bromination of 1,10-Phenanthroline*

For the synthesis of the tri- or tetra-bromo derivatives of 1,10-phenanthroline (**5** and **6**), we used excess amounts of sulfur dichloride (4×), pyridine (4×), and bromine (4.8×), as shown in Exp. **I** (Table 1). The reaction mixture was worked up with aqueous sodium hydroxide, passed through a short silica gel column, crystallised, and finally subjected to gradient column chromatography (CC), gradually eluting with chloroform and chloroform containing 5 % v/v acetone. The actual yields after CC for the major products **5** and **6** were 1.80 g (19 %) and 1.28 g (11 %), respectively. The minor products **1**–**4** were isolated in low yields. A greater excess amount of sulfur dichloride (8×, Exp. **II**, Table 1) resulted in decreased yields for derivatives **5** and **6**. In reactions where the dibromoderivatives of 1,10-phenanthroline (**3** and **4**) were the desired products, we decreased the excess amount of bromine (2.4×) used in the reaction mixture (Exp. **III**, Table 1). Likewise, the raw material was treated with aqueous sodium hydroxide, passed through a short silica gel column, crystallised, and finally subjected to double gradient CC, first eluting with chloroform then

**Table 1. Experimental data for the bromination of 1,10-phenanthroline monohydrate (4.50 g, 22.7 mmol) in 1-chlorobutane (200 mL) under reflux (105–110°C) over 12 h**

| Exp. # | $SCl_2$ [mmol] | $S_2Cl_2$ [mmol] | Pyridine [mmol] | $Br_2$ [mmol] | Yield[A] [g] | Yield of product isolated by column chromatography[B] [%] | | | | | | Yield[C] [%] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **6** | **5** | **4** | **3** | **2** | **1** | |
| **I** | 90 | – | 90 | 110 | 4.65 | 11 | 19 | 3 | 1 | 2 | 1 | 77 |
| **II** | 180 | – | 90 | 110 | 2.61 | 7 | 10 | 1 | 1 | 2 | 2 | 79 |
| **III** | 90 | – | 90 | 55 | 3.73 | – | 10 | 9 | 17 | 1 | 1 | 82 |
| **IV** | 5 | – | 40 | 70 | 3.05 | – | 4 | 20 | 3 | 2 | 1 | 75 |
| **V** | – | 74 | 73 | 72 | 7.59 | – | 2 | 2 | 14 | 40 | 32 | 70 |
| **VI**[D] | – | 74 | 73 | 72 | 7.14 | – | 3 | 3 | 13 | 63 | 6 | 76 |

[A]Crude yield of the mixture of products used for column chromatography.
[B]The yields shown in **I**–**V** correspond to those of starting material 1,10-phenanthroline monohydrate; yields of <1 % were neglected.
[C]Recovered yield after column chromatography.
[D]Experimental data shown in **VI** were taken from [16] for comparison.

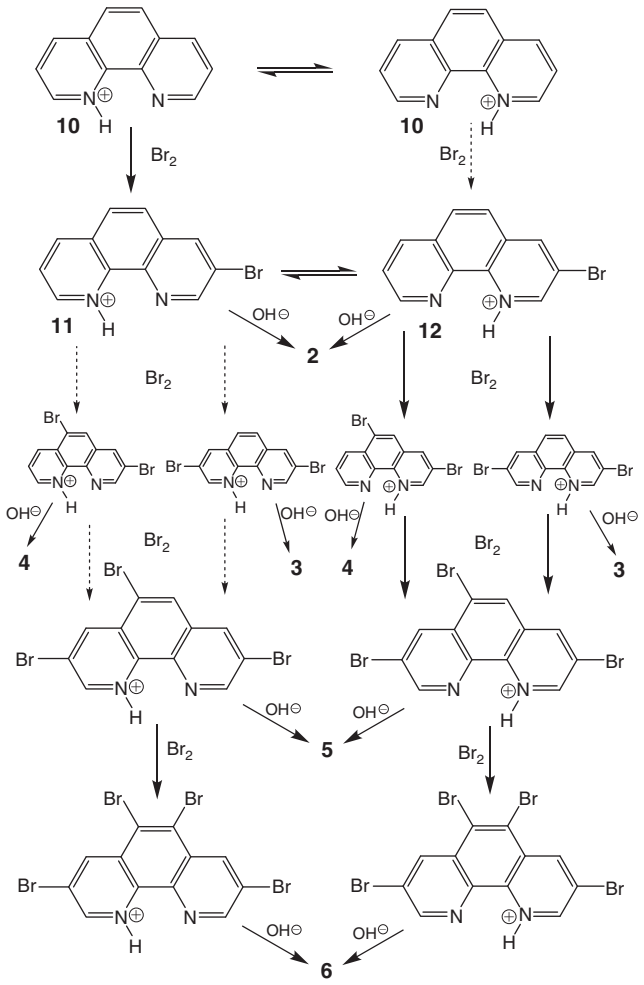



**Scheme 4.** Proposed 1,10-phenanthrolin-1-ium salt-type intermediates **7**, **8**, and **9** formed from reaction between **1** and $S_2Cl_2$, $SCl_2$, and $SOCl_2$, respectively. Compound **8** is in equilibrium with intermediates **8a** and **8b**, and its bromination leads to **2**.

with chloroform containing 5 % v/v acetone. Consequently, derivatives **4**, **2**, and **1** were first separated, while fractions containing **3** and **5** underwent further CC, eluting with chloroform then with chloroform containing 2 % v/v acetone. The difficult separation of **3** and **5** is expected. It has been reported[16] that these compounds cannot be purified by re-crystallisation because of the formation of a crystal mixture of **3** and **5** in a 3 : 1 molar ratio. They must be further purified by CC, which is challenging because of their similar $R_F$ values. Derivatives **3**, **4**, and **5** were obtained in yields of 1.32 g (17 %), 0.68 g (9 %), and 0.95 g (10 %), respectively. The minor products **1** and **2** were isolated in low yields (Table 1). Lower amounts of sulfur dichloride and pyridine in the reaction mixture (Exp. **IV**) promoted the formation of **4** as the major product. This compound was obtained in a yield of 1.56 g (20 %), whereas by-products **1**–**3** and **5** were obtained in low yields. To compare the results of the experiments using sulfur dichloride ($SCl_2$) with those using sulfur chloride ($S_2Cl_2$), Exp. **V** was performed, in which 1,10-phenanthroline monohydrate was reacted with sulfur chloride. Previously reported data[16] for the bromination of 1,10-phenanthroline using $S_2Cl_2$ are shown (Exp. **VI**, Table 1) for comparison. A short comment should be made about the designation of the isolated material **1** in experiments **I**–**V** (Table 1, Scheme 3). In this discussion, we describe this compound as 'product or by-product' to emphasise that 1,10-phenanthroline monohydrate is used as starting material. Experimental work proved that during bromination and isolation, the starting material loses a water molecule. As expected, in the case of experiment **VI**, isolated **1** is recovered as a starting material. Comparison between experiments **I**–**IV** and **V**–**VI** shows that the bromination of 1,10-phenanthroline monohydrate using sulfur dichloride is more efficient than bromination involving sulfur chloride. The actual yields of compounds **3**–**6** varied between 10 and 20 % after CC (calculated on the basis of the starting material **1** monohydrate). From this perspective, the procedure involving $SCl_2$ as the catalyst can be recommended for the syntheses of compounds **4** and **5**. For the synthesis of **3**, the aforementioned procedure[6–11] whereby $S_2Cl_2$ is used as the catalyst is more convenient, whereas the procedure using $SOCl_2$ as a strong Lewis acid[14] (see below) is the most convenient for the preparation of **6**. All synthesised compounds, **2**–**6**, were obtained with good purity (see $^1$H, $^{13}$C NMR, and Fourier transform infrared (FTIR) data in the Supplementary Material) and were fully characterised (yield, melting point, elemental analysis, $^1$H and $^{13}$C NMR, and FTIR). Heteronuclear (C, H) shift correlated 2D NMR spectra (HETCOR) enabled us to distinguish between the aromatic carbons substituted with hydrogen atoms and non-substituted carbon atoms (those that were either brominated or only connected to carbon atoms). This tool proved to be very helpful throughout this study.

### *Proposed Reaction Mechanism*

The development of the synthesis procedure was the main objective of this work, instead of mechanistic studies. Nevertheless, we propose a reaction mechanism based on the published approaches and previous knowledge. Garcia et al.[17] reported the bromination of pyridine and quinoline in the presence of $S_2Cl_2$ or $SOCl_2$. They proposed the formation of a protonated pyridinium salt-type reaction intermediate, which exists as an equilibrium mixture of the 1,4-dihydropyridine derivative and the pyridine addition product. Similarly, 1,10-phenanthrolin-1-ium salt-type intermediates **7**, **8**, or **9** may be expected when **1** reacts with sulfur chloride, sulfur dichloride, or thionyl chloride, respectively (Scheme 4). For compound **8**, we propose that an equilibrium between 1,4-dihydrophenanthroline (**8a**) and its addition product with pyridine (**8b**) exists. In our experiments (Table 1), it was established that $SCl_2$ must be added before the addition of pyridine (see the Experimental section) to avoid reduction in the yield and efficiency of the bromination reaction. These results support the importance of the **8a** ↔ **8b** equilibrium mentioned in Scheme 4 and the literature.[17] Thomas[16] used molecular modelling with the RHF-STO-3G method, as well as some synthetic approaches to explain the bromination of 1,10-phenanthroline to produce **2** and **3**. Calculations suggested that in singly protonated 1,10-phenanthrolin-1-ium (**10**), the electron density is concentrated on the non-protonated ring; thus, bromination to 8-bromo-1,10-phenanthrolin-1-ium (**11**) is more likely than the formation of 3-bromo-1,10-phenanthrolin-1-ium (**12**). Electrophilic aromatic substitutions are directed towards regions of high electron density in an aromatic substrate. Synthetic investigation of the bromination of 1*N*-methyl-1,10-phenanthroline supported the calculated results. The higher calculated stability of **11** compared with that of **12** and fast proton shuttling between *N*1 and *N*10 were also considered in the reported




**Scheme 5.** General mechanism for 1,10-phenanthroline bromination,[16] resulting in products **2**–**6**, considering the following: (i) the bromination is much more probable on the non-protonated ring (solid arrows) than on the protonated ring (dashed arrows); and (ii) proton shuttling between *N*1 and *N*10.

mechanism. In spite of the fact that such a mechanism does not explain the rate of bromination or the distribution of products, we believed that it is a reasonable explanation for the bromination reaction in the presence of $SCl_2$ yielding bromo derivatives **2**–**6**.

The reaction mechanism shown in Scheme 5 assumes the formation of a 1,10-phenanthrolin-1-ium salt-type intermediate in the first step and proton shuttling between *N*1 and *N*10 in the second step. Both literature approaches[16,17] are complementary and served as a draft of the proposed mechanism shown in Scheme 5.

## Conclusion

We achieved the bromination of 1,10-phenanthroline monohydrate in the presence of $SCl_2$ yielding products **3**–**6**, depending on the reaction conditions (Table 1). The results were compared with those of bromination reactions in the presence of $S_2Cl_2$. Compound **3** is obtained through bromination in the presence of $SCl_2$ or $S_2Cl_2$ (Table 1), whereas the preparation of the highly brominated materials **4**–**6** are only possible in the presence of $SCl_2$. The bromination of 1,10-phenanthroline in the presence of $S_2Cl_2$ led to products **2** and **3** only. On the other hand, the monobrominated product **2** can be obtained from bromination in the presence of $S_2Cl_2$. These results suggest that the formation of a 1,10-phenanthrolin-1-ium salt-type intermediate (**10**) is important for efficient bromination. It seems that $SCl_2$ is a stronger Lewis acid than $S_2Cl_2$ (cf. the structures of **7** and **8** in Scheme 4). Perhaps the equilibrium reaction $2SCl_2 \leftrightarrow S_2Cl_2 + Cl_2$ is responsible for the higher activity of sulfur dichloride compared with that of sulfur chloride. The strongest Lewis acid is likely $SOCl_2$, which promotes the formation of the salt-type intermediate **9** in the first step and affords the fully brominated compound **6** as the only product.[18] In conclusion, the bromination efficiencies of the selected catalysts (Lewis acids) may be ranked as follows: $S_2Cl_2 < SCl_2 < SOCl_2$. Sulfur chloride ($S_2Cl_2$) is convenient for the preparation of compounds **2** and **3**, sulfur dichloride ($SCl_2$) is useful for the preparation of compounds **3**–**6**, and thionyl chloride ($SOCl_2$) may be used for the preparation of compound **6** only. The identification and purities of all materials were determined by $^1H$ and $^{13}C$ NMR and FTIR (see Supplementary Material). These spectral data conveniently complement the lack of such information in the literature. Brominated 1,10-phenanthrolines can serve as functional ligands for both transition and lanthanide metals, as monomer units for polymers or macromolecular networks, and/or as compounds in organic syntheses.

## Experimental

### *General*

The starting material 1,10-phenanthroline monohydrate (mp 102–103°C) was purchased from TCI. The 1,10-phenanthroline (mp 116–117°C) and other chemicals were purchased from Sigma–Aldrich or LachNer (Czech Republic), and were used directly without purification. Silica gel 60 (0.063–0.200 mm, Merck) was used for column chromatography (column diameter: 3–4 cm; column length: 60 cm). TLC was performed on Silica gel 60 $F_{254}$ aluminium sheets (Merck), and the $R_F$ values have the usual meaning (i.e. $R_F$ = distance travelled by substance/distance travelled by solvent front). $^1H$ and $^{13}C$ NMR spectra were measured in $CDCl_3$ on an upgraded Bruker Advance DPX-300 spectrometer at 300.13 ($^1H$) and 75.45 ($^{13}C$) MHz using hexamethyldisiloxane as internal standard. Heteronuclear (C, H) shift correlated 2D spectra (HETCOR) were measured in $CDCl_3$ using the same equipment. FTIR spectra were measured on a Perkin–Elmer Paragon 1000 PC Fourier transform infrared spectrometer by means of diamond attenuated total reflectance (ATR).

### *Procedure Involving Sulfur Dichloride ($SCl_2$, Exp. **I**–**IV**, Table 1)*

1,10-Phenanthroline monohydrate (4.50 g, 22.7 mmol) was dissolved in 1-chlorobutane (160 mL) under argon. Then, sulfur dichloride (Table 1) and pyridine (Table 1) were added over 10 min. Finally, a solution of bromine (Table 1) in 1-chlorobutane (40 mL) was added dropwise, and the reaction mixture was refluxed (110°C) for 12 h. After cooling, the reaction flask was placed in a refrigerator overnight resulting in the precipitation of a yellow solid. An aqueous solution of 10 % NaOH (200 mL) and chloroform (200 mL) were added to the solid, and the mixture was stirred vigorously. The organic phase was separated and passed through a short silica gel column (~10–15 cm) before drying over $Na_2SO_4$.

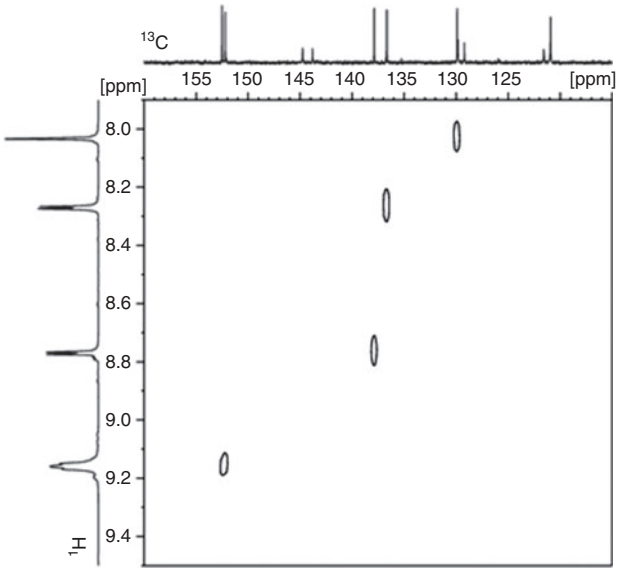



**Fig. 1.** 2D HETCOR $^{13}C$ spectrum versus $^{1}H$ NMR spectrum of 3,5,8-tribromo-1,10-phenanthroline **5**.

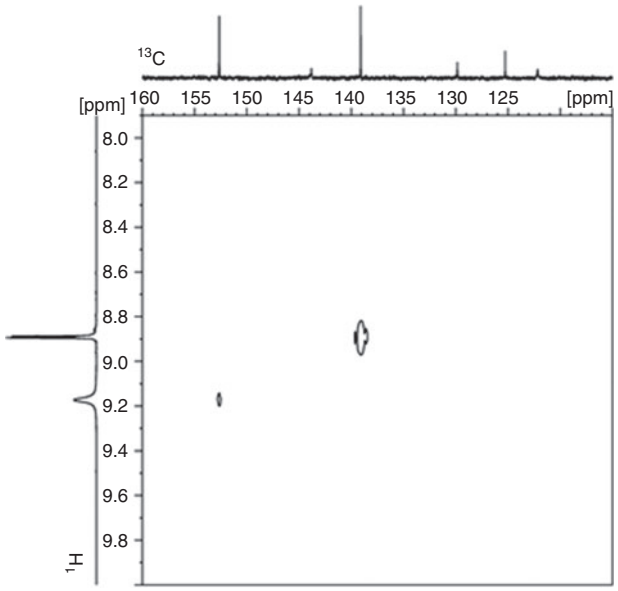



**Fig. 2.** 2D HETCOR $^{13}C$ spectrum versus $^{1}H$ NMR spectrum of 3,5,6,8-tetrabromo-1,10-phenanthroline **6**.

### *3,5,8-Tribromo-1,10-phenanthroline **5** and 3,5,6,8-Tetrabromo-1,10-phenanthroline **6***

Sulfur dichloride (9.26 g, 90 mmol), pyridine (7.11 g, 90 mmol), and bromine (17.6 g, 110 mmol) were mixed accordingly (Exp. **I**, Table 1). $Na_2SO_4$ was removed by filtration, the solvent was evaporated, and a solid was crystallised (charcoal) from 1,2-dichloroethane/chloroform (4 : 1) to afford a yellow crystalline solid (yield: 4.65 g). The crude material was subjected to gradient chromatography eluting with $CHCl_3$ then $CHCl_3$ containing 5 % v/v acetone. The corresponding fractions were combined and characterised as compounds **5** and **6** (major products) and compounds **1**–**4** (minor products) (Table 1, Exp. **I**) as follows:

#### *3,5,8-Tribromo-1,10-phenanthroline **5***

Yield: 1.80 g (19 %), mp 290–291°C (lit. 290°C[16]). $\nu_{max}$(ATR)/cm$^{-1}$ 3039, 2920, 1581, 1480, 1412, 1272, 1204, 1104, 1034, 937, 914, 891, 805, 732, 622, 560, 530. $\delta_H$ (300.1 MHz, $CDCl_3$) 9.13–9.18 (broad peak, 2H, H2+H9), 8.77 (d, *J* 2.1, 1H, H4), 8.27 (d, *J* 2.1, 1H, H7), 8.03 (s, 1H, H6). $\delta_C$ (75 MHz, $CDCl_3$) 120.9 (C3+C8), 121.6 (C5), 129.2 (C4a), 129.8 (C6a), 129.9 (C6), 136.7 (C7), 137.9 (C4), 143.8 (C10a), 144.7 (C10b), 152.2 (C2), 152.5 (C9) all aromatic. Anal. Calc. for $C_{12}H_5N_2Br_3$ (416.9): C 34.57, H 1.21, N 6.72, Br 57.50. Found: C 34.71, H 1.12, N 6.66, Br 57.83. The HETCOR spectrum ($CDCl_3$) of **5** is shown in Fig. 1.

#### *3,5,6,8-Tetrabromo-1,10-phenanthroline **6***

Yield: 1.28 g (11 %), mp 354–355°C (lit. 356–357°C[7], lit. 355–356°C[18]). $\nu_{max}$(ATR)/cm$^{-1}$ 3022, 1577, 1472, 1405, 1266, 1103, 959, 915, 887, 825, 730, 595, 566, 537. $\delta_H$ (300.1 MHz, $CDCl_3$) 9.17 (s, 2H, H2+H9), 8.89 (d, *J* 2.4, 2H, H4+H7). $\delta_C$ (75 MHz, $CDCl_3$) 122.1 (C3+C8), 125.3 (C5+C6), 129.8 (C4a+C6a), 139.1 (C4+C7), 143.8 (C10a+C10b), 152.6 (C2+C9) all aromatic. Anal. Calc. for $C_{12}H_4N_2Br_4$ (495.8): C 29.07, H 0.81, N 5.65, Br 64.46. Found: C 29.14, H 0.73, N 5.64, Br 64.51.

The minor products **1**, **2**, **3**, and **4** were obtained in yields of 0.06 g (1 %), 0.12 g (2 %), 0.07 g (1 %), and 0.24 g (3 %), respectively. Their analyses and spectra are discussed below. The HETCOR spectrum ($CDCl_3$) of **6** is shown in Fig. 2.

### *3,6-Dibromo-1,10-phenanthroline **4***

Sulfur dichloride (0.51 g, 5 mmol), pyridine (3.16 g, 40 mmol), and bromine (11.2 g, 70 mmol) were mixed accordingly (Exp. **IV**, Table 1). $Na_2SO_4$ was removed by filtration, the solvent was evaporated, and the residue was dissolved in 1,1,2-trichloroethylene. The raw product was crystallised by addition of petrolether (yield: 3.05 g). The crude material was purified by gradient chromatography eluting with $CH_2Cl_2$ then $CH_2Cl_2$ containing 10 % v/v acetone. The corresponding fractions were combined and characterised as compound **4** (major product) and compounds **1**–**3** and **5** (minor products) (Table 1, Exp. **IV**):

#### *3,6-Dibromo-1,10-phenanthroline **4***

Yield: 1.56 g (20 %), mp 248–249°C (lit. 247–248°C[7]). $\nu_{max}$(ATR)/cm$^{-1}$ 3027, 1589, 1577, 1492, 1411, 1382, 1204, 1097, 1031, 911, 894, 799, 733, 554, 473. $\delta_H$ (300.1 MHz, $CDCl_3$) 9.19–9.15 (m, 2H, H2+H9), 8.60 (dd, *J* 8.1, 1.7, 1H, H4), 8.25 (d, *J* 2.4, 1H, H7), 7.99 (s, 1H, H5), 7.72 (dd, *J* 8.4, 4.5, 1H, H8). $\delta_C$ (75 MHz, $CDCl_3$) 120.6 (C3), 122.4 (C6), 124.1 (C8), 128.1 (C4a), 128.6 (C5), 129.8 (C6a), 136.1 (C7), 136.5 (C4), 144.1 (C10a), 146.6 (C10b), 151.4 (C2), 151.7 (C9) all aromatic. Anal. Calc. for $C_{12}H_6N_2Br_2$ (338.0): C 42.64, H 1.79, N 8.29, Br 47.28. Found: C 42.75, H 1.73, N 8.41, Br 47.51.

The minor products **1**, **2**, **3**, and **5** were obtained in yields of 0.04 g (1 %), 0.10 g (2 %), 0.22 g (3 %), and 0.37 g (4 %), respectively. Their analyses and spectra are discussed below (**1**–**3**) or above (**5**). The HETCOR spectrum ($CDCl_3$) of **4** is shown in Fig. 3.

### *3,8-Dibromo-1,10-phenanthroline **3***

Sulfur dichloride (9.26 g, 90 mmol), pyridine (7.11 g, 90 mmol), and bromine (8.80 g, 55 mmol) were mixed accordingly (Exp. **III**, Table 1). $Na_2SO_4$ was removed by filtration, the solvent was evaporated, and a solid crystallised (charcoal) from 1,1,2-trichloroethylene giving a yellow crystalline solid (yield: 3.73 g).

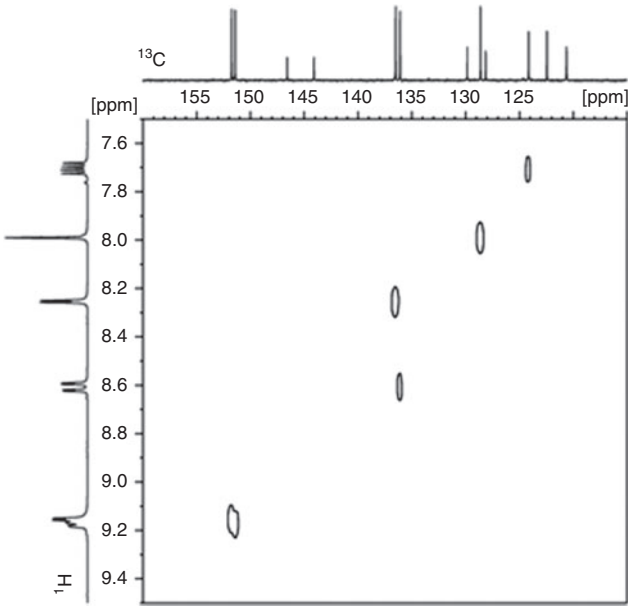



**Fig. 3.** 2D HETCOR $^{13}$C spectrum versus $^{1}$H NMR spectrum of 3,6-dibromo-1,10-phenanthroline **4**.

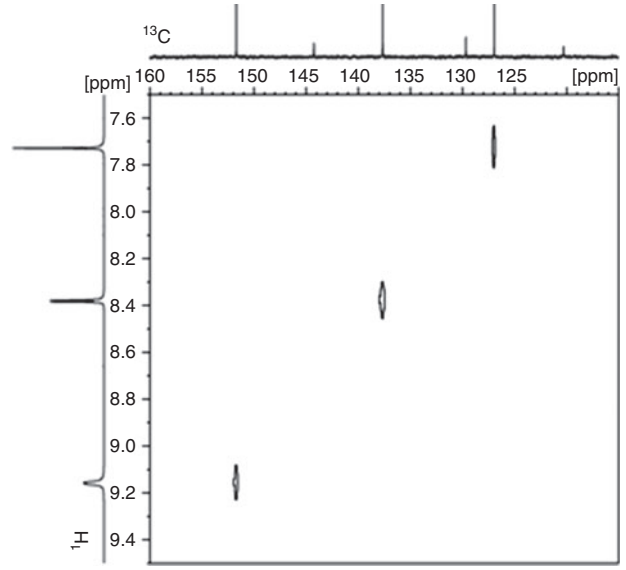



**Fig. 4.** 2D HETCOR $^{13}$C spectrum versus $^{1}$H NMR spectrum of 3,8-dibromo-1,10-phenanthroline **3**.

The raw material was chromatographed eluting with $CHCl_3$ containing 5 % v/v acetone and compounds **4**, **2**, and **1** were obtained. The fractions containing **3** and **5** were chromatographed further eluting with $CHCl_3$ then $CHCl_3$ containing 2 % v/v acetone to obtain purified **3** and **5** (Table 1, Exp. **III**) as follows:

### *3,8-Dibromo-1,10-phenanthroline **3***

Yield: 1.32 g (17 %), mp 279–280°C (lit. 221–222°C[7], lit. 270–273°C[10], lit. 270–272°C[14], lit. 284–286°C[15], lit. 270°C[16]). $\nu_{max}$(ATR)/cm$^{-1}$ 3025, 1585, 1477, 1412, 1374, 1207, 1101, 1034, 905, 891, 776, 720, 509. $\delta_H$ (300.1 MHz, $CDCl_3$) 9.14 (d, *J* 2.4, 2H, H2+H9), 8.36 (d, *J* 2.4, 2H, H4+H7), 7.70 (s, 2H, H5+H6). $\delta_C$ (75 MHz, $CDCl_3$) 120.2 (C3+C8), 126.9 (C5+C6), 129.6 (C4a+C6a), 137.6 (C4+C7), 144.1 (C10a+C10b), 151.6 (C2+C9) all aromatic. Anal. Calc. for $C_{12}H_6N_2Br_2$ (338.0): C 42.64, H 1.79, N 8.29, Br 47.28. Found: C 42.67, H 1.54, N 8.23, Br 47.07.

The side-products **1**, **2**, **4**, and **5** were obtained in yields of 0.03 g (1 %), 0.08 g (1 %), 0.68 g (9 %), and 0.95 g (10 %), respectively. Their analyses and spectra are discussed below (**1** and **2**) or above (**4** and **5**). The HETCOR spectrum ($CDCl_3$) of **3** is shown in Fig. 4.

### *Procedure Involving Sulfur Chloride ($S_2Cl_2$, Exp. **V**, Table 1)*

1,10-Phenanthroline monohydrate (4.50 g, 22.7 mmol) was dissolved in 1-chlorobutane (160 mL) under argon; and sulfur chloride (74 mmol), pyridine (73 mmol), and bromine (72 mmol) in 1-chlorobutane (40 mL) were added gradually. The reaction mixture was refluxed (110°C) for 12 h. After cooling, the reaction flask was placed in a refrigerator overnight, resulting in the precipitation of a yellow solid. An aqueous solution of 10 % NaOH (200 mL) and chloroform (200 mL) were added to the solid, and the mixture was stirred vigorously. The organic phase was separated and dried over $Na_2SO_4$. The chloroform was removed under vacuum, and the yellow solid was dried to a constant weight (yield: 7.59 g). The raw material was chromatographed in chloroform to yield the major products (**1**–**3**) and minor products (**4** and **5**).

### *3,8-Dibromo-1,10-phenanthroline **3***

Yield: 1.05 g (14 %), mp 279–280°C. The elemental analysis and spectral data were the same as those shown above, and confirmed the structure of **3**.

### *3-Bromo-1,10-phenanthroline **2***

Yield: 2.35 g (40 %), mp 168–170°C (lit. 169–170°C[7], lit. 164–167°C[10], lit. 165°C[16]). $\nu_{max}$(ATR)/cm$^{-1}$ 3018, 2940, 1577, 1493, 1415, 1374, 1208, 1095, 1025, 895, 865, 830, 725, 637, 508, 467. $\delta_H$ (300.1 MHz, $CDCl_3$) 9.18–9.15 (m, 2H, H2+H9), 8.35 (d, *J* 2.4, 1H, H4), 8.21 (dd, *J* 8.1, 1.8, 1H, H7), 7.79 (d, *J* 9.0, 1H, H5), 7.66 (d, *J* 8.7, 1H, H6), 7.63 (dd, *J* 8.1, 4.4, 1H, H8). $\delta_C$ (75 MHz, $CDCl_3$) 119.9 (C3), 123.4 (C8), 125.5 (C5), 128.0 (C6), 128.6 (C4a), 129.7 (C6a), 136.1 (C7), 137.5 (C4), 144.5 (C10a), 146.0 (C10b), 150.8 (C2), 151.2 (C9) all aromatic. Anal. Calc. for $C_{12}H_7N_2Br$ (259.1): C 55.63, H 2.72, N 10.81, Br 30.84. Found: C 55.82, H 2.54, N 10.87, Br 31.07.

### *1,10-Phenanthroline **1***

Yield: 1.32 g (32 %), mp 114–115°C (Aldrich material 114–117°C, lit. 103°C[16], lit. 116°C[19]). $\nu_{max}$(ATR)/cm$^{-1}$ 3374, 3026, 2933, 1587, 1558, 1501, 1418, 1343, 1215, 1136, 1090, 852, 733, 703, 618. $\delta_H$ (300.1 MHz, $CDCl_3$) 9.18 (dd, *J* 4.2,1.8, 2H, H2+H9), 8.23 (dd, *J* 8.1, 1.5, 2H, H4+H7), 7.77 (s, 2H, H5+H6), 7.62 (dd, *J* 7.8, 4.3, 2H, H3+H8). $\delta_C$ (75 MHz, $CDCl_3$) 123.1 (C3+C8), 126.6 (C5+C6), 128.7 (C4a+C6a), 136.0 (C4+C7), 146.3 (C10a+C10b), 150.4 (C2+C9) all aromatic. Anal. Calc. for $C_{12}H_8N_2$ (180.2): C 79.98, H 4.47, N 15.54. Found: C 80.08, H 4.32, N 15.74.

The minor products **4** and **5** were obtained in yields of 0.15 g (2 %) and 0.19 g (2 %), respectively. Their analyses were the same as those shown above.

## Supplementary Material

$^{1}$H and $^{13}$C NMR and FTIR spectra of samples **1**–**6** are available on the Journal's website.

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## References

[1] M. Pandrala, F. Li, L. Wallace, P. J. Steel, B. Moore II, J. Autschbach, J. G. Collins, F. R. Keene, *Aust. J. Chem.* **2013**, *66*, 1065. doi:10.1071/CH13264

[2] X. He, G. Yang, X. Sun, L. Xie, L. Tan, *Aust. J. Chem.* **2013**, *66*, 1406. doi:10.1071/CH13329

[3] D. Tzalis, Y. Tor, *Tetrahedron Lett.* **1995**, *36*, 6017. doi:10.1016/0040-4039(95)01190-S

[4] M. Karnahl, S. Krieck, H. Gorls, S. Tschierlei, M. Schmitt, J. Popp, D. Chartrand, G. S. Hanan, R. Goarke, J. G. Vos, S. Rau, *Eur. J. Inorg. Chem.* **2009**, 4962. doi:10.1002/EJIC.200900310

[5] V. Dénes, R. Chira, *J. Prakt. Chemie* **1978**, *320*, 172. doi:10.1002/PRAC.19783200124

[6] A. R. Katritzki, R. Taylor, in *Advances in Heterocyclic Chemistry* (Eds A. R. Katritzki, R. Taylor) **1990**, Vol. 47, Ch. 11, pp. 382–387 (Academic Press, Inc.: San Diego, California 92201).

[7] F. H. Case, *J. Org. Chem.* **1951**, *16*, 941. doi:10.1021/JO01146A018

[8] H. R. Snyder, H. E. Freier, *J. Am. Chem. Soc.* **1946**, *68*, 1320. doi:10.1021/JA01211A065

[9] T. Yamamoto, Y. Saitoh, K. Anzai, H. Fukumoto, T. Tasuda, Y. Fujiwara, B.-K. Choi, K. Kubota, T. Miyamae, *Macromolecules* **2003**, *36*, 6722. doi:10.1021/MA0302659

[10] D. Tzalis, Y. Tor, S. Failla, J. S. Siegel, *Tetrahedron Lett.* **1995**, *36*, 3489. doi:10.1016/0040-4039(95)00572-T

[11] Y. Saitoh, T. Koizumi, K. Osakada, T. Yamamoto, *Can. J. Chem.* **1997**, *75*, 1336. doi:10.1139/V97-160

[12] C. Dietrich-Buchecker, M. C. Jimenéz, J.-P. Sauvage, *Tetrahedron Lett.* **1999**, *40*, 3395. doi:10.1016/S0040-4039(99)00501-8

[13] S. J. P. Bousquet, D. W. Bruce, *J. Mater. Chem.* **2001**, *11*, 1769. doi:10.1039/B103150N

[14] N. S. Baek, H. K. Kim, Y. Lee, J. Kang, T. J. Kim, G. T. Hwang, B. H. Kim, *Thin Solid Films* **2002**, *417*, 111. doi:10.1016/S0040-6090(02)00585-0

[15] J. W. Ciszek, J. M. Tour, *Tetrahedron Lett.* **2004**, *45*, 2801. doi:10.1016/J.TETLET.2004.02.028

[16] C. W. Thomas, *Ruthenium–DNA Hybrid Materials for Supramolecular Synthesis and Investigations into Osmotic Effects in Ionomeric Polymer–Metal Composites*, UMI 3021196 **2001**, Ph.D. Thesis, University of California, San Diego.

[17] E. E. Garcia, C. V. Gresco, I. M. Hunsberger, *J. Am. Chem. Soc.* **1960**, *82*, 4430. doi:10.1021/JA01501A079

[18] G. Manolikakes, A. Gavryushin, P. Knochel, *J. Org. Chem.* **2008**, *73*, 1429. doi:10.1021/JO702219F

[19] K. Madeja, *J. Prakt. Chemie* **1962**, *17*, 97. doi:10.1002/PRAC.19620170113