Synthesis and Functionalisation of 5-Substituted Neocuproine Derivatives

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2,9-Dimethyl-1,10-phenanthroline (neocuproine, **1**) was functionalised selectively in the 5-position. Silylation of the methyl groups followed by bromination in the 5-position was carried out to give the bis(*tert*-butyldimethylsilyl)-substituted neocuproine **3** and 5-bromo-2,9-dimethyl-1,10-phenanthroline (**4**) after deprotection. Compounds **3** and **4** are versatile building blocks for the construction of 5-substituted neocuproines. Palladium-catalysed couplings (Suzuki, Sonogashira, Buchwald/Hartwig) can be utilized to connect different substituents to the 1,10-phenanthroline moiety (**5**–**7**). These substituents may carry additional functional groups that allow the further connection of the 5-substituted neocuproines to form other molecules.

Introduction

1,10-Phenanthroline and its derivatives, such as 2,9-dimethyl-1,10-phenanthroline (**1**, neocuproine), are important ligands for the complexation of metal ions.[1–3] Due to this property they play an important role in different areas of supramolecular chemistry, such as self-assembly and catalysis.[4–9] In combination with early transition metals, they usually form complexes reversibly, while in combination with heavy transition metals, such as ruthenium, kinetically stable complexes are mostly observed.[10]

If their complexing ability is to be exploited for the construction of larger supramolecular entities, the 1,10-phenanthroline system must be further substituted, preferentially on the opposite site of the binding region, i.e. in positions 5 and 6. While a number of 5-substituted 2,9-unsubstituted 1,10-phenanthrolines are known, there are remarkably few examples of 5-substituted neocuproines, and, for instance, 5-bromo-2,9-dimethyl-1,10-phenanthroline (**4**) has not yet been synthesised.[11]

There are two main problems when synthesising neocuproine derivatives: (i) many derivatives are poorly soluble, which hinders their synthesis and isolation, and (ii) the methyl groups in the 2- and 9-positions are reactive − they can be attacked by radicals and by bases, and they can also easily be oxidized.

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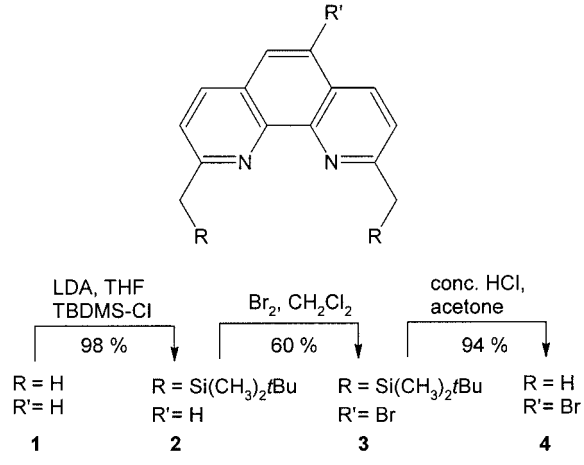
Results and Discussion

To avoid side reactions at the methyl groups of neocuproine (**1**), we substituted them with silyl groups. This has three effects: the solubility of all products is enhanced, the methyl groups are protected against many side reactions by steric hindrance, and the silyl groups can easily be removed under acidic conditions, thereby re-establishing the 2,9-dimethyl substitution.

Neocuproine (**1**) was first doubly deprotonated with LDA.[12] Reaction with *tert*-butylchlorodimethylsilane (TBDMS-Cl) resulted in the doubly silylated product **2**. In contrast to unsubstituted neocuproine (**1**), the bromination products of derivative **2** are much easier to purify.[13] The tailing effects, which are caused by strong interactions of the 1,10-phenanthroline nitrogen atoms with the silica or alumina used for chromatography, are minimised by the steric demand of the silyl protecting groups. Thus, upon reaction of **2** with bromine, the hydrogen atom in the 5-position is substituted in an addition–elimination mechanism at the



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5,6-double bond, and **3** can be isolated in useful yield. The regioselectivity (5-substitution) was determined by 2D NMR spectroscopy and verified by X-ray analysis (see Figure 1). As found with many 1,10-phenanthrolines, solvent included in the crystals was found spectroscopically and in elemental analyses of **3**. The general tendency of 1,10-phenanthrolines to include solvent molecules such as water or methanol can be seen from their X-ray structures.

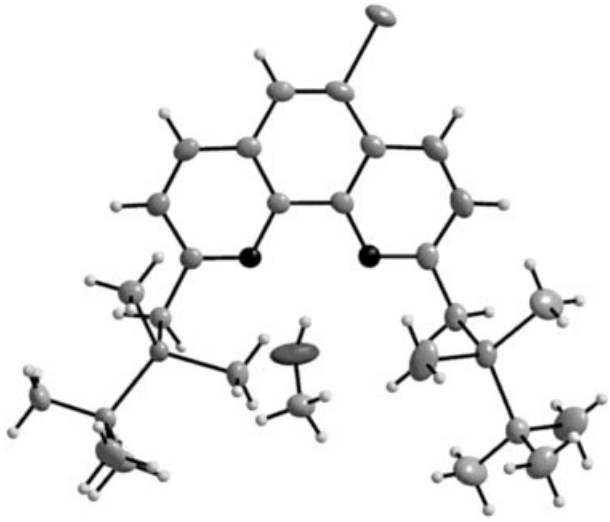


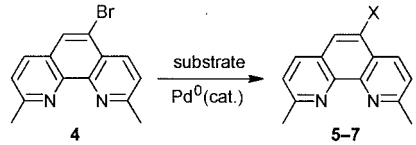
Figure 1. X-ray structure of 5-bromo-2,9-bis[(*tert*-butyldimethyl-silyl)methyl]-1,10-phenanthroline (**3**) ($C_{26}H_{39}BrN_2Si_2 \cdot CH_3OH$, recrystallised from methanol). The structure confirms the attachment of the bromo substituent in the 5-position and shows the steric demand of the silyl protecting group; the complexation tendency of the phenanthroline moiety for small, polar solvent molecules is also clearly visible.

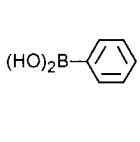
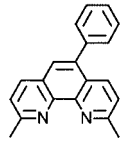
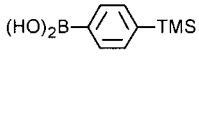
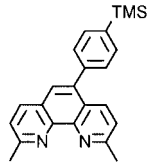
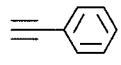
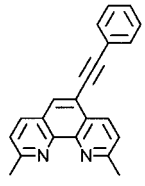
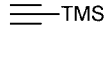
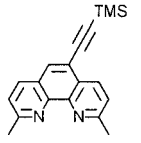
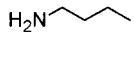
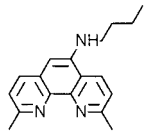
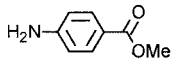
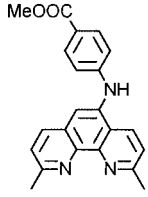
Deprotection of the silyl groups under acidic conditions gives access to the hitherto unknown[11] 5-bromo-1,10-dimethyl-1,10-phenanthroline (**4**) in 55% yield based on neocuproine (**1**).

The 5-bromo-substituted compound **4**, and compound **3**, are interesting intermediates for the extension of the 1,10-phenanthroline system because they should allow all kinds of palladium-catalysed cross-coupling reactions.[14,15] We tested three of these reactions: the Suzuki coupling,[16–18] the Sonogashira coupling[19–22] and the amination according to Buchwald et al.[23] and Hartwig.[24] In all cases we tested a standard coupling partner: phenylboronic acid, phenylacetylene and *n*-butylamine, respectively. In addition, we used coupling partners that carry other functional groups (a trimethylsilyl-substituted phenylboronic acid, a trimethylsilyl-substituted acetylene and an aniline carrying an additional ester group), which allow further substitution of the coupling products.

All except one coupling reaction with 5-bromoneocuproine (**4**) worked very well and gave six new 5-substituted 1,10-phenanthrolines **5**–**7**. One such compound (**5a**) was known before but had been synthesised by a different route.[25] All new compounds were fully characterised. The reaction conditions used were those described in the literature and were not optimised. These conditions and the yields are summarised in Table 1.

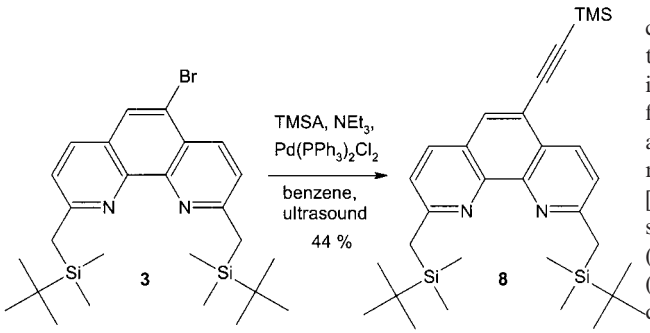
Table 1. Selective modification of neocuproine in the 5-position using three different palladium-catalysed couplings with the 5-bromo-substituted neocuproine **4** (Suzuki, Sonogashira, Buchwald/Hartwig).



Substrate	Product		Cond.	Time [h]	Yield [%]
		**5a**	a	18	65
		**5b**	b	24	71
		**6a**	c	3.5	44
		**6b**	d	24 *	≈ 3
		**7a**	e	1	54
		**7b**	e	4	46

[a] [$Pd(PPh_3)_4$], 1,2-dimethoxyethane/H_2O, $Ba(OH)_2$, reflux. [b] [$Pd(PPh_3)_4$], 1,2-dimethoxyethane/H_2O, Cs_2CO_3, reflux. [c] [$PdCl_2(PPh_3)_2$], DMF/NEt_3, CuI, ultrasound. [d] [$PdCl_2(PPh_3)_2$], DMF/NEt_3 or benzene/NEt_3, CuI, ultrasound, various temp. [e] [$Pd_2(dba)_3$], *rac*-BINAP, NaO*t*Bu, reflux; * various reaction times up to max. 24 h.

In the case of the reaction of **4** with trimethylsilylacetylene (TMSA), the coupling product **6b** was detected in the MALDI mass and NMR spectra in the crude product mixture but it could not be isolated as a pure compound. In this case, the TBDMS-substituted precursor **3** was used in the Sonogashira coupling reaction instead, the coupling of which to give **8** could be carried out in 44% yield.



An X-ray structure analysis was carried out with **8** as a model compound (see Figure 2).

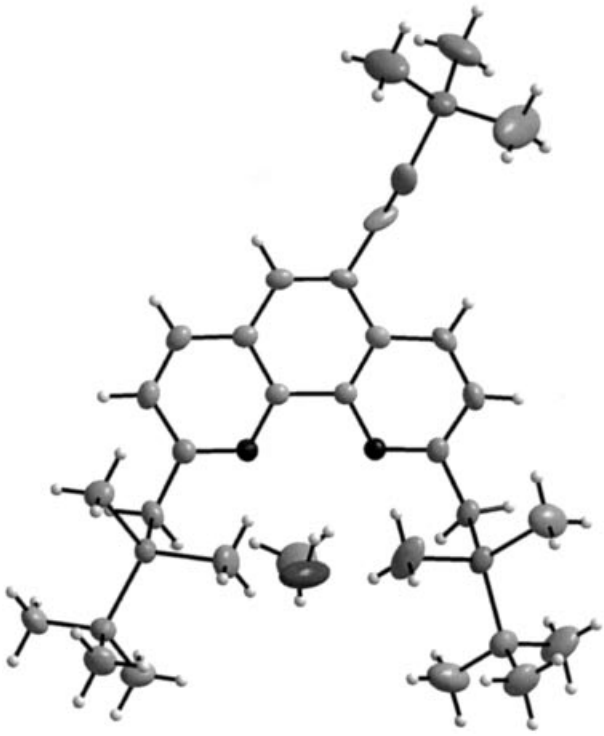


Figure 2. X-ray structure of 2,9-bis[(*tert*-butyldimethylsilyl)methyl]-5-[(trimethylsilyl)ethynyl]-1,10-phenanthroline (**8**) ($C_{31}H_{48}N_2Si_3$·CH_3OH, recrystallised from methanol).

Conclusions

5-Bromo-2,9-dimethyl-1,10-phenanthroline (**4**) is a versatile building block for the construction of 5-substituted neocuproines. Various palladium-catalysed reactions can be exploited for the connection of different substituents with the 1,10-phenanthroline scaffold. These substituents can carry further functional groups, which should allow the connection of the 5-substituted neocuproines to other molecules.

Experimental Section

General Remarks: All reactions requiring dry solvents were carried out using standard Schlenk techniques under an argon atmosphere. Dry solvents were either purchased or dried with suitable desiccants: DMF (Fluka), dichloromethane and triethylamine were distilled from calcium hydride, tetrahydrofuran was distilled from lithium aluminium hydride, and benzene and toluene were distilled from molten sodium. The following reagents are commercially available and were used without further purification: methyl 4-aminobenzoate (Aldrich), phenylboronic acid (Aldrich), *rac*-BINAP [*rac*-2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl, Aldrich], bis(triphenylphosphane)palladium(II) dichloride (Fluka), bromine (Aldrich), *tert*-butylchlorodimethylsilane (Fluka), *n*-butylamine (Acros), lithium diisopropylamide (Fluka, 2 M solution in tetrahydrofuran/heptane/ethylbenzene), neocuproine (2,9-dimethyl-1,10-phenanthroline, **1**, Chempur), phenylacetylene (Fluka), sodium *tert*-butoxide (Acros), tetrakis(triphenylphosphane)palladium(0) (Fluka), 4-(trimethylsilyl)phenylboronic acid (Aldrich), trimethylsilylacetylene (Fluka), tris(dibenzylideneacetone)dipalladium(0)–chloroform adduct (Fluka). Column chromatography was carried out on either basic or neutral alumina (Fluka, 0.05–0.15 mesh). Neutral alumina (Merck, F254) and silica (Aldrich, Merck type 7749) were used for chromatotron chromatography. All products were characterised by ^{1}H NMR and IR spectroscopy and mass spectrometry. New compounds were further characterised by ^{13}C NMR spectroscopy and elemental analysis or high resolution mass spectrometry (HR-MS). NMR spectra were recorded on a Bruker AM 300 (300 MHz) or Bruker DRX 500 (500 MHz) spectrometer using tetramethylsilane as internal standard. IR spectra were obtained with a Perkin–Elmer 1600 Series Fourier Transform spectrometer. Mass spectra were recorded on a Finnigan MAT 8230. Elemental analyses were carried out on a Perkin–Elmer Elemental Analyser 240 or HEKAtech GmbH EA3000CHNS.

2,9-Bis[(*tert*-butyldimethylsilyl)methyl]-1,10-phenanthroline(2): A solution of neocuproine (**1**; 4.17 g, 20.0 mmol) in dry tetrahydrofuran (90 mL) was cooled to 0 °C under argon. A 2 M solution of lithium diisopropylamide (60.0 mL, 120 mmol) was then added dropwise. The cooling bath was removed and the solution was stirred for 1 h. A solution of *tert*-butylchlorodimethylsilane (6.18 g, 41.0 mmol) in dry tetrahydrofuran (35 mL) was slowly added at room temperature and the mixture was stirred for another 30 min. The reaction was quenched by addition of water (30 mL) while cooling. More water (40 mL) was added, the organic layer separated and the aqueous layer was extracted with dichloromethane (2 × 30 mL). Solvent was removed and the residue was filtered through basic alumina (eluent: dichloromethane). After removal of the solvent in vacuo, the remaining yellow oil was dried in vacuo (<0.1 mbar) and recrystallised from *n*-pentane at –18 °C to give 8.61 g (98%) of **2**, m.p. 78 °C. IR (KBr): $\tilde{\nu}$ = 2953, 2927 cm^{-1} (aliph. C–H), 1591 (arom. C=C), 1490, 1469 (aliph. C–H), 844, 808 (arom. C–H). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.2 Hz, 2 H, Phen-$H^{4,7}$), 7.59 (s, 2 H, Phen-$H^{5,6}$), 7.27 (d, J = 8.2 Hz, 2 H, Phen-$H^{3,8}$), 2.77 (s, 4 H, -CH_2-), 0.95 [s, 18 H, -C(CH_3)$_3$], 0.00 [s, 12 H, -Si(CH_3)$_2$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$):δ = 162.05 (Phen-$C^{2,9}$), 145.56 (Phen-$C^{10a,b}$), 135.37 (Phen-$C^{4,7}$), 125.78 (Phen-$C^{4a,6a}$), 124.56 (Phen-$C^{3,8}$), 122.75 (Phen-$C^{5,6}$), 27.46 (Phen-CH_2), 26.54 [SiC(CH_3)$_3$], 17.01 [SiC(CH$_3$)$_3$], –6.08 (Si-CH_3) ppm. MS (CI, 70 eV): m/z (%) = 437 (100) [MH$^+$], 380 (1) [MH$^+$ – C(CH$_3$)$_3$], 379 (5) [M$^+$ – C(CH$_3$)$_3$]. $C_{26}H_{40}N_2Si_2$ (436.79): calcd. C 71.50, H 9.23, N 6.41; found C 71.65, H 9.37, N 6.37.

5-Bromo-2,9-bis[(*tert*-butyldimethylsilyl)methyl]-1,10-phenanthroline (3): A solution of 2,9-bis[(*tert*-butyldimethylsilyl)methyl]-1,10-phenanthroline (**2**; 7.13 g, 16.3 mmol) in dry dichloromethane (80 mL) was heated to reflux under argon. A solution of bromine (2.51 mL, 48.9 mmol) in dry dichloromethane was then added within 15 min and the reaction mixture was heated to reflux for another 45 min. 2 N NaOH (50 mL) was added while cooling and

stirring vigorously. After addition of more 2 N NaOH (30 mL), the organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 30 mL). The combined organic layer was washed with saturated brine (40 mL), dried with sodium sulfate and solvent was removed in vacuo. The crude product (brown oil) was filtered through neutral alumina (eluent: dichloromethane) and recrystallised from methanol to give 5.00 g (60%) of **3**, m. p. 58 °C. IR (KBr): $\tilde{\nu}$ = 3447 cm^{-1} (MeO–H), 2925 (aliph. C–H), 1602 (arom. C=C), 1489 (aliph. C–H), 1140 (MeC–O), 840 (arom. C–H). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.41 (d, J = 8.5 Hz, 1 H, Phen-H^4), 7.94 (s, 1 H, Phen-H^6), 7.92 (d, J = 8.3 Hz, 1 H, Phen-H^7), 7.34 (d, J = 8.5 Hz, 1 H, Phen-H^3), 7.28 (d, J = 8.3 Hz, 1 H, Phen-H^8), 2.80 (s, 2 H, PhenC^2-CH_2), 2.76 (s, 2 H, PhenC^9-CH_2), 0.95 [s, 9 H, PhenC^{2}CH$_2$Si-C(CH_3)$_3$], 0.94 [s, 9 H, PhenC^{9}CH$_2$Si-C(CH_3)$_3$], –0.01 [s, 6 H, PhenC^{2}CH$_2$Si(CH_3)$_2$], –0.02 [s, 6 H, PhenC^{9}CH$_2$Si-(CH_3)$_2$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$):δ = 163.07 (Phen-C^2), 162.75 (Phen-C^9), 146.08 (Phen-C^{10b}), 145.02 (Phen-C^{10a}), 135.14 (Phen-C^4), 134.50 (Phen-C^7), 127.75 (Phen-C^6), 126.12 (Phen-C^{6a}), 124.95 (Phen-C^{4a}), 123.51 (Phen-C^3), 123.34 (Phen-C^8), 118.76 (Phen-C^5), 27.70 (PhenC^9-CH$_2$), 27.46 (PhenC^2-CH$_2$), 26.89 [PhenC^{2}CH$_2$Si-C(CH$_3$)$_3$], 26.51 [PhenC^{9}CH$_2$Si-C(CH$_3$)$_3$], 17.04 [PhenC^{2}CH$_2$Si-C(CH$_3$)$_3$], 17.03 [PhenC^{9}CH$_2$Si-C(CH$_3$)$_3$], –6.07 [PhenC^{2}CH$_2$Si(CH$_3$)$_2$], –6.09 [PhenC^{9}CH$_2$Si(CH$_3$)$_2$] ppm. MS (CI, 70 eV): m/z (%) = 517, 515 (80, 85) [MH$^+$], 459, 457 (8, 10) [MH$^+$ – tBu], 237 (29) [MH$^+$ – Br]. $C_{26}H_{39}BrN_2Si_2$·0.6 CH_3OH (534.90): calcd. C 59.73, H 7.80, N 5.24; found C 59.74, H 7.87, N 5.22.

X-ray Crystal Structure Determination of 3: Empirical formula $C_{26}H_{39}BrN_2Si_2$·CH_3OH, mol. mass 547.72 g mol^{-1}, colourless block, a = 10.255(1) Å, b = 10.070(1) Å, c = 13.934(1) Å, α = 66.54(1)°, β = 71.60(1)°, γ = 84.64(1)°, V = 1500.3 (2) Å^3, T = 150 K, $\rho_{calcd.}$ = 1.212 g·cm^{-3}, μ = 1.47 mm^{-1}, triclinic, space group $P\bar{1}$ (no. 2), Z = 2, STOE imaging plate diffraction system (IPDS), Mo-K_α (λ = 0.71073 Å), 13 267 measured reflections in the range 3° ≤ 2θ ≤ 56°, 6771 independent reflections used for refinement and 5293 reflections with $I \geq 2\sigma(I)$, R_{int} = 0.0405. Structure solution was performed with SHELXL-97, and structure refinement against F^2 with SHELXL-97. 310 Refined parameters, R for all reflections with $I \geq 2\sigma(I)$ = 0.0406, wR^2 for all reflections = 0.1052, GoF = 1.027, residual electron density 0.49/–0.56 Å^{-3}. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealised geometry and refined with isotropic displacement parameters using the riding model. The bromo substituent is disordered and was refined using a split model.

5-Bromo-2,9-dimethyl-1,10-phenanthroline (4): Concentrated hydrochloric acid (2 mL) was added to a solution of 5-bromo-2,9-bis-[(*tert*-butyldimethylsilyl)methyl]-1,10-phenanthroline (**3**; 4.50 g, 8.73 mmol) in acetone (25 mL) and the reaction mixture was stirred for 3 h at room temperature. 2 N NaOH was added until the solution was basic, and the precipitate was filtered off, washed with water and dried in vacuo (<0.1 mbar) to give 2.36 g (94%) of **4**, m. p. 172 °C. IR (KBr): $\tilde{\nu}$ = 2938 cm^{-1} (aliph. C–H), 1604 (arom. C=C), 1492 (aliph. C–H), 874, 820 (arom. C–H). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.53 (d, J = 8.5 Hz, 1 H, Phen-H^4), 8.04 (d, J = 8.2 Hz, 1 H, Phen-H^7), 8.03 (s, 1 H, Phen-H^6), 7.58 (d, J = 8.5 Hz, 1 H, Phen-H^3), 7.50 (d, J = 8.2 Hz, 1 H, Phen-H^8), 2.97 (s, 3 H, PhenC^2-CH_3), 2.93 (s, 3 H, PhenC^9-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$):δ = 160.18 (Phen-C^2), 159.88 (Phen-C^9), 145.74 (Phen-C^{10b}), 144.70 (Phen-C^{10a}), 136.05 (Phen-C^4), 135.32 (Phen-C^7), 128.58 (Phen-C^6), 127.03 (Phen-C^{6a}), 126.00 (Phen-C^{4a}), 124.25 (Phen-C^3), 124.10 (Phen-C^8), 119.65 (Phen-C^5), 25.91 (PhenC^9-CH$_3$), 25.62 (PhenC^2-CH$_3$) ppm. MS (EI, 70 eV): m/z (%) = 288, 286 (98, 100) [M$^+$], 207 (35) [M$^+$ – Br]. $C_{14}H_{11}BrN_2$ (287.16): calcd. C 58.56, H 3.86, N 9.76; found C 58.31, H 3.99, N 9.70.

2,9-Dimethyl-5-phenyl-1,10-phenanthroline (5a): A suspension of 5-bromo-2,9-dimethyl-1,10-phenanthroline (**4**; 101 mg, 350 μmol), tetrakis(triphenylphosphane)palladium(0) (40.6 mg, 35.0 μmol), phenylboronic acid (48.8 mg, 400 μmol) and $Ba(OH)_2$·$8H_2O$ (221 mg, 700 μmol) in dimethoxyethane/water (10:1, 10 mL) was heated to reflux for 18 h under argon. After dilution with water (30 mL) and addition of dichloromethane (30 mL), the organic layer was separated. The aqueous layer was extracted with dichloromethane (30 mL) and the combined organic layer was dried with sodium sulfate. After removal of the solvent in vacuo, the crude product was purified by column chromatography (basic alumina; eluent: dichloromethane) to give 65.0 mg (65%) of **5a**, m. p. 165 °C (158–159 °C[25]). IR (KBr): $\tilde{\nu}$ = 2989 cm^{-1} (aliph. C–H), 1586 (arom. C=C), 1492 (aliph. C–H), 891, 823 (arom. C–H). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.16 (d, J = 8.5 Hz, 1 H, Phen-H^4), 8.13 (d, J = 8.2 Hz, 1 H, Phen-H^7), 7.65 (s, 1 H, Phen-H^6), 7.55–7.46 (m, 5 H, Ar-$H^{2,3,4,5,6}$), 7.52 (d, J = 8.2 Hz, 1 H, Phen-H^8), 7.43 (d, J = 8.5 Hz, 1 H, Phen-H^3), 2.97 (s, 3 H, PhenC^2-CH_3), 2.96 (s, 3 H, PhenC^9-CH_3) ppm. MS (EI, 70 eV): m/z (%) = 284 (100) [M$^+$].

2,9-Dimethyl-5-[4-(trimethylsilyl)phenyl]-1,10-phenanthroline (5b): A suspension of 5-bromo-2,9-dimethyl-1,10-phenanthroline (**4**; 750 mg, 2.61 mmol), tetrakis(triphenylphosphane)palladium(0) (302 mg, 261 μmol), 4-(trimethylsilyl)phenylboronic acid (557 mg, 2.87 mmol) and Cs_2CO_3 (1.70 g, 5.22 mmol) in dimethoxyethane/water (10:1, 55 mL) was heated to reflux for 24 h under argon. After dilution with water (50 mL) and addition of dichloromethane (50 mL), the organic layer was separated. The aqueous layer was extracted twice with dichloromethane (50 mL) and the combined organic layer was dried with sodium sulfate. After removal of the solvent in vacuo, the crude product was purified by column chromatography (neutral alumina; eluent: cyclohexane/ethyl acetate, 10:1) to give 660 mg (71%) of **5b**, m. p. 205 °C. IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1} (aliph. C–H), 1588, 1552 (arom. C=C), 1488 (aliph. C–H), 852, 835 (arom. C–H). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.19 (d, J = 8.5 Hz, 1 H, Phen-H^4), 8.11 (d, J = 8.2 Hz, 1 H, Phen-H^7), 7.68 (ddd, J = 8.1, J = 1.8, J = 1.4 Hz, 2 H, Ar-$H^{3,5}$), 7.64 (s, 1 H, Phen-H^6), 7.51 (ddd, J = 8.1, J = 1.8, J = 1.4 Hz, 2 H, Ar-$H^{2,6}$), 7.50 (d, J = 8.2 Hz, 1 H, Phen-H^8), 7.42 (d, J = 8.5 Hz, 1 H, Phen-H^3), 2.96 (s, 3 H, PhenC^2-CH_3), 2.95 (s, 3 H, PhenC^9-CH_3), 0.35 [s, 9 H, Si(CH_3)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$):δ = 159.31 (Phen-C^9), 159.07 (Phen-C^2), 145.48 (Phen-C^{10b}), 144.78 (Phen-C^{10a}), 140.02 (Ar-C^4), 139.65 (Ar-C^1), 137.77 (Phen-C^5), 136.26 (Phen-C^7), 134.78 (Phen-C^4), 133.49 (Ar-$C^{3,5}$), 129.30 (Ar-$C^{2,6}$), 126.26 (Phen-C^{6a}), 125.89 (Phen-C^{4a}), 125.52 (Phen-C^6), 123.76 (Phen-C^8), 123.17 (Phen-C^3), 25.98 (PhenC^9-CH$_3$), 25.80 (PhenC^2-CH$_3$), –1.06 [Si(CH$_3$)$_3$] ppm. MS (EI, 70 eV): m/z (%) = 356 (73) [M$^+$], 341 (100) [M$^+$ – CH_3]. $C_{23}H_{24}N_2Si$·0.4H_2O·0.3 C_6H_{12} (389.00): calcd. C 76.57, H 7.36, N 7.20; found C 76.63, H 7.10, N 7.02.

2,9-Dimethyl-5-phenylethynyl-1,10-phenanthroline (6a): 5-Bromo-2,9-dimethyl-1,10-phenanthroline (**4**; 101 mg, 350 μmol), bis(triphenylphosphine)palladium(II) dichloride (12.3 mg, 17.5 μmol) and CuI (6.67 mg, 35.0 μmol) were dissolved in a mixture of dry DMF (10 mL) and dry triethylamine (2.50 mL). Oxygen was removed from the solution by sonication under a flow of argon for 30 min. After dropwise addition of phenylacetylene (53.6 mg, 525 μmol), the mixture was left to react whilst applying ultrasound for 3.5 h. After addition of water (20 mL), the precipitate was filtered off and dissolved in dichloromethane (30 mL). The solution was dried with sodium sulfate, and solvent was removed in vacuo. The crude pro-

duct was purified by column chromatography (basic alumina; eluent: dichloromethane) and recrystallised from chloroform/*n*-pentane to give 47.2 mg (44%) of **6a**, m.p. 128 °C. IR (KBr): $\tilde{\nu}$ = 2983 cm^{-1} (aliph. C–H), 1604 (arom. C=C), 1484 (aliph. C–H), 885, 832, 749 (arom. C–H). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.70 (d, J = 8.4 Hz, 1 H, Phen-H^4), 8.08 (d, J = 8.3 Hz, 1 H, Phen-H^7), 8.00 (s, 1 H, Phen-H^6), 7.63–7.68 (m, 2 H, Ar-$H^{2,6}$), 7.58 (d, J = 8.4 Hz, 1 H, Phen-H^3), 7.49 (d, J = 8.3 Hz, 1 H, Phen-H^8), 7.39–7.44 (m, 3 H, Ar-$H^{3,4,5}$), 2.97 (s, 3 H, PhenC^2-CH_3), 2.95 (s, 3 H, PhenC^9-CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$):δ = 160.17 (Phen-C^9), 159.77 (Phen-C^2), 145.21 (Phen-C^{10a}), 144.99 (Phen-C^{10b}), 136.03 (Phen-C^7), 134.91 (Phen-C^4), 131.68 (Ar-$C^{2,6}$), 129.70 (Phen-C^6), 128.75 (Ar-C^4), 128.49 (Ar-$C^{3,5}$), 126.46 (Phen-C^{4a}), 126.16 (Phen-C^{6a}), 123.88 (Phen-C^8), 123.79 (Phen-C^3), 122.78 (Ar-C^1), 118.69 (Phen-C^5), 94.65 (Phen-C≡C), 86.19 (Phen-C≡C), 25.99 (PhenC^9-CH$_3$), 25.83 (PhenC^2-CH$_3$) ppm. MS (EI, 70 eV): m/z (%) = 308 (100) [M^+]. HR-MS (EI, 70 eV) for $C_{22}H_{16}N_2$: calcd. 308.13135; found 308.13134 (diff. = 0.0 ppm). $C_{21}{}^{13}CH_{16}N_2$: calcd. 309.13470; found 309.13443 (diff. = 0.9 ppm).

***N*-Butyl-(2,9-dimethyl-1,10-phenanthrolin-5-yl)amine (7a):** A solution of 5-bromo-2,9-dimethyl-1,10-phenanthroline (**4**; 101 mg, 350 μmol), tris(dibenzylideneacetone)dipalladium(0)–chloroform adduct (18.1 mg, 17.5 μmol), *rac*-BINAP (21.8 mg, 35.0 μmol), *n*-butylamine (102 mg, 1.40 mmol) and sodium *tert*-butoxide (47.1 mg, 490 μmol) in dry toluene (10 mL) was heated to 80 °C for 1 h under argon. The reaction mixture was allowed to cool to room temperature and the solvent was removed in vacuo. The residue was taken up in dichloromethane (25 mL) and water (25 mL) was added. The organic layer was washed with saturated brine (20 mL), dried with sodium sulfate and the solvent was removed in vacuo. The crude product was filtered through basic alumina (eluent: dichloromethane) and further purified by chromatography (chromatotron, neutral alumina; eluent: cyclohexane/ethyl acetate, 2:1) to yield 53 mg (54%) of **7a**, m.p. 186 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3301 cm^{-1} (N–H), 2926 (aliph. C–H), 1604 (arom. C=C), 1498 (aliph. C–H), 831 (arom. C–H). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.14 (d, J = 8.5 Hz, 1 H, Phen-H^4), 7.91 (d, J = 8.2 Hz, 1 H, Phen-H^7), 7.47 (d, J = 8.5 Hz, 1 H, Phen-H^3), 7.35 (d, J = 8.2 Hz, 1 H, Phen-H^8), 6.64 (s, 1 H, Phen-H^6), 4.23 (s, 1 H, NH), 3.33 (m_c, 2 H, NHCH_2), 2.93 (s, 3 H, PhenC^2-CH_3), 2.85 (s, 3 H, PhenC^9-CH_3), 1.80 (m_c, 2 H, NHCH$_2$CH_2), 1.55 (m_c, 2 H, CH_2CH$_3$), 1.01 (t, J = 7.3 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$):δ = 158.87 (Phen-C^2), 155.00 (Phen-C^9), 146.00 (Phen-C^{10b}), 140.69 (Phen-C^{10a}), 140.60 (Phen-C^5), 134.21 (Phen-C^7), 128.65 (Phen-C^4), 128.43 (Phen-C^{6a}), 123.68 (Phen-C^8), 122.44 (Phen-C^3), 120.01 (Phen-C^{4a}), 99.86 (Phen-C^6), 43.96 (NHCH$_2$CH$_2$), 31.47 (NHCH$_2$$CH_2$), 25.73 (PhenC^2-$CH_3$), 25.56 (PhenC^9-$CH_3$), 20.55 ($CH_2CH_3$), 13.98 (CH$_2$$CH_3$) ppm. MS (EI, 70 eV): m/z (%) = 279 (75) [M^+], 236 (100) [M^+ – C_3H_7]. HR-MS (EI, 70 eV) for $C_{18}H_{21}N_3$: calcd. 279.17355; found 279.17350 (diff. = 0.2 ppm). $C_{17}{}^{13}CH_{21}N_3$: calcd. 280.17691; found 280.17690 (diff. = 0.0 ppm).

Methyl 4-[(2,9-Dimethyl-1,10-phenanthrolin-5-yl)amino]benzoate (7b): A solution of 5-bromo-2,9-dimethyl-1,10-phenanthroline (**4**; 101 mg, 350 μmol), tris(dibenzylideneacetone)dipalladium(0)–chloroform adduct (18.1 mg, 17.5 μmol), *rac*-BINAP (21.8 mg, 35.0 μmol), methyl 4-aminobenzoate (106 mg, 700 μmol) and sodium *tert*-butoxide (47.1 mg, 490 μmol) in dry toluene (10 mL) was heated to reflux for 4 h under argon. The reaction mixture was allowed to cool to room temperature and solvent was removed in vacuo. The residue was taken up in dichloromethane (25 mL) and water (25 mL) was added. The organic layer was washed with saturated brine (20 mL), dried with sodium sulfate and solvent was removed in vacuo. The crude product was filtered through basic alumina (eluent: dichloromethane) and further purification by chromatography (chromatotron, silica; eluent: dichloromethane/methanol, 2:1), afforded 57.2 mg (46%) of **7b**, m.p. 239 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3227 cm^{-1} (N–H), 2913 (aliph. C–H), 1716 (C=O), 1600 (arom. C=C), 1512 (aliph. C–H), 849 (arom. C–H). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.31 (d, J = 8.5 Hz, 1 H, Phen-H^4), 8.01 (d, J = 8.2 Hz, 1 H, Phen-H^7), 7.93 (ddd, J = 8.9, 2.5, 2.0 Hz, 2 H, Ar-$H^{2,6}$), 7.62 (s, 1 H, Phen-H^6), 7.46 (d, J = 8.2 Hz, 1 H, Phen-H^8), 7.44 (d, J = 8.5 Hz, 1 H, Phen-H^3), 6.91 (ddd, J = 8.9, 2.5, 2.0 Hz, 2 H, Ar-$H^{3,5}$), 6.43 (s, 1 H, NH), 3.88 (s, 3 H, COOCH_3), 2.92 (s, 3 H, PhenC^2-CH_3), 2.91 (s, 3 H, PhenC^9-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$):δ = 166.92 (COOCH$_3$), 159.77 (Phen-C^2), 158.68 (Phen-C^9), 149.49 (Ar-C^4), 146.26 (Phen-C^{10b}), 143.69 (Phen-C^{10a}), 135.54 (Phen-C^7), 134.33 (Phen-C^5), 131.56 (Ar-$C^{2,6}$), 131.42 (Phen-C^4), 126.76 (Phen-C^{6a}), 123.90 (Ar-C^8), 123.49 (Phen-C^{4a}), 123.33 (Phen-C^3), 121.39 (Ar-C^1), 117.22 (Phen-C^6), 115.01 (Ar-$C^{3,5}$), 25.77 (PhenC^2-CH$_3$), 25.74 (PhenC^9-CH$_3$) ppm. HR-MS (EI, 70 eV) for $C_{22}H_{19}N_3O_2$: calcd. 356.14774; found 357.14820 (diff. = –1.3 ppm). $C_{21}{}^{13}CH_{19}N_3O_2$: calcd. 358.15109; found 358.15280 (diff. = –4.8 ppm).

2,9-Bis[(*tert*-butyldimethylsilyl)methyl]-5-[(trimethylsilyl)ethynyl]-1,10-phenanthroline (8): 5-Bromo-2,9-bis[(*tert*-butyldimethylsilyl)methyl]-1,10-phenanthroline (**3**; 1.61 g, 3.12 mmol) was dissolved in a mixture of dry benzene (50 mL) and dry triethylamine (10 mL). Oxygen was removed by sonication under a flow of argon for 15 min. Trimethylsilylacetylene (1.30 mL, 9.36 mmol), CuI (59.4 mg, 312 μmol) and bis(triphenylphosphane)palladium(II) dichloride (109 mg, 156 μmol) were added and the reaction mixture was warmed to 50 °C for 18 h whilst applying ultrasound. The solvents were removed in vacuo and the residue was dissolved in dichloromethane (50 mL). The organic layer was washed with 2 M aqueous potassium cyanide (50 mL) and water (50 mL), dried with sodium sulfate, and the solvent was removed in vacuo. The crude product was purified by column chromatography (neutral alumina; eluent: cyclohexane/ethyl acetate, 40:1) and recrystallised from methanol to give 47.2 mg (44%) of **8**, m.p. 128 °C. IR (KBr): $\tilde{\nu}$ = 2952 cm^{-1} (aliph. C–H), 2146 (C≡C), 1602 (arom. C=C), 1484 (aliph. C–H), 874, 844 (arom. C–H). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.48 (d, J = 8.4 Hz, 1 H, Phen-H^4), 7.94 (d, J = 8.3 Hz, 1 H, Phen-H^7), 7.86 (s, 1 H, Phen-H^6), 7.35 (d, J = 8.4 Hz, 1 H, Phen-H^3), 7.26 (d, J = 8.3 Hz, 1 H, Phen-H^8), 2.77 (s, 2 H, PhenC^2-CH_2), 2.76 (s, 2 H, PhenC^9-CH_2), 0.94 [s, 9 H, PhenC^{2}CH$_2$Si-C(CH_3)$_3$], 0.94 [s, 9 H, PhenC^{9}CH$_2$Si-C(CH_3)$_3$], 0.34 [s, 9 H, C≡C-Si-(CH_3)$_3$], –0.02 [s, 12 H, PhenC^{2,9}CH$_2$Si-(CH_3)$_2$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$):δ = 163.25 (Phen-C^9), 162.54 (Phen-C^2), 145.63 (Phen-C^{10a}), 145.11 (Phen-C^{10b}), 135.29 (Phen-C^7), 134.05 (Phen-C^4), 129.66 (Phen-C^6), 125.51 (Phen-C^{4a}), 125.04 (Phen-C^{6a}), 123.16 (Phen-$C^{3,8}$), 117.53 (Phen-C^5), 102.24 (Phen-C≡C-TMS), 99.34 (Phen-C≡C-TMS), 27.78 (PhenC^9-CH$_2$), 27.48 (PhenC^2-CH$_2$), 26.54 [PhenC^{2,9}CH$_2$Si-C(CH$_3$)$_3$], 17.06 [PhenC^{2,9}CH$_2$Si-C(CH$_3$)$_3$], 0.09 [Si-(CH$_3$)$_3$], –6.06 [PhenC^{2,9}CH$_2$Si-(CH$_3$)$_2$] ppm. MS (CI, 70 eV): m/z (%) = 533 (100) [MH^+], 475 (41) [MH^+ – *tert*-butyl], 419 (10) [MH^+ – 2 *tert*-butyl]. $C_{31}H_{48}N_2Si_3$·1.9CH_3OH (593.87): calcd. C 66.54, H 9.44, N 4.72; found C 66.44, H 9.09, N 4.93.

X-ray Crystal Structure Determination of 8: Empirical formula $C_{31}H_{48}N_2Si_3$·CH_3OH, mol. mass 565.03 g mol^{-1}, colourless plate, a = 10.428(1) Å, b = 11.314(1) Å, c = 15.695(2) Å, α = 85.61(1)°, β = 89.88(1)°, γ = 75.43(1)°, V = 1786.6 (3) Å^3, T = 170 K, $\rho_{calcd.}$ = 1.050 g cm^{-3}, μ = 1.6 mm^{-1}, triclinic, space group $P\bar{1}$ (no. 2), Z = 2, STOE imaging plate diffraction system (IPDS), Mo-K_α (λ = 0.71073 Å), 12 919 measured reflections in the range of 3° ≤ 2θ ≤ 50°, 5918 independent reflections used for refinement and 4536

reflections with $I \geq 2\sigma(I)$, $R_{int} = 0.0716$. Structure solution was performed with SHELXL-97 and structure refinement against F^2 with SHELXL-97. 344 Refined parameters, R for all reflections with $I \geq 2\sigma(I) = 0.0614$, wR^2 for all reflections = 0.1743, GoF = 1.021, residual electron density 0.78/–0.47 Å^{-3}. All non hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealised geometry and refined with isotropic displacement parameters using the riding model.

CCDC-249494 (for **3**) and -249495 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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