Synthesis of 2-(substituted methyl)quinolin-8-ols and their complexation with Sn(II)

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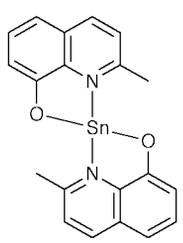
A new method for the synthesis of 2-(substituted methyl)quinolin-8-ol is described. 2-Methyl-8-methoxyquinoline **3** was prepared as a key building block; lithiation of **3** with LDA and subsequent addition of alkyl halides followed by reaction in 48% HBr afforded the 2-alkylquinolin-8-ols **6a**,**b**. On the other hand, the use of alkanediyl dihalides as the electrophile gave bis(quinolin-8-ol) derivatives containing an alkyl bridge **12**. The complexation of 2-alkyl-8-hydroxyquinolines with $SnCl_2$ in alkaline methanol produced the bis(quinolin-8-ol) complexes **13a**,**b**, whereas in the case of the bis(quinolin-8-ol) derivatives, intractable solids were obtained. The molecular structure of **13b** was elucidated by X-ray analysis.

Introduction

As an *N*,*O*-bidentate ligand, quinolin-8-ol is used for the identification of metals.[1] Its applications as a component for molecular electronic devices[2] and as a new supramolecular motif[3] are of current interest. Recently, we determined the unique nonplanar two-blade-screw structure of the bis(2-methylquinolin-8-olato)tin(II) complex **1** by X-ray analysis.[4]



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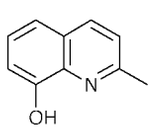

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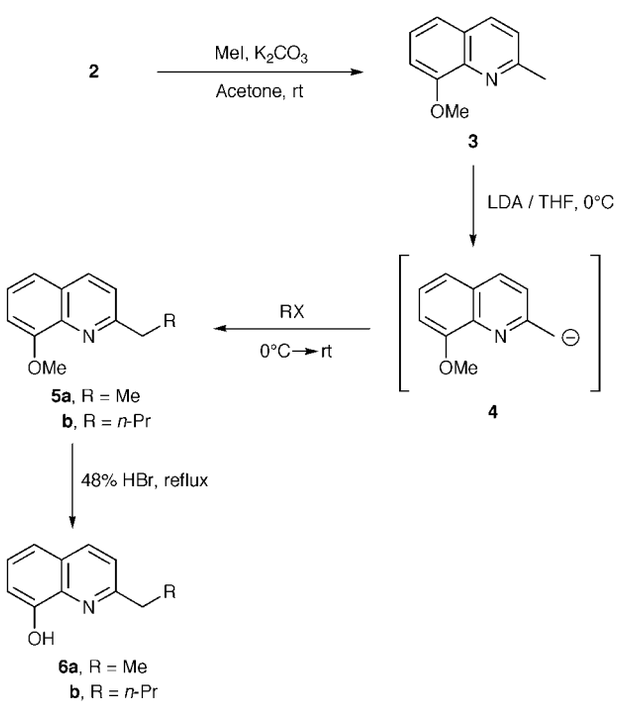
The interesting structural characteristics led us to investigate the steric effect of the substituent at the 2-position in the quinolin-8-olate ligand. However, to date, there have been only a few reports on the preparation of quinolin-8-ols possessing a substituent at the 2-position.[5] In recent years, we have studied the synthesis of new 2-substituted-quinolin-8-ols and their complexes. It is known that a carbanion derived from 2-methylquinoline by deprotonation reacts with electrophiles to give the corresponding substituted methyl derivatives.[6] Therefore we intended to adopt the methodology for the synthesis of OH-protected quinolin-8-ol. We report here a new method for the preparation of 2-(substituted methyl)quinolin-8-ol derivatives, using 2-methylquinolin-8-ol **2** as the starting material, and their complexation with Sn(II).

Results and discussion

We needed a temporary protecting group for the quinolinol that was stable under basic conditions and that could be removed by acidic reagents. A methyl group was introduced as a protecting group because 8-methoxyquinoline can be easily converted to quinolin-8-ol with HBr under reflux.[7] We therefore regarded 8-methoxy-2-methylquinoline **3** as a key building block. However, few practical methods for the synthesis of **3** have been reported so far.[8,9] We have succeeded in a simple and convenient preparation of **3** by reaction of **2** with iodomethane in acetone in the presence of K_2CO_3 in 90% yield (Scheme 1). Reaction of



Scheme 1

3 with LDA generated the carbanion **4** as an intermediate, and subsequent addition of iodomethane or 1-bromopropane produced the 2-(substituted methyl)quinolines 2-ethyl-8-methoxyquinoline **5a** or 2-butyl-8-methoxyquinoline **5b** in 45 and 73% yields, respectively (Scheme 1). It is known that treatment of 2-methylquinolines with a strong base such as LDA yields stable quinolin-2-ylmethanide carbanions such as **4**. However, use of *n*-butyllithium as a nucleophilic strong base affords

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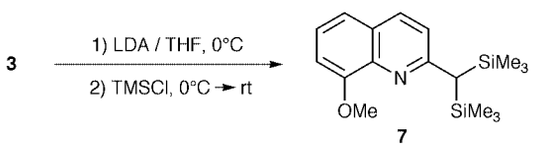
a butyl adduct as the main product because *n*-butyllithium attacks the carbon atom of quinoline at the 2-position. These results suggest that the development of the synthesis of a variety of 2-(substituted methyl)quinolines could be promising with other electrophiles. Deprotection by treatment of **5a**,**b** with 48% HBr under reflux furnished the corresponding quinolin-8-ol derivatives, 2-ethylquinolin-8-ol **6a**[5] and 2-*n*-butylquinolin-8-ol **6b**[5] in 52 and 77% yield, respectively (Scheme 1). This synthetic path has offered a simple method for synthesis of 2-(substituted methyl)quinolin-8-ols.

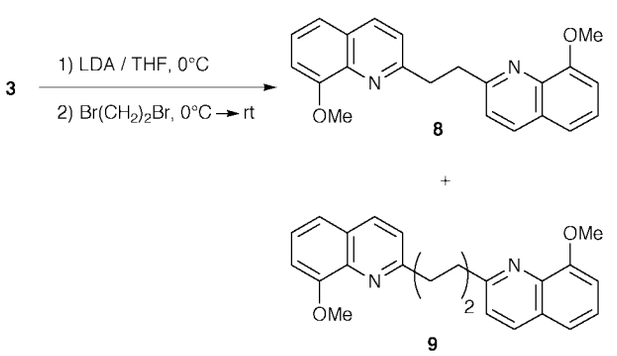
Interestingly, quenching of the carbanion **4** with trimethylsilyl chloride gave a complex mixture, and only 2-bis(trimethylsilyl)methyl-8-methoxyquinoline **7** could be isolated (Scheme 2). Although we tried various reaction conditions (different



Scheme 2

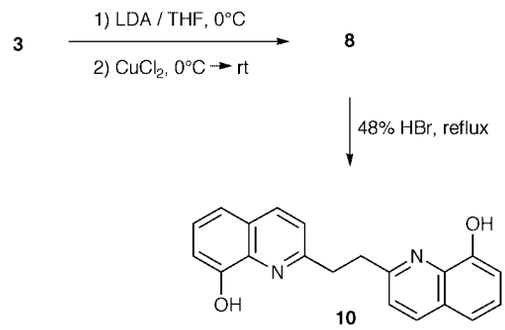
concentrations of LDA and trimethylsilyl chloride; different temperatures and times), mono- and tris(trimethylsilyl)methylquinolines were never obtained. This result seems strange since, in the case of 2-methylpyridine, mono-, bis- and tris(trimethylsilyl) compounds can be prepared according to the proportion of base and electrophile added.[10] Although the oxygen atom of 8-methoxyquinoline is probably involved in lithiation and disproportionation of the carbanion, we were not able to explain this result.

Next we tried the synthesis of other 2-(substituted methyl)-quinoline compounds. The bis(quinolin-8-ol) derivative is a prospective metallo-supramolecular ligand.[3] However, the complexes of quinolin-8-ol with many metal ions have not been utilized in the field of metallo-supramolecular chemistry since they are formed in the *trans*-planar conformation. On the other hand, the bis(quinolin-8-olato)tin(II) complex has a non-planar screw-like structure.[4] Therefore, the tin(II) complex of the bis(quinolin-8-ol) derivative seems a more likely candidate for a new supramolecular architecture such as a neutral double-stranded helix. We therefore attempted the synthesis of bis(quinolin-8-ol) derivatives by use of alkanediyl dihalides as the electrophile in the reaction depicted in Scheme 1. First we performed the reaction of the carbanion derived from **3** and LDA with 1,2-dibromoethane (Scheme 3). However, we



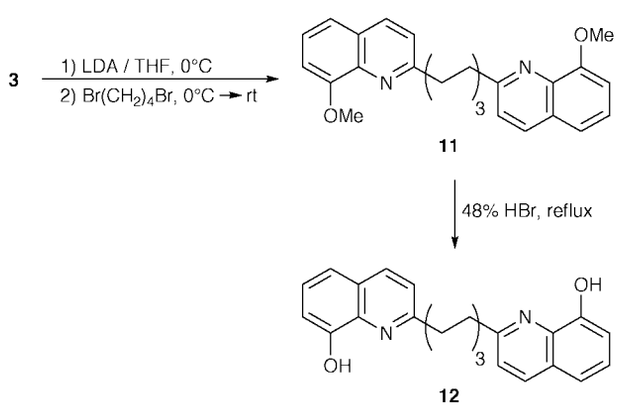
Scheme 3

gained a mixture of two products, the ethylene-bridged bis-(8-methoxyquinoline) **8** (homo-coupling product) and the tetramethylene-bridged bis(8-methoxyquinoline) **9** (substitution product), which were identified from their ^{1}H NMR and MS spectra. We repeated the reaction carefully but still failed to isolate **9** exclusively. Separation of **8** and **9** was impossible because they had the same R_f values, and so we abandoned the isolation of **9**. As Jones and Russell had reported that the ethylene-bridged bis-quinoline compound was formed in the presence of oxygen,[11] we prepared the bis(8-methoxyquinoline) derivative with the ethylene spacer **8** by coupling with an oxidizing reagent. Treatment of **3** with LDA followed by addition of $CuCl_2$ yielded the homo-coupling product **8** in 18% yield. The bis(8-methoxyquinoline) derivative **8** was then heated with 48% HBr to give a bis(quinolin-8-ol) derivative **10** in 80% yield (Scheme 4). In order to synthesize a bis(quinolin-8-ol) deriv-



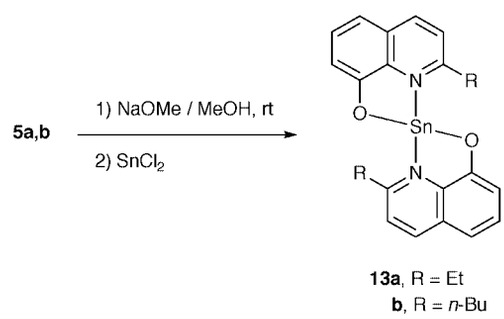
Scheme 4

ative containing a longer linkage than ethylene, we carried out the reaction with a longer alkanediyl dihalide. The action of **3** on LDA followed by addition of 1,4-dibromobutane afforded only the bis(8-methoxyquinoline) derivative with a hexamethylene spacer **11** in 73% yield; deprotection with 48% HBr subsequently yielded the bis(quinolin-8-ol) derivative **12** in 95% yield (Scheme 5).



Scheme 5

We examined the complexing ability of the prepared quinolin-8-ol molecules as ligands with Sn(II). Reaction of quinolinolates derived from **5a**,**b** with $SnCl_2$ produced the stable yellow solids **13a**,**b** in 69 and 35% yields, respectively (Scheme 6). In contrast, complexation of the bis(quinolin-8-ol) derivatives



Scheme 6

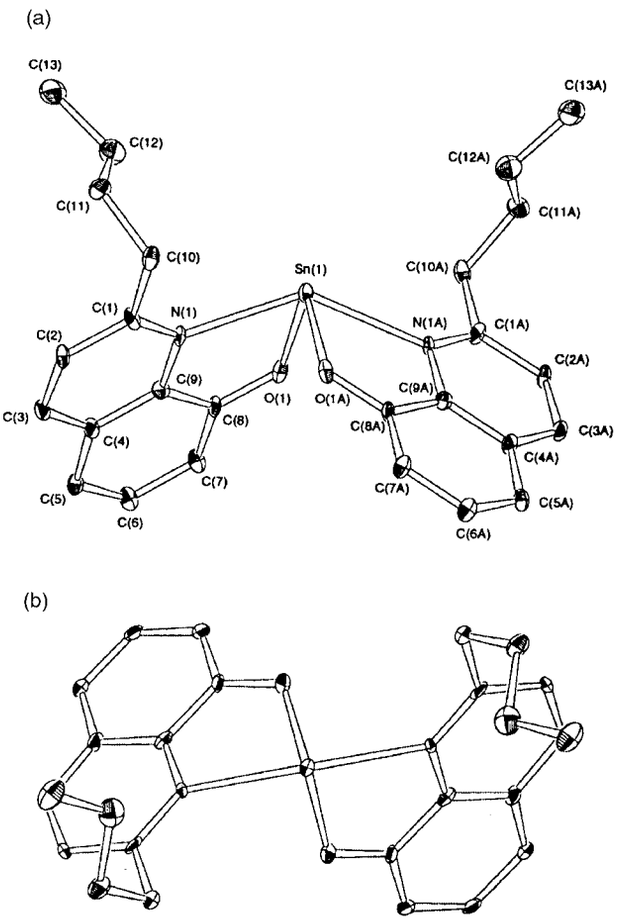
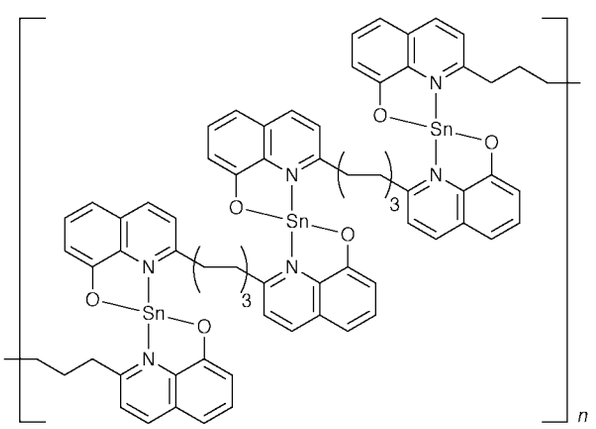


Fig. 1 Molecular structure of **13b** showing 50% probability displacement ellipsoids, in (a) side view and (b) top view. H atoms have been omitted for clarity.

10 and **12** with Sn(II) gave yellow solids, but we could not identify them by NMR, MS and elemental analysis because the solids obtained were insoluble in any organic solvents, and were slightly inflammable.

A polymeric complex containing the bis(quinolin-8-ol) derivative and Sn(II), such as **14**, is probably formed under the



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conditions we used. To avoid this troublesome characterization, the design and synthesis of soluble bis(quinolin-8-ol) ligands are required. Fortunately, we succeeded in our X-ray analysis of **13b**. The molecular structure showed some interesting features (Fig. 1). Complex **13b** has a non-planar, two-bladed conformation and a C_2 axis lying on the bisectors of the N–Sn–N [138.2(2)°] and O–Sn–O [96.0(2)°] bond angles due to the effect of the lone pair of electrons on Sn(II), indicating the presence of axial asymmetry.[4] The dihedral angle between the two ligands is nearly vertical at 85.9°. The molecular structure of the bis(quinolin-8-olato)tin(II) fragment in **13b** was almost identical with that of **1**. The effect of one lone pair of electrons was observed in the ^{1}H NMR spectrum; thus the signals of the methylene protons at C(10) and C(11) exhibited two broad singlets at 2.02 and 3.34 ppm, respectively. The alkyl group of C(11), C(12) and C(13) is almost perpendicular to the plane of the quinoline and C(10). The orientation of the two alkyl groups looks like part of a double helix. The intermolecular distances for C(10)–C(10A), C(11)–C(11A), C(12)–C(12A) and C(13)–C(13A) are 7.35, 8.68, 7.30 and 9.37 Å, respectively. The almost equal length of C(10)–C(10A) and C(12)–C(12A) suggests that the complex with longer alkyl chains may form alkyl double-helicates.

Conclusion

We have presented a new method for the synthesis of 2-alkylquinolin-8-ols and bis(quinolin-8-ol) derivatives with alkyl linkages. The method would be useful in preparation of other quinolin-8-ols substituted at the 2-position. The complexation chemistry of the prepared quinolin-8-ols was also examined. The bis(quinolin-8-ol)–Sn(II) complexes were difficult to identify. The Sn(II) complex of 2-butylquinolin-8-ol was characterized by X-ray analysis and showed a unique structure like part of a double helix. Bis(quinolin-8-olato)tin(II) may now become a new component in metallo-supramolecular chemistry.

Experimental

All reactions were carried out under a nitrogen atmosphere unless indicated otherwise. Mps were determined on a Yanaco Melting Point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker DRX500 FT spectrometer at 500 MHz or on a JEOL EX270 FT spectrometer at 270 MHz, respectively. Chemical shifts are given in ppm; coupling constants, *J*, are quoted in Hz. Electron impact mass spectra were obtained at 70 eV on a Shimadzu QP-1000EX or a Shimadzu GC/MS-QP5000 by a direct-inlet system. Elemental analysis was carried out on a Yanaco MT-5 CHN recorder. High resolution mass determinations (HRMS) were obtained on a Shimadzu Kratos Concept 1s mass spectrometer. THF was distilled from $LiAlH_4$ prior to use. 1.5 M LDA·THF in cyclohexane was purchased from Aldrich. All other reagents were used without purification.

2-Methyl-8-methoxyquinoline (3)[8]

To a mixture of 2-methylquinolin-8-ol (8.01 g, 50.3 mmol) and K_2CO_3 (39.5 g, 286 mmol) in acetone (100 ml), a solution of iodomethane (11.4 g, 80.1 mmol) in acetone (20 ml) was added. In the dark, the reaction mixture was stirred at rt for 12 h. After filtration, the resulting solution was evaporated. Short column chromatogaphy on silica gel with chloroform and recrystallization from hexane–AcOEt (5:1) gave **3** (7.84 g, 90%) as a white solid; mp 127–128 °C (lit.,[8] 122–124 °C); δ_H (270 MHz, $CDCl_3$) 2.80 (s, 3H, CH_3), 7.40 (d, 1H, *J* 8.6, 3-quinH), 7.49 (dd, 1H, *J* 7.9 and 7.6, 6-quinH), 7.58 (dd, 1H, *J* 7.6 and 1.3, 7-quinH), 7.80 (dd, 1H, *J* 7.9 and 1.3, 5-quinH), 8.01 (d, 1H, *J* 8.6, 4-quinH) (Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.06; H, 6.52; N, 8.01%).

2-Ethyl-8-methoxyquinoline (5a)

To an ice-cooled solution of **3** (1.73 g, 10.0 mmol) in THF (20 ml), 1.5 M LDA·THF in cyclohexane (10 ml) was added dropwise, and the mixture was stirred for 1 h at 0 °C. Iodomethane (2.14 g, 15.1 mmol) was then added dropwise. After removal of

the ice-bath, the reaction mixture was allowed to warm to rt and was then stirred for 2 h. The resulting mixture was poured into water, extracted with chloroform, washed with brine, and dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel using hexane–AcOEt (2:1) and recrystallized from hexane to afford **5a** (835 mg, 45%) as a pale yellow solid; mp 70–71 °C; δ_H (270 MHz, $CDCl_3$) 1.40 (t, 3H, *J* 7.6, CH_3), 3.08 (q, 2H, *J* 7.6, CH_2), 4.07 (s, 3H, OCH_3), 7.03 (dd, 1H, *J* 7.9 and 1.6, 7-quinH), 7.32–7.42 (m, 3H, 3,5,6-quinH), 8.04 (d, 1H, *J* 8.5, 4-quinH); *m*/*z* (EI) 157 (44%), 158 (39), 186 (100), 187 (M^+, 66).

2-Ethylquinolin-8-ol (6a)[5]

A mixture of **5a** (620 mg, 3.3 mmol) and 48% HBr (5 ml) was refluxed for 24 h. After cooling to rt, the mixture was neutralized with 5% NaOH and then a pale green precipitate was observed. The precipitate was extracted with chloroform, washed with brine, and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel using hexane–AcOEt (2:1) to yield **6a** as a pale yellow oil (298 mg, 52%); δ_H (270 MHz, $CDCl_3$) 1.39 (t, 3H, *J* 7.6, CH_3), 2.99 (q, 2H, *J* 7.6, CH_2), 7.13 (dd, 1H, *J* 7.6 and 1.3, quinH), 7.25–7.40 (m, 3H, 3,5,6-quinH), 8.03 (d, 1H, *J* 8.6, 4-quinH); *m*/*z* (EI) 172 (100%), 173 (M^+, 98); HRMS (EI) calcd for $C_{11}H_{11}NO$ 173.08406; found 173.08344.

2-Butyl-8-methoxyquinoline (5b)

The title compound **5b** was prepared by the procedure used for **5a**. Reaction of **3** (1.04 g, 6.00 mmol) and 1-bromopropane (1.10 g, 9.00 mmol) with 1.5 M LDA·THF (7.20 mmol) gave **5b** (937 mg, 73%) as a pale yellow solid; mp 32–33 °C; δ_H (270 MHz, $CDCl_3$) 0.96 (t, 3H, *J* 7.3, CH_3), 1.45–1.80 (m, 4H), 3.04 (t, 2H, *J* 8.1, CH_2), 4.07 (s, 3H, OCH_3), 7.02 (dd, 1H, *J* 7.3 and 1.7, 7-quinH), 7.25–7.40 (m, 3H, 3,5,6-quinH), 8.03 (d, 1H, *J* 8.6, 4-quinH); *m*/*z* (EI) 173 (100%), 186 (27), 214 (24), 215 (M^+, 14).

2-*n*-Butylquinolin-8-ol (6b)[5]

The title compound **6b** was prepared by the procedure used for **6a**. Reaction of **5b** (800 mg, 3.97 mmol) with 48% HBr (20 ml) gave **6b** (612 mg, 77%) as a pale yellow oil; δ_H (270 MHz, $CDCl_3$) 0.97 (t, 3H, *J* 7.3, CH_3), 1.42–1.80 (m, 4H), 2.96 (t, 2H, *J* 7.6, CH_2), 7.14 (d, *J* 7.3, 1H, 7-quinH), 7.25–7.40 (m, 3H, 3,5,6-quinH), 8.03 (d, 1H, *J* 8.6, 4-quinH); *m*/*z* (EI) 159 (100%), 172 (21), 186 (15), 201 (M^+, 18); HRMS (EI) calcd for $C_{13}H_{15}NO$ 201.11536; found 201.11629.

2-Bis(trimethylsilyl)methyl-8-methoxyquinoline (7)

To an ice-cooled solution of **3** (349 mg, 2.02 mmol) in THF (10 ml), 1.5 M LDA·THF in cyclohexane (3.0 ml) was added dropwise, and the mixture was stirred at 0 °C for 1 h. Then trimethylsilyl chloride (548 mg, 5.04 mmol) was added dropwise. The reaction mixture was stirred at 0 °C for 30 min, and after removal of the ice-bath it was allowed to warm to rt and was stirred for 1 h. The resulting mixture was poured into water, extracted with chloroform, washed with brine, and dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed twice on silica gel using hexane–AcOEt (3:1) to afford **7** (222 mg, 45%) as a white solid; mp 63–65 °C; δ_H NMR (270 MHz, $CDCl_3$) 0.08 (s, 18H, $2Si(CH_3)_3$), 2.40 (s, 1H, SiCH), 4.04 (s, 3H, OCH_3), 7.03 (dd, 1H, *J* 7.6 and 1.7, 7-quinH), 7.27–7.31 (m, 3H, 3,5,6-quinH), 7.90 (d, 1H, *J* 8.6, 4-quinH); *m*/*z* (FAB) 318 ($M^+ + H$); HRMS (FAB) calcd for $C_{17}H_{28}NO_2Si_2$ 318.17095; found 318.17070.

1,2-Bis(8-methoxyquinolin-2-yl)ethane (8)

To an ice-cooled solution of **3** (346 mg, 2.00 mmol) in THF (5 ml), 1.5 M LDA·THF in THF (5 ml) was added dropwise. The mixture was stirred at 0 °C for 1 h, then $CuCl_2$ (323 mg, 2.40 mmol) was added. After removal of the ice-bath, the reaction mixture was allowed to warm to rt and stirred for 26 h. To remove the precipitates of Cu salts, the mixture was filtered. The filtrate was poured into water, extracted with chloroform, washed with brine, and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel using chloroform–AcOEt (3:1) to yield **8** as a pale yellow solid (63 mg, 18%); mp 174.5–175 °C; δ_H (270 MHz, $CDCl_3$) 3.61 (s, 4H, $2CH_2$), 4.11 (s, 6H, $2OCH_3$), 7.06 (dd, 2H, *J* 7.1 and 1.3, 2 × 7-quinH), 7.33–7.45 (m, 6H, 2 × 3,5,6-quinH), 8.04 (d, 2H, *J* 8.6, 2 × 4-quinH); *m*/*z* (EI) 344 (M^+, 100), 186 (86); HRMS (EI) calcd for $C_{22}H_{20}N_2O_2$ 344.15248; found 344.15379.

1,2-Bis(8-hydroxyquinolin-2-yl)ethane (10)

The title compound **10** was prepared by the procedure used for **6a**. Reaction of **8** (63 mg, 0.19 mmol) with 48% HBr (10 ml) gave **10** (47 mg, 80%) as a pale yellow solid; mp 201.5–202 °C; δ_H (270 MHz, $CDCl_3$) 3.59 (s, 4H, $2CH_2$), 7.14 (dd, 2H, *J* 7.1 and 1.3, 2 × 7-quinH), 7.30 (dd, 2H, *J* 7.3 and 1.3, 2 × 5-quinH), 7.35–7.42 (m, 2H, 2 × 3,6-quinH), 8.06 (d, 2H, *J* 8.3, 2 × 4-quinH); *m*/*z* (FAB) 317 ($M^+ + H$) (Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.92; H, 5.11; N, 8.68%).

1,6-Bis(8-methoxyquinolin-2-yl)hexane (11)

The title compound **11** was prepared by the procedure used for **5a**. Reaction of **3** (1.04 g, 6.00 mmol) and 1,4-dibromobutane (698 mg, 3.30 mmol) with 1.5 M LDA·THF (7.20 mmol) gave **11** (937 mg, 73%) as a pale yellow solid; mp 89.5–90 °C; δ_H (270 MHz, $CDCl_3$) 1.50 (t, 4H, *J* 7.3 Hz, $2CH_2$), 1.83 (s, 4H, $2CH_2$), 3.03 (t, 4H, *J* 8.1, $2CH_2$), 4.07 (s, 6H, $2OCH_3$), 7.03 (dd, 2H, *J* 7.3 and 1.8, 2 × 7-quinH), 7.30–7.42 (m, 6H, 2 × 3,5,6-quinH), 8.02 (d, 2H, *J* 8.3, 2 × 4-quinH); *m*/*z* (EI) 173 (100%), 186 (43), 200 (14), 400 (M^+, 12) (Anal. Calcd for $C_{26}H_{28}N_2O_2$: C, 77.97; H, 7.05; N, 6.99. Found: C, 77.83; H, 7.27; N, 6.91%).

1,6-Bis(8-hydroxyquinolin-2-yl)hexane (12)

The title compound **12** was prepared by the procedure used for **6a**. Reaction of **11** (631 mg, 1.58 mmol) with 48% HBr (40 ml) gave **12** (557 mg, 95%) as a pale green solid; mp 93–94 °C; δ_H (270 MHz, $CDCl_3$) 1.47 (sextet, 4H, *J* 7.6, $2CH_2$), 1.85 (t, 4H, *J* 7.6 Hz, $2CH_2$), 2.96 (t, 4H, *J* 7.6, 2 × CH_2), 7.14 (dd, 2H, *J* 7.6 and 1.3, 2 × 7-quinH), 7.26–7.37 (m, 6H, 2 × 3,5,6-quinH), 8.03 (d, 2H, *J* 7.9, 2 × 4-quinH); *m*/*z* (EI) 172 (100%), 186 (11), 372 (M^+, 28) (Anal. Calcd for $C_{24}H_{24}N_2O_2$: C, 77.39; H, 6.49; N, 7.52. Found: C, 77.46; H, 6.55; N, 7.57%).

Bis(2-ethylquinolin-8-olato)tin(II) (13a)

To 2-ethylquinolin-8-ol **6a** (298 g, 1.72 mmol) in methanol (3 ml), sodium (41 mg, 1.79 mmol) was added. After evolution of hydrogen gas ceased, tin(II) chloride (162 mg, 0.85 mmol) in methanol (5 ml) was added and the mixture was stirred for 1 h at room temperature. Filtration afforded a yellow solid (185 mg, 69%); mp 176–178 °C; δ_H 1.59 (t, 6H, *J* 7.6, $2CH_3$), 3.39 (br s, 4H, $2CH_2$), 6.90 (d, 2H, *J* 7.6, 2 × 7-quinH), 7.00 (d, 2H, *J* 7.5, 2 × 5-quinH), 7.34 (d, 2H, *J* 7.6 and 7.5, 2 × 6-quinH), 7.39 (d, 2H, *J* 8.4, 2 × 3-quinH), 8.19 (d, 2H, *J* 8.4, 2 × 4-quinH); MS (FAB) *m*/*z* 464 (M^+) (Anal. Calcd for $C_{22}H_{20}N_2O_2Sn$: C, 57.06; H, 4.35; N, 6.05. Found: C, 57.34; H, 4.50; N, 6.13%).

Bis(2-butylquinolin-8-olato)tin(II) (13b)

The title compound **13b** was prepared by the procedure used for **13a**. Treatment of 2-*n*-butylquinolin-8-ol **6b** (544 mg, 2.70 mmol) with $SnCl_2$ (256 mg, 1.35 mmol) in alkaline methanol

solution afforded **13b** (494 mg, 35%) as a yellow solid; mp 149.5–150 °C; δ_H (500 MHz, $CDCl_3$) 1.03 (t, 6H, *J* 7.6, $2CH_3$), 1.56 (sextet, 4H, *J* 7.6, $2CH_2$), 2.02 (br s, 4H, $2CH_2$), 3.34 (br s, 4H, $2CH_2$), 6.88 (d, 2H, *J* 7.9, 2 × 7-quinH), 7.00 (d, 2H, *J* 8.0, 2 × 5-quinH), 7.30–7.47 (m, 4H, 2 × 3,6-quinH), 8.16 (d, 2H, *J* 8.4, 2 × 4-quinH); *m*/*z* (FAB) 519 (M^+) (Anal. Calcd for $C_{26}H_{28}N_2O_2Sn$: C, 60.14; H, 5.44; N, 5.40. Found: C, 59.94; H, 5.45; N, 5.37%).

X-Ray crystal structure determination of complex 13b

Crystal data: $C_{26}H_{18}N_2O_2Sn$, $M_r = 519.21$, monoclinic, *C*2/*c*, $a = 11.836(1)$, $b = 19.401(2)$, $c = 10.580(1)$ Å, $\beta = 110.81(1)°$, $V = 2271.0(4)$ Å^3, $D_x = 1.518$ g cm^{-3}, $Z = 4$, $\mu = 11.5$ cm^{-1}, $T = 75$ K.† A yellow needle prepared by slow evaporation from Et_2O was used for data collection with a Rigaku RAXIS-IV imaging plate area detector with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71070$ Å) from a rotating-anode generator operating at 50 kV and 100 mA. Indexing was performed from 3 oscillation images which were exposed for 5 minutes. The data were collected to a maximum 2θ value of 51.3°. In a total of 156° range, 13 oscillation images were collected, each of which was exposed for 30 minutes. A total of 2135 reflections was collected. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[12] and expanded using a Fourier technique.[13] Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1997 observed reflections ($I > 3\sigma(I)$) and 141 variable parameters and converged with $R = 0.050$ and $R_w = 0.067$. All calculations were performed with teXsan for Windows.[14]

† CCDC reference number 207/391. See http://www.rsc.org/suppdata/p1/a9/a908636f for crystallographic files in .cif format.

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References

1 J. P. Phillips, *Chem. Rev.*, 1956, **51**, 271.
2 C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913.
3 M. Albrecht and O. Blau, *Synthesis*, 1997, 213.
4 C. Kitamura, A. Yoneda, K. Sugiura and Y. Sakata, *Acta Crystallogr., Sect. C*, 1999, **55**, 876.
5 H. Kaneko and K. Ueno, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 1910.
6 Z. Ziegler and H. Ziegler, *Justus Liebigs Ann. Chem.*, 1931, **485**, 174.
7 F. E. King and J. A. Sherred, *J. Chem. Soc.*, 1942, 415.
8 C. M. Leir, *J. Org. Chem.*, 1977, **42**, 911.
9 M. Kawase and Y. Kikugawa, *Chem. Pharm. Bull.*, 1981, **29**, 1615.
10 R. I. Papasergio, B. W. Skelton, P. Twiss and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1990, 1661.
11 A. M. Jones and C. A. Russell, *J. Chem. Soc.* (*C*), 1969, 2246.
12 SIR92: A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, M. C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435.
13 DIRDIF94: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, The DIRDIF94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.
14 teXsan for Windows: Crystal Structure Analysis Package, Molecular Structure Corporation, 1997.

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