Di(8-hydroxyquinoline) Derivatives for Supramolecular Chemistry: Syntheses and Solid State Superstructures

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Abstract: The synthesis of the di(8-hydroxyquinoline) derivatives **8–14** is described. Hereby, spacers of different length and nature (alkyl or amide) are introduced. The geometric features of the compounds are changed by connection of the bridging groups to different positions of the 8-hydroxyquinoline moiety. The derivatives thus obtained possess a high potential as ligands for metallo-supramolecular chemistry. In the solid state the alkyl-bridged compounds adopt a polymeric structure by formation of hydrogen-bridges between self-complementary hydroxyquinoline units. The overall structure of the polymer is controlled by the spacer. Introduction of an amide group in 7-position of the quinoline leads to intramolecular hydrogen bonds and suppresses the formation of "dimeric" di(8-hydroxyquinoline) units.

Key words: 8-hydroxyquinoline, hydrogen bonds, supramolecular chemistry, hydrogen bonded polymers, chelating ligands

8-Hydroxyquinoline (**1**) easily can be prepared either by the Skraup, the Friedländer or by the Doebner-von Miller reaction.[1] With various metal ions it forms homoleptic coordination compounds (oxinates) which possess low solubility in polar solvents. Thus **1** frequently is used for analytical purposes or for the extraction of metal ions (e.g. Ga(III)).[2,3] Just recently the 8-hydroxyquinoline moiety was introduced in metallo-supramolecular chemistry to form mono- or dinuclear complexes. Hereby the molecular recognition of specific metal cations or the self-assembly of defined supramolecular aggregates were of major interest. Baret[4] and Hiratami[5] prepared 8-hydroxyquinoline TRIPODS as complexing agents for different metal ions. Recently we described the ethylene-linked di(8-hydroxyquinoline) ligand **3** and developed an example for the new principle of "dynamic combinatorial chemistry".[6,7]

In addition to its ability to form coordination compounds, 8-hydroxyquinoline (**1**) shows a further feature which is valuable for supramolecular chemistry. 8-Hydroxyquinoline (**1**) possesses a hydrogen bond donor/acceptor motif which is self-complementary. Consequently, in the solid state **1** forms a dimer $(\mathbf{1})_2$ by H-bridges between the oxygen atom of one and the nitrogen atom of the other molecule. Hereby a non-covalently linked ten membered ring is obtained.[8] Consequently, di(8-hydroxyquinolines) can act as monomers to form polymeric structures in the solid state. The monomers are connected via hydrogen bridges

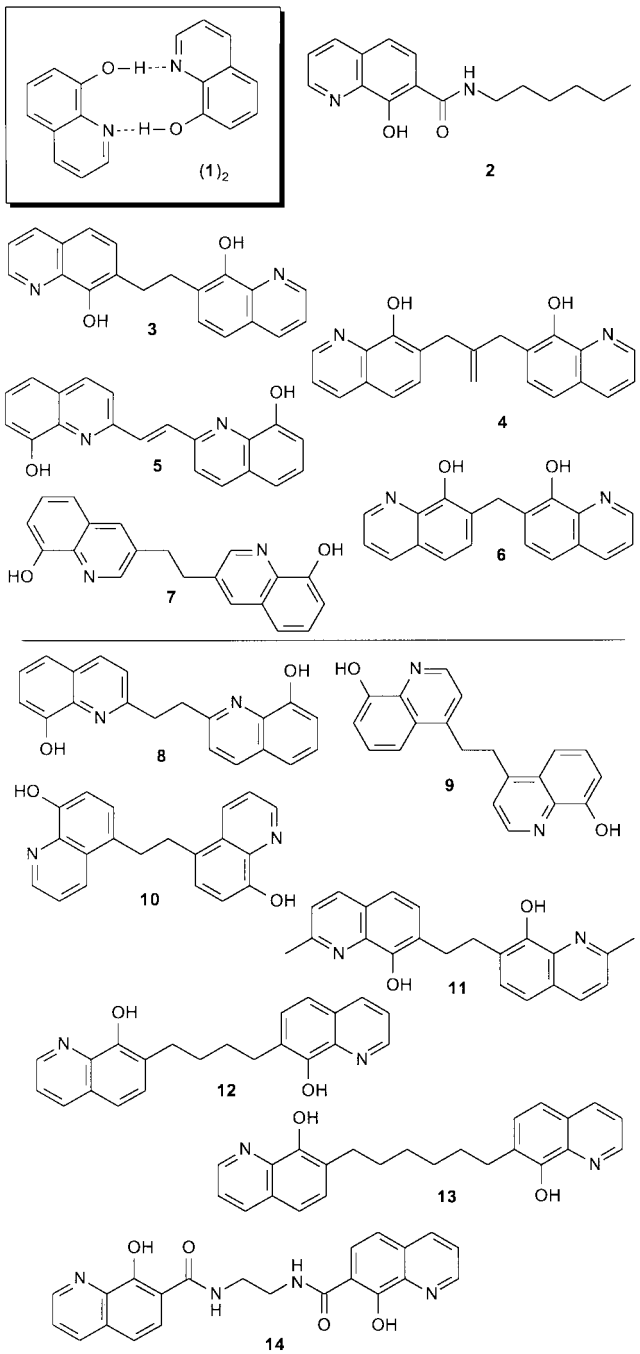


Figure 1 8-Hydroxyquinoline derivatives **1–14** discussed in this study

Biographical Sketches

Markus Albrecht (born 1964) studied Chemistry in Würzburg and Münster and obtained his Dr. rer. nat. in 1992 (Prof. G. Erker). After one year as a postdoctoral fellow in Berkeley (Prof. K. N. Raymond) he moved to Karlsruhe and received his habilitation in 1997. His work on the metal-directed self-assembly of metallo-supramolecular aggregates was honoured with the "ADUC-Jahrespreis für Habilitanden" and with a Heisenberg-fellowship of the DFG.

Oliver Blau was born in 1969 in Karlsruhe. He studied chemistry in Karlsruhe and obtained his Dr. rer. nat in summer 1999. For his work on hydroxyquinoline derivatives he got the "Wolff & Sohn Award" of the University of Karlsruhe.

Karen Witt was born in 1972 in Berlin. She studied chemistry in Karlsruhe and obtained her diploma in 1998. Currently she is performing research in the group of Dr. Albrecht to obtain a Dr. rer. nat in chemistry.

Elina Wegelius, born in 1973, studied chemistry in Jyväskylä (Finland) and finished her diploma thesis on synthetic calixarene ionophores in 1997. She is currently completing her doctorate on the X-ray crystallography of organic and organometallic structures under the supervision of Prof. K. Rissanen. Her work is supported by The Graduate School of Inorganic Material Chemistry (Ministry of Education in Finland).

Maija Nissinen, born in 1974, studied chemistry in Jyväskylä (Finland). In 1997 she finished her diploma thesis on piperazine macrocycles and the synthesis of chiral piperazines. She is currently completing her doctorate on the X-ray crystallography of organic structures under the supervision of Prof. K. Rissanen. Her work is supported by The Graduate School of Bioorganic Chemistry (Ministry of Education in Finland).

Kari Rissanen, born in 1959, studied chemistry in Jyväskylä (Finland) and got his doctorate in 1990 on solid state structural studies of organic compounds. In 1991 he was appointed as a Docent (Privat Dozent) in Chemistry at the University of Jyväskylä. In 1993 he was appointed as an associate professor (C3 professor) in organic chemistry at the University of Joensuu. Since 1995 he has worked as a full professor (C4) and the Head of the Laboratory of Organic Chemistry at the University of Jyväskylä. His research interest vary from Structural Chemistry into synthetic Supramolecular and Organic Chemistry.

Roland Fröhlich, born in 1952, studied chemistry in Münster and Cologne and received his Dr. rer. nat. in 1982. After postdoctoral studies in the crystallographic institute of the University of Karlsruhe he worked as a sales and application manager for Enraf Nonius. Since 1993 he is a senior scientist at the University of Münster and since 1994 a docent for X-ray crystallography at the University of Jyväskylä.

while the structure of the polymeric strand is dictated by the nature of the spacer.

In preliminary investigations we could show that alkyl-bridged di(8-hydroxyquinoline) derivatives **3** and **4** form polymeric superstructures in the solid state. While the compound **3** forms a "doubly wound" polymer,[6] derivative **4**, which was first synthesized by Hiratami et al,[9] leads to a zigzag-type structure (Figure 2).[7]

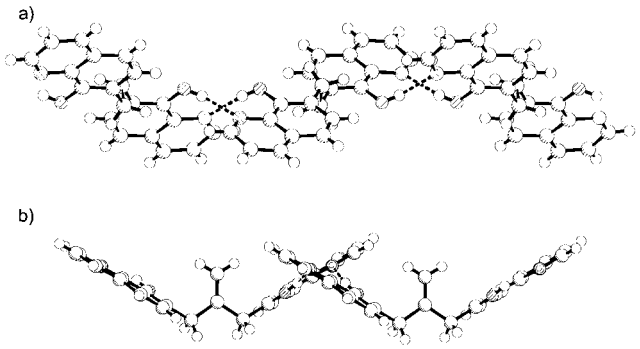


Figure 2 The hydrogen bonded polymeric structure of **3** ("doubly wound", (a)) and **4** ("zigzag", (b)) in the solid state

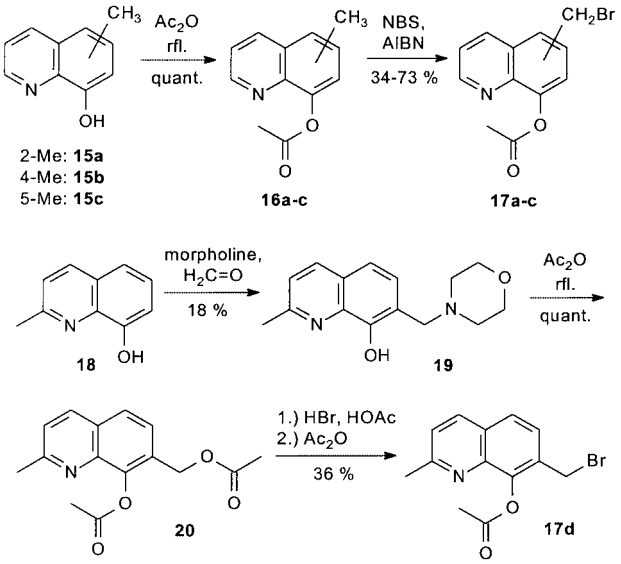
However the *E*-alkene bridged di(8-hydroxyquinoline) derivative **5** does not show such a polymeric structure. Probably due to steric reasons only hydrogen bonding between the phenolic units occurs.[10]

Herein we describe the syntheses of a number of alkyl-bridged di(8-hydroxyquinoline) derivatives **8–13** and of an analogous compound **14** with an amide linkage in the spacer. Related derivatives were described earlier by us (**3,7**)[6] and others (**4–6**).[9–11] The X-ray structure of the amide substituted 8-hydroxyquinoline **2** shows that the possibility of intramolecular hydrogen bonding suppresses the intermolecular formation of hydrogen bridged ten membered rings. Additionally two representative X-ray structures of the polymeric strands of **6** and **8** are discussed, which lead to a concept for the control of the polymeric superstructure in the solid state.

Results and Discussion

Syntheses of Di(8-hydroxyquinoline) Derivatives

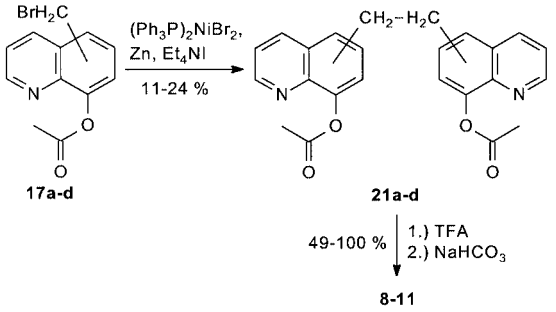
The structure of (metallo)-supramolecular aggregates highly depends on the geometric features of the molecular components.[12] To introduce different geometries in $(CH_2)_2$-linked di(8-hydroxyquinoline) derivatives we synthesized the compounds **8–10**. The spacers are connected to different positions of the hydroxyquinoline moiety. In derivative **11** additional methyl groups are present which should introduce steric constraints during the self-assembly of supermolecules. For the preparation of the ethylene-linked compounds **8–11** we followed a route which was developed by us[13] using a Ni-catalyzed homocoupling of benzyl bromides[14] which was described by Iyoda and Oda[15] in the keystep of the reaction sequence. Therefore appropriate benzyl bromides **17a–d** had to be prepared first.



Scheme 1

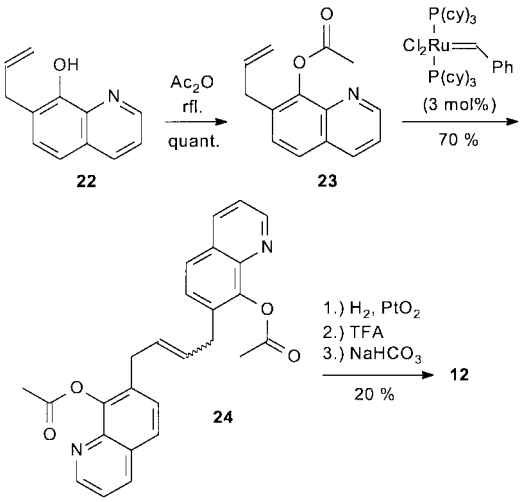
The syntheses of 8-acetoxyquinolines which bear bromomethyl substituents in 2- (**17a**), 4- (**17b**) or 5-position (**17c**) were performed starting from the hydroxyquinoline derivatives **15**.[3,16,17] After quantitative acylation of the hydroxy function, the bromo substituent was introduced by Wohl-Ziegler reaction with *N*-bromosuccinimide (NBS) and α,α'-azabisisobutyronitrile (AIBN) in CCl_4. The compounds were obtained in 34% (**17a**), 38% (**17b**), and 73% (**17c**) respectively. The corresponding methyl-substituted derivative **17d** was prepared starting from chinaldine (**18**). A Mannich-type reaction of **18** with formaline and morpholine in 18% yield introduces a *N*-morpholinomethyl group in 7-position of **19**. By reaction with acetic anhydride the *N*-morpholinomethyl substituent is quantitatively transformed into an acetoxymethyl group. Simultaneously the hydroxy function is protected as an acetate. The diacetate **20** reacts with HBr in glacial acetic acid to obtain bromide **17d** after workup in 36% yield.[13] However, **19d** easily can be obtained over three steps (starting from **18**) without purification of the intermediates **19** or **20**.

The benzyl bromides **17** are coupled in a mild homocoupling procedure following the protocol of Iyoda and Oda[15] by using the $(Ph_3P)_2NiBr_2/Zn/Et_4NI$ system.[14] However due to solubility problems the yields of the acetyl protected hydroxyquinoline derivatives **21a–d** are low (11–24%). Deprotection is performed by reaction with trifluoroacetic acid followed by workup under basic conditions. In the case of **8, 9** and **11** this reaction proceeds quantitatively while **10** (low solubility) is obtained in only 49% yield.



Scheme 2

To introduce a $(CH_2)_4$-spacer, we started from 7-allyl-8-hydroxyquinoline (**22**) (which can be easily prepared by Claisen rearrangement of 8-allyloxyquinoline)[18] and protected the hydroxy functionality by reaction with acetic anhydride. In the following step a C4-spacer was obtained by metathesis reaction with Grubbs catalyst.[19] Derivative **24** was prepared in 70% yield as a mixture of the double bond isomers (ratio of 6:1).

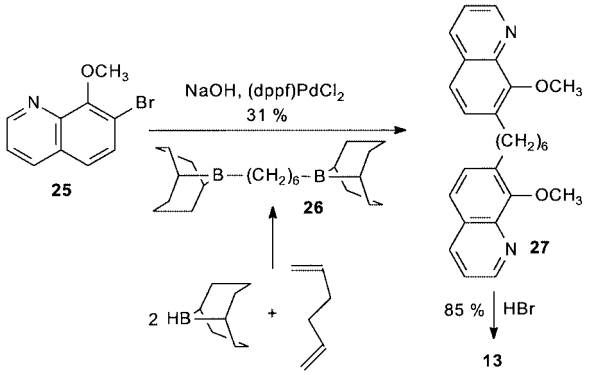


Scheme 3

In the final step the alkene moiety of **24** was reduced with hydrogen in the presence of platinum dioxide[20] and the protecting groups were removed subsequently to obtain **12** in 20% yield. Here the low yields are due to the sensitivity of the hydroxyquinoline unit. As a side reaction reduction of the heterocyclic portion could be observed.

Establishment of a $(CH_2)_6$-spacer[21] to obtain **13** is achieved by a double Suzuki reaction.[22]

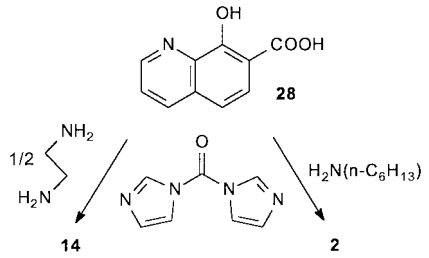
Hexa-1,5-diene can be hydroborated twice by reaction with 9-BBN.[22] The resulting diboron compound **26** in situ is coupled with 7-bromo-8-methoxyquinoline (**25**)[23] in the presence of sodium hydroxide and $(dppf)PdCl_2$ as catalyst. The derivative **27** which by this procedure is obtained in 31% yield is deprotected by ether cleavage with HBr to yield the di(hydroxyquinoline) derivative **13** in 85% yield. This Suzuki coupling strategy for the synthesis of alkyl-



Scheme 4

bridged di(8-hydroxyquinoline) compounds opens a way to prepare analogous derivatives with even longer spacer length.

For comparison we additionally synthesized one di(8-hydroxyquinoline) derivative **14** with amide units in the spacer. Compound **14** was obtained in 85% yield by reaction of 7-carboxy-8-hydroxyquinoline (**28**) with ethylenediamine in the presence of carbonyl diimidazole as coupling reagent.[4] By analogous reaction of **28** with hexylamine the mono(8-hydroxyquinoline) derivative **2** was prepared in 89% yield.



Scheme 5

The Solid State Structures of 2–4, 6 and 8

As already described, 8-hydroxyquinoline (**1**) forms a dimeric structure in the solid state.[8] In the amide substituted compound **2** an additional functionality, which can form hydrogen bonds, is introduced and should influence the structure of the compound in the solid state.

In the crystal, **2** forms an intramolecular hydrogen bond between the phenolic OH group and the amide carbonyl function leading to a favorable six membered ring (Figure 3a). Similar intramolecular interactions were already observed in e.g. related catechol amide derivatives.[24]

Additional intermolecular hydrogen bonding occurs between the nitrogen atom of the quinoline moiety and the amide proton of **2**. This shows that in derivatives like **2** (or **14**) no hydrogen bonded ten membered rings are formed. The OH group is blocked by intramolecular bridging with

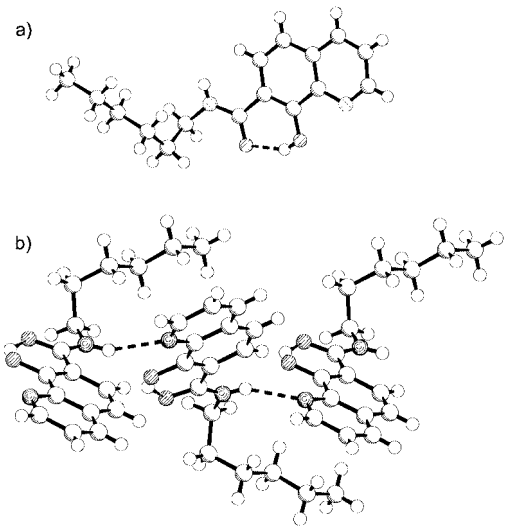


Figure 3 Representations of the molecular structure of the monomeric **2** (a) and of the hydrogen bonded network (b) in the solid state

the carbonyl oxygen atom and the resulting H-donor/acceptor functions are able to undergo other interactions (Figure 3b).

In case of the alkyl bridged derivatives no such intramolecular binding can occur. Therefore polymeric strands are formed which possess as connecting units doubly hydrogen bridged ten membered rings.[25]

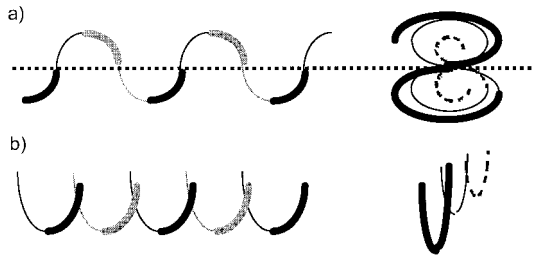


Figure 4 Schematic representation of a "doubly wound" polymer (a) and of a "zigzag" polymer (b)

Figure 4 shows schematic representations of the structures of the polymeric chains of the already described X-ray structures of **3** (a) and **4** (b) (see Figure 2). In the case of **3** the ethylene spacer leads to a "Z"-type structure of the monomer. Hydrogen bridging between monomers results in a polymeric chain which is "doubly wound". This means that the polymeric chain contains alternating left and right turns as it is depicted in Figure 4a (left: side view; right: view along the polymer chain).[6]

Compound **4** on the other hand adopts a "V"-type monomer structure which in the polymer leads to a zigzag chain as it is shown in Figure 4b.[7]

Our assumption was, that the structure of the polymer is controlled by the nature of the spacer. In case of alkyl spacers the preferred zigzag conformation should lead to "Z"-type monomers if an even number of carbon atoms are in the spacer while an odd number should prefer the "V"-type structure. Consequently the "Z"-type monomers should form polymers as it is shown in Figure 4a while the "V"-type monomers should lead to polymers as depicted in Figure 4b. To check this perception we crystallized the $(CH_2)_2$-bridged derivative **8** and the CH_2-bridged **6** and performed additional X-ray structural analyses.

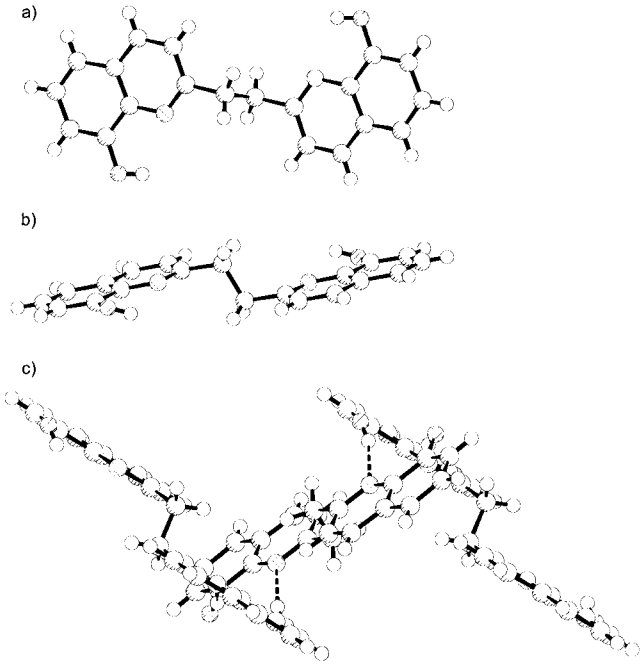


Figure 5 The solid state structure of **8** (monomer: top view (a), side view (b); polymeric strand (c)).

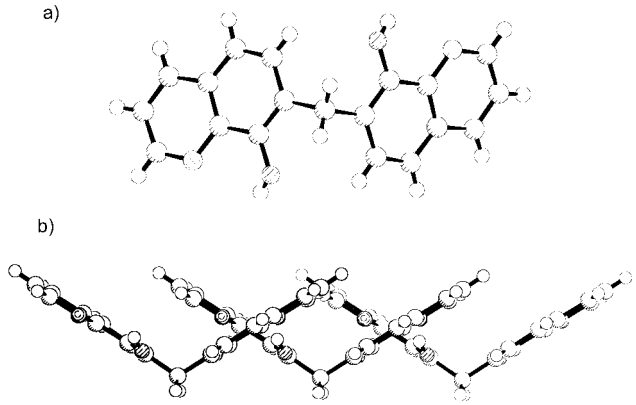


Figure 6 The solid state structure of **6** (monomer (a), polymeric strand (b))

Derivative **8** possesses an ethylene spacer which is attached to the 2-positions of the two 8-hydroxyquinoline moieties. Figure 5 shows the structure of the monomeric (a: top view, b: side view) and polymeric structure (c) in the solid state. As expected the monomer adopts a "Z"-type structure and forms a polymeric chain which is "doubly wound" as shown in Figure 4a.

In contrast to **8** the derivative **6** which is depicted in Figure 6 possesses only one methylene group in the spacer. Therefore **6** adopts a "V"-type structure leading to a "zig-zag" polymer (Figure 4b).

Thus, for polymeric **6** a structure is observed which is closely related to the one of compound **4**.

Conclusion

We described the preparation of a number of di(8-hydroxyquinoline) derivatives which are potential candidates as building blocks for supramolecular as well as metallo-supramolecular chemistry.[26] The compounds show a broad variation in their geometry, the spacer length and the nature of the spacer (alkyl versus amide linkage). As key steps in the reaction sequences different transition metal catalysed coupling reactions were performed. At the moment investigations towards the coordination behavior and the formation of supramolecular coordination compounds are going on in our laboratories.

In the second part of this paper we showed that our alkyl bridged compounds by hydrogen bonding are able to form polymeric strands in the solid state. The structure of the polymers highly depends on the length of the spacer. Compounds with an even number of atoms in the spacer lead to a "doubly wound" kind of polymer while derivatives with an odd number of spacer atoms result in a "zig-zag" polymer chain. A similar structural control mechanism was observed earlier by us in the formation of dinuclear helicates from alkyl-bridged ligands with an even number of atoms in the spacer. An odd number on the other hand favours the formation of the corresponding meso-helicate.[27]

If an amide group is connected to the 7-position of the quinoline, intramolecular hydrogen bonding takes place and suppresses the formation of ten membered rings.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 500, AM 400, or WM 250 NMR spectrometer using DEPT techniques for the assignment of the multiplicity of carbon atoms. FT-IR spectra were recorded by diffuse reflection (KBr) on a Bruker IFS spectrometer. Mass spectra (EI, 70 eV or FAB(+), 3-NBA as matrix) were taken on a Finnigan MAT 90 mass spectrometer. Elemental analyses were obtained with a Heraeus CH*N-O*-Rapid analyzer. Solvents were purified by standard methods. Melting points: Büchi 535 (uncorrected). Air sensitive compounds were prepared and handled under Ar using Schlenk techniques.

Methylquinolin-8-yl Acetates (16); General Procedure
8-Hydroxymethylquinoline **15**[3,16,17] is refluxed in Ac_2O (50 mL) for 15 h. The mixture is evaporated and the residue is dissolved in CH_2Cl_2, washed with aq $NaHCO_3$, dried ($MgSO_4$) and taken to dryness to obtain methylquinolin-8-yl acetates **16**.

2-Methylquinolin-8-yl Acetate (16a)
Yield: Quant.; yellow oil.

^{1}H NMR ($CDCl_3$): δ = 8.02 (d, *J* = 8.4 Hz, 1 H), 7.65 (dd, *J* = 1.5, 8.0 Hz, 1 H), 7.44 (t, *J* = 8.0 Hz, 1 H), 7.44 (d, *J* = 1.5 Hz, 1 H), 7.27 (d, *J* = 8.4 Hz, 1 H), 2.72 (s, 3 H), 2.51 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 170.0 (C), 159.4 (C), 146.9 (C), 140.6 (C), 136.0 (CH), 127.7 (C), 125.5 (CH), 125.2 (CH), 122.6 (CH), 121.3 (CH), 25.7 (CH_3), 21.0 (CH_3).

IR (KBr): ν = 3390, 3053, 2922, 1771, 1601, 1502, 1431, 1368, 1203, 1082, 761 cm^{-1}.

MS: m/z (%) = 201 (2) $[M]^+$, 159 (100) $[M–C_2H_2O]^+$.

HRMS (EI, 70 eV): $C_{12}H_{11}NO_2$ (201.23): requires: M 201.0790; found M^+201.0779.

4-Methylquinolin-8-yl Acetate (16b)
Yield: Quant.; brown solid; mp 83-85 °C.

^{1}H NMR ($CDCl_3$): δ = 8.75 (d, *J* = 4.0 Hz, 1 H), 7.84 (dd, *J* = 1.0, 8.3 Hz, 1 H), 7.49 (dd, *J* = 7.6, 8.3 Hz, 1 H), 7.42 (dd, *J* = 1.0, 7.6 Hz, 1 H), 7.21 (d, *J* = 4.0 Hz, 1 H), 2.64 (s, 3 H), 2.49 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 169.7 (C), 150.0 (CH), 147.6 (C), 144.4 (C), 140.9 (C), 129.5 (C), 125.7 (CH), 122.4 (CH), 121.9 (CH), 121.1 (CH), 20.9 (CH_3), 18.7 (CH_3).

IR (KBr): ν = 3062, 3041, 2986, 2936, 1763, 1508, 1370. 1222, 1206, 1172, 1156, 836, 757 cm^{-1}.

MS: m/z (%) = 201 (2) $[M]^+$, 159 (100) $[M–C_2H_2O]^+$.

HRMS (EI, 70 eV): $C_{12}H_{11}NO_2$ (201.23): requires: M 201.0790; found M^+201.0797.

$C_{12}H_{11}NO_2$ (201.23):	calc.	C 71.63	H 5.51	N 6.96
	found	C 71.32	H 5.63	N 6.47

5-Methylquinolin-8-yl Acetate (16c)
Yield: Quant.; brown solid; mp 77–78 °C.

^{1}H NMR ($CDCl_3$): δ = 8.98 (dd, *J* = 1.6, 4.2 Hz, 1 H), 8.33 (dd, *J* = 1.6, 8.5 Hz, 1 H), 7.47 (dd, *J* = 4.2, 8.5 Hz, 1 H), 7.35 (s, 2 H), 2.65 (s, 3 H), 2.50 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 170.1 (C), 149.9 (CH), 145.4 (C), 141.0 (C), 133.2 (CH), 132.8 (C), 128.7 (C), 126.5 (CH), 121.4 (CH, double intensity), 21.0 (CH_3), 18.4 (CH_3)

IR (KBr): ν = 3037, 2931, 1756, 1501, 1371, 1210, 1063, 902, 795 cm^{-1}.

MS: m/z (%) = 201 (2) $[M]^+$, 159 (100) $[M–C_2H_2O]^+$.

HRMS (EI, 70 eV): $C_{12}H_{11}NO_2$ (201.23): requires: M 201.0790; found M^+201.0800.

$C_{12}H_{11}NO_2 \cdot ½\ H_2O$:	calc.	C 68.56	H 5.75	N 6.66
	found	C 68.55	H 5.68	N 6.44

(Bromomethyl)quinolin-8-yl Acetate (17a–c); General Procedure
8-Acetoxymethylquinoline (**16**, approx. 10 mmol) is dissolved in CCl_4 (15 mL) under Ar, 1 equiv. of NBS (*N*-bromosuccinimide) and of AIBN (50 mg) are added and the mixture is refluxed overnight. Solvent is evaporated and the residue is dissolved in CH_2Cl_2 (150 mL), washed with aq $NaHCO_3$ (3 x 50 mL), dried ($MgSO_4$) and solvent is removed in vacuo. The crude product is purified by column chromatography (silica gel, hexane / EtOAc 5:1).

2-(Bromomethyl)quinolin-8-yl Acetate (17a)
Yield: 34%; yellow solid; mp 71–73 °C.

^{1}H NMR ($CDCl_3$): δ = 8.15 (d, *J* = 8.6 Hz, 1 H), 7.68 (dd, *J* = 1.4, 8.2 Hz, 1 H), 7.58 (d, *J* = 8.6 Hz, 1 H), 7.52 (dd, *J* = 7.6, 8.2 Hz, 1 H), 7.45 (dd, *J* = 1.4, 7.6 Hz, 1 H), 4.69 (s, 2 H), 2.52 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 169.8 (C), 156.9 (C), 147.4 (C), 140.2 (C), 137.2 (CH), 128.5 (C), 126.7 (CH), 125.6 (CH), 121.9 (CH), 34.5 (CH_2), 21.0 (CH_3).

IR (KBr): ν = 3060, 1768, 1502, 1370, 1204, 1077, 827, 690 cm^{-1}.

MS: m/z (%) = 279 (1) $[M]^+$, 158 (100) $[M–C_2H_2OBr]^+$.

HRMS (EI, 70 eV): $C_{12}H_{10}NO_2Br$ (280.12): requires: M 278.9895; found M^+278.9875.

$C_{12}H_{10}NO_2Br$:	calc.	C 51.45	H 3.60	N 5.00
	found	C 51.91	H 3.70	N 5.04

4-(Bromomethyl)quinolin-8-yl Acetate (17b)
Yield: (38%); green solid (containing approx. 15% of **16b**).

^{1}H NMR ($CDCl_3$): δ = 8.86 (d, *J* = 4.4 Hz, 1 H), 8.01 (dd, *J* = 1.2, 8.5 Hz, 1 H), 7.63 (dd, *J* = 7.6, 8.5 Hz, 1 H), 7.47 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.43 (d, *J* = 4.4 Hz, 1 H), 4.81 (s, 2 H), 2.51 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 170.0 (C), 150.2 (CH), 147.9 (C), 142.6 (C), 141.7 (C), 127.3 (C), 126.8 (CH), 122.0 (CH), 121.9 (CH), 121.6 (CH), 28.2 (CH_2), 21.0 (CH_3).

MS: m/z (%) = 281 (1) $[M]^+$, 158 (100) $[M–C_2H_2OBr]^+$.

HRMS (EI, 70 eV): $C_{12}H_{10}NO_2Br$ (280.12): requires: M 278.9895; found M^+278.9881.

4-(Bromomethyl)quinolin-8-yl acetate (**17b**) is used without further purification.

5-(Bromomethyl)quinolin-8-yl Acetate (17c)
Yield: 73%; light brown solid; mp 134–135 °C.

^{1}H NMR ($CDCl_3$): δ = 8.95 (dd, *J* = 1.6, 4.2 Hz, 1 H), 8.47 (dd, *J* = 1.6, 8.6 Hz, 1 H), 7.58 (d, *J* = 7.7 Hz, 1 H), 7.54 (dd, *J* = 4.2, 8.6 Hz, 1 H), 7.36 (d, *J* = 7.7 Hz, 1 H), 4.88 (s, 2 H), 2.50 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 169.6 (C), 150.6 (CH), 148.3 (C), 141.7 (C), 132.5 (CH), 131.8 (C), 127.8 (CH), 127.6 (C), 121.9 (CH), 121.8 (CH), 121.0 (CH), 29.7 (CH_2), 21.0 (CH_3).

IR (KBr): ν = 3492, 1759, 1505, 1227, 1207, 1151, 1063, 907, 788, 704 cm^{-1}.

MS: m/z (%) = 279 (1) $[M]^+$, 158 (100) $[M–C_2H_2OBr]^+$.

HRMS (EI, 70 eV): $C_{12}H_{10}NO_2Br$ (280.12): requires: M 278.9895; found M^+278.9883.

$C_{12}H_{10}NO_2Br \cdot ½\ H_2O$:	calc.	C 49.85	H 3.83	N 4.84
	found	C 49.79	H 3.91	N 4.76

2-Methyl-7-(morpholin-4-ylmethyl)quinolin-8-ol (19)
2-Methylquinolin-8-ol **18** (5.00 g, 31.4 mmol) is dissolved in EtOH (90 ml) and morpholine (2.73 ml, 31.4 mmol) and formaline (3.70 ml, 53.4 mmol) are added. The mixture is stirred for 15 h at r.t. and solvent is removed in vacuo. The crude product is purified by column chromatography (gradient: $CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH 49:1); yield: 1.45 g (18%); yellow oil.

^{1}H NMR ($CDCl_3$): δ = 7.88 (d, *J* = 8.4 Hz, 1 H), 7.17 (d, *J* = 8.4 Hz, 1 H), 7.14 (d, *J* = 8.4 Hz, 1 H), 7.12 (d, *J* = 8.4 Hz, 1 H), 3.77 (s, 2 H), 3.70 (t, *J* = 4.7 Hz, 4 H), 2.68 (s, 3 H), 2.54 (br s, 4 H).

^{13}C NMR ($CDCl_3$): δ = 157.4 (C), 151.7 (C), 138.2 (C), 135.7 (CH), 126.8 (CH), 126.3 (C), 122.1 (CH), 117.3 (C), 117.1 (CH), 66.9 (CH_2), 60.0 (CH_2), 52.9 (CH_2), 25.2 (CH_3).

MS: m/z (%) = 258 (1) $[M]^+$, 73 (100) $[M–C_4H_7NO]^+$.

HRMS (EI, 70 eV): $C_{15}H_{18}N_2O_2$ (258.32): requires: M 258.1368; found M^+258.1355.

7-[(Acetyloxy)methyl]-2-methylquinolin-8-yl Acetate (20)
2-Methyl-7-(morpholin-4-ylmethyl)quinolin-8-ol (**19**) (1.45 g, 5.74 mmol) is refluxed for 15 h in Ac_2O (20 mL). After evaporation of the solvent, the remaining oil is dissolved in CH_2Cl_2 (50 mL), washed with aq $NaHCO_3$ (3 times), dried ($MgSO_4$), and the CH_2Cl_2 is removed in vacuo; yield: 1.57 g (quant.); brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.93 (d, *J* = 8.5 Hz, 1 H), 7.57 (d, *J* = 8.5 Hz, 1 H), 7.45 (d, *J* = 8.5 Hz, 1 H), 7.20 (d, *J* = 8.5 Hz, 1 H), 5.23 (s, 2 H), 2.64 (s, 3 H), 2.47 (s, 3 H), 2.04 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 170.5 (C), 129.3 (C), 159.4 (C), 145.2 (C), 140.2 (C), 135.6 (CH), 127.8 (C), 127.3 (C), 125.9 (CH), 125.0 (CH), 122.6 (CH), 61.1 (CH_2), 25.4 (CH_3), 20.6 (CH_3), 20.5 (CH_3).

IR (KBr): ν = 3366, 2965, 2927, 2859, 2586, 1770, 1742, 1609, 1513, 1431, 1368, 1233, 1199, 1085, 1028 cm^{-1}.

MS: m/z (%) = 273 (5) $[M]^+$, 231 (100) $[M–C_2H_2O]^+$, 189 (13) $[M–C_4H_4O_2]^+$.

HRMS (EI, 70 eV): $C_{15}H_{15}NO_4$ (273.29): requires: M 273.1001; found M^+273.1015.

7-(Bromomethyl)-2-methylquinolin-8-yl Acetate (17d)
7-[(Acetyloxy)methyl]-2-methylquinolin-8-yl acetate (**20**) (2.50 g, 9.58 mmol) is dissolved in CH_2Cl_2 (25 mL) and a 30% solution of HBr in glacial acetic acid (75 mL) is added. After 3 days at r.t. Ac_2O (9.5 ml) is added. Volatile components are removed in vacuo and the residue is purified by column chromatography (silica gel, hexane/EtOAc 1:2); yield: 1.00 g (36%); yellow solid; mp 162–164 °C.

^{1}H NMR ($CDCl_3$): δ = 8.01 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1 H), 7.49 (d, *J* = 8.5 Hz, 1 H), 7.29 (d, *J* = 8.4 Hz, 1 H), 4.62 (s, 2 H), 2.73 (s, 3 H), 2.57 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 169.3 (C), 159.9 (C), 145.2 (C), 140.3 (C), 136.1 (CH), 129.7 (C), 127.6 (C), 126.9 (CH), 125.6 (CH), 123.0 (CH), 27.2 (CH_2), 25.6 (CH_3), 20.9 (CH_3).

IR (KBr): ν = 3047, 2986, 1769, 1444, 1428, 1372, 1213, 1204, 1176, 1081, 842 cm^{-1}.

MS: m/z (%) = 293 (1) $[M]^+$, 251 (7) $[M–C_2H_2O]^+$, 158 (100) $[M–C_2H_2OBr]^+$.

HRMS (EI, 70 eV): $C_{13}H_{12}NO_2Br$ (294.15): requires: M 293.0052; found M^+293.0065.

$C_{13}H_{12}NO_2Br$ (294.15):	calc.	C 53.08	H 4.11	N 4.76
	found	C 52.57	H 4.31	N 4.14

1,2-Di(8-acetoxyquinolinyl)ethane (21); General Procedure
Dibromobis(triphenylphosphane)nickel (350 mg, 0.47 mmol), tetraethylammonium iodide (2.43 g, 9.43 mmol) and activated zinc (925 mg, 14.1 mmol) are suspended in anhyd THF (20 mL) under Ar.[15] The mixture is stirred for 3 h and a solution of (bromomethyl)quinolin-8-yl acetate **17** (3.14 mmol) in THF (20 mL) is added. After 3 h the solvent is removed in vacuo and the residue is chromatographed (silica gel, hexane / EtOAc 1:2).

1,2-Di(8-acetoxyquinolin-2-yl)ethane (21a)
Yield: 17%; yellow solid; mp 130 °C.

^{1}H NMR ($CDCl_3$): δ = 7.99 (d, *J* = 8.5 Hz, 2 H), 7.63 (dd, *J* = 1.7, 7.9 Hz, 2 H), 7.44 (dd, *J* = 7.5, 7.9 Hz, 2 H), 7.41 (dd, *J* = 1.7, 7.5 Hz, 2 H), 7.27 (d, *J* = 8.5 Hz, 2 H), 3.55 (s, 4 H), 2.51 (s, 6 H).

^{13}C NMR ($CDCl_3$): δ = 169.8 (C), 161.7 (C), 147.2 (C), 140.5 (C), 136.0 (CH), 128.0 (C), 125.5 (CH), 125.3 (CH), 122.4 (CH), 121.1 (CH), 37.4 (CH_2), 20.9 (CH_3).

IR (KBr): ν = 3391, 3062, 2913, 1756, 1503, 1433, 1208, 1076, 835, 755 cm^{-1}.

MS: m/z (%) = 400 (1) $[M]^+$, 159 (100) $[M–C_{14}H_{11}NO_3]^+$.

HRMS (EI, 70 eV): $C_{24}H_{20}N_2O_4$ (400.43): requires: M 400.1423; found M^+400.1415.

$C_{24}H_{20}N_2O_4 \cdot {}^1/_4\ H_2O$:	calc.	C 71.19	H 5.10	N 6.92
	found	C 70.83	H 5.20	N 6.96

1,2-Di(8-acetoxyquinolin-4-yl)ethane (21b)
Yield: 18%; yellow solid; mp 206–208 °C.

^{1}H NMR ($CDCl_3$): δ = 8.79 (d, *J* = 4.3 Hz, 2 H), 7.91 (dd, *J* = 1.0, 8.5 Hz, 2 H), 7.57 (dd, *J* = 7.5, 8.5 Hz, 2 H), 7.47 (dd, *J* = 1.0, 7.5 Hz, 2 H), 7.20 (d, *J* = 4.3 Hz, 2 H), 3.52 (s, 4 H), 2.52 (s, 6 H).

^{13}C NMR ($CDCl_3$): δ = 169.9 (C), 150.2 (CH), 148.2 (C), 146.6 (C), 141.5 (C), 128.6 (C), 126.4 (CH), 121.5 (CH), 121.4 (CH), 121.2 (CH), 32.3 (CH_2), 21.1 (CH_3).

IR (KBr): ν = 1767, 1593, 1507, 1221, 1199, 1175, 856, 756 cm^{-1}.

MS: m/z (%) = 400 (1) $[M]^+$, 316 (100) $[M–C_4H_4O_2]^+$.

HRMS (EI, 70 eV): $C_{24}H_{20}N_2O_4$ (400.43): requires: M 400.1423; found M^+400.1399.

$C_{24}H_{20}N_2O_4 \cdot ½\ H_2O$:	calc.	C 70.40	H 5.17	N 6.84
	found	C 70.09	H 5.17	N 6.74

1,2-Di(8-acetoxyquinolin-5-yl)ethane (21c)
Yield: 11%; yellow solid; mp 231–233 °C.

^{1}H NMR ($CDCl_3$): δ = 8.92 (dd, *J* = 1.5, 4.2 Hz, 2 H), 8.24 (dd, *J* = 1.5, 8.5 Hz, 2 H), 7.41 (dd, *J* = 4.2, 8.5 Hz, 2 H), 7.35 (d, *J* = 7.8 Hz, 2 H), 7.32 (d, *J* = 7.8 Hz, 2 H), 3.45 (s, 4 H), 2.51 (s, 6 H).

^{13}C NMR ($CDCl_3$): δ = 169.9 (C), 150.1 (CH), 146.2 (C), 141.4 (C), 135.9 (C), 132.1 (CH), 127.9 (C), 126.0 (CH), 121.5 (CH), 121.1 (CH), 29.7 (CH_2), 21.1 (CH_3).

IR (KBr): ν = 3430, 2925, 2855, 1762, 1365, 1213, 1065, 902, 786, 700 cm^{-1}.

FAB(+) MS: m/z (%) = 401 (10) $[MH]^+$.

1,2-Di(8-acetoxy-2-methylquinolin-7-yl)ethane (21d)
Yield: 24%; white solid; mp 158–160 °C.

^{1}H NMR ($CDCl_3$): δ = 7.97 (d, *J* = 8.4 Hz, 2 H), 7.53 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 7.24 (d, *J* = 8.4 Hz, 2 H), 3.11 (s, 4 H), 2.72 (s, 6 H), 2.57 (s, 6 H).

^{13}C NMR ($CDCl_3$): δ = 170.0 (C), 159.3 (C), 144.7 (C), 140.7 (C), 135.9 (CH), 133.4 (C), 127.4 (CH), 126.3 (C), 125.0 (CH), 122.0 (CH), 31.1 (CH_2), 25.8 (CH_3), 20.9 (CH_3).

IR (KBr): ν = 3404, 1770, 1509, 1368, 1201, 1170, 1077, 841 cm^{-1}.

MS: m/z (%) = 428 (2) $[M]^+$, 386 (18) $[M–C_2H_2O]^+$, 344 (7) $[M–C_4H_4O_2]^+$, 172 (100) $[M–C_{15}H_{14}NO_3]^+$.

HRMS (EI, 70 eV): $C_{26}H_{24}N_2O_4$ (428.49): requires: M 428.1736; found M^+428.1724.

$C_{26}H_{24}N_2O_4$:	calc.	C 72.88	H 5.65	N 6.54
	found	C 72.41	H 5.80	N 6.51

1,2-Di(8-hydroxyquinolinyl)ethane; General Procedure
1,2-Di(8-acetoxyquinolinyl)ethane **21** (approx. 0.5 mmol) is dissolved in MeOH (10 mL) and 10 drops of TFA are added. The mixture is stirred for 3 days at r.t. and then the solvent is evaporated. The residue is dissolved in CH_2Cl_2 (30 mL), washed with aq $NaHCO_3$ (3 times), dried ($MgSO_4$) and solvent is removed in vacuum.

1,2-Di(8-hydroxyquinolin-2-yl)ethane (8)
Yield: Quant.; yellow solid; mp 164 °C.

^{1}H NMR ($CDCl_3$): δ = 8.20 (br s, 2 H), 8.05 (d, *J* = 8.4 Hz, 2 H), 7.39 (pseudo t, *J* = 7.7 Hz, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 7.28 (dd, *J* = 1.0, 7.7 Hz, 2 H), 7.14 (dd, *J* = 1.0, 7.7 Hz, 2 H), 3.58 (s, 4 H).

^{13}C NMR ($CDCl_3$): δ = 159.4 (C), 151.8 (C), 137.7 (C), 136.4 (CH), 126.9 (CH), 122.5 (CH), 117.7 (CH), 109.9 (CH), 37.0 (CH_2); one C is not observed.

IR (KBr): ν = 2939, 1570, 1509, 1455, 1443, 1273, 1247, 839, 752, 699 cm^{-1}.

MS: m/z (%) = 316 (100) $[M]^+$.

HRMS (EI, 70 eV): $C_{20}H_{16}N_2O_2$ (316.36): requires: M 316.1212; found M^+316.1198.

$C_{20}H_{16}N_2O_2 \cdot H_2O$:	calc.	C 71.84	H 5.43	N 8.38
	found	C 72.28	H 5.12	N 8.14

X-ray Structural Analysis of 1,2-Di(8-hydroxyquinolin-2-yl)ethane (8)
X-ray quality crystals of **8** were obtained from CH_2Cl_2. $C_{20}H_{16}N_2O_2$, *M* = 316.35 gmol^{-1}, monoclinic, *a* = 13.242(3), *b* = 11.454(3), *c* = 10.442(2) Å, β = 107.49(2)°, *V* = 1510.6(6) Å^3, *C*2/c, μ(CuK_α) = 0.732 mm^{-1}, *Z* = 4, D_c = 1.391 g cm^{-3}, *F*(000) = 664, *T* = 223(2) K. Data were recorded with a Enraf Nonius CAD4 diffractometer. 1618 collected reflections, 1530 unique reflections [999 $I > 2\sigma(I)$] were used for refinement. *Lp* correction. Psi scan absorption correction used (T_{min} = 92.7, T_{max} = 99.7%). Structure solution by direct methods (SHELXS97[28]), refinement on F^2 (SHELXL97[29]). The hydrogen positions are of riding model with fixed isotropic *U*. *R* = 0.0430, wR^2 = 0.1055 [$I > 2\sigma(I)$], *R* = 0.0891, wR^2 = 0.1232 (all data) for 110 parameters. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 120867.

1,2-Di(8-hydroxyquinolin-4-yl)ethane (9)
Yield: 49%; white solid; m.p. 270 °C.

^{1}H NMR ($CDCl_3$): δ = 9.72 (s, 2 H), 8.71 (d, *J* = 4.4 Hz, 2 H), 7.59 (d, *J* = 8.3 Hz, 2 H), 7.46 (dd, *J* = 7.7, 8.3 Hz, 2 H), 7.40 (d, *J* = 4.4 Hz, 2 H), 7.08 (d, *J* = 7.7 Hz, 2 H), 3.49 (s, 4 H).

^{13}C NMR ($CDCl_3$): δ = 153.8 (C), 147.6 (CH), 147.0 (C), 138.5 (C), 127.8 (C), 127.5 (CH), 121.5 (CH), 113.5 (CH), 110.8 (CH), 31.5 (CH_2).

IR (KBr): ν = 3307, 1516, 1406, 1270, 1220, 1168, 743 cm^{-1}.

MS: m/z (%) = 316 (100) $[M]^+$.

HRMS (EI, 70 eV): $C_{20}H_{16}N_2O_2$ (316.36): requires: M 316.1212; found M^+316.1201.

$C_{20}H_{16}N_2O_2 \cdot ¾\ H_2O$:	calc.	C 72.82	H 5.35	N 8.49
	found	C 72.86	H 5.34	N 8.09

1,2-Di(8-hydroxyquinolin-5-yl)ethane (10)
Yield: Quant.; yellow solid; mp >285 °C.

^{1}H NMR ($CDCl_3$): δ = 8.82 (dd, *J* = 1.4, 4.1 Hz, 2 H), 8.43 (dd, *J* = 1.4, 8.6 Hz, 2 H), 7.53 (dd, *J* = 4.1, 8.6 Hz, 2 H), 7.25 (d, *J* = 7.8 Hz, 2 H), 6.96 (d, *J* = 7.8 Hz, 2 H), 3.27 (s, 4 H).

^{13}C NMR ($CDCl_3$): δ = 151.8 (C), 147.6 (CH), 138.7 (C), 132.6 (CH), 127.7 (C), 127.3 (CH), 127.0 (C), 121.6 (CH), 110.6 (CH), 32.7 (CH_2).

IR (KBr): ν = 3345, 2546, 1923, 1670, 1622, 1507, 1477, 1370, 837, 698 cm^{-1}.

FAB(+) MS: m/z (%) = 317 (7) $[M+H]^+$.

$C_{20}H_{16}N_2O_2 \cdot ½\ H_2O$:	calc.	C 73.83	H 5.27	N 8.61
	found	C 74.04	H 4.89	N 9.46

1,2-Di(8-hydroxy-2-methylquinolin-7-yl)ethane (11)
Yield: Quant.; white solid; mp 177–178 °C.

^{1}H NMR ($CDCl_3$): δ = 8.46 (br s, 2 H), 7.98 (d, *J* = 8.3 Hz, 2 H), 7.29 (d, *J* = 8.3 Hz, 2 H), 7.24 (d, *J* = 8.3 Hz, 2 H), 7.18 (d, *J* = 8.3 Hz, 2 H), 3.26 (s, 4 H), 2.73 (s, 6 H).

^{13}C NMR ($CDCl_3$): δ = 156.7 (C), 148.8 (C), 137.4 (C), 136.1 (CH), 129.0 (CH), 125.1 (C), 123.7 (C), 121.8 (CH), 116.8 (CH), 30.3 (CH_2), 24.9 (CH_3).

IR (KBr): ν = 3362, 1511, 1455, 1443, 1250, 839, 688, 613 cm^{-1}.

MS: m/z (%) = 344 (40) $[M]^+$, 127 (100) $[M–C_{11}H_{10}NO]^+$.

HRMS (EI, 70 eV): $C_{22}H_{20}N_2O_2$ (344.41): requires: M 344.1525; found M^+344.1537.

$C_{22}H_{20}N_2O_2 \cdot ½\ H_2O$:	calc.	C 74.77	H 5.99	N 7.93
	found	C 75.54	H 6.05	N 7.92

7-Allylquinolin-8-yl Acetate (23)

7-Allylquinolin-8-ol (**22**)[18] (6.93 g, 37.5 mmol) is refluxed in Ac_2O (50 mL) for 15 h. Solvent is removed in vacuum and the residue is dissolved in CH_2Cl_2, washed with H_2O, dried ($MgSO_4$) and the CH_2Cl_2 is evaporated; yield: 8.50 g (quant.); green oil.

^{1}H NMR ($CDCl_3$): δ = 8.90 (dd, *J* = 1.6, 4.2 Hz, 1 H), 8.10 (dd, *J* = 1.6, 8.3 Hz, 1 H), 7.64 (d, *J* = 8.5 Hz, 1 H), 7.42 (d, *J* = 8.5 Hz, 1 H), 7.36 (dd, *J* = 4.2, 8.3 Hz, 1 H), 5.97 (m, 1 H), 5.15 (m, 2 H), 3.54 (m, 2 H), 2.52 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 169.5 (C), 150.4 (CH), 144.8 (C), 141.3 (C), 135.9 (CH), 135.4 (CH), 132.3 (C), 128.3 (CH), 128.1 (C), 125.4 (CH), 121.1 (CH), 116.7 (CH_2), 34.8 (CH_2), 20.9 (CH_3).

IR (KBr): ν = 1762, 1501, 1463, 1365, 1203, 1173, 1078, 914, 836, 804 cm^{-1}.

MS: m/z (%) = 227 (3) $[M]^+$, 170 (100) $[M–C_2HO_2]^+$.

HRMS (EI, 70 eV): $C_{19}H_{27}NO$ (227.26): requires: M 227.0946; found M^+227.0936.

1,4-Di(8-acetoxyquinolin-7yl)but-2-ene (24)

A solution of 7-allylquinolin-8-yl acetate (**23**) (850 mg, 3.75 mmol) in CH_2Cl_2 (5 mL) under Ar slowly is added to the metathesis catalyst benzylidene dichlorobis(tricyclohexylphosphane)ruthenium(II)[19] (100 mg, 0.12 mmol) in CH_2Cl_2 (5 mL). The mixture is refluxed for 15 h and solvent is removed in vacuo. The crude product can be used without further purification or can be purified by column chromatography (silica gel, gradient: hexane / EtOAc 1:1 → EtOAc); yield: 560 mg (70%); brown solid; two isomers:1:6.

^{1}H NMR ($CDCl_3$): δ = 8.84 (d, *J* = 4.3 Hz, 2 H), 7.99 (d, *J* = 7.9 Hz, 2 H), 7.56 (d, *J* = 8.4 Hz, 2 H), 7.36 (d, *J* = 8.4 Hz, 2 H), 7.24 (dd, *J* = 4.3, 7.9 Hz, 2 H), 5.76 / 5.72 (m, Σ 2 H), 3.71 / 3.51 (d, *J* = 4.7 Hz (each), Σ 4 H), 2.48 (s, 6 H).

^{13}C NMR ($CDCl_3$): δ (major isomer) = 169.6 (C), 150.4 (CH), 144.8 (C), 141.3 (C), 135.9 (CH), 132.5 (C), 129.4 (CH), 128.4 (CH), 128.1 (C), 125.5 (CH), 121.1 (CH), 33.6 (CH_2), 20.9 (CH_3); δ(minor isomer) = 150.5 (CH), 144.7 (CH), 132.7 (C), 128.2 (CH), 127.9 (C), 125.6 (CH), 121.2 (CH), 28.4 (CH_2).

IR (KBr): ν = 3041, 2934, 1762, 1499, 1463, 1365, 1205, 1172, 1081, 837 cm^{-1}.

MS: m/z (%) = 426 (1) $[M]^+$.

HRMS (EI, 70 eV): $C_{26}H_{22}N_2O_4$ (426.47): requires: M 426.1580; found M^+426.1596.

$C_{26}H_{22}N_2O_4 \cdot H_2O$:	calc.	C 70.26	H 5.44	N 6.30
	found	C 70.39	H 5.15	N 6.18

1,4-Di(8-hydroxyquinolin-7yl)butane (12)

Platinum dioxide (150 mg) is added to a solution of **24** (750 mg, 1.76 mmol) in CH_2Cl_2/EtOH (20 mL, 1:1) and the mixture is stirred under an atmosphere of H_2 for 4.5 h. The solvent is removed in vacuo and the residue is applied to column chromatography (silica gel, gradient: hexane/EtOAc 1:2 → MeOH). The obtained 1,4-di(8-acetoxyquinoline)butane immediately is dissolved in MeOH and 10 drops of TFA are added. After 3 days at r.t. the solvent is removed and the residue is dissolved in CH_2Cl_2, washed with aq $NaHCO_3$, dried and the solvent is removed; yield: 110 mg (20%); green solid; mp 172–174 °C.

^{1}H NMR ($CDCl_3$): δ = 8.74 (d, *J* = 3.2 Hz, 2 H), 8.28 (br s, 2 H), 8.11 (d, *J* = 8.1 Hz, 2 H), 7.37 (dd, *J* = 3.2, 8.1 Hz, 2 H and d, *J* = 8.5 Hz, 2 H), 7.27 (d, *J* = 8.5 Hz, 2 H), 2.93 (m, 4 H), 1.84 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 149.1 (C), 147.7 (CH), 138.1 (C), 135.9 (CH), 129.9 (CH), 126.8 (C), 124.3 (C), 120.9 (CH), 117.1 (CH), 29.8 (CH_2), 29.7 (CH_2).

IR (KBr): ν = 3333, 2859, 1504, 1470, 1405, 1371, 1283, 1239, 1118, 832, 825, 673 cm^{-1}.

MS: m/z (%) = 344 (75) $[M]^+$, 159 (100) $[M–C_{12}H_{11}NO]^+$.

HRMS (EI, 70 eV): $C_{22}H_{20}N_2O_2$ (344.41): requires: M 344.1525; found M^+344.1511.

1,2-Di(8-methoxyquinoline-7-yl)hexane (27)

At 0 °C a 0.5 M solution of 9-BBN in THF (4.88 mL, 2.44 mmol) is added to hexa-1,5-diene (0.15 ml, 1.22 mmol) in anhyd THF (2 mL).[22] The mixture is allowed to warm to r.t. and is stirred for 4.5 h. A mixture of aq 3 M NaOH (2.5 mL), THF (10 mL), $PdCl_2$(dppf) (116 mg, 0.15 mmol) and **25** (580 mg, 2.44 mmol) is added to the in situ prepared **26** and the solution is refluxed for 15 h. Solvents are evaporated and the residue is chromatographed (silica gel, hexane / ethyl acetate 5:1); yield: 150 mg (31%); beige solid; mp 94–96 °C.

^{1}H NMR ($CDCl_3$): δ = 8.91 (d, *J* = 3.5 Hz, 2 H), 8.10 (d, *J* = 8.3 Hz, 2 H), 7.49 (d, *J* = 8.3 Hz, 2 H), 7.37 (d, *J* = 8.3 Hz, 2 H), 7.34 (dd, *J* = 3.5, 8.3 Hz, 2 H), 4.10 (s, 6 H), 2.85 (t, *J* = 7.8 Hz, 4 H), 1.70 (m, 4 H), 1.47 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 153.3 (C), 149.3 (CH), 142.7 (C), 136.2 (CH), 135.4 (C), 129.0 (CH), 128.3 (C), 122.9 (CH), 120.4 (CH), 62.4 (CH_3), 30.7 (CH_2), 30.1 (CH_2), 29.5 (CH_2).

IR (KBr): ν = 3417, 2941, 2922, 2855, 1499, 1465, 1435, 1230, 1111, 1086, 830, 809, 705 cm^{-1}.

MS: m/z (%) = 400 (100) $[M]^+$.

HRMS (EI, 70 eV): $C_{26}H_{28}N_2O_2$ (400.52): requires: M 400.2151; found M^+400.2135.

$C_{26}H_{28}N_2O_2 \cdot ½\ H_2O$:	calc.	C 76.25	H 7.14	N 6.84
	found	C 76.09	H 7.25	N 6.38

1,2-Di(8-hydroxyquinoline-7-yl)hexane (13)

1,2-Di(8-methoxyquinoline-7-yl)hexane (**27**) (110 mg, 0.27 mmol) for 2 h is refluxed in 48% HBr (8 mL). The solution is neutralized by addition of $NaHCO_3$ and extracted with CH_2Cl_2 (3 x 50 mL). The organic layer is dried ($MgSO_4$) and evaporated to drieness; yield: 90 mg (85%); grey solid; mp 138 °C.

^{1}H NMR ($CDCl_3$): δ = 8.75 (d, *J* = 3.1 Hz, 2 H), 8.15 (d, *J* = 8.0 Hz, 2 H), 7.39 (d, *J* = 3.1, 8.0 Hz, 2 H), 7.36 (d, *J* = 8.3 Hz, 2 H), 7.28 (d, *J* = 8.3 Hz, 2 H), 2.86 (t, *J* = 7.7 Hz, 4 H), 1.73 (m, 4 H), 1.47 (t, J = 6.8 Hz, 4 H).

^{13}C NMR ($CDCl_3$): δ = 148.8 (C), 147.2 (CH), 157.3 (C), 136.6 (CH), 130.1 (CH), 126.9 (C), 125.4 (C), 120.7 (CH), 117.2 (CH), 30.0 (CH_2), 29.9 (CH_2), 29.4 (CH_2).

IR (KBr): ν = 3312, 2926, 2861, 2850, 1506, 1466, 1407, 1288, 1231, 823, 715 cm^{-1}.

MS: m/z (%) = 372 (27) $[M]^+$, 159 (100) $[M–C_{14}H_{15}NO]^+$.

HRMS (EI, 70 eV): $C_{24}H_{24}N_2O_2$ (372.47): requires: M 372.1838; found M^+372.1853.

$C_{24}H_{24}N_2O_2 \cdot H_2O$:	calc.	C 73.20	H 6.20	N 6.39
	found	C 73.82	H 6.71	N 7.17

***N*-Hexyl-8-hydroxyquinoline-7-carboxamide (2)**

8-Hydroxyquinoline-7-carboxylic acid (**28**) (500 mg, 2.64 mmol) and carbonyl diimidazole (470 mg, 2.91 mmol) are refluxed in an-

hyd THF (50 ml) for 1 h under Ar. Hexylamine (350 μL, 2.64 mmol) in THF (4 mL) is added to the refluxing mixture, which after completion of the addition is heated overnight. Solvent is removed and the residue is dissolved in CH_2Cl_2, washed with aq NH_4Cl and brine, dried ($MgSO_4$) and evaporated in vacuum; yield: 604 mg (89%); yellow solid; mp 94 °C.

^{1}H NMR ($CDCl_3$): δ = 8.82 (d, *J* = 3.8 Hz, 1 H), 8.45 (br s, 1 H), 8.12 (d, *J* = 8.5 Hz, 2 H), 7.90 (s, 1 H), 7.45 (dd, *J* = 3.8, 8.5 Hz, 1 H), 7.32 (d, *J* = 8.5 Hz, 1 H), 3.52 (m, 2 H), 1.66 (m, 2 H), 1.41 (m, 2 H), 1.31 (m, 4 H), 0.88 (m, 3 H).

^{13}C NMR ($CDCl_3$): δ = 166.2 (C), 152.7 (C), 148.5 (CH), 138.7 (C), 136.1 (CH), 130.1 (C), 127.0 (CH), 123.2 (CH), 117.5 (CH), 113.8 (C), 40.0 (CH_2), 31.5 (CH_2), 29.6 (CH_2), 26.8 (CH_2), 22.6 (CH_2), 14.0 (CH_3).

IR (KBr): ν = 3276, 2927, 1598, 1497, 1406, 1328, 1288, 1212, 1106, 931, 796, 744 cm^{-1}.

MS: m/z (%) = 272 (42) $[M]^+$, 172 (100).

HRMS (EI, 70 eV): $C_{16}H_{20}N_2O_2$ (272.35): requires: M 272.1525; found M^+272.1512.

$C_{16}H_{20}N_2O_2$:	calc.	C 70.56	H 7.40	N 10.29
	found	C 70.09	H 7.51	N 10.19

X-ray Structural Analysis of *N*-Hexyl-8-hydroxyquinoline-7-carboxamide (2)

$C_{16}H_{20}N_2O_2$, *M* = 272.34 $gmol^{-1}$, monoclinic, *a* = 10.021(1), *b* = 11.996(1), *c* = 12.257(1) Å, β = 103.44(1)°, *V* = 1433.1(2) Å^3, $P2_1/n$, $\mu(MoK_\alpha)$ = 0.084 mm^{-1}, *Z* = 4, D_c = 1.262 g cm^{-3}, *F*(000) = 584, *T* = 173(2) K. Data were recorded with a Nonius Kappa CCD diffractometer. 16750 collected reflections, 2925 unique reflections [2131 $I > 2\sigma(I)$] were used for refinement. The data were processed with Denzo.[30] *Lp* correction. No absorption correction was applied. Structure solution by direct methods (SHELXS97[28]), refinement on F^2 (SHELXL97[29]). The hydrogen positions are of riding model with fixed isotropic *U*. *R* = 0.0457, wR^2 = 0.1067 [$I > 2\sigma(I)$], *R* = 0.0700, wR^2 = 0.1193 (all data) for 186 parameters. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 120865.

1,2-*N,N'*-Di(8-hydroxyquinolin-7-carboxamide)ethane (14)

8-Hydroxyquinoline-7-carboxylic acid (**28**) (500 mg, 2.64 mmol) and carbonyl diimidazole (470 mg, 2.91 mmol) are refluxed in anhyd THF (50 ml) for 1 h under Ar. Ethylenediamine (80 mg, 1.32 mmol) in anhyd THF (5 mL) is added to the refluxing mixture, which after completion of the addition is refluxed overnight. Solvent is removed and the residue is washed with H_2O and MeOH and dried in vacuo; yield: 341 mg (64%); beige solid; mp >280 °C.

^{1}H NMR (DMS*O*-d_6): δ = 9.07 (m, 2 H), 8.91 (m, 2 H), 8.34 (m, 2 H), 7.97 (m, 2 H), 7.63 (m, 2 H), 7.41 (m, 2 H), 3.32 (br, 4 H).

^{13}C NMR (DMS*O*-d_6): δ = 168.7 (C), 157.1 (C), 149.1 (CH), 139.2 (C), 135.0 (CH), 130.7 (C), 125.0 (CH), 123.5 (CH), 116.8 (CH), 112.4 (C), 38.9 (CH_2).

IR (KBr): ν = 3335, 3068, 2943, 1598, 1559, 1434, 1384, 1224, 1127, 941, 747 cm^{-1}.

MS: m/z (%) = 402 (2) $[M]^+$, 145 (100).

HRMS (EI, 70 eV): $C_{22}H_{18}N_4O_4$ (402.41): requires: M 402.1328; found M^+402.1305.

$C_{22}H_{18}N_4O_4 \cdot ½\ H_2O$:	calc.	C 64.23	H 4.65	N 13.62
	found	C 63.92	H 4.77	N 13.60

X-ray Structural Analysis of Di(8-hydroxyquinolin-2-yl)methane (6)

Compound **6** was prepared as described in the literature.[11] X-ray quality crystals of **6** were obtained from CH_2Cl_2. $C_{19}H_{14}N_2O_2$, *M* = 302.32 $gmol^{-1}$, triclinic, *a* = 8.591(2), *b* = 13.237(3), *c* = 14.479(3) Å, α = 67.38(3), β = 87.37(3), γ = 87.94(3)°, *V* = 1518.0(6) Å^3, *P*-1, $\mu(CuK_\alpha)$ = 0.704 mm^{-1}, *Z* = 4, D_c = 1.323 g cm^{-3}, *F*(000) = 632, *T* = 223(2) K. Data were recorded with an Enraf Nonius CAD4 diffractometer. 6626 collected reflections, 6192 unique reflections [2996 $I > 2\sigma(I)$] were used for refinement. *Lp* correction. Psi scan absorption correction used (T_{min} = 72.0, T_{max} = 93.3%). Structure solution by direct methods (SHELXS97[28]), refinement on F^2 (SHELXL97[29]). The hydrogen positions are of riding model with fixed isotropic *U*. *R* = 0.0581, wR^2 = 0.1644 [$I > 2\sigma(I)$], *R* = 0.1551, wR^2 = 0.2000 (all data) for 419 parameters. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 120866.

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