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Synthesis of Homo- and Heteroditopic 8-Hydroxyquinoline Ligands

Markus Albrecht,*[a] Olga Osetska,[a] and Roland Fröhlich[b]

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The Claisen rearrangement is a versatile reaction for the preparation of either isobutenylidene- or *n*-butenylidene-bridged bis(8-hydroxyquinoline) ligands for supramolecular chemistry. The Hiratani–double-Claisen rearrangement of the appropriate isobutenylidene bis(aryl) ethers enables the formation of either symmetrical or unsymmetrical ligand systems with two tridentate or one bi- and one tridentate quinoline-based chelating units. Claisen rearrangement of quinoline allyl ether followed by Grubbs metathesis affords the symmetric ligand with an elongated spacer between the chelates. The described ligands are of interest for the self-assembly of homo- and heterodinuclear near-IR-emitting lanthanide complexes.

Introduction

Optical and display devices,[1] as well as luminescent probes and sensors[2] based on lanthanide ion containing precursors, are in the focus of attention of recent supramolecular chemistry. Their elaboration requires precise design of molecular edifies with multiple light-absorbing groups.[3] Hereby the preparation of homo- and heterodinuclear complexes is of special interest due to the possibility that the emitting properties of the compounds can be manipulated.[4]

As a striking example, Piguet and Bünzli described a benzimidazole–pyridine ligand system that can form up to tetranuclear lanthanide(III) helicates in a simple self-assembly step by mixing the ligands and the metal salts. Heterodinuclear f–d complexes were obtained by the introduction of unsymmetrical ligands with a tridentate as well as a bidentate binding site for the different kinds of metal ions. The ligand system allows the positioning of the metals in well-defined distances to each other.[5] Following this approach, it should be of interest to introduce other ligand systems to allow variation in the electronic properties or the metal–metal separation. However, further heterodinuclear helicates containing lanthanides are not described in the literature. This is probably due to the lack of reliable synthetic pathways that can result in reasonable amounts of the necessary ligands.

The unique electron-transport and light-emitting properties of the well-established tris(8-hydroxyquinolinate) aluminium complex allow its utilization as an active medium in OLEDs (organic light emitting devices).[6] Preliminary studies in our lab showed that near-infrared luminescence is observed with the amide modified 8-hydroxyquinoline ligands **1c** (Figure 1),[7] in which the intrinsically bidentate 8-hydroxyquinoline unit is extended to be tridentate.[8] Excitation of the ligand is followed by energy transfer (ET) to the metal and subsequently the typical emission[9] of the lanthanide ion is detected. Particularly, the trischelate complexes of bromide derivatives of ligand **1c** with Er^{III}, Nd^{III} and Yb^{III} demonstrated a quite intensive metal-centred luminescence in the near-IR region.[10]

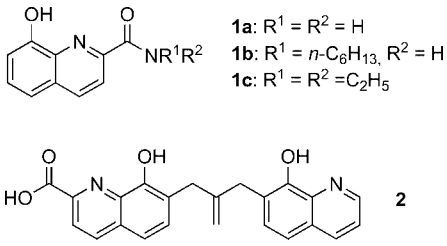

Figure 1. 8-Hydroxyquinoline ligands with one (**1a**–**c**) or two (**2**) quinoline units.

As a prototype for the formation of triple-stranded dinuclear d–f helicates compound **2** was synthesized. The attempted preparation of a La^{III}/Zn^{II} complex failed, and a double-stranded dinuclear zinc(II) complex was isolated.[11] This fact and the successful use of the parent symmetric bis(8-hydroxyquinoline) derivative for the self-assembly of Al^{III}, Ga^{III} or Fe^{III} triple-stranded helicates[12] make unsymmetrical derivatives of **2** valuable precursors for d–f complexes.

Now we report the synthesis of a series of homo- and heteroditopic 8-hydroxyquinoline-based receptors. They contain an amide or a carboxylate moiety at the tridentate

[a] Institut für Organische Chemie, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany
E-mail: markus.albrecht@oc.rwth-aachen.de
[b] Organisch-Chemisches Institut, Universität Münster, Corrensstrasse 40, 48149 Münster, Germany
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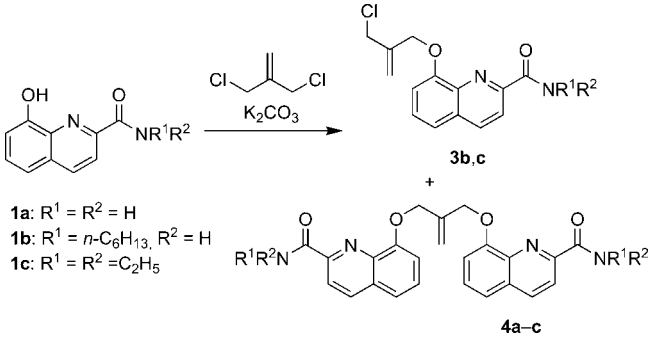
coordination site for the complexation of Ln^{3+} ions or an 8-hydroxyquinoline unit as an alternative bidentate segment for addressing transition- or *p*-block metal ions.

Results and Discussion

For the preparation of bis(8-hydroxyquinoline) derivatives, the Claisen rearrangement was chosen as an effective way to functionalize 8-hydroxyquinoline derivatives in the 7-position and to introduce an "anchor group" for the establishment of the spacer. The Hiratani–double-Claisen rearrangement offers a simple method, in which two new C–C bonds are formed simultaneously in high yields, which results in a bridge between the phenol moieties.[13] In the reaction sequence an ether is initially formed in a Williamson synthesis by coupling of 3-chloro-2-chloromethylpropene with two equivalents of an appropriate phenol. It is also possible to successively attach different phenolic moieties to the isobutenylidene. In the rearrangement reaction the ether is heated neat to yield the isobutenylidene-bridged diphenols. This reaction was applied by the Hiratani group for different purposes.[14] For example, biscatechol as well as bis(8-hydroxyquinoline) ligands were synthesized.[15]

To obtain ligand systems containing tridentate lanthanide binding sites, amides **1a**–**b** were prepared first following published procedures.[16] Amidation of the corresponding acid with diethylamine in the presence of HBTU [2-(1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate] afforded **1c** (60% yield).

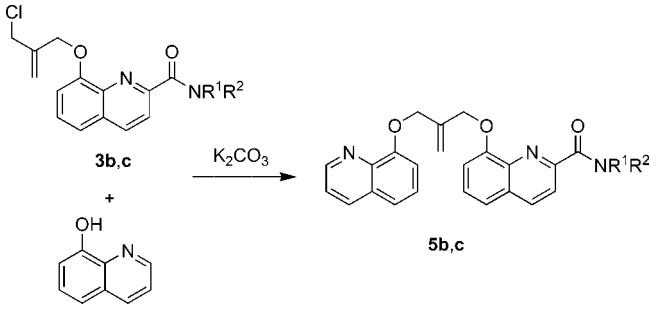
The Williamson ether coupling of **1a**–**c** with 3-chloro-2-chloromethylpropene provided us with the possibility to obtain monoethers **3** as well as diethers **4** by choosing the correct stoichiometry between reactants. However, in a 1:1 reaction of "unsubstituted" amide **1a** with 3-chloro-2-chloromethylpropene only diether **4a** was isolated in 17% yield. The probably formed monoether **3a** could not be obtained after workup. Only products of hydrolysis of the CH_2–Cl bond were identified by NMR spectroscopy and ESI MS after column chromatography. (Scheme 1)



Scheme 1. Preparation of precursors **3b**,**c** and **4a**–**c** for the Hiratani–double-Claisen rearrangement.

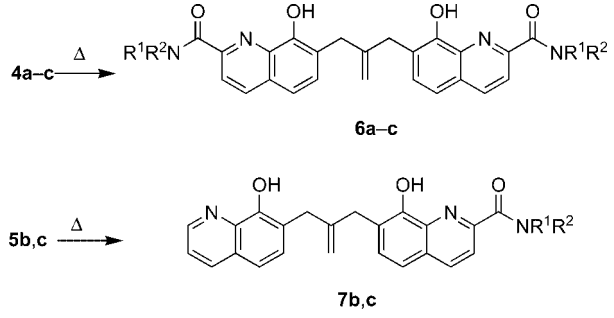
By applying the same stoichiometry between the starting materials as before, the reaction of amides **1b**,**c** furnished a mixture of **3b** (28%) and **4b** (59%) or **3c** (46%) and **4c** (41%), respectively. Attempts to form only one of the two products by applying different stoichiometries failed, and the reaction was optimized to obtain both useful building blocks, which can be easily separated by column chromatography.

Monoethers **3b**,**c** afforded in a successive substitution of chloride by unsubstituted 8-hydroxyquinoline unsymmetrical diethers **5b**,**c** in 77 and 82% yield, respectively (Scheme 2).



Scheme 2. Preparation of unsymmetrical diethers.

Finally, all monosubstituted ethers **4a**–**c** and tetrasubstituted diethers **5b**,**c** were converted into isobutenylidene-bridged dihydroxyquinoline derivatives **6a**–**c** and **7b**,**c**, respectively. The reaction proceeded smoothly within 5–7 h by thermal rearrangement at 170–175 °C under an atmosphere of N_2. The yields of this highly specific step are close to quantitative (88–100%; Scheme 3). The compounds were often obtained in analytically pure form. Where necessary, they can be purified by crystallization or column chromatography.



Scheme 3. Hiratani–double-Claisen rearrangement providing symmetric **6a**–**c** as well as unsymmetrical **7b**,**c** 8-hydroxyquinoline derivatives.

From our early studies on the parent unsubstituted isobutenylidene-bridged bis(8-hydroxyquinoline), we knew that the compounds form interesting hydrogen bonded polymeric networks in the solid state.[17] Therefore, the molecular structure of **6c** was also determined by X-ray diffraction (Figure 2).

As can be seen in Figure 2a, the isobutenylidene unit adopts a twisted conformation[18] connecting the two hydroxyquinoline moieties, which show the expected intramolecular O–H···N hydrogen bonds. Because of the bulkiness of the diethylamide moieties, dimerization of the 8-hydroxyquinoline units cannot occur as found in related unsubsti-

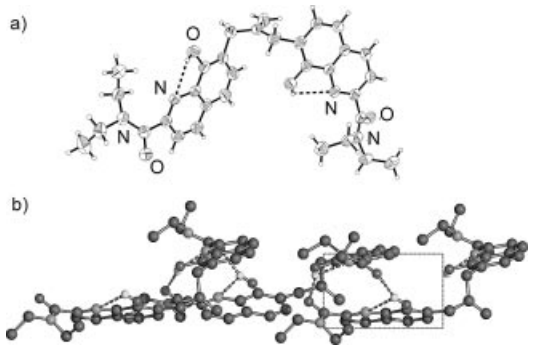


Figure 2. (a) The molecular structure of **6c** in the solid state; (b) the polymeric hydrogen-bonded structure is shown for three molecules of **6c**, which highlights the hydrogen-bonding pattern for two adjacent 2-amido-8-hydroxyquinoline units of different molecules; H atoms except OH are omitted for clarity.

tuted derivatives. Therefore, in the present case, the O–H···N additionally binds to an amide oxygen atom of a neighbouring molecule that is twisted out of the plane of the quinoline (Figure 2b). In addition, the bridging hydrogen is also forced to be off plane of the usually observed planar five-membered ring.[19] The relative orientations of the quinolines, which are connected by hydrogen bonds, indicate that aromatic π–π stacking might additionally stabilize this arrangement. The "dimerization" of the single units of the ditopic molecule results in a polymeric structure in the solid state.

The Hiratani–double-Claisen rearrangement offers an attractive way to establish a spacer unit between two hydroxyquinoline moieties with three carbon atoms in the chain. To obtain variation in the distance between the two binding sites it would be of interest to introduce bridges of different size.

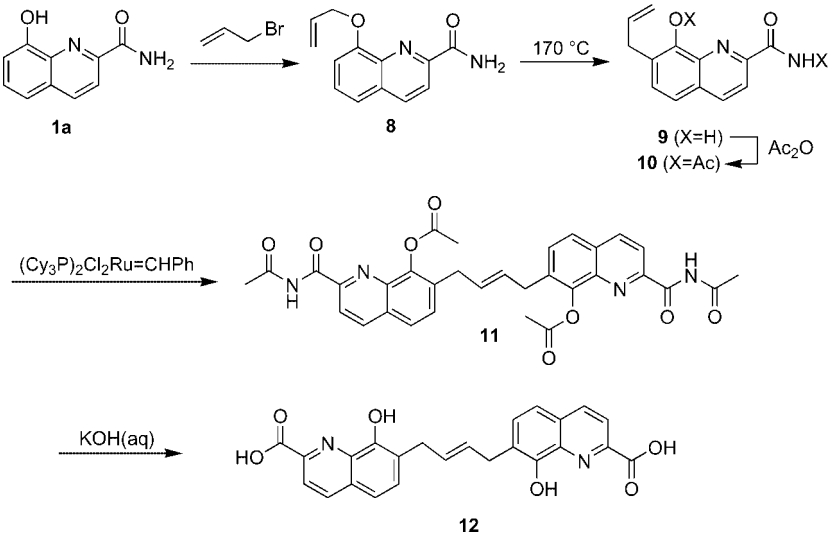
An alternate approach to connect identical tridentate 8-hydroxyquinoline units can be envisaged by using a Claisen rearrangement followed by olefin metathesis homodimerization. Therefore, an allyl group was attached to 8-hydroxyquinoline-2-carboxamide (**1a**). The resulting ether **8** underwent Claisen rearrangement at 170 °C under a nitrogen atmosphere to afford the C-allylated 8-hydroxyquinoline derivative **9** in quantitative yield. Compound **9** was converted into acetate **10** by treatment with acetic anhydride. The amide substituent was acetylated simultaneously during this reaction (Scheme 4).

"Homodimerization" of **10** by intermolecular metathesis with the first generation Grubbs catalyst resulted in bis(8-hydroxyquinoline-2-carboxamide) **11** with the *n*-butenylidene spacer connecting the 7-positions of the quinoline rings. Flash chromatography afforded two fractions: (1) a mixture of *Z* and *E* isomers in 18% yield [similar results were obtained with a simple bis(8-acetoxyquinoline) alkene analogue];[14] (2) one pure isomer in a yield of 26%. Only the latter isomerically pure *E* product **11** was employed in the final transformation. The assignment of the *Z* and *E* isomers was done by NMR spectroscopy by using a recently described technique. Nonequivalence of the two vinylic protons was observed for those located at an H–C=^{13}C–H unit.[20] $^{3}J_{H,H}$ coupling constants of 10.2 or 15.6 Hz are observed for the *Z* and *E* isomers of **11**, respectively.

The reaction sequence was completed by hydrolytic cleavage of the acetyl groups at the phenolate functions and simultaneous hydrolysis of the *N*-acetamido substituents with aqueous KOH in pyridine to afford the symmetrical bis(8-hydroxyquinoline-2-carboxylic acid) derivative **12** in sufficient yield (64%).[21] The introduction of negatively charged carboxylates, which possess high affinity to the hard Ln^{III} ions, in the terminal positions of the oxine cores should affect the Ln ligand bond strength leading to the stabilization of charged helicate complexes possibly even in water.[22]

Conclusions

Thus, we described two efficient pathways for the preparation of modified ditopic 8-hydroxyquinoline ligand sys-



Scheme 4.

tems, which are of paramount interest in metallosupramolecular chemistry as useful building blocks for luminescent helicates. Both protocols can be applied to a wide range of substrates as the carboxamide group, and for example the ester functionality, are tolerated. Currently, the investigations towards the generation of more extended (*tri*- and *tetra*topic) 8-hydroxyquinoline-based ligands, in which the rigidity control will be gained through the different connectors (in particular, flexible ones), are in progress and our ligands are introduced in coordination studies.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded with a Varian Inova 400 or Mercury 300 NMR spectrometer. FTIR spectra were recorded with a Bruker IFS spectrometer (KBr or neat). Mass spectra (EI, 70 eV, FAB) were taken with a Finnigan MAT 95 or 212 mass spectrometer. Elemental analyses were obtained with a Heraeus CHN-O-Rapid analyzer. Melting points were measured with a Büchi B-540 and are uncorrected. For compounds with sharp melting points, only one temperature is given, whereas in the other cases an interval is listed. Preparative column chromatography was performed with Merck silica gel 60, particle size 0.040–0.063 mm (230–400 mesh, flash). Compounds **1a** and **1b** were prepared as described earlier.[16]

***N*,*N*-Diethyl-8-hydroxyquinoline-2-carboxamide (1c):** 8-Hydroxyquinoline-2-carboxylic acid (1.00 g, 5.29 mmol, 1 equiv.), HBTU (2.41 g, 6.35 mmol, 1.2 equiv.) and *N*-ethyldiisopropylamine (0.75 g, 1.00 mL, 5.8 mmol, 1.1 equiv.) were stirred in acetonitrile (50 mL) for 30 min at room temp. $HNEt_2$ (0.39 g, 0.55 mL, 5.33 mmol, 1 equiv.) dissolved in MeCN (2 mL) was added, and the mixture was stirred for 2 d at room temp. After removal of the solvent in vacuo, the oily brown residue was dissolved in CH_2Cl_2 (100 mL) and washed with saturated aqueous solution of NH_4Cl, saturated aqueous solution of $NaHCO_3$, H_2O and brine. After drying (Na_2SO_4), the solvent was removed under reduced pressure. The crude product was purified by column chromatography (EtOAc/*n*-hexane, 1:4) to yield a white solid (0.77 g, 60%). M.p. 104 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08 (d, J = 8.4 Hz, 1 H), 8.03 (br. s, 1 H), 7.56 (d, J = 8.4 Hz, 1 H), 7.33 (t, J = 8.0 Hz, 1 H), 7.18 (dd, J = 8.0, 1.2 Hz, 1 H), 7.08 (dd, J = 8.0, 1.2 Hz, 1 H), 3.50 (q, J = 7.0 Hz, 2 H), 3.25 (q, J = 7.0 Hz, 2 H), 1.19 (t, J = 7.0 Hz, 3 H), 1.10 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.9 (C), 151.9 (C), 151.8 (C), 136.8 (CH), 136.0 (C), 128.2 (CH), 127.8 (C), 120.5 (CH), 117.5 (CH), 110.5 (CH), 42.8 (CH_2), 39.7 (CH_2), 14.1 (CH_3), 12.4 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3316, 2978, 1618, 1567, 1489, 1459, 1320, 1207, 11.85, 1161, 850, 759 cm^{-1}. MS (EI, DIP): m/z = 244.1 [M]$^+$. $C_{14}H_{16}N_2O_2$ (244.3): calcd. C 68.83, H 6.60, N 11.47; found C 68.99, H 6.62, N 11.93.

8,8′-(2-Methylenepropane-1,3-diyl)bis(oxy)bis(quinoline-2-carboxamide) (4a): To a solution of **1a** (0.50 g, 2.66 mmol, 1 equiv.) in DMF (30 mL) was added K_2CO_3 (1.84 g, 13.31 mmol, 5 equiv.) and 3-chloro-2-chloromethylpropene (0.33 g, 2.66 mmol, 1 equiv.). The resulting suspension was stirred at 90 °C overnight. The solvent was evaporated under reduced pressure; the remaining residue in CH_2Cl_2 was washed with water and dried with Na_2SO_4. After removing the solvent, the crude residue was again dissolved in CH_2Cl_2 (30 mL), heated at reflux and then cooled to room temp. The precipitate was collected by filtration, washed with CH_2Cl_2 and dried to provide **4a** as a white powder (0.10 g, 17%). M.p. 203 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.30 (d, J = 8.5 Hz, 2 H), 8.26 (d, J = 8.5 Hz, 2 H), 8.12 (br. s, 2 H), 7.50 (dd, J = 8.2, 7.4 Hz, 2 H), 7.45 (dd, J = 8.2, 1.3 Hz, 2 H), 7.21 (dd, J = 7.4, 1.3 Hz, 2 H), 5.63 (s, 2 H), 5.58 (br. s, 2 H), 5.06 (s, 4 H) ppm. IR (KBr): $\tilde{\nu}$ = 3441, 1696, 1566, 1470, 1375, 1324, 1254, 1099, 753 cm^{-1}. MS (EI, DIP): m/z = 428.0 [M]$^+$. $C_{24}H_{20}N_4O_4 \cdot H_2O$ (446.4): calcd. C 64.57, H 4.97, N 12.55; found C 64.36, H 5.12, N 12.47.

8-[2-(Chloromethyl)allyloxy]-*N*-(*n*-hexyl)quinoline-2-carboxamide (3b) and 8,8′-(2-Methylenepropane-1,3-diyl)bis(oxy)bis[*N*-(*n*-hexyl)-quinoline-2-carboxamide] (4b): K_2CO_3 (0.71 g, 5.14 mmol, 5 equiv.) and 3-chloro-2-chloromethylpropene (0.13 g, 1.03 mmol, 1 equiv.) were added to the solution of **1b** (0.28 g, 1.03 mmol, 1 equiv.) in acetone (50 mL). The resulting suspension was heated at reflux for 24 h. The solvent was evaporated in vacuo; the remaining residue was dissolved in CH_2Cl_2, washed with water and dried with Na_2SO_4. Separation by flash chromatography (EtOAc/*n*-hexane, 1:2) afforded **3b** (R_f = 0.39; 0.104 g, 28%) and **4b** (R_f = 0.07; 0.181 g, 59%) as colourless oils. Data for **3b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.36 (br. t, J = 5.5 Hz, 1 H), 8.31 Hz (d, J = 8.5 Hz, 1 H), 8.23 (d, J = 8.5 Hz, 1 H), 7.46 (m, 2 H), 7.12 (dd, J = 7.2, 1.6 Hz, 1 H), 5.51 (s, 1 H), 5.46 (s, 1 H), 4.88 (s, 2 H), 4.30 (s, 2 H), 3.51 (m, 2 H), 1.66 (m, 2 H), 1.42 (m, 6 H), 0.87 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.3 (C), 154.2 (C), 148.8 (C), 140.5 (C), 138.6 (C), 137.23 (CH), 130.4 (C), 127.9 (CH), 120.2 (CH), 119.3 (CH), 117.5 (CH_2), 110.7 (CH), 69.1 (CH_2), 45.0 (CH_2), 39.5 (CH_2), 31.4 (CH_2), 29.5 (CH_2), 26.6 (CH_2), 22.5 (CH_2), 13.9 (CH_3) ppm. MS (EI, DIP): m/z = 360.2 [M + H]$^+$. Data for **4b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.37 (br. t, J = 6.0 Hz, 2 H), 8.27 (d, J = 8.4 Hz, 2 H), 8.18 (d, J = 8.4 Hz, 2 H), 7.39 (m, 4 H), 7.12 (dd, J = 6.8, 2.0 Hz, 2 H), 5.57 (s, 2 H), 4.99 (s, 4 H), 3.36 (m, 4 H), 1.46 (m, 4 H), 1.21 (m, 12 H), 0.77 (t, J = 6.8 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.2 (C), 154.2 (C), 148.7 (C), 139.7 (C), 138.4 (C), 137.1 (CH), 130.3 (C), 127.8 (CH), 120.0 (CH), 119.2 (CH), 115.8 (CH_2), 110.3 (CH), 69.6 (CH_2), 39.4 (CH_2), 31.3 (CH_2), 29.4 (CH_2), 26.5 (CH_2), 22.3 (CH_2), 13.8 (CH_3) ppm. MS (EI, DIP): m/z = 596.7 [M]$^+$.

8-[2-(Chloromethyl)allyloxy]-*N*,*N*-(diethyl)quinoline-2-carboxamide (3c) and 8,8′-(2-Methylenepropane-1,3-diyl)bis(oxy)bis[*N*,*N*-(diethyl)quinoline-2-carboxamide] (4c): The compounds were prepared according to the procedure described for **3b/4b** by treating **2c** (0.775 g, 3.17 mmol) with 3-chloro-2-chloromethylpropene (0.40 g, 3.17 mmol) in acetone (50 mL) in the presence of K_2CO_3 (2.19 g, 15.85 mmol). Compounds **3c** and **4c** were separated by column chromatography (EtOAc/*n*-hexane, 1:1) to yield **3c** as a colourless oil (R_f = 0.89; 0.486 g, 46%) and **4c** as a sticky white solid (R_f = 0.49; 0.352 g, 41%). Data for **3c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, J = 8.5 Hz, 1 H), 7.77 (d, J = 8.5 Hz, 1 H), 7.46 (t, J = 8.0 Hz, 1 H), 7.25 (dd, J = 8.0, 1.3 Hz, 1 H), 7.11 (dd, J = 8.0, 1.3 Hz, 1 H), 5.43 (s, 1 H), 5.42 (s, 1 H) 4.88 (s, 2 H), 4.27 (s, 2 H), 3.59 (q, J = 7.1 Hz, 2 H), 3.53 (q, J = 7.1 Hz, 2 H), 1.29 (t, J = 7.1 Hz, 3 H), 1.28 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.2 (C), 154.3 (C), 153.0 (C), 140.2 (C), 138.3 (C), 136.6 (CH), 129.1 (C), 127.35 (CH), 121.4 (CH), 119.9 (CH), 117.8 (CH_2), 110.2 (CH), 69.9 (CH_2), 45.1 (CH_2), 43.5 (CH_2), 40.7 (CH_2), 14.5 (CH_3), 13.9 (CH_3) ppm. MS (EI, DIP): m/z = 332.1 [M]$^+$. Data for **4c**: M.p. 62 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16 (d, J = 8.6 Hz, 2 H), 7.73 (d, J = 8.6 Hz, 2 H), 7.40 (m, 4 H), 7.14 (d, J = 6.9 Hz, 2 H), 5.51 (s, 2 H), 4.97 (s, 4 H), 3.55 (q, J = 7.1 Hz, 4 H), 3.46 (q, J = 7.1 Hz, 4 H), 1.25 (t, J = 7.1 Hz, 6 H), 1.21 (t, J = 7.1 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.4 (C), 154.5 (C), 153.1 (C), 139.5 (C), 138.4 (C), 136.6 (CH), 129.1 (C), 127.4 (CH), 121.2 (CH), 119.7 (CH), 116.3 (CH_2), 110.3 (CH), 69.4 (CH_2), 43.4 (CH_2), 40.5 (CH_2), 14.4 (CH_3), 12.7 (CH_3) ppm. IR

(KBr): $\tilde{\nu}$ = 3488, 2968, 2932, 1628, 1563, 1477, 1378, 1319, 1256, 1209, 1104, 840, 756 cm^{-1}. MS (EI, DIP): *m*/*z* = 540.3 [M]$^+$. $C_{32}H_{36}N_4O_4$ (540.7): calcd. C 71.09, H 6.71, N 10.36; found C 71.10, H 6.97, N 9.95.

***N*-Hexyl-8-{2-[(quinolin-8-yloxy)methyl]allyloxy}quinoline-2-carboxamide (5b):** K_2CO_3 (0.20 g, 1.44 mmol, 5 equiv.) and 8-hydroxyquinoline (0.083 g, 0.57 mmol, 2 equiv.) were added to a solution of **3b** (0.103 g, 0.29 mmol, 1 equiv.) in acetone (25 mL). The suspension was heated at reflux overnight, and the solvent was then evaporated under reduced pressure. The crude residue was taken up in CH_2Cl_2 (50 mL) and washed once with water. The organic phase was dried with Na_2SO_4. Evaporation of the solvent and purification by column chromatography (EtOAc/*n*-hexane, 1:2 to 1:0) gave an oily colourless product (0.103 g, 77%), which was crystallized from *n*-hexane/CH_2Cl_2 (1:1) to obtain a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.86 (dd, *J* = 4.2, 1.7 Hz, 1 H), 8.33 (br. t, *J* = 5.8 Hz, 1 H), 8.25 Hz (d, *J* = 8.7 Hz, 1 H), 8.16 (d, *J* = 8.6 Hz, 1 H), 8.04 (dd, *J* = 8.1, 1.7 Hz, 1 H), 7.34 (m, 5 H), 7.14 (dd, *J* = 5.7, 3.2 Hz, 1 H), 7.07 (dd, *J* = 6.9, 1.9 Hz, 1 H), 5.54 (s, 1 H), 5.50 (s, 1 H), 5.06 (s, 2 H), 4.93 (s, 2 H), 3.35 (dd, *J* = 13.7, 6.6 Hz, 2 H), 1.46 (m, 2 H), 1.20 (m, 6 H), 0.75 (t, *J* = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.4 (C), 154.3 (C), 154.2 (C), 149.3 (CH), 148.8 (C), 139.7 (C), 138.6 (C), 137.2 (CH), 135.9 (CH), 130.4 (C), 129.5 (C), 127.9 (CH), 126.5 (CH), 121.6 (CH), 120.1 (CH), 119.9 (CH), 119.3 (CH), 116.0 (C), 117.5 (CH_2), 110.3 (CH), 109.8 (CH), 69.6 (CH_2), 69.5 (CH_2), 39.5 (CH_2), 31.4 (CH_2), 29.5 (CH_2), 26.6 (CH_2), 22.5 (CH_2), 14.0 (CH_3) ppm. MS (EI, DIP): *m*/*z* = 469.2 [M]$^+$. $C_{29}H_{31}N_3O_3$ (469.6): calcd. C 74.18, H 6.65, N 8.95; found C 74.23, H 6.82, N 8.67.

***N*,*N*-Diethyl-8-{2-[(quinolin-8-yloxy)methyl]allyloxy}quinoline-2-carboxamide (5c):** Following the procedure for the synthesis of **5b**, product **5c** was obtained by treating **3c** (0.48 g, 1.44 mmol, 1 equiv.) with 8-hydroxyquinoline (0.42 g, 2.90 mmol, 2 equiv.) in acetone (50 mL) in the presence of K_2CO_3 (1.00 g, 7.20 mmol, 5 equiv.) as a yellow oil (0.53 g, 82%). This compound was crystallized from *n*-hexane/CH_2Cl_2 (1:1). M.p. 117 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.92 (dd, *J* = 4.2, 1.7 Hz, 1 H), 8.16 (d, *J* = 8.7 Hz, 1 H), 8.09 (dd, *J* = 8.4, 1.7 Hz, 1 H), 7.74 (d, *J* = 8.7 Hz, 1 H), 7.34 (m, 5 H), 7.17 (t, *J* = 4.4 Hz, 1 H), 7.12 (dd, *J* = 6.9, 2.0 Hz, 1 H), 5.52 (s, 2 H), 5.06 (s, 2 H), 4.97 (s, 2 H), 3.56 (q, *J* = 7.2 Hz, 2 H), 3.47 (q, *J* = 7.1 Hz, 2 H), 1.25 (t, *J* = 7.1 Hz, 3 H), 1.21 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.3 (C), 154.3 (C), 153.9 (C), 153.0 (C), 149.0 (CH), 140.1 (C), 139.3 (C), 138.3 (C), 136.5 (CH), 135.6 (CH), 129.2 (C), 129.0 (C), 127.3 (CH), 126.4 (CH), 121.3 (CH), 121.0 (CH), 119.8 (CH), 119.6 (CH), 116.1 (CH_2), 110.2 (CH), 109.8 (CH), 69.4 (CH_2), 69.2 (CH_2), 43.3 (CH_2), 40.4 (CH_2), 14.3 (CH_3), 12.6 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2928, 1617, 1465, 1373, 1316, 1254, 1103, 755 cm^{-1}. MS (EI, DIP): *m*/*z* = 441.2 [M]$^+$. $C_{27}H_{27}N_3O_3$ (441.5): calcd. C 73.45, H 6.16, N 9.52; found C 73.19, H 6.30, N 9.24.

General Procedure for the Thermal Claisen Rearrangement

A compound was placed in a Schlenk flask; the rearrangement proceeded at 170–180 °C without solvent under a nitrogen atmosphere for 5–7 h.

7,7′-(2-Methylenepropane-1,3-diyl)bis(8-hydroxyquinoline-2-carboxamide) (6a): Compound **6a** was prepared according to the general procedure (180 °C, 7 h). The product can be additionally purified by recrystallization from DMF by the slow addition of *i*PrOH to give a white powder in a quantitative yield M.p. 291 °C (dec.). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.03 (s, 2 H), 9.13 (br. s, 2 H), 8.45 (d, *J* = 8.5 Hz, 2 H), 8.10 (d, *J* = 8.5 Hz, 2 H), 7.64 (br. s, 2 H), 7.49 (d, *J* = 8.5 Hz, 2 H), 7.45 (d, *J* = 8.5 Hz, 2 H), 4.76 (s, 2 H), 3.60 (s, 4 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 165.7, 150.6, 147.5, 146.6, 137.1, 136.1, 131.1, 127.8, 121.9, 118.0, 116.6, 112.1, 35.6 ppm. IR (KBr): $\tilde{\nu}$ = 3445, 3287, 1669, 1572, 1447, 1385, 1327, 1237, 1080, 714, 553 cm^{-1}. MS (ESI): *m*/*z* = 429.3 [M + H]$^+$. $C_{24}H_{20}N_4O_4{\cdot}2H_2O$ (464.4): calcd. C 62.06, H 5.21, N 12.06; found C 62.27, H 4.96, N 11.67.

7,7′-(2-Methylenepropane-1,3-diyl)bis[*N*-(hexyl)-8-hydroxyquinoline-2-carboxamide] (6b): Compound **6b** was prepared according to the general procedure from **4b** (0.15 g, 0.25 mmol). The glass-like slightly yellow residue **6b** was purified by column chromatography (EtOAc/*n*-hexane, 1:1) to afford a yellowish solid (0.132 g, 88%). M.p. 112–115 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28 Hz (d, *J* = 8.5 Hz, 2 H), 8.22 (d, *J* = 8.5 Hz, 2 H), 8.04 (br. t, *J* = 6.0 Hz, 2 H), 8.01 (s, 2 H), 7.44 (d, *J* = 8.5 Hz, 2 H), 7.31 (d, *J* = 8.5 Hz, 2 H), 4.85 (s, 2 H), 3.66 (s, 4 H), 3.51 (dd, *J* = 13.6, 6.7 Hz, 4 H), 1.64 (m, 4 H), 1.37 (m, 4 H), 1.29 (m, 8 H), 0.86 (t, *J* = 6.8 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.6 (C), 149.8 (C), 147.6 (C), 146.5 (C), 137.1 (CH), 136.3 (C), 131.4 (CH), 128.1 (C), 122.21 (C), 118.8 (CH), 117.2 (CH), 112.9 (CH_2), 39.8 (CH_2), 36.1 (CH_2), 31.4 (CH_2), 29.6 (CH_2), 26.6 (CH_2), 22.4 (CH_2), 13.9 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3291, 2927, 2857, 1653, 1542, 1505, 1450, 1231, 1181, 1087, 858, 725, 665 cm^{-1}. MS (EI, DIP): *m*/*z* = 596.2 [M]$^+$. $C_{36}H_{44}N_4O_4$ (596.8): calcd. C 72.46, H 7.43, N 9.39; found C 72.04, H 7.88, N 8.95.

7,7′-(2-Methylenepropane-1,3-diyl)bis(*N*,*N*-diethyl-8-hydroxyquinoline-2-carboxamide) (6c): Compound **6c** was prepared according to the general procedure from **4c** (0.30 g, 0.55 mmol). The brown oily product **6c** was purified by column chromatography (EtOAc/*n*-hexane, 1:2 to 1:1 to 1:0) to afford a white solid (0.282 g, 94%). M.p. 106 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8.6 Hz, 2 H), 8.04 (br. s, 2 H), 7.63 (d, *J* = 8.4 Hz, 2 H), 7.43 (d, *J* = 8.4 Hz, 2 H), 7.30 (d, *J* = 8.6 Hz, 2 H), 4.87 (s, 2 H), 3.65 (s, 4 H), 3.63 (q, *J* = 7.0 Hz, 4 H), 3.40 (q, *J* = 7.0 Hz, 4 H), 1.31 (t, *J* = 7.0 Hz, 6 H), 1.22 (t, *J* = 7.0 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.3 (C), 152.3 (C), 149.6 (C), 146.4 (C), 137.0 (CH), 136.3 (C), 130.9 (CH), 126.8 (C), 122.0 (C), 120.3 (CH), 117.1 (CH), 113.0 (CH_2), 43.1 (CH_2), 40.1 (CH_2), 36.0 (CH_2), 14.6 (CH_3), 12.8 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2936, 2877, 1611, 1483, 1444, 1375, 1108, 845 cm^{-1}. MS (EI, DIP): *m*/*z* = 540.2 [M]$^+$. $C_{32}H_{36}N_4O_4$ (540.3): calcd. C 71.09, H 6.71, N 10.36; found C 70.83, H 7.08, N 10.04. HRMS: calcd. for $C_{32}H_{36}N_4O_4$ 540.27366; found 540.27374.

X-ray Crystal Structure Analysis of 6c: Formula $C_{32}H_{36}N_4O_4$, *M* = 540.65, colourless crystal 0.25 × 0.25 × 0.25 mm, *a* = 25.2787(9) Å, *b* = 8.5927(2) Å, *c* = 13.3004(4) Å, *V* = 2889.01(15) Å^3, $\rho_{calcd.}$ = 1.243 g cm^{-3}, μ = 0.666 mm^{-1}, empirical absorption correction ($0.851 \leq T \leq 0.851$), *Z* = 4, orthorhombic, space group *P*na2$_1$ (No. 33), λ = 1.54178 Å, *T* = 223 K, ω and *f* scans, 19293 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 4828 independent (R_{int} = 0.041) and 4650 observed reflections [$I \geq 2\sigma(I)$], 367 refined parameters, R = 0.032, wR_2 = 0.082, max. residual electron density 0.10 (–0.11) e Å^{-3}, Flack parameter 0.41(16), hydrogen atoms calculated and refined riding.

Data set was collected with a Nonius Kappa CCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN,[23] absorption correction Denzo,[24] structure solution SHELXS-97,[25] structure refinement SHELXL-97,[26] graphics XP (BrukerAXS, 2000) and SCHAKAL.[27]

CCDC-649294 contains 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.

8-Hydroxy-7-[2-(8-hydroxyquinolin-7-ylmethyl)allyl]quinoline-2-carboxylic Acid Hexylamide (7b): Compound **7b** was prepared according to the general procedure from **5b** (0.08 g, 0.17 mmol). The purification of the brown residue was performed by column chromatography (EtOAc/*n*-hexane, 1:1) to provide a pale solid (0.075 mg, 94%). M.p. 57–64 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.74 (m, 1 H), 8.29 (d, J = 8.4 Hz, 1 H), 8.23 (d, J = 8.4 Hz, 1 H), 8.13 (br. t, J = 5.8 Hz, 1 H), 8.07 (dd, J = 8.3, 1.6 Hz, 1 H), 7.46 (d, J = 8.4 Hz, 1 H), 7.38 (d, J = 8.4 Hz, 1 H), 7.35 (d, J = 8.4 Hz, 1 H), 7.31 (d, J = 8.4 Hz, 1 H), 7.23 (d, J = 8.4 Hz, 1 H), 4.87 (m, 2 H), 3.66 (s, 4 H), 3.50 (m, 2 H), 1.63 (m, 2 H), 1.31 (m, 6 H), 0.85 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.2 (C), 149.5 (C), 148.0 (C), 147.7 (CH), 146.6 (C), 138.1 (C), 137.3 (CH), 136.3 (C), 135.9 (CH), 131.6 (CH), 129.9 (CH), 128.3 (C), 127.1 (C), 122.5 (C), 121.1 (CH), 121.0 (C), 119.1 (CH), 117.4 (CH), 117.1 (CH), 112.9 (CH_2), 39.8 (CH_2), 36.1 (CH_2), 36.1 (CH_2), 31.5 (CH_2), 29.7 (CH_2), 26.7 (CH_2), 22.5 (CH_2), 14.0 (CH_3) ppm, one quarternary C atom could not be observed. IR (KBr): $\tilde{\nu}$ = 3305, 2925, 2856, 1651, 1542, 1504, 1453, 1372, 1233, 1179, 1089, 894, 827, 667 cm^{-1}. MS (EI, DIP): m/z = 469.2 $[M]^+$. $C_{29}H_{31}N_3O_3$ (469.6): calcd. C 74.18, H 6.65, N 8.95; found C 74.23, H 6.82, N 8.67.

***N*-Diethyl-8-hydroxy-7-{2-[(8-hydroxyquinolin-7-yl)methyl]allyl}-quinoline-2-carboxamide (7c):** Compound **7c** was prepared according to the general procedure from **5c** (0.50 g, 1.13 mmol). The purification of the brown residue was performed by column chromatography (EtOAc/*n*-hexane, 1:2 to 1:1 to 1:0) to provide a white solid (0.485 mg, 97%). M.p. 65–66 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.69 (dd, J = 4.1, 1.6 Hz, 1 H), 8.14 (d, J = 8.5 Hz, 1 H), 8.06 (dd, J = 8.2, 1.6 Hz, 1 H), 7.98 (br. s, 1 H), 7.59 Hz (d, J = 8.4 Hz, 1 H), 7.39 Hz (d, J = 8.5 Hz, 1 H), 7.39 (d, J = 8.5 Hz, 1 H), 7.33 (m, 2 H), 7.23 (m, 2 H), 4.83 (s, 1 H), 4.82 (s, 1 H), 3.61 (s, 4 H), 3.58 (q, J = 7.2 Hz, 2 H), 3.36 (q, J = 7.1 Hz, 2 H), 1.27 (t, J = 7.2 Hz, 3 H), 1.19 Hz (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.1 (C), 152.0 (C), 149.3 (C), 147.5 (CH), 146.4 (C), 137.9 (C), 136.9 (CH), 136.1 (C), 135.7 (CH), 130.9 (CH), 129.8 (CH), 126.9 (C), 126.7 (C), 122.0 (C), 120.9 (C), 120.9 (C), 120.2 (CH), 120.2 (CH), 117.0 (CH), 117.0 (CH) 112.8 (CH_2), 43.1 (CH_2), 40.1 (CH_2), 36.1 (CH_2), 36.0 (CH_2), 14.6 (CH_3), 12.9 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3382, 3323, 2925, 1615, 1463, 1463, 1374, 1207, 1089, 882, 830, 777, 663 cm^{-1}. MS (EI): m/z = 441.1 $[M]^+$. $C_{27}H_{27}N_3O_3$ (441.2): calcd. C 73.45, H 6.16, N 9.52; found C 74.09, H 6.51, N 9.27. HRMS: calcd. for $C_{27}H_{27}N_3O_3$ 441.20524; found 441.20543.

8-Allyloxyquinoline-2-carboxylic Acid Amide (8): To a solution of **2a** (0.338 g, 1.80 mmol, 1 equiv.) in DMF (25 mL) was added allylbromide (2.19 g, 18 mmol, 10 equiv.) and K_2CO_3 (2.5 g, 18 mmol, 10 equiv.). The resulting mixture was stirred at 90 °C overnight, evaporated to dryness and then partitioned between CH_2Cl_2 and water. The organic extract was dried with Na_2SO_4 and concentrated in vacuo. The crude oily product was purified by flash chromatography (CH_2Cl_2/acetone, 5:1) to afford a white crystalline solid (0.251 g, 88%). M.p. 121 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (br. s, 1 H), 8.25 (d, J = 8.6 Hz, 1 H), 8.15 (m, 1 H), 7.41 (m, 1 H), 7.33 (d, J = 8.5 Hz, 1 H), 6.99 (d, J = 7.7 Hz, 1 H), 6.76 (s, 1 H), 6.13 (m, 1 H), 5.48 (dq, J = 17.3, 1.5 Hz, 1 H), 5.29 (dq, J = 10.7, 1.5 Hz, 1 H), 4.71 (d, J = 4.1 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.1 (C), 154.1 (C), 147.9 (C), 138.4 (C), 136.9 (CH), 132.6 (CH), 130.2 (C), 128.0 (CH), 119.4 (CH), 119.0 (CH), 117.7 (CH_2), 109.8 (CH), 69.5 (CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 3426, 1684, 1584, 1464, 1369, 1251, 1086, 990, 504 cm^{-1}. MS (EI, DIP): m/z = 228.0 $[M]^+$. $C_{13}H_{12}N_2O_2$ (228.0): calcd. C 68.41, H 5.30, N 12.27; found C 68.08, H 5.02, N 12.45.

7-Allyl-8-hydroxyquinoline-2-carboxylic Acid Amide (9): Heating of **8** (0.25 g, 1.10 mmol) under an atmosphere of N_2 at 170 °C for 6 h led to the pure product as an off-white solid in quantitative yield (0.25 g,). M.p. 198 °C. ^{1}H NMR (300 MHz, CD_3OD): δ = 8.33 (d, J = 8.4 Hz, 1 H), 8.13 (d, J = 8.4 Hz, 1 H), 7.43 (d, J = 8.4 Hz, 1 H), 7.36 (d, J = 8.4 Hz, 1 H), 6.06 (m, 1 H), 5.07 (m, 2 H), 3.61 (dt, J = 6.7, 1.5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.5 (C), 151.8 (C), 148.6 (C), 138.6 (CH), 138.3 (C), 137.7 (CH), 132.5 (CH), 129.9 (C), 124.4 (C), 119.3 (CH), 118.2 (CH), 116.0 (CH_2), 35.0 (CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 3414, 3307, 3191, 1710, 1672, 1598, 1564, 1509, 1451, 1388, 1234, 1189, 1095, 992, 912, 856 cm^{-1}. MS (EI, DIP): m/z = 228.1 $[M]^+$. $C_{13}H_{12}N_2O_2$ (228.2): calcd. C 68.41, H 5.30, N 12.27; found C 68.82, H 5.20, N 12.20.

8-Acetyloxy-2-*N*-acetylcarboxylic Acid Amide (10): A suspension of **9** (0.25 g, 1.10 mmol) in acetic anhydride (30 mL) was heated at reflux overnight. After evaporation of the solvent, the oily residue was suspended in water, neutralized with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was dried with Na_2SO_4, filtered and concentrated in vacuo before column chromatography (EtOAc/*n*-hexane, 1:5) to afford a white crystalline solid (0.292 g, 85.5%). M.p. 96 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.42 (br. s, 1 H), 8.34 (d, J = 8.5 Hz, 1 H), 8.25 (d, J = 8.5 Hz, 1 H), 7.74 (d, J = 8.5 Hz, 1 H), 7.57 (d, J = 8.5 Hz, 1 H), 5.95 (m, 1 H), 5.17 (m, 1 H), 5.14 (t, J = 1.5 Hz, 1 H), 3.56 (dt, J = 6.6, 1.5 Hz, 2 H), 2.64 (s, 3 H), 2.57 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.5 (C), 169.1 (C), 162.3 (C), 147.3 (C), 144.8 (C), 139.1 (C), 138.1 (CH), 134.0 (CH), 133.8 (C), 130.9 (CH), 129.4 (CH_2), 125.1 (CH), 118.7 (CH), 117.1 (C), 34.7 (CH_2), 25.2 (CH_3), 20.7 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3308, 1767, 1701, 1468, 1374, 1281, 1198, 865, 748 cm^{-1}. MS (EI): m/z = 312.1 $[M]^+$. $C_{17}H_{16}N_2O_4$ (312.0): calcd. C 65.38, H 5.16, N 8.97; found C 65.79, H 5.69, N 9.02.

7-[4-(8-Acetoxy-2-acetylcarbamoylquinolin-7-yl)but-2-enyl]-2-acetylcarbamoylquinolin-8-yl Acetate (11): To a solution of **10** (0.25 g, 0.93 mmol, 1 equiv.) in absolute CH_2Cl_2 (5 mL) under an inert atmosphere of N_2 was added benzylidenebis(tricyclohexylphosphane)dichlororuthenium (0.038 g, 0.046 mmol, 0.05 equiv.) in absolute CH_2Cl_2 (5 mL). The mixture was heated at reflux for 12 h and then stirred at room temp. for another 12 h. The solvent was removed in vacuo. The crude product was directly subjected to column chromatography (EtOAc/*n*-hexane, 1:2 to 1:1 to 1:0 to MeOH). The fraction with R_f = 0.16 (fraction from EtOAc/*n*-hexane, 1:1 to 1:0) contained a mixture of *Z* and *E* isomers, which was recrystallized from $CHCl_3$/MeOH (2:1) to yield white solid flakes (0.043 g, 18%). The fraction washed out with MeOH afforded a single compound that was washed with MeOH to give a white solid (62 mg, 26%). M.p. 268 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.42 (br. s, 2 H), 8.37 (d, J = 8.5 Hz, 2 H), 8.29 (d, J = 8.5 Hz, 2 H), 7.77 (d, J = 8.5 Hz, 2 H), 7.56 (d, J = 8.5 Hz, 2 H), 5.73 (dt, J = 3.8, 2.2 Hz, 2 H), 3.55 (d, J = 5.0 Hz, 4 H), 2.65 (s, 6 H), 2.53 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 171.7 (C), 169.2 (C), 162.4 (C), 147.4 (C), 144.9 (C), 139.2 (C), 138.2 (CH), 134.0 (C), 131.0 (CH), 129.5 (C), 129.2 (CH), 125.2 (CH), 118.8 (CH), 33.5 (CH_2), 25.2 (CH_3), 20.2 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3312, 1755, 1699, 1472, 1375, 1281, 1213, 1075, 861, 744 cm^{-1}. MS (EI+, DIP): m/z = 554.1 $[M - CH_3CO^-]^+$. $C_{32}H_{28}N_4O_8$ (596.6): calcd. C 64.42, H 4.73, N 9.39; found C 64.19, H 5.09, N 9.24.

7,7′-(But-2-ene-1,4-diyl)bis(quinolin-8-ol-2-carboxylic Acid) (12): A solution of aqueous KOH (20%, 0.5 mL) was added to **11** (0.05 g, 0.084 mmol) suspended in a mixture of pyridine (2 mL) and water (0.5 mL). The reddish solution was heated at reflux for 1 h and then stirred at room temp. for another 12 h. The mixture was neu-

tralized with dilute HCl until pH ca. 6–7. The precipitate thus formed was filtered off and purified by recrystallization from THF/MeOH (3:1) to furnish a pale solid (0.023 g, 64%). M.p. 285 °C (dec.). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.42 (d, J = 8.5 Hz, 2 H), 8.11 (d, J = 8.5 Hz, 2 H), 7.49 (d, J = 8.2 Hz, 2 H), 7.43 (d, J = 8.2 Hz, 2 H), 5.85 (s, 2 H), 3.61 (s, 4 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 166.3, 150.8, 138.2, 136.8, 133.1, 132.1, 129.5, 128.5, 123.9, 120.0, 117.5, 32.7 ppm. IR (KBr): $\tilde{\nu}$ = 3386, 3024, 1669, 1593, 1458, 1375, 1271, 1192, 1157, 1131, 976, 931, 793 cm^{-1}. MS (EI, DIP): m/z = 430.1 [M]$^+$. MS (ESI): m/z = 453.2 [M + Na]$^+$. $C_{24}H_{18}N_2O_6$ (430.4): calcd. C 66.97, H 4.22, N 6.51; found C 67.06, H 4.67, N 7.02.

Supporting Information (see footnote on the first page of this article): Two dimensional NMR spectrum for the assignment of the *E* configuration of **11**.

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