Homo- and Heterodinuclear Luminescent Helicates

Von der Fakultät für Mathematik, Informatik und Naturwissenschaften der Rheinisch-Westfälischen Technischen Hochschule Aachen zur Erlangung des akademischen Grades einer Doktorin der Naturwissenschaften genehmigte Dissertation

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   Chem. Commun. **2007**, *18*, 1834-1836.

6. M. Albrecht, O. Osetska, R. Fröhlich
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   Eur. J. Org. Chem. **2007**, *29*, 4902-4908.

7. M. Albrecht, O. Osetska, R. Fröhlich, J.-C. G. Bünzli, A. Aebischer, F. Gumy, J. Hamacek
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Моїм дорогим батькам,

To my dear Parents,

Anna and Volodimir Ossietzky

Contents

1. Introduction

Graceful ease, precision and perfection, with which nature builds up and maintains unique and complicated biological structures, has always wondered humans, stirring their ambitions in striving to realize and even emulate natural paradigms. Biomimetic chemistry[1] and nanotechnology[2] are the terms introduced in the scientific community to define or distinguish research, which concerns itself with mimicking the essence of biosystems by developing artificial analogues, or with elaboration of functioning molecular devices which operate on the nanometer scale.[3] A biological concept of self-recognition of molecular components and their self-organization into supramolecular entities is considered crucial for the expression of specific properties.[4] Tobacco mosaic virus,[5] protein ferritin,[6] ribosomes, mitochondria, rhinovirus[7] etc. as well as the well-known and intensively studied DNA double helix[8] are striking examples of "strict self-assembly"[9] in nature. Supramolecular chemistry is the discipline, which studies the phenomena of these supramolecules using synthetic principles exclusively driven by noncovalent interactions.[10] In this consideration, giant artificial molecular architectures are constructed by simultaneous and highly convergent assembly of predisposed subunits and held together by additive or cooperative intermolecular forces (van der Waals / hydrophobic, hydrogen bonding or π-π stacking / electrostatic interactions). To optimize complementarity and integrity in the shape and properties attributed to biological systems, dynamics and reversibility between constituents in the assembling systems are required; the shift in an equilibrium leads to the final product representing the thermodynamic minimum.[11] Kinetic lability of alternative coordinative bonds also allows the reorganization of multicomponent species and promotes the self-correction during the assemblage, considerably decreasing the number of defects and precluding inappropriate routes such as

[1] E. C. Constable, *Nature* **1990**, *346*, 314.
[2] J.-M. Lehn, *Angew. Chem.* **1990**, *102*, 1347.
[3] R. P. Feyman, *Eng. Sci.* **1960**, *23*, 22.
[4] D. Philp, F. Stoddart, *Angew. Chem.* **1996**, *108*, 1243; *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 1154.
[5] A. Klug, *Angew. Chem.* **1983**, *95*, 579.
[6] D. L. Caulder, K. N. Raymond, *Acc. Chem. Res.*, **1999**, *32*, 975.
[7] A. Cann, *Principles of Molecular Virology*, 2nd ed.; Academic Press: New York, **1997**.
[8] C. R. Calladine, H. R. Drew, *Understanding DNA: The Molecule and how it works*, Academic Press: New York, 2nd ed.; **1997**.
[9] J. S. Linsey, *New J. Chem.* **1991**, *15*, 153.
[10] (a) G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, *254*, 1312. (b) P. Tecilla, R. P. Dixon, G. Slobodkin, D. S. Alavi, D. H. Waldeck, A. D. Hamilton, *J. Am. Chem. Soc.* **1990**, *112*, 9408. (c) J.-M. Lehn, *Chem. Eur.* J. **2000**, *6*, 2097.
[11] D. S. Lawrence, T. Jiang, M. Levett, *Chem. Rev.* **1995**, *95*, 2229.

unfavourable aggregation.[12] Moreover, metal-ligand interactions possess high directionality and are of moderate strength, therefore providing an option for traditional biological motifs in molecular recognition.[13] If the variable geometries and stereochemical preferences at metal centers match the binding possibilities of pre-organized / predisposed multidentate organic ligands a well-defined and predictable fascinating artificial supramolecular architecture might be produced.[14]

1.1. Helicates in Supramolecular Chemistry

During the last 100 years the coordination chemistry principles found by *Alfred Werner*,[15] developed further by *Lewis* and *Sidgwick*[16] (introduction of the concept of metal-ligand interaction through sharing of an electron pair), and contributed to by *Curtis,*[17] *Jäger*,[18] and *Busch*[19] (macrocycles, popularization of "template effect"), have been finally acknowledged by awarding the Nobel Prize to *Cram*[20] (cyclophanes, spherands, carcerands, host-guest chemistry), *Pederson*[21] (crown ethers, molecular recognition), and *Lehn*[22] (cryptands, introduction of the term "supramolecular chemistry") in 1987. The fundamental research in the area of metallosupramolecular chemistry unravels its enormous potential in the construction of complex unnatural systems (two-dimensional grids, ladders, racks, metallocyclic polygons, polyhedra, circular helicates, intertwined catenanes, rotaxanes, knots etc.), emerging from scientists' imagination and creativity to represent a kind of an art in chemistry.

Probably the most spectacular and inspiring example of self-recognition and self-organization in nature is provided by nucleic base-pairing that occurs in DNA strands due to hydrogen bonding.[23] Additionally, the overall DNA structure is stabilized by π-π stacking interactions

[12] J.-M. Lehn, *Supramolecular Chemistry – Concepts and Perspectives*, Wiley–VCH, Weinheim, **1995**.
[13] (a) E. C. Constable, *Angew. Chem*. **1991**, *103*, 1483; *Angew. Chem., Int. Ed. Engl*. **1991**, *30*, 1450. (b) E. C. Constable, *Chem. Ind*. **1994**, 56.
[14] (a) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev*. **2000**, *100*, 853. (b) G. F. Swiegers, T. J. Malefetse, *Chem. Rev*. **2000**, *100*, 3483. (c) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa, K. Biradha, *Chem. Commun*. **2001**, 509. (d) P. J. Steel, *Acc. Chem. Res*. **2005**, *38*, 243.
[15] (a) A. Werner, *New Ideas in Chemistry*, E. P. Hedley, London, **1911**. (b) A. Werner, *Z. Anorg. Chem.* **1893**, *3*, 267.
[16] (a) G. A. Melson, *Coordination Chemistry of Macrocyclic Compounds*, Plenum, New York, **1979**. (b) L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, **1989.**
[17] (a) N. F. Curtis, *J. Chem. Soc*. **1960**, 4409. (b) N. F. Curtis, Y. M. Curtis, H. K. Powell, *J. Chem. Soc. A* **1966**, 1015.
[18] E. G. Jäger, *Z. Chem.* **1968**, *8*, 392.
[19] M. C. Thompson, D. H. Busch, *J. Am. Chem. Soc*. **1992**, *114*, 9197.
[20] D. J. Cram, *Angew. Chem*. **1988**, *100*, 1041.
[21] (a) C. J. Pederson, *J. Am. Chem. Soc*. **1967**, *89*, 2495. (b) C. J. Pederson, *Angew. Chem* **1988**, *100*, 1041.
[22] (a) J.-M. Lehn, *Science*, **1985**, *227*, 849. (b) J.-M. Lehn, *Angew. Chem*. **1988**, *100*, 91.
[23] (a) J. D. Watson, F. H. C. Crick, *Nature*, **1953**, *171*, 737. (b) W. Saenger, *Principles of Nucleic Acid Structure*, Springer: New York, **1984**.

between neighbouring base-pairs.[24] Like many proteins it adopts helical substructures - α-helices. DNA is commonly illustrated in three forms - A and B with right-, and Z with left-handed helicity, causing the chirality of the helical screw and enabling the formation of a double helix. The corresponding nomenclature was proposed by *Cahn*, *Ingold*, and *Prelog* labelling right- and left-handed forms as P ("plus") and M ("minus"), respectively.[25]

The helix formation mechanism associated with biological principles of self-organization has been applied to metal complexes, where "the molecular information stored in strands"[12] is transferred in an assembly under the assistance of an appropriate metal coordinator. These artificial supramolecular architectures were termed helicates (*Lehn*, 1987).[26] In the last twenty years helicate chemistry has made a formidable step from simple oligobipyridine-based double helicates, selected by the appropriate amount of Cu^{I} metal centres,[26] to homo- and heteropolynuclear triple- and quaternary stranded linear, circular, or polymeric systems, exhibiting already certain magnetic or spectroscopic properties and intended for various stimulating applications.[27] Probably the *positive cooperativity* and the *"self-self selection"* discovered by *Lehn* et al.[28] became a milestone in the development of metal helicates: the above-mentioned spherical d^{10} Cu^{I}, which prefers pseudotetrahedral coordination with 2,2'-bipyridine, organizes a set of D_2-symmetrical double stranded helicates by selection of the predisposed ether-linked segmental ligands (**1**) from a random mixture (Figure 1).

Similar findings, or another example of positive cooperativity, were reported by *Raymond*: selective self-assembly of three individual homoleptic helical products by reaction of the ligands, possessing different length and conformational rigidity of the spacers between two binding sites, with Ga^{III} under an appropriate 3 : 2 ligand to metal ion stoichiometry.[29]

As the next step, the nucleoside unit was embedded in the periphery of bipyridine ligand, whereas the charged moieties for Cu^{I} are positioned within the interior.[30] Amazingly, the final deoxyribonucleohelicate structure, where the nucleobases are on the outside of the copper helix, is reminiscent of *Pauling's* (erroneous) structural model for DNA, proposed in 1953.[31]

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[24] G. Ebert, *Biopolymere*, Teubner, Stuttgart **1992**.
[25] R. S. Cahn, C. K. Ingold, V. Prelog, *Angew. Chem*. **1966**, *78*, 413; *Angew. Chem*., *Int. Ed. Engl*. **1966**, *5*, 385.
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[27] (a) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005. (b) M. Albrecht, *Chem. Rev*. **2001**, *101*, 3457.
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[29] D. Caulder, K. N. Raymond, *Angew. Chem*. **1997**, *109*, 1508.
[30] U. Koert, M. M. Harding, J.-M. Lehn, *Nature* **1990**, *346*, 339.
[31] L. Pauling, R. B. Corey, *Nature* **1953**, *171*, 346.

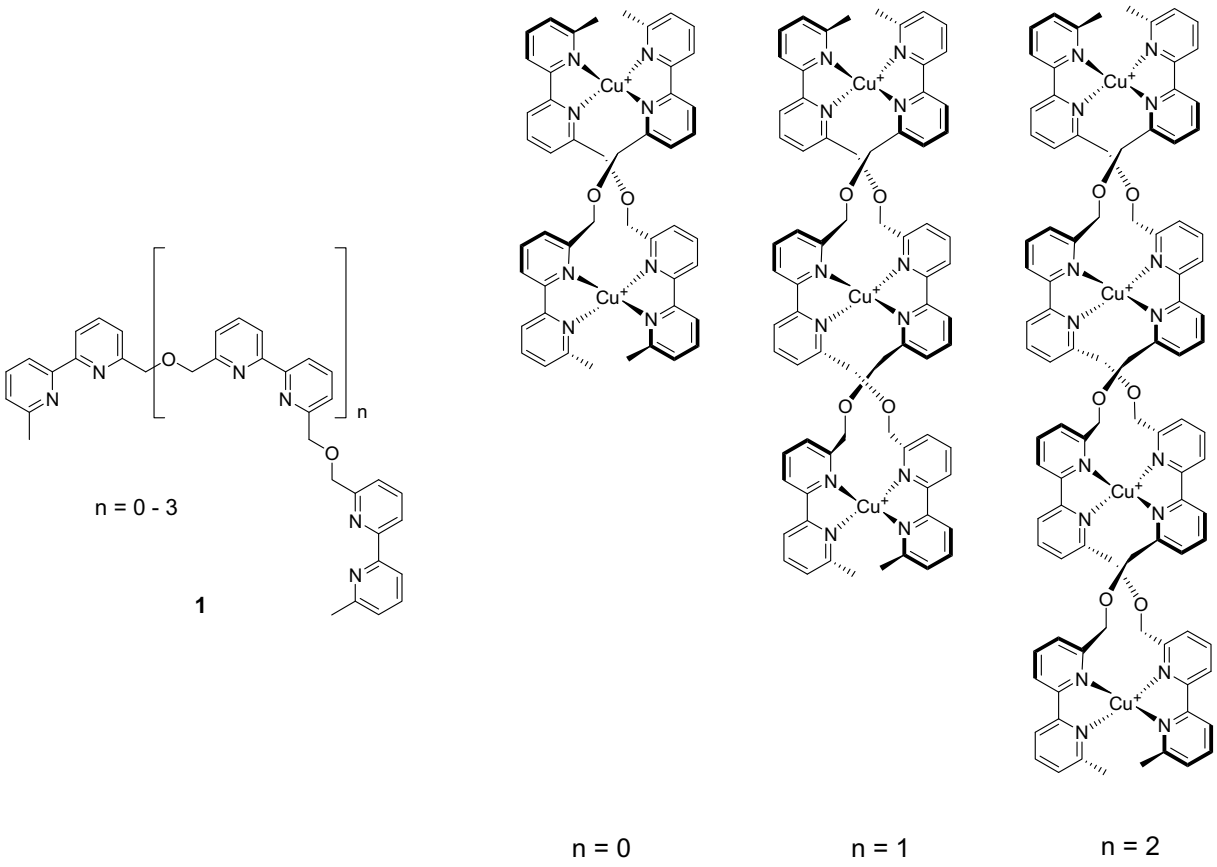
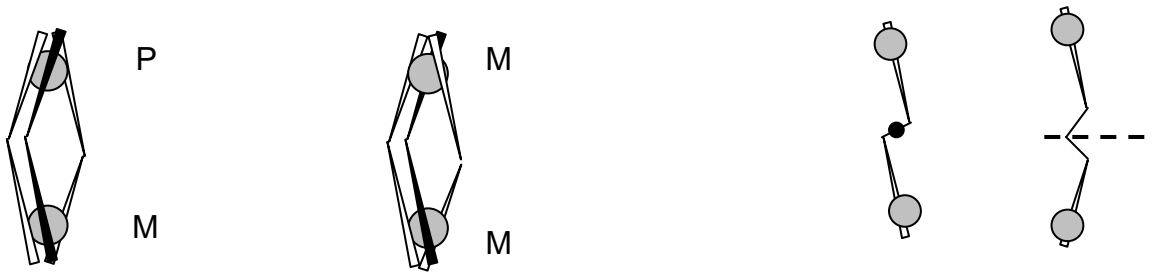


Figure 1. An example of positive cooperativity and self-selection in the self-assembly of the Cu(I) double helices from a mixture of oligobipyridine strands **1**.[26, 32]

Another interesting experiment was reported by *Lehn*, involving oligobipyridine ligands, which owing to different steric requirements (alternating rigidity / flexibility) react with a stoichiometric mixture of Cu^{I} and Ni^{II}, leading to the double-stranded copper and triple-stranded nickel helicates. This striking example represents the self-assembly of 11 participating in whole process particles of 4 different kinds of units resulting in only two well-defined supramolecules.[32]

In all these cases described above, the chiral and helical properties of helicates are deduced from the P/M combination of metal centres, if the intrinsic helicity at the ligand spacer is neglected. Thus, the chirality of helicates can be developed from the same absolute configurations of complex units; the opposite configurations correspond to the achiral meso-form of helicate (Figure 2).

[32] R. Krämer, J.-M. Lehn, A. Marquis-Rigault, *Proc. Natl. Acad. Sci. USA* **1993**, *90*, 5394.



achiral side-by-side *meso*-form (C_{3h}) chiral helical form (D_3) C_2 axis mirror plane σ

Figure 2. Helical and chiral properties of triple-stranded dinuclear helicates with C_2 symmetrical ligands.

Figure 3. Regulation of the chirality at helicates by altering a number of CH_2 units.

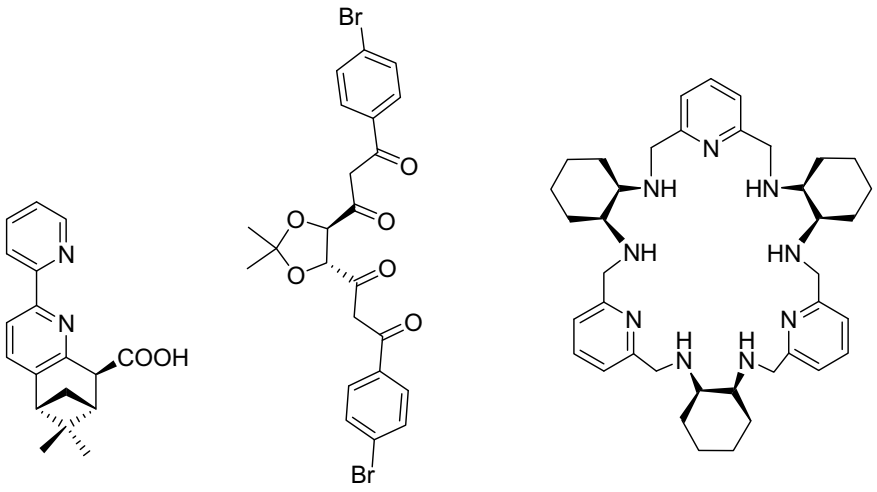
An "*odd-even principle*"[33] for the stereoselective preparation of helicates was applied to metallohelicates by *Albrecht*.[34] A set of ligands containing methylene units in the spacer was analyzed relying on the control of diastereo- (for *meso*-helicate[34,35]) or homotopic (for chiral helicate) protons of CH_2 groups in NMR spectra. It was suggested, that an odd number of methylene units in the linkage provides an internal mirror symmetry plane in the molecule, which might lead to the *meso*-form of the helicate. An even number of CH_2 groups brings C_2 symmetry axis for the adopted conformation giving rise to the chiral helicate (Figure 3).[36]

The described strategy is partially in agreement with *Raymond's* "*symmetry interactions*" model developed for the rational design of a M_2L_3 (M = metal, L = ligand) helicates possessing a D_3 symmetry. The latter implies the perpendicular to each other oriented C_3 and C_2 axes and parallel positioned chelate planes lying on the same helical axis.[6,37] But the author warned about the possible strong influence of other factors (e. g., template effect) on the final conformation of the product by suppression of enthalpy parameters. An inversion of the stereochemistry can occur yielding the thermodynamically more favoured helicate. [38]

Another, different approach to the chirality in helicates, is the involvement of intrinsically chiral ligands with an incorporated asymmetric C centre. For instance, enantiomerically pure

[33] J. H. Brewster, *Top. Curr. Chem*. **1974**, *47*, 29.
[34] M. Albrecht, *Chem. Eur. J*. **2000**, 6*,* 3485.
[35] (a) E. C. Constable, M. Neuburger, L. Whall, M. Zehnder, *New J. Chem*. **1998**, *22*, 219. (b) W. Zarges, J. Hall, J.-M. Lehn, C. Bolm, *Helv. Chem. Acta* **1991**, *74*, 1843.
[36] (a) M. Albrecht, I. Janser, H. Houjou, R. Fröhlich, *Chem. Eur. J*. **2004**, *10*, 2839. (b) M. Albrecht, I. Janser, R. Fröhlich, *Chem. Commun*. **2005**, 157. (c) M. Albrecht, I. Janser, A. Lützen, M. Hapke, R. Fröhlich, P. Weis, *Chem. Eur. J*. **2005**, *11*, 5742. (d) M. Albrecht, O. Blau, R. Fröhlich, *Chem. Eur. J*. **1999**, *5*, 48.
[37] D. Caulder, K. N. Raymond, *J. Chem. Soc., Dalton Trans*. **1999**, 1185.
[38] J. Xu, T. N. Parac, K. N. Raymond, *Angew. Chem*. **1999**, *111*, 3055.

strands (pinene-derived[39] and chiragen-type[40] ligands, e.g., (+)-**2**-H,[40b] bis-ß-diketonate,[41] e.g., *R,R*-**3**,[41] macrocyclic, e.g., L_{RRRRRR}-**4**-H_6, [42] derivatives etc.) induce the formation of diastereomers according to the helical turn at the ligand unit. Moreover, the attempts of chiral self-recognition (homo- and heterorecognition) between so-called "mixture of instructed ligands" were reported.[40a]



(+)-**2**-H *R,R*-**3** L_{RRRRRR}-**4**-H_6

Figure 4. Chiral linear (+)-**2**-H, *R,R*-**3** and macrocyclic L_{RRRRRR}-**4**-H_6 ligands.

1.2. Lanthanide Helicates. From Homo- to Heteropolymetallic systems

An impressive number of publications concerning the helicate systems appeared in the literature since the first helicate structure for a Cu complex was proposed (*Harris* and *McKenzie*, 1969)[43]; many intensive efforts are still focused on the study and predictive concept of self-assembly processes. *Piguet*, *Bernardinelli*, and *Williams*[44] developed a new type of segmental ligands like **5 (**Figure 5) bearing pyridine and benzimidazole structural components which enable tridentate as well as bidentate binding units. They are connected by

[39] (a) H. Mürner, A. Von Zelewsky, G. Hopfgartner, *Inorg. Chim. Acta* **1998**, *271*, 36. (b) P. Baret, D. Gaude, G. Gellon, J.-L. Pierre*, New J. Chem*. **1997**, *21*, 1255.
[40] (a) O. Mamula, A. Von Zelewsky, P. Brodard, C.-W. Schläpfer, G. Bernardinelli, H. Stoeckli-Evans, *Chem. Eur. J.* **2005**, *11*, 3049. (b) O. Mamula, M. Lama, H. Stoeckli-Evans, and S. Shova, *Angew. Chem., Int. Ed.* **2006***, 45,* 4940. (c) M. Lama, O. Mamula, G. S. Kottas, F. Rizzo, L. De Cola, A. Nakamura, R. Kuroda, H. Stoeckli-Evans, *Chem. Eur. J.* **2007**, *13*, 7358.
[41] (a) M. Albrecht, S. Schmidt, M. deGroot, P. Weis, R. Fröhlich, *Chem. Commun*. **2003**, 2526. (b) M. Albrecht, S. Dehn, G. Raabe, R. Fröhlich, *Chem. Commun*. **2005**, 5690.
[42] J. Gregoliński, J. Lisowski, *Angew. Chem*., **2006**, *118*, 6268.
[43] C. M. Harris, E. D. McKenzie, *J. Chem. Soc. (A)* **1969**, 746.
[44] G. Bernardinelli, C. Piguet, A. F. Williams, *Angew. Chem.* **1992**, *104*, 1626; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1622.

a methylene spacer which provides a helical twist within the ligand. An increase in the denticity of the coordination moiety requires more variable coordination numbers different from the banal tetrahedral or octahedral geometries of d- or p-block elements. Lanthanide ions Ln(III) (Ln = La-Lu) are optimal candidates which possess coordination numbers predominantly of 8-10, and despite their uncertain stereochemical preferences, Ln(III) tend to the nine coordinate environment.

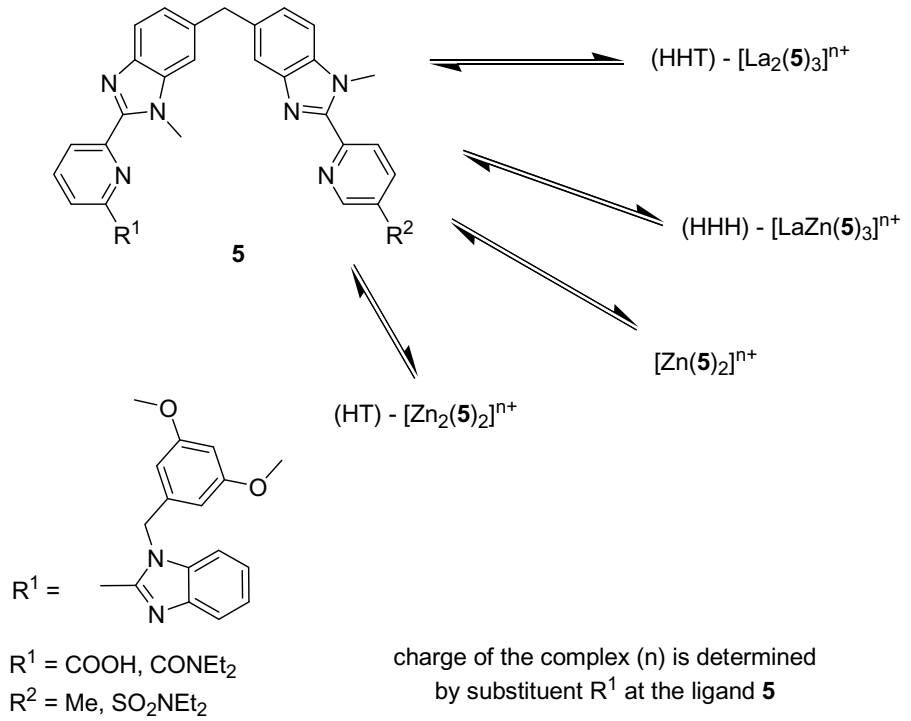


Figure 5. Self-assembly of the ligand **5** with La(III) and Zn(II) in solution.

1.2.1. d/f-Helicates

A wide range of stable triple-stranded bimetallic 4f-4f and 3d-4f helicates was designed varying the end groups in order to correlate hardness / softness and size discrimination of the binding cavity, and/or to affect the affinity to the certain kind of elements (p-, d-, f-).[45]

For instance, it was shown how the replacement of the terminal benzimidazole unit by a carboxamide group affects the affinity to the d-block elements increasing remarkably the tendency to coordinate Ln(III). Thus, the selectivity improvement resulted in the quantitative formation of target heterodimetallic (HHH)-$[ZnLa(\mathbf{5})_3]^{n+}$ species (Figure 5). But at the same

[45] (a) J.-C. G. Bünzli, C. Piguet, *Chem. Soc. Rev.* **2005**, *34*, 1048. (b) J.-C. G. Bünzli, C. Piguet, *Chem. Rev.* **2002**, *102*, 1897-1928. (c) C. Piguet, J.-C. G. Bünzli, *Chem. Soc. Rev.* **1999**, *28*, 347.

time the *negative cooperativity*[46] can preclude the formation of well-defined helicate assemblies resulting in homodimetallic either antiparallel oriented side-by-side complexes, e.g., $[Zn_2(\mathbf{5})_2]^{n+}$, or triple stranded HHT-helicates, e.g., (HHT)-$[La_2(\mathbf{5})_3]^{n+}$.[47] Finally, an implementation of carboxylate in the periphery of the ligands is crucial for the establishment of Ln-ligand bonds, strong enough to compete with water molecules stabilizing the complexes in aqueous medium.[47,48] But it is noteworthy, that the additional negatively charged oxygen donor can considerably decrease the formation constant in solution and cause the distortion from the regular structure, which is traced back to the electrostatic repulsions between coordinated carboxylates.[49]

Another spectacular aspect related to the thermodynamic control in the ligand design was elucidated by *Bünzli* and *Piguet*. They described the electronic effects arising from the introduction of the strongly withdrawing sulphonamide group on the pyridine moiety (Figure 5, $R^2 = SO_2NEt_2$). The latter thus loses the affinity to Ln (III), due to σ-accepting capacity of SO_2NEt_2 and tends to coordinate d-elements (especially soft and electron-rich Fe^{2+}, Ni^{2+}, Zn^{2+}) involving π-back donation from filled d-orbitals. The σ/π - compensation effect dramatically influences the electronic structure of the bidentate domain enabling the tuning of Fe^{2+} and Ni^{2+} spectroscopical and magnetical properties induced by intermetallic d-f electrostatic or mechanical coupling. Therefore the spin crossover behaviour of iron spin states can be observed from Eu(III) luminescence spectra and analyzed by attribution of critical temperatures (T_c) to certain entropic parameters. Moreover, the polar nature of the sulfonamide group allows the design of tuneable thermal switches, which can function in polar solvents (H_2O, alcohols), anticipating the practical applications in sensors and signalling materials.[47, 50]

1.2.2. f/f-Helicates

Whereas the chemical properties are enhanced in homobinuclear lanthanide complexes due to concentration effect if compared with monometallic parent compounds, the spectroscopic and magnetic properties very often remain unchanged. Therefore the inexorable demand of

[46] (a) R. Ziessel, A. Harriman, J. Suffert, M.-T. Youinou, A. De Cian, J. Fischer, *Angew. Chem*. **1997**, *109*, 2612; *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 2509. (b) R. Ziessel, *Coord. Chem. Rev*. **2001**, *216*, 195.
[47] (a) C. Piguet, C. Edder, S. Rigault, G. Bernardinelli, J.-C. G. Bünzli, *J. Chem. Soc. Dalton Trans*. **2000**, 3999. (b) C. Edder, C. Piguet, J.-C. G. Bünzli, G. Hopfgartner, *Chem. Eur. J*. **2001**, *7*, 3014. (c) C. Piguet, E. Rivara-Minten, G. Hopfgartner, J.-C. G. Bünzli, *Helv. Chim. Acta* **1995**, *78*, 1651. (d) C. Piguet, J.-C. G. Bünzli, G. Bernardinelli, G. Hopfgartner, S. Petoud, O. Schaad, *J. Am. Chem. Soc* **1996**, *118*, 6681.
[48] M. Elhabiri, R. Scopelliti, J.-C. G. Bünzli, C. Piguet, *J. Am. Chem. Soc*. **1999**, *121*, 10747.
[49] I. Grenthe, *J. Am. Chem. Soc.* **1961**, *83*, 360.
[50] C. Edder, C. Piguet, G. Bernardinell, J. Mareda, C. Bochet, J.-C. G. Bünzli, G. Hopfgartner, *Inorg. Chem.* **2000**, *39*, 5059.

heterodi- and heteropolymetallic systems, for example helicates, became an inspiring factor for supramolecular chemists. The initial attempts to complex symmetric ditopic ligands with a mixture of different Ln(III) salts resulted in a statistical mixture of homo- and heterodimetallic complexes, which could be separated by selective recrystallization or ion-exchange chromatography.[51] The isolation of pure heteropolymetallic species requires the elaboration of suitable synthetic approaches. Currently, three main strategies for producing 4f-4f' heterobimetallic edifies are envisaged:

1) the "selective crystallization";[51c]
2) the selective reaction of kinetically inert monometallic complex (Ln(III) containing macrocycle-porphyrin and phthalocyanin,[52] linked calix-[4]arene,[53] or cyclen,[54] e.g., **6**, Figure 6) with a second Ln(III) ion;

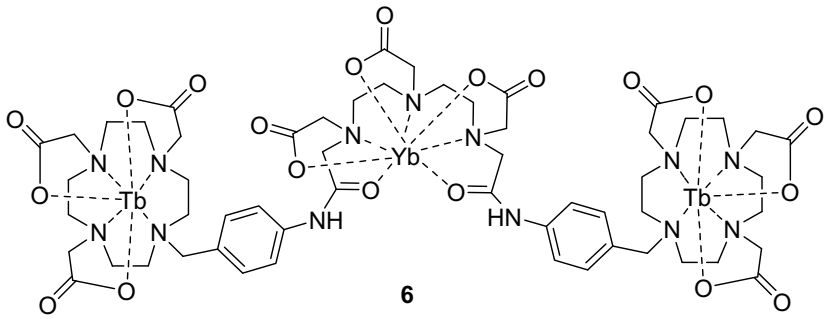


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Figure 6. Neutral heterometallic TbYbTb-complex **6**, in which intramolecular Tb → Yb energy transfer processes result in the efficient sensitization of NIR Yb(III)-centered emission.[54d]

3) the selective recognition of a Ln(III) heteropair by a polytopic receptor possessing different compartments in a decisive self-assembly step.

Probably the last pathway, adopted by *Piguet* and co-workers, is the most reliable and well-proven one. But it still remains challenging enough, because the simultaneous recognition of a specific Ln(III) in the presence of other rare-earth(III) cations is limited due to the diminutive differences in size within the Ln(III) row (0.184 Å between La(III) and Lu(III), 0.01-0.02 Å

[51] (a) P. Froidevaux, J.-C. G. Bünzli, *J. Phys. Chem*. **1994**, *98*, 8. (b) J. Coates, P. G. Sammes, R. M. West, J. *Chem. Soc. Chem. Commun*. **1995**, 1107. (c) J.-P. Costes, F. Dahan, A. Dupuis, S. Lagrave, J. P. Laurent*, Inorg. Chem*. **1998**, *37*, 153.
[52] N. Ishikawa, T. Iino, Y. Kaizu, *J. Am. Chem. Soc*. **2002**, *124*, 11440.
[53] M. P. O. Wolbers, F. C. J. M. Van Veggel, R. H. M. Heeringa, J. W. Hofstraat, F. A. J. Geurts, G. J. Vanhummel, S. Harkema, D. N. Reinhoudt, *Liebigs Ann*. **1997**, 2587.
[54] (a) V. Jacques, J. F. Desreux, *Top. Curr. Chem*. **2002**, *221*, 123. (b) S. J. A. Pope, A. M. Kenwright, S. L. Heath, S. Faulkner, *Chem. Commun*. **2003**, 1550. (c) S. J. A. Pope, A. M. Kenwright, V. A. Boote, S. Faulkner, *Dalton Trans.* **2003**, 3780. (d) S. Faulkner, S. J. A. Pope, *J. Am. Chem. Soc*. **2003**, *125*, 10526.

between two consecutive Ln(III). Another important aspect is the control of qualitative and quantitative speciation in solution - formation of HHH (strands for head-to-head-to-head) *versus* HHT (strands for head-to-head-to-tail) and homo- *vs* heterodimetallic species. The subtle interplay between steric and electronic parameters influences the affinity of the predisposed receptor's segment for the particular Ln(III) ion to be incorporated into a target helicate. Conscious efforts are dedicated to the design of unsymmetrical ligands involving the introduction of substituents (Hal, NEt_2) in the pyridyl moiety of pyridine-benzimidazole receptors or altering systematically the end group (benzimidazole / ester / amide / carboxylate) like in Figure 5. An appreciable selectivity (LaEu, EuLu, LaEr, PrEr hetero pairs) was attained with increasing difference in the ionic radius (up to 70 % for $\Delta r_i \sim 0.1$ Å).[55] Recently *Bünzli* and others demonstrated how slight tuning in the donor / acceptor strength of various substituents in the ligand framework can extremely affect the HHH ↔ HHT equilibrium ($\Delta E \sim 5$ kJ · mol^{-1}). [56] The stabilization of HHH species is provided by the combination of two important factors:

1) small differences in the large ion-dipole Ln-X interactions (these are the strongest interactions which are necessary for the insertion and fixation of lanthanides(III) inside the structure);
2) the difference in interligand interactions (e.g., interstrand π-π interactions).

But the quantitative selectivity still remains an inspiring enigma which must be solved.

1.3. Lanthanides as Luminescence Source

One of the most fascinating and attractive features of some of the lanthanides is their ability to luminesce. Luminescence is, first of all, a natural phenomenon (luminous stones, corals, animals-fireflies, glow worms, jellyfish etc.). In 1888 *Wiedemann* applied the term "luminescence" to define the light emission which does not originate from a temperature increase.[57] Nowadays, light emission processes are usually described as fluorescence (for singlet-to-singlet transitions) or phosphorescence (for singlet-to-triplet transitions). Most of the Ln(III) ions exhibit luminescence - either fluorescence (Pr, Nd, Ho, Er, Yb) or phosphorescence (Sm, Eu, Tb, Dy, Tm, Gd). The spectroscopical uniqueness of lanthanides implies the emission to be due to intraconfigurational f-f transitions. 4f-Orbitals are shielded

[55] (a) N. André, R. Scopelliti, G. Hopfgartner, C. Piguet, J.-C. G. Bünzli, *Chem. Commun.* **2002**, 214. (b) N. André, T. B. Jensen, R. Scopelliti, D. Imbert, M. Elhabiri, G. Hopfgartner, C. Piguet, J.-C. G. Bünzli, *Inorg. Chem.* **2004**, *43*, 515.
[56] T. B. Jensen, R. Scopelliti, J.-C. G. Bünzli, *Inorg. Chem*. **2006**, *45*, 7806.
[57] E.N. Harvey, *A History of Luminescence. From the Earliest Times Until 1900*, American Philosophical Society, Philadelphia, **1957**.

from the environment by the closed $5s^2 5p^6$ sub-shell, preventing an external perturbation of the electronic configuration by, for example, coordinated ligands in the immediate vicinity. This results in the easily recognizable narrow-band emission with a negligible Stokes shift as well as in the long lifetimes of the excited states. But f-f transitions are parity-forbidden (Laporte's rule) and have extremely low absorption coefficients ($\varepsilon < 1\ M^{-1} \cdot cm^{-1}$). Therefore an intense source (laser) at a precise wavelength is usually required for the *direct* excitation of Ln(III) emitting levels.[58]

However, the weak light absorption, which results in the weak luminescence, can be circumvented by the *indirect* excitation. In 1942 *Weissman* observed a typical intensive Eu(III) red luminescence from its salicylaldehyde complex and described it as "antenna effect".[59] 20 years thereafter *Crosby* and *Whan* postulated a common and generally accepted sensitization mechanism of lanthanide-centred luminescence by energy transfer (ET) from the strongly absorbing organic chromophore in the immediate environment of Ln(III) ion (Figure 7).[60]

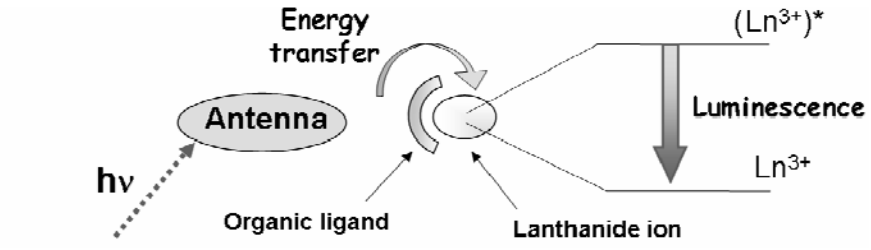

Figure 7. The basic principle of the complex performance implying efficient *indirect* sensitization of the lanthanide(III) photoluminescence.

The stepwise energy flow involves the excitation of the attached organic ligand to the singlet state S_1, followed by intersystem crossing ISC to the triplet state T_1. Then energy transfers to the resonance states of the Ln ion, which finally undergo radiative deactivation resulting in the characteristic line-like emission (Figure 8).

[58] (a) W. T. Carnall, In Handbook on the *Physics and Chemistry of Rare Earths*; K. A. Gschneidner Jr., L. Eyring; North-Holland; Amsterdam, The Netherlands, **1979**, Vol. 3, Chapter 24. (b) G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals*, Wiley, New York, **1968**. (c) R. T. Wegh, A. Meijerink, R.-J. Lamminmäki, J. Hölsa, *J. Luminescence* **2000**, *87-89*, 1002.
[59] S. I. Weissman, *J. Chem. Phys*. **1942**, *10*, 214.
[60] (a) G. A. Crosby, R. E. Whan, R. M. Alire, *J. Chem. Phys.* **1961**, *34*, 743. (b) G. A. Crosby, R. E. Whan, J. J. Freeman, *J. Am. Chem. Soc*. **1962**, *66*, 2493.

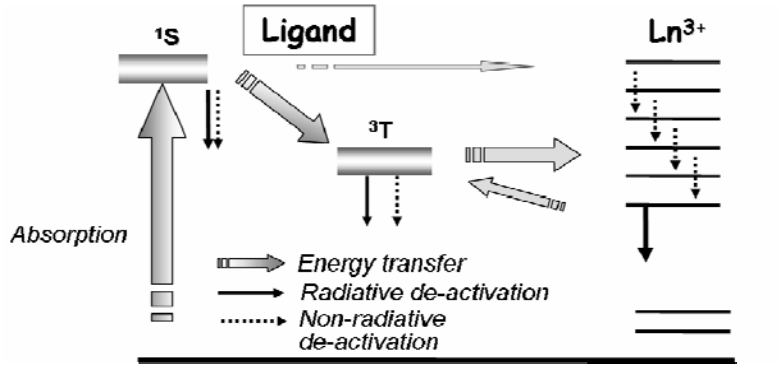

Figure 8. Schematic representation of the energy transfer process in a lanthanide complex.[45]

An important characteristic describing the efficiency of the emission processes is *luminescence quantum yield (Q)*. *Fery-Forgues* and *Lavabre* defined it as a ratio of the amount of emitted photons to the amount of absorbed photons.[61] The luminescence of the lanthanide complexes reflects an overall sensitization mechanism and needs a more specific equation to adequately describe it:

$$Q^{L}_{Ln} = \eta_{sens} \cdot Q^{Ln}_{Ln} = \eta_{isc} \cdot \eta_{et} \cdot Q^{Ln}_{Ln},$$

where Q^{L}_{Ln} depicts the quantum yield upon the *indirect* ligand excitation, Q^{Ln}_{Ln} is the inherent quantum yield detected upon *direct* Ln(III) excitation, the η_{sens} parameter is contributed by η_{isc} describing the efficacy of the ISC process and by η_{et} representing the followed and final step of energy flow-$^3\pi\pi^*$-Ln energy transfer.

The mechanism of ET from sensitizer itself was also widely discussed,[62] and the availability of two pathways has been envisaged:

1) *Dexter's*[63] (or exchange) pathway suggests double forward-and-back electron transfer and can be considered as internal redox process; it requires satisfying overlap of the ligand and metal orbitals;
2) *Förster's*[64] (or dipole-dipole) pathway relates to the coupling of two dipole moments, one of the T_1 state, another one of the 4f-orbitals.

[61] S. Fery-Forgues, D. Lavabre, *J. Chem. Educ*. **1999**, *76*, 1260.
[62] (a) G. F. G. De Sá, O. L. Malta, C. D. Donega, A. M. Simas, R. L. Longo, P. A. Santa-Cruz, E. F. da Silva, *Coord. Chem. Rev.* **2000***, 196,* 165. (b) M. Latva, H. Takalo, V. M. Mukkala, C. Matachescu, J.-C. Rodriquez-Ubis, J. Kankare, *J. Lumin.* **1997,** *75*, 149. (c) F. R. Gonçalves e Silva, R. L. Longo, O. L. Malta, C. Piguet, J.-C. G.Bünzli, *Phys. Chem. Chem. Phys.* **2000**, *2*, 5400.
[63] D. L. Dexter, *J. Chem. Phys*. **1953**, *21*, 836.
[64] T. Förster, *Discuss. Faraday Soc.* **1959**, *27*, 7.

Dexter's model was found to take place in certain Yb complexes (for example, those of modified proteins) relying on the probable transient reduction of Yb(III) to Yb(II).[65] *Förster's* theory is more likely for Ln(III) ions; it was used by *Horrocks* to investigate the donor-metal ion distances in protein systems.[66] But besides these general rules, some other important principles for the design of Ln(III) complexes have to be taken into account:

1) the lowest T_1 state of an organic "antenna" should be located slightly above the resonance levels of the lanthanide ($\Delta E \sim 2500\text{-}5000\ cm^{-1}$) adjusting the energy gap in between, which is responsible for the feasibility of energy flow;[67]
2) the chromophore must be close enough to the metal to overcome the distance dependence of the ET and to avoid the deactivation of T_1, e.g., by oxygen;
3) the lanthanide centre must be well protected from the penetration of solvent molecules (H_2O, alcohols etc.) into the first coordination sphere, because metal luminescence (especially in the NIR region) is severely quenched by the high-energy vibrational modes of the O-H, C-H, N-H oscillators.[68]

1.4. Quinolines: Prominent Features and Peculiarities

For a long time 8-hydroxyquinoline (oxine, 8-HQ) was known only because of its excellent coordination properties with a wide range of metals including lanthanides allowing its use for gravimetric analysis.[69] The poor solubility of quinolinate metal complexes enabled its application also as an extraction agent.[70] Only in 1987 8-hydroxyquinoline was acknowledged as spectroscopically important object due to the valuable contribution of *Tang* and *Van Slyke*, who introduced a new injection type of electroluminescent device and used the aluminium tris(8-hydroxyquinolinate) complex [Al(8-Q)$_3$] (**7**, Figure 9) as an active medium there.

[65] (a) A. Beeby, S. Faulkner, J. A. G. Williams, *J. Chem. Soc., Dalton Trans.* **2002**, 1918. (b) W. D. Horrocks, J. P. Bolender, W. D. Smith, R. M. Supkowski, *J. Am. Chem. Soc.* **1997**, 119, 5972. (c) F. R. Gonçalves e Silva, O. L. Malta, C. Reinhard, H.-U. Güdel, C. Piguet, J. E. Moser, J.-C. G.Bünzli, *J. Phys. Chem. A* **2002**, *106*, 1677.
[66] R. M. Supkowski, J. P. Bolender, W. D. Smith, L. E. L: Reynolds, W. Horrocks, *Coord. Chem. Rev.* **1999**, *185*, 307.
[67] S. Sato, M. Wada, *Bull. Chem. Soc. Jpn*. **1970**, *43*, 1955.
[68] A. Beeby, I. M. Clarkson, R. S. Dickins, S. Faulkner, D. Parker, L. Royle, A. S. de Sousa, G. Williams, M. Woods, *J. Chem. Soc. Perkin Trans*. **1999**, *2,* 493.
[69] (a) T. I. Pirtea, *Z. Anal. Chem.* **1936**, *107*, 191. (b) W. W. Wendlandt, *Anal. Chim. Acta* **1956**, *15*, 109. (c) E. R. Birnbaum, J. H. Forsberg, *Gmelin Handbook of Inorganic Chemistry, Sc, Y, La-Lu Rare Earth Elements*; Springer - Verlag: Berlin, **1982**, Part D2, pp 5-24.
[70] (a) R. G. W. Hollingshead, *Oxine and its Derivatives*, Butterworths, London **1954**. (b) H. Schmidbaur, J. Lettenbauer, D. L. Wilkinson, G. Müller, and O. Kumberger, *Z. Naturforsch.* **1991**, *46b*, 901.

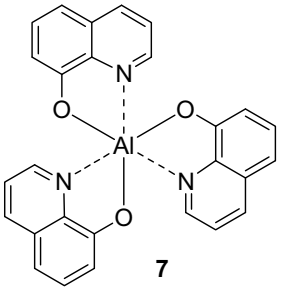

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Figure 9. Structure of tris(8-quinolinate)aluminium(III) [Al(8-Q)$_3$] **7** - a molecular semiconductor used in thin-film electroluminescent devices.

The complex performs as electron transport / emitting layer and exhibits intensive green electroluminescence.[71] Later on, *Gillin* and *Curry* (1999) tested the Er analogue of [Al(8-Q)$_3$] and demonstrated its advantages as a 1.5 μm light source, potentially interesting in optical amplification or as an OLED component operating at telecom wavelengths.[72]

Further studies on this complex were carried out by *Suzuki*, who highlighted the sensitization of Er-centered luminescence in [Er(8-Q)$_3$] and suggested, that it is provoked by ligand-to-metal ET.[73]

It is noteworthy, that only the 1 : 3 stoichiometry of Ln/8-HQ was presumed until 2004, when *Van Deun* reported synthetic routes for the preparation of pure trimeric, tris, and tetrakis complexes, and the dependence of their photophysical properties on the structure.[74] Additionally, halogen substitution on the quinoline scaffold as an efficient tool to enhance the NIR photoluminescence intensity was proposed (e.g., up to 30 % increase of metal-centered emission was reported for an Er complex with a 5,7-dihaloquinoline derivative).[75]

Referring to all these investigations, it was postulated that the triplet state T_1 of quinolinate located at 18 000 cm^{-1} is suitable for the efficient sensitization of only NIR luminescence. This motivated *Imbert* to develop a new approach to the binding mode of quinolines and to design tetrapodal ligands **Tsox** and **TsoxMe** (**8**) possessing four quinolinate chromophores which provide tight coordination surrounding the Ln(III) (Figure 10).[76]

[71] C. W. Tang, S. A. Van Slyke, *Appl. Phys. Lett*. **1987**, *51*, 913.
[72] W. P. Gillin, R. J. Curry, *Appl. Phys. Lett*. **1999**, *74*, 798.
[73] H. Suzuki, Y. Hattori, T. Iizuka, K. Yuzawa, N. Matsumoto, *Thin Solid Films* **2003**, 288.
[74] R. Van Deun, P. Fias, P. Nockemann, A Schepers, T. N. Parac-Vogt, K. Van Hecke, L. Van Meervelt, K. Binnemans, *Inorg. Chem.* **2004**, *43*, 8461.
[75] R. Van Deun, P. Fias, K. Binnemans, C. Görller-Walrand, *Phys. Chem. Chem. Phys.* **2003***, 5,* 2754.

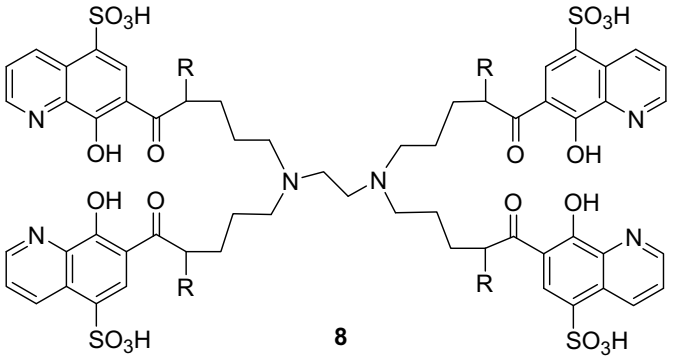

Figure 10. 8-Hydroxyquinoline based podands designed for the sensitisation of the luminescence of NIR emitters.[76]

Moreover, four sulfonate groups were introduced into the quinolinate core for solubility of the ligand in water. The desired 1 : 1 podates demonstrated sizeable quantum yields in water (largest one documented for Yb complexes in aqueous solution $Q^{L}_{Yb} = 0.18$ %) making their potential especially attractive for *in vivo* applications (e.g., coupling to human serum albumin).[76]

From the supramolecular point of view, 8-hydroxyquinolines represent an emerging field of scientific interest. Recently, *Lehn* reported an example of a heterometallic [2×2] grid formation in a single toposelective self-assembly step with participation of quinolinate-based ligand **9**-H containing two different coordination subunits. Octahedral Zn(II) and tetrahedral Cu(II) are selectively accommodated by tri- and bidentate binding sites, respectively, sharing a common pyrimidine fragment (Figure 11). This complex architecture can adopt four distinct conformational and optical states serving as a model of optoionic molecular switching devices and providing an access to logic gate operations in semiochemistry.[77]

[76] (a) D. Imbert, S. Comby, A.-S. Chauvin, J.-C. G. Bünzli, *Chem. Commun.* **2005**, 1432. (b) S. Comby, D. Imbert, A.-S. Chauvin, J.-C. G. Bünzli, *Inorg. Chem.* **2006**, *45*, 732. (c) S. Comby, D. Imbert, C. Vandevyver, J.-C. G. Bünzli, *Chem. Eur. J.*, **2007**, *13*, 936

[77] (a) A. Petitjean, N. Kuritsakas, J.-M. Lehn, *Chem. Commun.* **2004**, 1168. (b) A. Petitjean, N. Kuritsakas, J.-M. Lehn, *Chem. Eur. J.* **2005**, *11*, 6818.

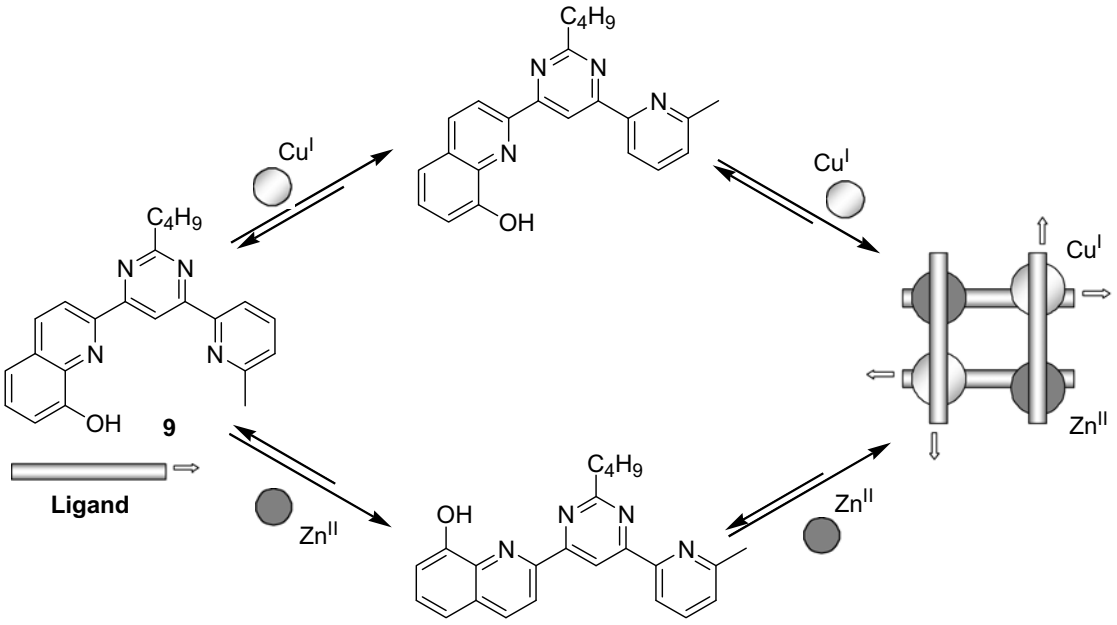

Figure 11. An example for the self-assembly of a molecular mixed metallic grid realized due to different binding segments of 8-hydroxyquinoline ligand **9**-H.[77]

But probably the most considerable impact on the development and deepest insight in advances of metallosupramolecular chemistry of 8-hydroxyquinolines belong to *Albrecht* and co-workers.[27b,78] An abundance of alkyl-bridged bis(8-hydroxyquinoline) helicating ligands connected by a spacer preferably in 7-position of the quinolinol body **10**-H_2 was developed.[79] p-/d-Block elements were involved in template directed dynamic combinatorial processes generating triple-stranded dinuclear helicates (Figure 12).[36d,80] The efficiency of metalla-cryptands' self-assembly was attributed to the correct ratio between size of template (usually alkali metal cation or NH_4^+) and length of linker as the controlling and regulating factor.[81]

[78] (a) M. Albrecht, R. Fröhlich, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 797. (b) M. Albrecht, M. Fiege, O. Osetska, *Coord. Chem. Rev*. **2007** (in print).
[79] (a) M. Albrecht, O. Blau, *Synthesis* **1997**, 213. (b) M. Albrecht, O. Blau, K. Witt, E. Wegelius, M. Nissinen, K. Rissanen, R. Fröhlich, *Synthesis* **1999**, *10*, 1819. (c) K. Hiratani, K. Kasuga, M. Goto, H. Uzawa, *J. Am. Chem. Soc.* **1997**, *119*, 12677.
[80] M. Albrecht, O. Blau*, Chem. Commun*. **1997**, 345. (b) M. Albrecht, O. Blau, J. Zauner, *Eur. J. Org. Chem*. **1999**, 3165.
[81] (a) M. Albrecht, O. Blau, R. Fröhlich, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4876. (b) M. Albrecht, O. Blau, E. Wegelius, K. Rissanen, *New J. Chem*. **1999**, *23*, 667.

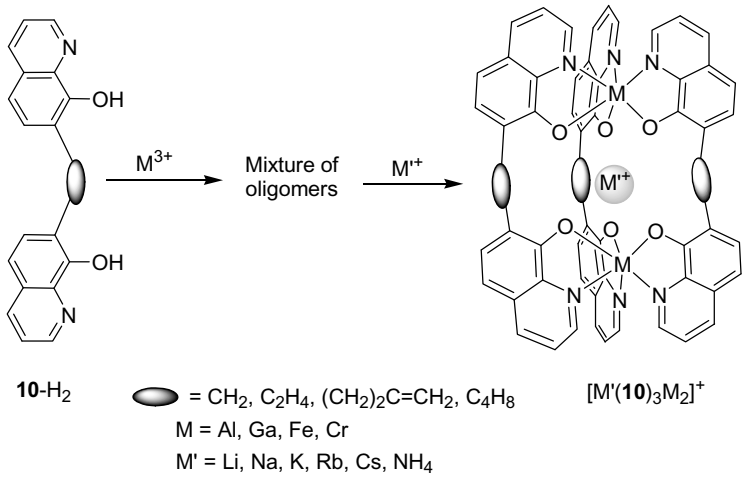

Figure 12. Alkyl-bridged bis-8-hydroxyquinoline ligands **10**-H_2 designed for the construction of triple-stranded helicates $[M'(\mathbf{10})_3M_2]^+$ in the template mediated self-assembly processes.

The amazing example of hierarchical formation of helicates due to electrostatically induced dimerization of negatively charged monomeric tris-quinolinate complexes with transition metals or Al^{3+} by three Li, or one Zn cations, inserted into alternative salicylate binding units, was also illustrated by *Albrecht* et al.[82]

1.5. Properties, Applications, Perspectives

1.5.1. Luminescent Helicates

In this chapter only the luminescence properties and applications related to the systems, discussed in Part 3, are considered.

The mimicking of natural structures is one of the concepts associated with molecular engineering and necessary for elaboration of nanoscale devices. The reproduction of the helicate motif has become a noticeable trend not only in synthetic biochemistry, but also in supramolecular chemistry. In seeking new exciting prospects, the luminescence phenomenon was anticipated as an advantageous principle in the design and fabrication of light-conversion molecular devices (LCMDs) working on the nanometric scale.[2] For that purpose, luminescent emitters (e.g, Ln(III) ions) must be incorporated into a supramolecular absorber (e.g., helicate).[83]

[82] (a) M. Albrecht, M. Fiege, M. Baumert, M. de Groot, R. Fröhlich, L. Russo, K. Rissanen, *Eur. J. Inorg. Chem*. **2007**, 609. (b) M. Albrecht, K. Witt, H. Röttele, R. Fröhlich, *Chem. Commun*. **2001**, 1330.

[83] (a) J.-C. Bünzli, G. R. Choppin (Eds.), *Lanthanide Probes in Life, Medical and Environmental Science*, Elsevier, Amsterdam, **1989**. (b) J.-M. Lehn, In *Frontiers in Supremolecular Chemistry and Photochemistry*; H.-J. Schneider, H. Dürr, (Eds.); VCH: Weinheim, **1991**, pp. 1-28. (c) N. Sabbatini, M. Guardigli, J.-M. Lehn, *Coord. Chem. Rev*. **1993**, *123*, 201.

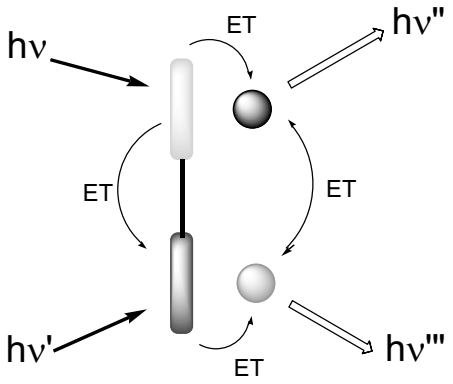

Figure 13. The schematic representation of energy flow in heterometallic lanthanide containing systems resulting in the emission of light at different wavelengths.

If the harvesting of light at one wavelength, its transfer, and reemission at another wavelength are performed independently by individual compartments of the complex, then the entire device operation can be easily optimized by modifying separately any of the compartments, and by extension or restriction of their mutual coupling (Figure 13). The fascinating spectroscopic and magnetic properties, as well as a wealth of promising applications encourage chemists to build up and study the library of luminescent helicates, particularly aesthetically appealing polymetallic[84] (for directional light-converting devices, fixation and reduction of nitrogen by hydrolytic catalysis in biological systems)[85], heterometallic 4f-4f (for luminescent sensors exhibiting intramolecular directional ET, the multiple fluoroimmunoassays, or the sensitive paramagnetic NMR probes possessing several sites with different crystal-field parameters), and 3d-4f edifies (for molecular magnets, the extension of the Ln-centred NIR luminescence lifetimes in order to improve the sensitivity of time-gated homogeneous fluoroimmunoassays) as well as quadruple-stranded complexes.[86]

1.5.2. Advantages of NIR Luminescence

A flurry of activity concerned with visible-emitting Eu(III) and Tb(III) complexes, well-known optical probes and fluoroimmunoassays, was documented in the literature during the last 40 years. In marked contrast, only recently has NIR luminescence of Nd(III), Er(III), Yb(III), Pr(III) been fully appreciated, although substantial drawbacks-low sensitization of

[84] (a) B. Bocquet, G. Bernardinelli, N. Ouali, F. Floquet, F. Renaud, G. Hopfgartner, C. Piguet, *Chem. Commun.* **2002**, 930. (b) K. Zeckert, J. Hamacek, J.-M. Senegas, N. Dalla-Favera, S. Floquet, G. Bernardinelli, C. Piguet, *Angew. Chem*. **2005**, *117*, 8168.
[85] (a) A. Tsubouchi, T. C. Bruice, *J. Am. Chem. Soc.* **1994**, *116*, 11614. (b) E. Campazzi, E. Solari, C. Floriani, R. Scopelliti, *Chem. Commun*. **1998**, 2603.
[86] (a) A. P. Bassett, S. W: Magennis, P. B. Glover, D. J. Lewis, N. Spencer, S. Parsons, R. M. Williams, L. De Cola, Z. Pikramenou, *J. Am. Chem. Soc.* **2004**, *126*, 9413. (b) M. Albrecht, S. Schmidt, S. Dehn, C. Wickleder, S. Zhang, A. P. Bassett, Z. Pikramenou, R. Fröhlich, *New J. Chem*. **2007**, *31*, 1755.

metal-centred luminescence and short lifetimes (ns to μs)-still have to be overcome.[87] In the last few years, the second limitation was elucidated in many reports: the population of the Ln(III) excited states can be achieved through the deactivation of d-block donors, commonly Ir (III),[88] Ru(II),[89] Os(II),[90] Re(I),[91] Pt(II),[92] or Cr(III)[93] in polynuclear d-f arrays. The demand for NIR luminescence is due to its use in telecommunication, optical amplification, silica-based fibre optic networks, laser design, LEDs etc.[94] But an even more important driving force is the request for non-invasive highly sensitive, easily resolvable and deep penetrating bioprobes for *in vivo* imaging. NIR lanthanide-based emitters are an option to the organic dyes commonly used as NIR fluorophores, able to couple to peptides and to exhibit emission spectra easily recognizable and separable from the background fluorescence.[95] With respect to bioprobes, Yb is particularly appealing because its $^2F_{5/2} \leftarrow {}^2F_{7/2}$ transition displays the Cotton effect which is employed to explore antibiotics.[96] Generally, the progress in the application of chiral luminescent probes for identification of chiral bioassays, *in cellulo* imaging potential or selective intercalation in DNA, relies on the availability of CD or CPL measurements of the signals induced by coupling of the luminescent probe with a chiral (biological) substrate.[97,98] For instance, *Pikramenou* designed the hetero-trimetallic Nd-Pt_2

[87] S. Comby, J.-C. G. Bünzli, *Lanthanide Near-Infrared Luminescence in Molecular Probes and Devices*. Ed.: K. A. Gschneidner, J.-C. G. Bünzli, V. K. Pecharsky, Handbook on the *Physics and Chemistry of Rare Earths* **2007**, Vol. 37, 217.
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[94] (a) S. Faulkner, S. J. A. Pope, B. P. Burton-Pye, *Appl. Spectrosc. Rev*. **2005**, *40*, 1-31. (b) J.-C. G. Bünzli, In *Spectroscopic Properties of Rare Earths in Optical Materials*; G. K. Lui, B. Jaquier; Eds.; Springer-Verlag: Berlin, **2005**, pp. 462-499. (c) R. Van Deun, P. Nockemann, C. Görller-Walrand, K. Binnemans, *Chem. Phys. Lett.* **2004,** *397*, 447. (d) J. W. Stouwdam, F. C. J. M. Van Veggel, *Nano Lett*. **2002**, *2*, 733.
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luminescent complex as a hairpin which bears intercalating groups for DNA recognition; flow linear dichroism (LD) was used to detect binding (angle and mode) of the complex to DNA.[99]

1.5.3. Organic Light-Emitting Diodes (OLEDs)

In this section the main features of OLED design, structure, characteristics, fabrication details, working principles, and application potentials will be briefly discussed, and then elucidated in the light of helicate peculiarities.

The paramount interest in these electroluminescent devices,[100] developed mostly for illuminators and displays with wide viewing angle, has to do with their low operating voltage, high brightness, efficiency, tunable emission, simplicity and low cost of fabrication, and applicability to any kind of substrate, even flexible ones. Organic light emitting diodes differ from their inorganic analogues already in the active component, using organic molecules instead of inorganic semiconductors. Typically, an OLED cell is built up of very thin layers deposited between electrodes. For that purpose, a variability of techniques can be employed: chemical vapour or plasma deposition, spin coating, Langmuir-Blodgett deposition etc. [Al(8-Q)$_3$] is found to be an ideal emitting element for OLED construction because of its stability, high carrier transport, and good heat resistance.

These specific properties of the aluminium chelate originate from its intrinsic structure consisting of two geometric isomers - meridional *mer* (C_1 symmetry) and facial *fac* (C_3 symmetry) with an energy difference of ~ 4 kcal/mol between them (Figure 14).[101] It results in the molecular disorder in the formed film giving rise to inhomogeneously broadened spectra. On the other hand, this co-existence may be prerequisite of thermal stability in the amorphous phase.[102] Many studies were focused on the specific synthesis and selective isolation of individual isomers. *fac*-[Al(8-Q)$_3$] is especially desirable in this context, because it exhibits blue-shifted emission with high quantum yields and acts as an efficient electron

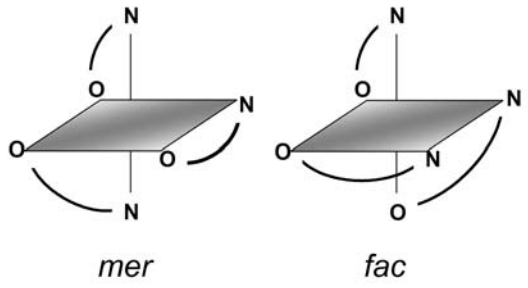

Figure 14. Schematic drawing of the [Al(8-Q)$_3$] geometrical isomers (*mer*: meridional, *fac*: facial)

[99] P. B. Glover, P. R. Ashton, L. J. Childs, A. Rodger, M. Kercher, R. M. Williams, L. De Cola, Z. Pikramenou, *J. Am. Chem. Soc.* **2003**, *125*, 9918.
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[102] A. Curioni, W. Andreoni, *IBM J. Res. Dev.* **2001**, *45*, 101.

trap, although it is a more problematic species to capture.[103] A reasonable strategy would be to resort to the well-defined molecular architectures, e.g., helicates, comprising of two or more Al complex fragments. This should bring the control and organization into the emissive medium.

The operation of an OLED can be generally described as a stepwise process: injected from opposite electrodes, the electron and hole recombine into an emissive layer to form an exciton in a singlet or triplet state (statistical distribution is 25 to 75 %). In turn, the exciton or another localized excited state relaxes releasing the light photon. Therefore, the efficiency of OLEDs is theoretically limited to 25 %. *Baldo* proposed a method to collect excitons quantitatively (100 %) using luminescent centers as excellent triplet harvesters.[104] Since this historical point, a bright future is foreseen for lanthanide-containing OLEDs.[105] Moreover, highly monochromatic emission of Ln(III) is considered as a tool to improve colour saturation in OLED-based displays. OLEDs employing NIR Ln(III) emission are thoroughly reviewed by *Bünzli*.[87]

[103] (a) M. Mucchini, M. A. Loi, K. Kenevey, R. Zamboni, N. Masciocchi, A. Sironi, *Adv. Mater*. **2004**, *16*, 861. (b) R. Katakura, Y. Koide, *Inorg. Chem*. **2006**, *45*, 2006.
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2. *Project Aim*

Luminescent helicates have gained momentum in metallosupramolecular chemistry since their fascinating optical, magnetic, and electronic properties can be approached in a single self-assembly step implicating lanthanide(III) ions and predisposed ligands. 8-Hydroxyquinolines are an appealing class of chelating units which only recently were shown to demonstrate their enormous potential in sensitization of NIR luminescence from the adequate f-elements (Nd^{3+}, Er^{3+}, Yb^{3+}). This work is concentrating on the development of bi-, tri- and tetradentate quinoline-based ligand systems and examination of their coordination behaviour towards rare-earths(III). The speciation in solution is observed by means of different spectroscopic methods (NMR, ESI MS, spectrophotometric titrations); solid state determinations of complex structures are provided by X-ray diffraction analysis.

The flexible and reliable synthetic pathways enabling functionalization of the quinoline scaffold by introducing appropriate donor groups (imine, amide, carboxylate) in the 2-position as well as halogen or aryl substituents in the 5- or both 5- and 7-positions are developed. Additionally, the Hiratani-double-Claisen rearrangement is extensively employed to combine tridentate (for addressing f-elements) and bidentate (for the recognition of p-/d-block metals) binding compartments within a single segmental receptor. Applicability of a wide range of substrates to the multistep reaction sequences allows modification of the ligand system and subsequently proper optimization of the helicate design focused on the facilitation of the intermetallic communication. Alternatively, the rigidity and conformation of the extended ligand strands can be controlled by altering the nature of connectors between chelating fragments. The tuning of the ligand coordination preferences simultaneously allows affecting photophysical properties of lanthanide(III) complexes. Therefore, the optic spectroscopic studies are performed in the solid state on mono- (Eu, Nd, Er, Yb) and dinuclear homo- Yb/Yb and heterometallic Yb/Al samples to deduce the intramolecular energy transfer processes occurring between different complex fragments and to explore the substitution effect on the luminescence efficiency.

The template effect often considered as a judicious factor governing helicating processes is partially elucidated in the context of its influence on the photoluminescence activity of the complexes.

Finally, the MW-methodology is tested on a series of precursors as a suitable option for the construction of a library of substituted quinoline heterocycles.

3. Results and Discussion

3.1. Aluminium Helicates

Within the last century artificial light revolutionized the living standards of people, which, in turn, governed the profound research in the field of organic electronics and extremely accelerated the progress in display and illumination technologies. The current activity embraced the "*small molecule*" SM OLEDs (*Tang*, *Van Slyke*, 1987),[71] π-conjugated polymer PLEDs (*Friend*, 1990),[106] doped guest-host molecular systems (*Wolak*, 2004),[107] and other semiconductor devices based on the organic thin-film electroluminescence. Organometallic SMOLEDs are appreciated because of their thermal and morphological stability, as well as the high purity of emitted colours. Among the luminescent chelates [Al(8-Q)$_3$] and its derivatives are the most privileged electroluminophores in OLEDs fabrication. Their semiconductor and emissive properties are ascribed to the lowest electronic π-π* transitions in the quinolinate and are defined by the HOMO and LUMO levels located on the phenoxide / pyridine side, respectively. *Anzenbacher* and co-workers demonstrated how emission colours and quantum yields of [Al(8-Q)$_3$] complex **7** can be tuned by introduction of electron-donating (Me, electron-rich arenes etc.) or electron-withdrawing (-F, -Cl, -CN, -SO_2NR_2, electron-deficient arenes etc.) substituents in the 5-position of the quinoline ligand. The correlation of the HOMO-LUMO energy gap, which is responsible for the optical properties of Al complexes, was established in accordance to the Hammett constants of attached substituents.[108]

Aluminium complexes as well as most of SM emissive materials are deposited by vacuum thermal evaporation technique. Although this method is well suitable to fabricate very thin amorphous infinite transparent films, it still has some serious drawbacks:

1) ashing problem during sublimation;
2) requirements of high vacuum (10^{-5}-10^{-7} Torr), which cause long down-times of device and are particularly challenging for full-colour displays.

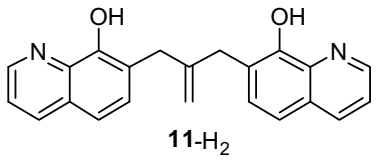
The low-cost manufacture, relying on solution processing techniques, such as spin coating or ink-jet printing, is especially attractive characteristic perceived in the industrial production of polymer LEDs-based lightning devices. An intelligent innovation would be to design and

[106] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N.Marks, C. Taliani, D. A. Dos Santos, J.-L. Bredas, M. Lögdlund, W. R. Salaneck, *Nature* **1999**, *397*, 121.
[107] M. A. Wolak, B. Jang, L. C. Palilis, Z. H. Kafafi, *J. Phys. Chem. B* **2004**, *108*, 5492.
[108](a) R. Pohl, V. A. Montes, J. Shinar, P. Anzenbacher, *J. Org. Chem*. **2004**, *69*, 1723. (b) R. Pohl, P. Anzenbacher, *Org. Lett*. **2003**, *5*, 2769.

prepare solution-processable SMOLEDs in analogy with PLEDs, for instance aluminium helicate-type macromolecules.

3.1.1. Synthesis and Characterization of Isobutenylidene-Bridged Highly Alkyl-Substituted Homoditopic Bidentate Ligands and their Aluminium Complexes

The tandem-double-Claisen rearrangement is an efficient method to establish the alkyl spacer in the 7-positions of the two phenolate moieties furnishing a ditopic symmetric receptor with two bidentate 8-hydroxyquinoline binding sites. Initially, the synthesis of isobutenylidene bridged bis-8-hydroxyquinoline **11**-H_2 was reported by *Hiratani*[109] and then extensively adopted by *Albrecht*. The simplest bis(8-hydroxyquinoline) **11**-H_2 was used as a model ligand system to study template-directed self-assembly of dinuclear triple-stranded Al, Ga, and Fe helicates (Figure 12).[81] However, their extremely low solubility (in DMSO or DMF) prevented any further investigations and/or applications.



11-H_2

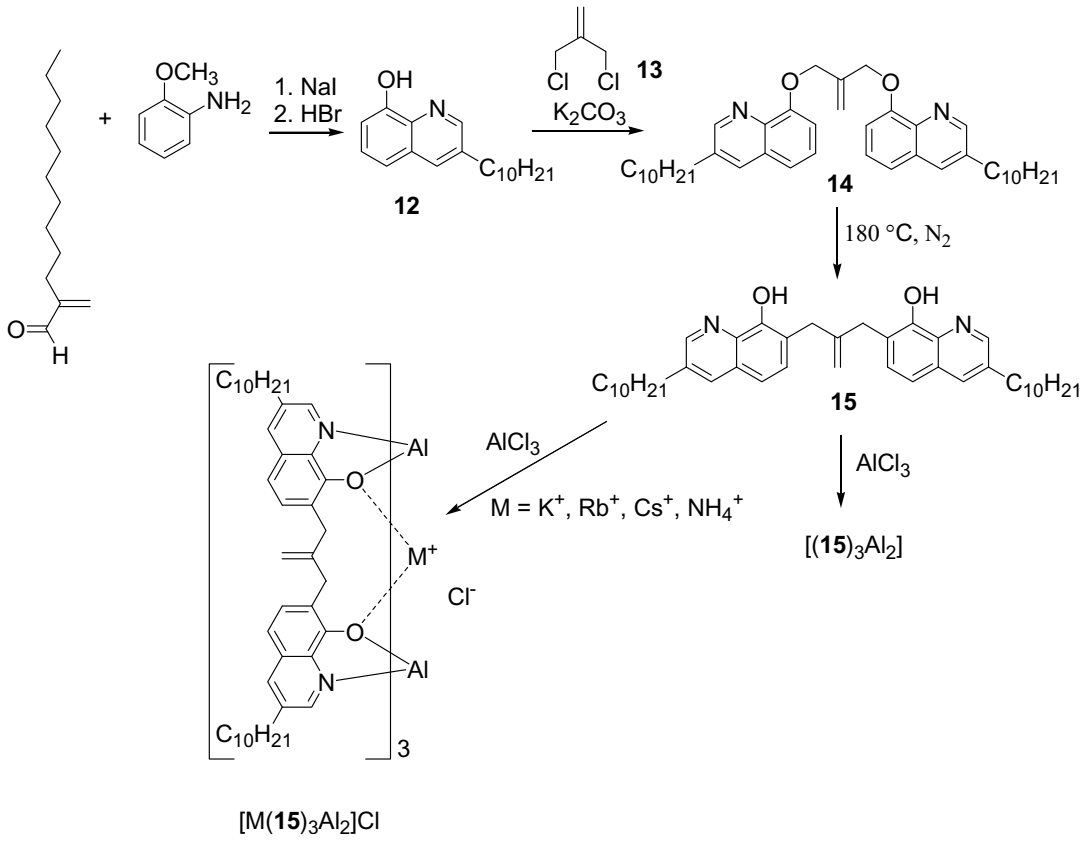
The introduction of alkyl groups into the quinoline core improves the ligand / complex solubility. The Skraup's synthesis proved to be the easiest way to functionalize the pyridine moiety of parent 8-hydroxyquinoline.[110] An appropriate synthetic procedure for the preparation of 3-*n*-decyl-8-hydroxyquinoline **12** was already described by *Blau*.[111] The Williamson ether coupling of derivative **12** with 3-chloro-2-chloromethyl-propene **13** in the presence of K_2CO_3 as base resulted in diether **14** which next underwent thermal rearrangement at 180 °C (Scheme 1). The conversion was complete within 7 h affording isobutenylidene-bridged bis(8-hydroxyquinoline) **15** in almost quantitative yield.

The ligand **15** was used to prepare a set of metalla-cryptates [M(**15**)$_3$Al$_2$]Cl (M = K^+, Rb^+, Cs^+, NH_4^+) in the template-mediated one-step self-assembly event. The reaction of **15**-H_2 with $AlCl_3$, and alkali metal or ammonium salt in a 3 : 2 : 6 ratio in a solvent mixture CH_2Cl_2 / MeOH / H_2O furnished the stable and in organic solvents well-soluble [M(**15**)$_3$Al$_2$]Cl complexes in moderate to high yields. [(**15**)$_3$Al$_2$] as a templateless species was obtained to clarify the possible influence of encapsulated cations on the coordination behaviour and optical properties of the aluminium cryptates.

Besides the participation in a dynamic combinatorial process and the important "size-selectivity" role, the templating cations may affect the EL spectra and the relative quantum

[109] K. Hiratani, T. Takahashi, K. Kasuga, H. Sugihara, K. Fujiwara, K. Ohashi, *Tetrahedron Lett.* **1995**, *36*, 5567.
[110] C. O'Murchu, *Synthesis* **1989**, 880
[111] O. Blau, *Dissertation*, Universität Karlsruhe, **1999**.

yields. Moreover, the high molecular weight of complexes is advantageous for their film forming properties. On the other hand, the excellent solubility of the aluminium helicates enables the film deposition using spin-casting directly from the $CHCl_3$ solution. Additionally, long alkyl chains preclude the unfavourable crystallization, which can occur in the emissive layer, and stabilize the amorphous phase.



Scheme 1. Synthesis of *n*-decyl substituted ligand **15**-H_2 and its metal complexes $[M(\mathbf{15})_3Al_2]Cl$ / $[(\mathbf{15})_3Al_2]$.

The ^1H NMR spectra give deeper insight into the template controlled self-assembly processes and speciation in solution (Figure 15). All templated helicates exhibit similar chemical shifts of the ligand proton signals, which are differently influenced upon coordination to the metal. Thus, the upfield shift of H^a is the most obvious one and has an anisotropic origin. Probably the ligand strands are slightly wrapped around aluminium centers, and coordinated quinolinates acquire a negligible tilt. However, the vicinity of neighbouring aromatics is experienced by quinolinate protons, an especially perceptible influence of the shielding effect is observed for H^a ($\Delta\delta \sim 2$ ppm for Rb^+, K^+, NH_4^+ templates). The signals of vinylic and benzylic protons are also shifted upfield; moreover, the latter appear as two doublets. This is ascribed to the diastereotopicity effect. It has been already shown by previous results that in

the related metalla-cryptates olefinic protons of the spacer are directed inside the complex cavity so that the close spatial proximity of the quinolinates causes an anisotropic shift.

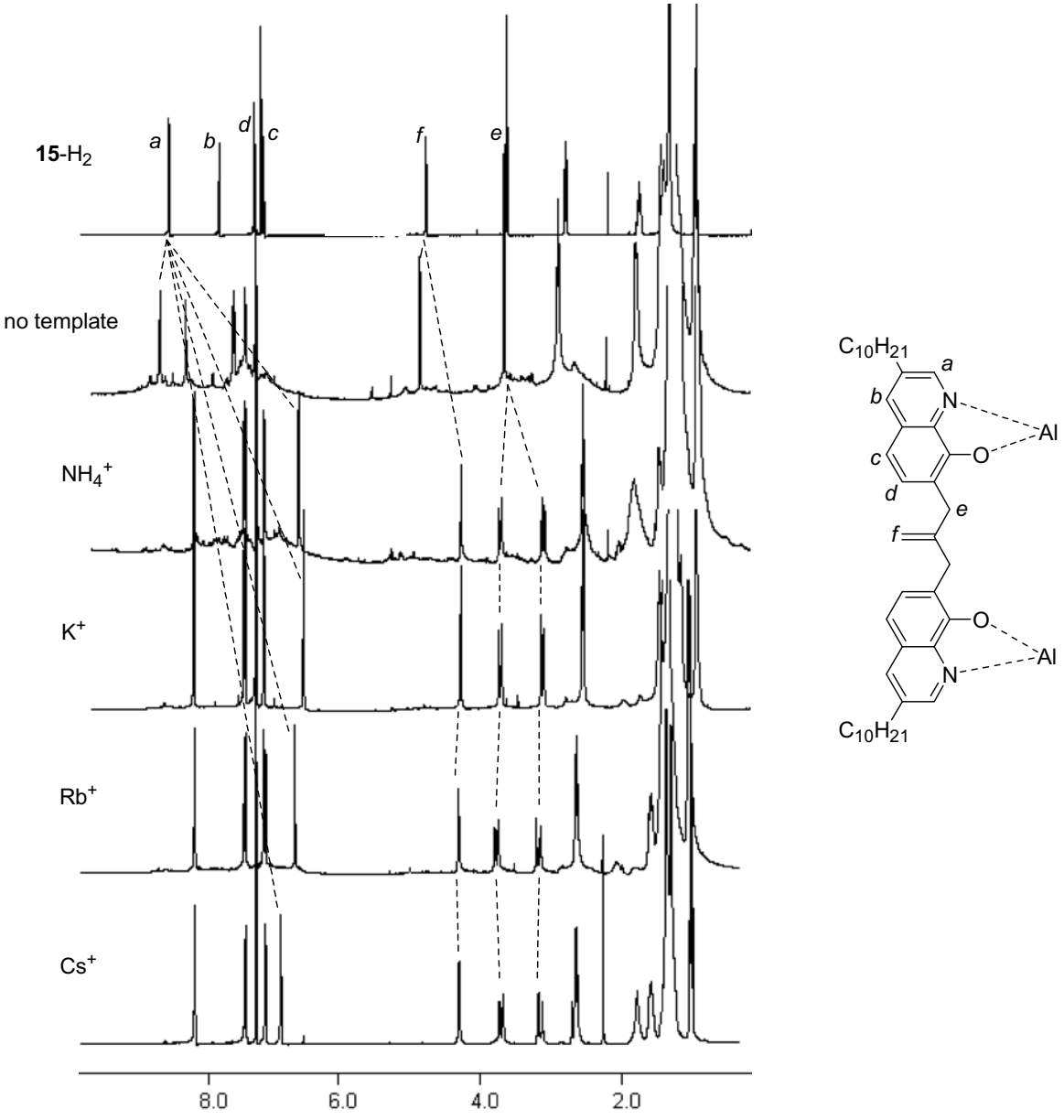


Figure 15. The comparison of ^{1}H NMR spectra of the ligand **15**-H_2 and [M(**15**)$_3$Al$_2$]Cl / [(**15**)$_3$Al$_2$] complexes.

The satisfactory yields indicate the efficiency of the helicating processes with the ligand **15**-H_2 and corresponding adjustment of the template size to the length of the isobutenylidene spacer. Thus, Cs and Rb cations are considered as the most preferable templates to be bound in the interior and to support the target helicate structure.

3.1.2. Photophysical Investigations of Alkyl Substituted Templated Aluminium Helicates

Electroluminescent (EL) devices with structure ITO / PEDOT : PSS / Poly(N-vinyl carbazole) (PVK): Derivative / Ca / Al were built by the group of Prof. Holloway / R. Torres (Figure 16), but no electroluminescence was detected from the device without PVK matrix.

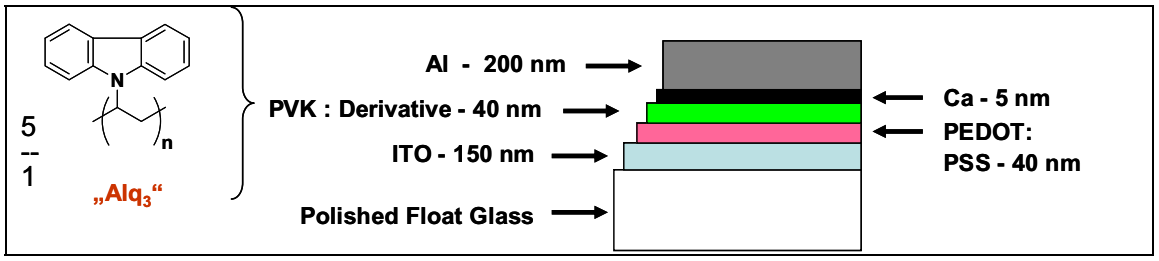


Figure 16. Configuration of the EL cell.

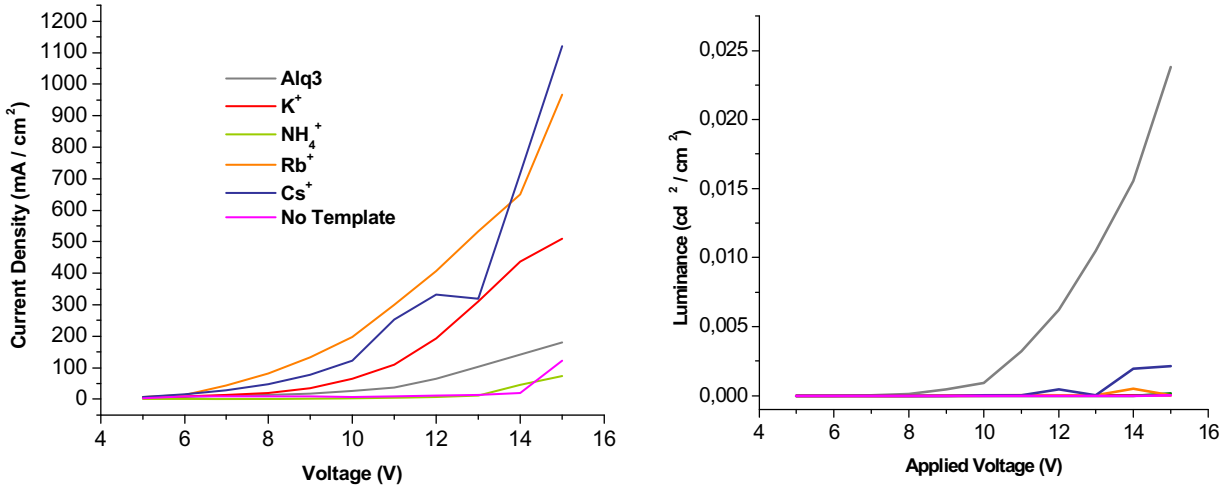


Figure 17. Luminance - current - voltage characteristics of OLED cells with the[M(**15**)$_3$Al$_2$]Cl / [(**15**)$_3$Al$_2$] emitters

PL emission data and relative quantum efficiencies in $CHCl_3$ (Φ_{PL}) are collected in Table 1. The electroluminescence is compared to a [Al(8-Q)$_3$] standard. The current-voltage-luminescence characteristics of the spin-coated thin film are displayed in Figure 17. The electroluminescence efficiency depends on the quality of the film and its carrier-transport capacity. The templated aluminium helicates show high current densities with minimal short-term luminance and low external quantum yields. It can be explained by quenching, which is attributed to the electronic traps from templating ionic species. The lack of conjugation on the

Table 1. Photophysical data in $CHCl_3$

complex	abs. λmax (nm)	emission λmax (nm)	rel. Φ_{PL}
$[Al(8\text{-}Q)_3]$	388	525	1.0
K^+	392	532	0.52
NH_4^+	389	533	0.41
Rb^+	389	539	0.49
Cs^+	392	532	0.66
no template	undetected	543	0.05

alkyl chains also exhibits an unfavourable effect on the luminescence. The reported results are not satisfying at the moment; but the fabrication of the film by solution-based processing of small macro-molecules of type $[M(\mathbf{15})_3Al_2]Cl$ was attempted, which would allow a cost-effective production of EL devices.

3.2. Bidentate Ligands for Coordination of the Lanthanides(III) Ions

Considerable progress in the development of lanthanide containing OLEDs was a motivating factor to incorporate Ln^{3+} into 8-hydroxyquinoline based dinuclear helicate-type complexes. Moreover, good solubility of ligand **15**-H_2 and its complexes would allow utilizing spin-coating techniques for the film fabrication. Recently the synthesis of the intensively fluorescent amphiphilic complex $[La(Q')_2(H_2O)_4Cl]$ (Q' = *N*-hexadecyl-8-hydroxyquinoline-2-carboxamide) was reported by *Ouyang*. The complex was used for the preparation of Langmuir-Blodgett films as effective emissive material for EL cells.[112] Thus, **15**-H_2 was involved in the coordination study with La^{3+}. It was expected that reaction of ligand with $LaCl_3$ in a 4 : 2 ratio in the presence of base Rb_2CO_3 should yield the quadruple stranded complex of composition $Rb_2[(\mathbf{15})_4La_2]$ according to the denticity of the ligand and coordination number at the metal center. Positive ESI MS of the product confirmed the target stoichiometry 2 : 4 La to ligand in the complex (MS (ESI+): m/z (%) = 2821.2 $[NaK(\mathbf{15})_4La_2]^+$, 88.5), but no indication of the Rb templation is observed. ^{1}H NMR spectrum is relatively poorly informative in order to make any suggestions about the structure of the compound.[113]

Therefore a simpler model for the prior investigation of coordination behaviour of 8-hydroxyquinolines with rare-earth elements was needed. The most reliable structural characterization of the complex helicate architectures can be provided by X-ray diffraction analysis. The ditopic bidentate ligand **11**-H_2 already demonstrated its potential in the

[112] J. Ouyang, L. Li, Z. Tai, Z. Lu, G. Wang, *Chem. Commun.* **1997**, 815.
[113] Complex was not isolated in analytically pure form.

crystallization experiments with pseudooctahedral Al^{3+}, Ga^{3+}, Cr^{+3}, or Fe^{3+} producing a series of templated dinuclear triple stranded helicates. A similar coordination behaviour was foreseen for bis(8-hydroxyquinoline) with respect to the lanthanide ions, but due to their size requirements and stereochemical preferences it was expected for **11**-H_2 to form quadruple stranded helicates. The ligand (4 equiv.) reacted with $LaCl_3$ (2 equiv.) in the presence of Rb_2CO_3 as base in methanol to yield a mixture of undefined species. The ^{1}H-NMR looked too intricate to make any assignments, but in ESI MS the peaks corresponding to the complex patterns $[(\mathbf{11})_4La_2]^{2-}$ and $[Rb(\mathbf{11})_4La_2]^-$ were found at m/z = 1639.9 and 1727.8, respectively. However, the major peak at m/z = 1299.3 is attributed to the $[(\mathbf{11})_3La_2]$ species. Upon the crystallization of this poorly characterized mixture from DMF solution on air, red crystals of X-ray quality were formed.[114] The crystal structure unravelled the tetranuclear hexa-stranded cluster $[La_4(\mathbf{11})_6(O_2)_2]^{2-}$ which is due to the helical wrapping of the ligands around metal ions can be termed as "cluster helicate" (Figure 18).[115]

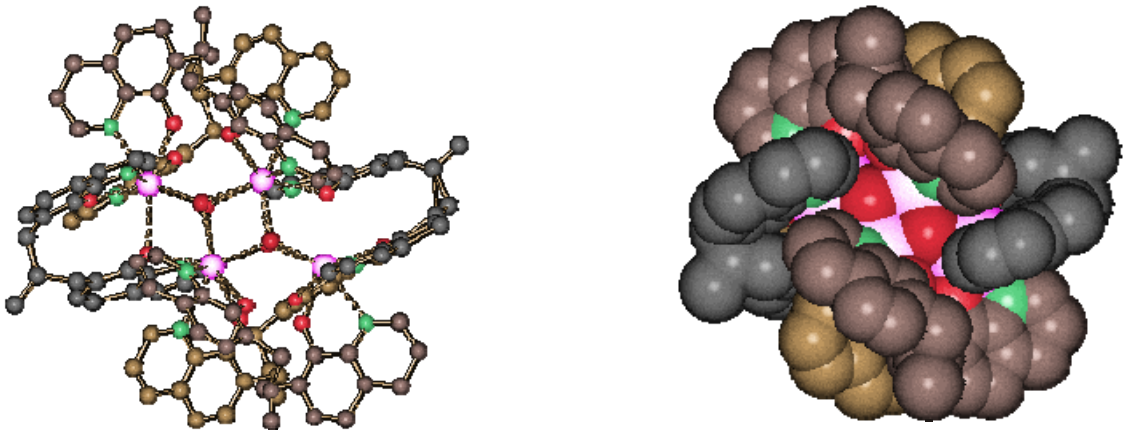


Figure 18. The molecular structure of the complex anion $[La_4(\mathbf{11})_6(O_2)_2]^{4-}$.

Four La^{3+} centers form an inner cluster core where two peroxodianions are bound in the interior by means of unusual side-on coordination to the lanthanum. This spectacular feature of the structure is described as μ_3-tris-η^2 coordination of each of the O_2 molecules to the three La^{3+} ions (two of them are bridging) (Figure 19). Related cases were previously reported for Sm^{3+}, Eu^{3+}, and Gd^{3+}.[116]

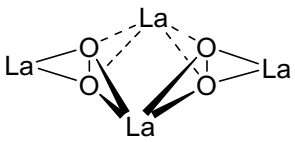


Figure 19. Arrangement of the inner cluster moiety.

[114] The complete crystallographic dataset could not be collected and the structure could not be fully resolved. Counterions are not observed.
[115] M. R. Bermejo, A. M. González-Noya, R. M. Pedrido, M. J. Romero, M. Vázques, *Angew. Chem*. **2005**, *117*, 4254; *Angew. Chem., Int. Ed.* **2005**, *44*, 4182.
[116] B. Neumüller, F. Weller, T. Gröb, K. Dehnicke, *Z. Anorg. Allg. Chem*. **2002**, *628*, 2365.

This unprecedented result can be attributed to the mismatch in the ligand denticity and the coordination number at the metal (in the present case eight- or nine-coordination is expected for La^{3+}), and serendipitous co-crystallization of random co-ligands, e.g., O_2. On the other hand, the dioxygen anion O_2^-, profiting as template, affects the global complexity and shifts it to the thermodynamically preferable maximum. Therefore, the formation of dimetallic triple stranded helicate with stoichiometry S = M/L = 2/3 = 0.66 (M = metal, L = ligand) and global complexity GC = 2 + 3 = 5 is precluded, and the template induced intramolecular interconversion results in the formation of alternative tetranuclear hexa-stranded cluster $[(\mathbf{11})_6La_4(O_2)_2]$ with S = 4/6 = 2/3 and G = 10.

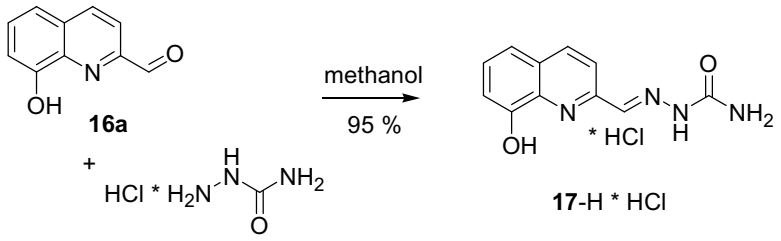
Control and prediction of the ligand coordination behaviour are two crucial factors for the design and selective formation of metallosupramolecular architectures. In the case of 8-hydroxyquinoline, its coordination mode can be easily specified by introducing suitable donor functionalities.

3.3. Tetradentate Quinolinate Ligands for the Coordination of Rare Earths(III)

3.3.1. Semicarbazone Ligand

3.3.1.1. Ligand synthesis and structure

The semicarbazone ligand **17**-H was prepared by condensation of 8-hydroxyquinoline-2-carboxaldehyde **16a** with semicarbazide hydrochloride (Scheme 2).



Scheme 2. Synthesis of **17**-H · HCl.

The X-ray crystallographic analysis showed that the molecular structure adopts a stretched conformation in plane and is stabilized due to *E*-configuration of the C=N double bond (Figure 20). The outward orientation of the carbonyl group is forced by intramolecularly bridged =N- and NH_2 units which are held together by means of hydrogen interactions. One methanol molecule is co-crystallized with the carbonyl group in an -O-H···O= binding manner. The pyridine moiety is protonated, yielding a cationic species; the chloride

counterion is H-bridged to the phenolate function. Therefore, the entire structure is supported by electrostatic interactions with remarkable hydrogen bonding contribution. The presence of base can easily destabilize the semicarbazone framework, which along with deprotonation of phenolate causes the high flexibility of the ligand (Figure 21). In turn, it enables a tetradentate coordination mode of the compound.

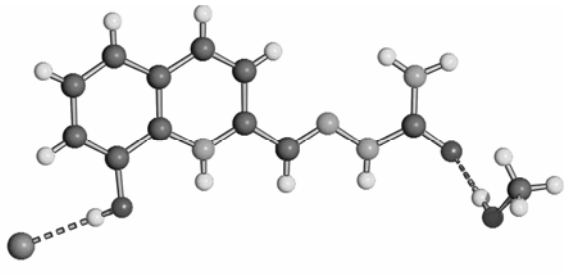


Figure 20. Structure of **17**-H • HCl • MeOH.

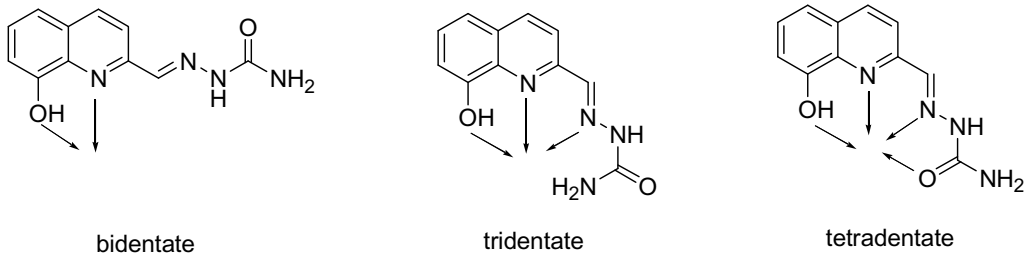
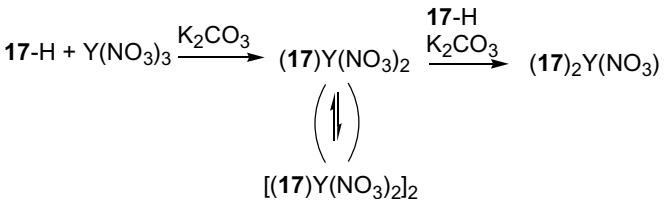


Figure 21. Possible conformations of **17**-H for bi-, tri-, and tetradentate coordination.

3.3.1.2. Speciation in solution

The NMR spectroscopic studies were performed in solution to observe the binding affinity of the ligand to the metals of different sizes, Y^{3+} *versus* La^{3+} (Scheme 3).



Scheme 3. Formation of yttrium(III) complexes of ligand **17**-H with a 1 : 1 (or 2 : 2) and 1 : 2 stoichiometry.

First of all, the speciation in the yttrium complex was monitored by ^{1}H NMR in DMSO-d_6. Mixing of the ligand and $Y(NO_3)_3$ in different ratios (1 : 1 → 4 : 1 ligand to metal) in the presence of base afforded complexes exhibiting spectra, from which two of the most informative are shown in Figure 22. At a 1 : 1 ratio the dominating set of signals (a) is ascribed to the coordinated ligand: δ = 8.44 (d, J = 8.5 Hz), 8.33 (s), 7.79 (d, J = 8.5 Hz), 7.39 (t, J = 7.7. Hz), 6.99 (d, J = 7.7 Hz), and 6.62 (d, J = 7.7 Hz). Another set of signals (b) is in

considerable minority. But it becomes prevalent at a 2 : 1 ratio: δ = 8.57 (s), 8.53 (d, J = 8.6 Hz), 7.90 (d, J = 8.6 Hz), 7.31 (t, J = 7.8 Hz), 6.99 (d, J = 7.8 Hz), and 6.36 (d, J = 7.8 Hz). Additionally, the insignificant amount of signals of a species (a) and of deprotonated ligand (*) are observed.

These NMR spectroscopic observations suggest that initially ligand coordinates to Y^{3+} resulting in a complex of 1 : 1 stoichiometry. But it tends to the 2 : 1 speciation upon further addition of the ligand. The respective complex of a 2 : 1 stoichiometry was detected by positive FAB MS (3-NBA) at m/z = 545 [(**17**)$_2Y^+$] with the correct isotopic pattern as the only species present in solution. The peak of a 1 : 1 complex was not found.

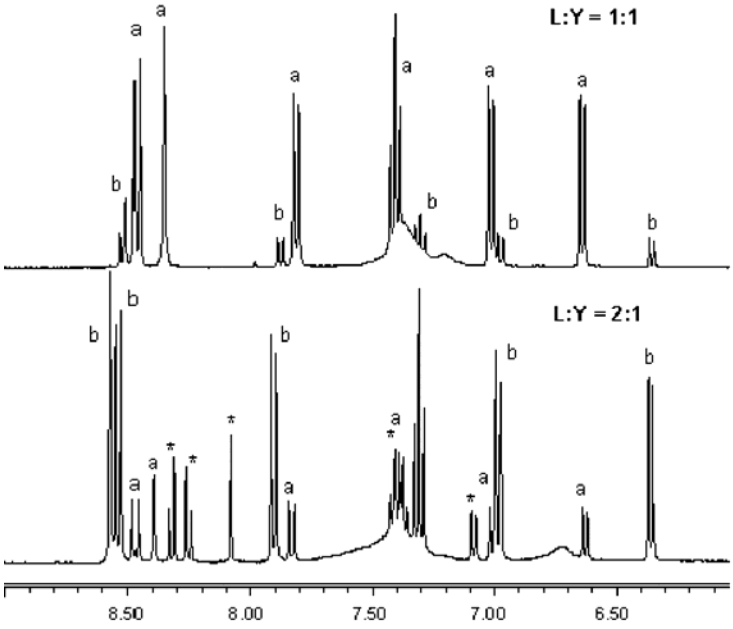


Figure 22. The comparison of ^{1}H NMR spectra of yttrium complexes of **17**-H obtained at different ligand L : Y ratios. Top: L : Y = 1 : 1, bottom: L : Y = 2 : 1. Complexes "(**17**)Y^{2+}" are marked by (a), "(**17**)$_2Y^+$" by (b); the asterisks indicate signals of deprotonated free ligand **17**.

Analogously, $La(NO_3)_3$ was involved in NMR studies with semicarbazone ligand **17**-H. The solution experiments resulted in a structured spectrum of only the 1 : 1 complex: δ = 8.37 (d, J = 8.4 Hz), 8.35 (s), 7.75 (d, J = 8.4 Hz), 7.36 (t, J = 7.9 Hz), 6.89 (d, J = 7.9 Hz), and 6.53 (d, J = 7.9 Hz). An increase in the ligand to metal ratio leads to the formation of a complex mixture which offers an intricate NMR spectrum.

Probably a 2 : 1 species is also formed, but the preferable 1 : 1 stoichiometry of the lanthanum complex can be traced back to size discrimination effect. In case of earlier lanthanides, the

coordination sphere will be rather filled with labile coligands (e.g., counterions, solvent molecules etc).

Only an X-ray analysis can give decisive structural information about a complex in the solid state because it is impossible to deduce from NMR spectra, whether the aggregation, e.g., dimerization, occurs in solution.

3.3.1.3. Crystal structure determination of complexes

In order to obtain necessary structural data a set of crystallization experiments was performed with ligand and some lanthanoid(III) salts at different ligand to metal ratios in the presence or absence of base / template. Two different crystallographic perspectives for yttrium(III) complexes were captured.

The structures of [(17)Y(NO$_3$)(DMF)$_2$]$_2$Cl$_2$ and [(17)La(NO$_3$)(MeOH)$_2$]$_2$(NO$_3$)$_2$

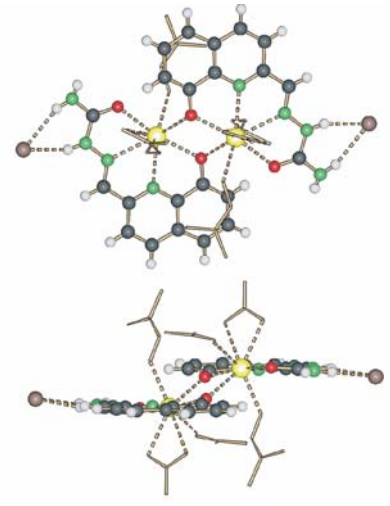


Figure 23. The structure of [(**17**)Y(NO$_3$)(DMF)$_2$]$_2$Cl$_2$ in the solid state. Top view (top) and side view (bottom). For clarity, solvent molecules as well as the nitrates are only indicated. (Y: yellow).

X-ray quality crystals of the 1 : 1 dimeric yttrium complex were obtained by slow diffusion of Et_2O in a DMF solution in the presence of NaCl. The complex crystallizes in the triclinic space group P1bar. The molecular structure of [(**17**)Y(NO$_3$)(DMF)$_2$]$_2$Cl$_2$ is represented in Figure 23.

Ligand **17** is bound to yttrium in a tetradentate manner through the pyridine N and phenolate anion of the quinolinate unit and the C=N- and C=O groups of the semicarbazone side chain. One DMF molecule occupies the orthogonal position relative to the ligand-plane from one side to the metal, while another DMF and bidentate nitrate are bound from the other. Dimerization of these monomeric fragments into a complex dication occurs through the phenolate oxygen atoms leading to a central four membered $(YO)_2$-ring with an Y···Y separation of 3.886 Å. At the dimerization site, a parallel alignment of the two identical coplanar moieties with a separation of *ca.* 2 Å takes place. Two chloride anions act as counterions, binding in a chelating fashion to the urea type unit of the semicarbazone side chain. [117]

[117] M. Boiocchi, L. Del Boca, D. E. Gomez, L. Fabbrizzi, M. Licchelli, and E. Monzani, *J. Am. Chem. Soc.,* **2004**, *126*, 16507.

The single crystals of $[(\mathbf{17})La(NO_3)(MeOH)_2]_2(NO_3)_2$ (Figure 24) are grown from methanol solution in the absence of additional salts (monoclinic, $P2_1/n$). The overall structure is analogous to the one described for $[(\mathbf{17})Y(NO_3)(DMF)_2]_2Cl_2$, but instead of DMF molecules and the chloride anions binding to the yttrium(III) center, the methanol and nitrate co-ligands are coordinated to the lanthanum(III). The La···La separation (3.980 Å) is notably long due to the bigger size of La^{3+} compared to Y^{3+}.

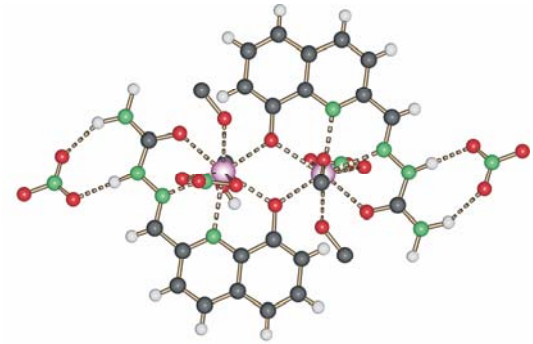
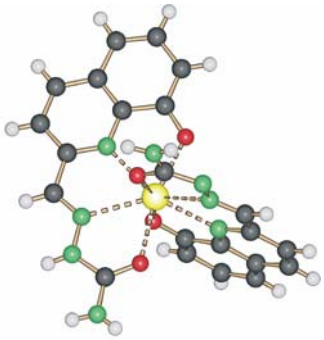


Figure 24. The structure of $[(\mathbf{17})La(NO_3)(MeOH)_2]_2(NO_3)_2$ in the solid state. Hydrogen atoms of the solvent molecules are omitted for clarity. (La: pink).

Although the X-ray analyses unravel that 1 : 1 yttrium(III) and lanthanum(III) complexes emerge as dimers in the solid state, it is not yet evident if either structure - dimeric or monomeric - is adapted by the complex in solution.

The structure of [(17)(17)'Y]

Single crystals of [(**17**)(**17**)**'**Y] were obtained upon vapour diffusion of Et_2O into a methanolic solution of $[(\mathbf{17})_2Y][NO_3]$. The compound crystallizes in the monoclinic space group $P2_1/n$. A mononuclear complex with a 2 : 1 ligand to metal stoichiometry is depicted in Figure 25. Typically the ligands are bound to the Y(III) in a tetradentate fashion. However, one of the ligands coordinates in its mono-deprotonated form (**17**), while the second one (**17**)' is doubly deprotonated. They occupy orthogonal positions to each other´s planes providing octacoordination at the yttrium(III) center.



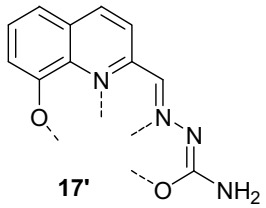


Figure 25. The solid state structure of [(**17**)(**17**)'Y] with ligand coordinated in its monodeprotonated (**17**) and bisdeprotonated (**17**)**'** forms.

Crystal structure analyses of erbium(III), holmium(III), and europium(III) complexes

After the solution and solid state investigations of the yttrium(III) and lanthanum(III) complexes, the coordination chemistry of **17**-H with f-elements has been subjected to further studies.

*The structures of [(**17**-H)$ErCl_3$] • MeOH and [(**17**-H)$HoCl_3$] • MeOH.* An erbium(III) or holmium(III) complex [(**17**-H)MCl_3] (M = Er, Ho) can be prepared by reaction of **17**-H with erbium(III) or holmium(III) triflate in a 1 : 1 ratio in the presence of KCl, or by simple mixing of the ligand and erbium(III) or holmium(III) chloride. X-ray quality crystals were obtained upon slow penetration of Et_2O vapours into MeOH solution.

Both complexes [(**17**-H)MCl_3] • MeOH (M = Er, Ho) crystallize in the monoclinic space group $P2_1/n$.

The complexes [(**17**-H)MCl_3] • MeOH (M = Er, Ho) adapt a distorted pentagonal bipyramidal geometry exhibiting heptacoordination at the metal ions (Figure 26). The ligand **17** binds in a tetradentate manner in the equatorial plane. Three chloride counterions fill up the two equatorial and one axial position at the metal center. Unusually, the phenolate moiety of the quinoline ligand remains protonated upon coordination and interacts with a molecule of methanol. This hydrogen bond differs in the two complexes. In the case of the erbium(III) compound, the proton is located close to the phenol oxygen (O-H = 0.83 Å) with a long distance to the methanol oxygen atom (Me(H)O···H = 1.66 Å). In the case of the holmium(III) complex, the bond is more symmetric (O-H = 1.15 Å, Me(H)O···H = 1.35 Å).[118]

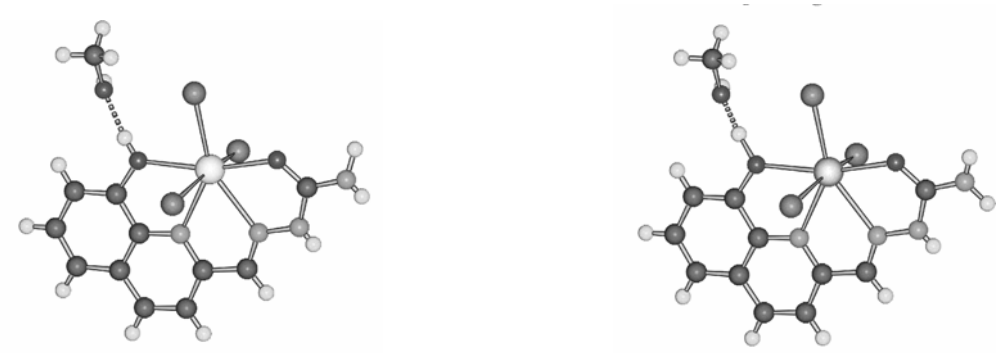


Figure 26. The structures of [(**17**-H)MCl_3] · MeOH [M = Er (left), Ho (right)] in the solid state.

*The structure of Na[μ-NO_3{(**17**)$Eu(NO_3)_2$}$_2$].* The compound K[μ-NO_3{(**17**)$Eu(NO_3)_2$}$_2$] was prepared by reaction of **17**-H with $Eu(NO_3)_3$ and K_2CO_3. But the single crystals of the europium(III) complex suitable for X-ray analysis could be obtained only for the corresponding protonated species by diffusion of Et_2O into a DMF solution of **17**-H, $NaHCO_3$, and $Eu(NO_3)_3$. This compound crystallizes in the tetragonal space group $I4_1/a$.

[118] T. Steiner, *Angew. Chem*. **2002**, *114*, 50; *Angew. Chem. Int. Ed.* **2002**, *41*, 48.

The molecular structure of the anionic dimer [μ-NO_3{(**17**)Eu$(NO_3)_2$}$_2$]$^-$ comprises of two neutral monomeric compartments [(**17**)Eu$(NO_3)_2$] (Figure 27). In each of them europium(III) is coordinated by the tetradentate ligand **17**, two bidentate nitrate ions from the "upper side" and one DMF molecule from the "down side" of the [(**17**)Eu]-plane. Two of those fragments are connected by one nitrate anion, which acts in a bis-bidentate manner: one of its oxygen atoms bridges both metal centers and each of two other nitrate oxygens binds to either of the europium(III) ions. In this complex, europium(III) centers exhibit an eleven coordination which is quite unusual and is realized due to the small bite angles of the nitrate ligands as well as of the ligand **17**. The proton could not be found by X-ray diffraction, but it is probably located at the phenolic oxygen atoms. The sodium acts as s a cation, which is disordered over three different positions.

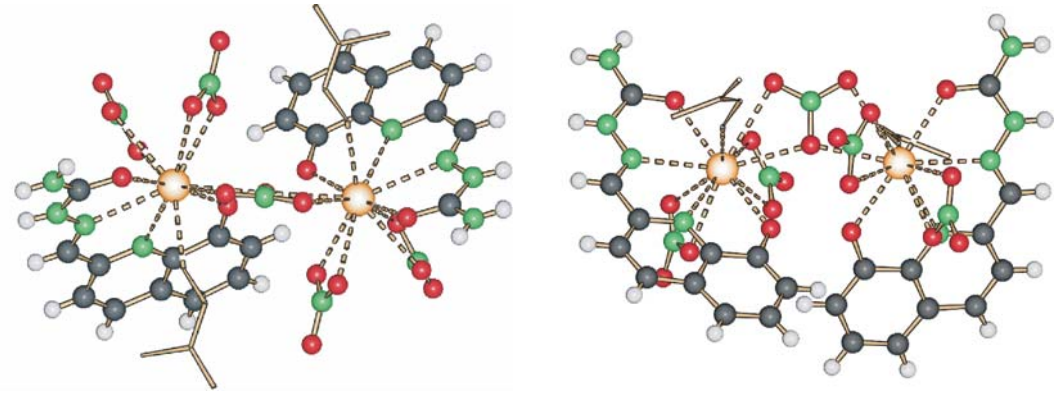
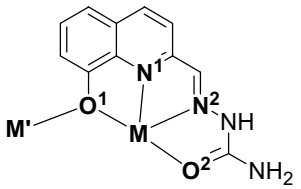


Figure 27. Two different views of the anion of Na[μ-NO_3{(DMF)(**17**)Eu$(NO_3)_2$}$_2$] in the solid state. (Eu: orange).

In summary, the semicarbazone derivative of 8-hydroxyquinoline **17**-H readily performs as a tetradentate ligand and is suitable for the coordination of rare-earth elements. NMR studies and X-ray crystallographic analyses reveal that a 1 : 1 stoichiometry is preferable in solution, as well as in the solid state (although an yttrium(III) complex was also isolated as a [ligand$_2$Y]$^+$ species) in spite of size discrimination in the lanthanoid row. Upon crystallization dimerization can occur often involving the phenolate oxygen as a bridging motif. Even in the protonated form the ligand retains its tetradentate mode. The coordination characteristics of the ligand depending on the central metal are listed in Table 2 for comparison.

Table 2. Comparison of the structural parameters of the tetradentate moiety of ligand **17** when binding to different metal centers.



	[(17)Y(NO$_3$)(DMF)$_2$]$_2^{2+}$	*[(17)(17')Y]*		*[(17)La(NO$_3$)(MeOH)$_2$]$_2^{2+}$*	*[(17-H)ErCl$_3$]*	*[(17-H)HoCl$_3$]*	*{(17)Eu(NO$_3$)$_{2.5}$DMF}*
O1-M	2.346(3)	2.330(3)	2.274(3)	2.425(3)	2.379(3)	2.395(3)	2.487(3)
N1-M	2.470(3)	2.442(4)	2.451(4)	2.541(3)	2.438(3)	2.455(3)	2.717(4)
N2-M	2.563(4)	2.483(4)	2.518(4)	2.620(3)	2.474(3)	2.486(3)	2.724(4)
O2-M	2.355(3)	2.311(3)	2.353(3)	2.414(4)	2.298(3)	2.310(3)	2.533(4)
O1-M'	2.354(3)			2.387(3)			
O1-M-N1	66.8(1)	67.2(1)	67.6(1)	65.5(1)	65.9(1)	65.6(1)	60.9(1)
N1-M-N2	61.4(1)	63.7(1)	62.7(1)	60.4(1)	63.9(1)	63.7(1)	58.1(1)
N2-M-O2	63.1(1)	64.2(1)	63.9(1)	60.9(1)	64.4(1)	64.1(1)	59.5(1)

3.3.2. Other (Thio-)Semicarbazone Derivatives

The interest in semicarbazone-containing ligand systems should not be limited to their exceptional coordination behaviour. The binding modes of the derivatives may be easily controlled by tuning the softness / hardness of the donor functions in the side chain C=O / S=O / O-CH_3 or at the phenolate side OH / OBn (Figure 28). Moreover, introduction of certain substituents, e.g., halogen atoms, in the quinolinate core may influence the electronic nature of the ligand (*vide infra*). Thus, the affinity to the different kinds of metals can be readily altered along a wide range.

Initially, the attention to the (thio)semicarbazone derivatives arose from their unique antimalarial, antibacterial (first report from *Alber*, 1954),[119] antivaccinal (first report from *Hamre*, 1950),[120] and antitubercular (first report from *Binswanger*, 1948)[121] activities. Many related compounds were tested, including 8-hydroxyquinoline derivatives,[122] and are now successfully included in medical applications as chemotherapeutic agents. Therefore, these and related systems are important objects for studies from the coordination point of view.

[119] A. Albert, *Brit. J. Exp. Path*. **1954**, *35*, 75.
[120] D. Hamre, J. Bernstein, R. Donovick, *Proc. Soc. Exper. Biol. & Med.* **1950**, *73*, 275.
[121] L. A. Binswanger, *Helv*. **1948**, *31*, 1975.
[122] J. Büchi, A. Aebi, A. Deflorin, H. Hurni, *Helv. Chim. Acta* **1956**, *39*, 1676.

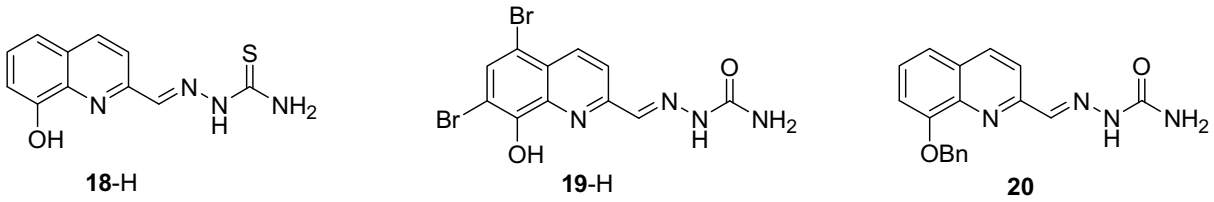


Figure 28. (Thio-)semicarbazone ligands **18**-H, **19**-H, **20**.

3.3.3. A SAMP Hydrazone Ligand and its Yttrium Complex

Excellent enantiomeric excesses are a destination point in asymmetric catalysis. The Ln(III) complexes were found to be particularly attractive and efficient for this purpose (e.g., in C-C coupling: Friedel-Crafts alkylation or acylation, hetero-Diels-Alder or Mannich reaction, aldol or Michael condensation, in polymerization, hydration processes etc.)[123] because of their Lewis acidity and diminished sensitivity to hydrolysis in comparison to traditional $AlCl_3$, $FeCl_3$, $SnCl_4$, $TiCl_4$. *Schneider* established the dependence of catalytic activity on the ionic radii of Ln(III):

1) its improvement for smaller cations;
2) its rapid decrease for heaviest Yb(III) and Lu(III) originating from problematic aggregation or clustering.[124]

In order to approach enantiomerically pure coordination compounds, the chirality should be introduced at the ligand. Taking inspiration from the previous results, SAMP hydrazone derivatives are considered as effective chiral auxiliaries to induce a helical twist at the ligand strand.[125]

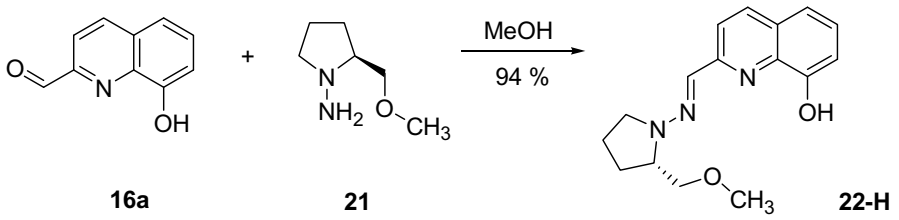
The hydrazone **22**-H was prepared in a simple condensation reaction of SAMP **21** with 8-hydroxyquinoline 2-carboxaldehyde **16a** in 94 % yield (Scheme 4).[126]

[123] (a) M. Shibasaki, H. Gröger, In *Topics in Organometallic Chemistry*; S. Kobayashi, Ed.; Springer-Verlag: Berlin-Heidelberg, **1999**, Vol. 2; pp 200-231. (b) K. Mikami, M. Tereda, H. Matsuzawa, *Angew. Chem*. **2002**, *114*, 3704; *Angew. Chem. Int. Ed.* **2002**, *41*, 3554. (c) M. Shibasaki, H. Sasai, T. Arai, *Angew. Chem.* **1997**, *109*, 1290. (d) S. Kobayashi, H. Ishitani, *J. Am. Chem. Soc.* **1994**, *116*, 4083; (e) S. Kobayashi, H. Ishitani, *Chem. Commun.* **1995**, 1379. (j) T. Hamada, K. Manabe, S. Ishikawa, S. Nagayama, M. Satoshi, S. Kobayashi, *J. Am. Chem. Soc*. **2003**, *125*, 2989.

[124] A. Roigk, R. Hettich, H.-J. Schneider, *Inorg. Chem*. **1998**, *37*, 751.

[125] (a) D. Enders, H. Eichenauer, *Chem. Ber.* **1979**, *112*, 2933. (b) D. Enders, P. Fey, H. Kipphardt, *Org. Synth.* **1987**, *65*, 173.

[126] For related pyridine SAMP-hydrazones see: (a) J. Ehlers, H. Dieck, *Z. Anorg. Allg. Chem.* **1988**, *560*, 80. (b) T. Mino, W. Imiya, M. Yamashita, *Synlett* **1997**, 583. (c) T. MinoY. Shirae, T. Yajima, M. Sakamoto, T. Fujita, *Heterocycles* **2006**, *68*, 1233. (d) For semicarbazone type ligands see e.g.: R. Pedrido, M. J. Romero, M. R. Bermejo, A. M. Gonzalez-Noya, M. Maneiro, M. J. Rodriguez, G. Zaragoza, *Dalton Trans.* **2006**, 5304.



Scheme 4. Synthesis of the SAMP hydrazone ligand **22**-H.

The new ligand was conceived as tetradentate coordinator but in contrast to **17-H** it possesses the weaker electron-donating ether moiety. Additionally, the chelating N,O unit in the side chain is elongated by one C atom.

A set of experiments with ligand **22**-H and different lanthanide(III) salts was performed under different conditions yielding usually undefined complex mixtures. Only the reaction of **22**-H with YCl_3 in methanol in the presence of K_2CO_3 as base gave a red powder, which exhibits in the ^{1}H NMR spectrum two sets of signals ascribed to the unsymmetrically bound ligands $(\mathbf{22})^-$. Positive ESI MS reveals the peak of $[(\mathbf{22})_2Y]^+$ at m/z = 657. X-Ray quality crystals of the complex were obtained upon slow evaporation of a CH_3CN / $CHCl_3$ solution. The crystallographic analysis showed that the two ligands are coordinated in a different way: one in a tetradentate as expected while another one binds to the Y(III) center monodentately through the phenolate oxygen atom (Figure 29). The latter ligand is extra fixed by hydrogen bridging between its protonated pyridine and the phenolate of the tetracoordinated hydrazone. This hydrogen atom involved in bonding can be detected by ^{1}H NMR spectroscopy at δ = 15.80 ppm. Additionally, the two *trans*-situated chloride coligands are binding to the yttrium(III) atom.

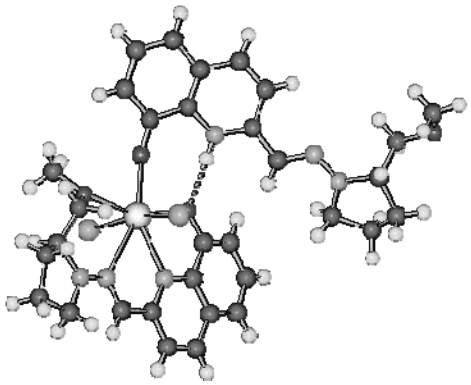


Figure 29. Molecular structure of $[(\mathbf{22})(\mathbf{22}\text{-H})YCl_2]$ as observed in the crystal.

In conclusion, the ligand **22**-H does not fully satisfy the coordination request of rare-earths(III) and is not reliable enough to provide effective Lewis acidic compounds.

3.4. Tridentate Ligands

The fascinating photophysical properties are anticipated from organized molecular architectures based on lanthanide(III) ions. However, the optimization of luminescence sensitization is usually associated with strict requirements for their design:

- kinetic inertness and thermodynamic stability of complexes;
- good protective environment at the Ln(III) emitter.

In order to achieve more specific and controllable coordination surrounding the luminescent center, the receptor must be preorganized to match the symmetry, geometry, and coordination numbers of the metal site. Consequently, due to facilitation of establishment of convergent non-covalent interactions the increased entropy value will be overcome in the self-assembly step. It is already well proven that three semirigid tricoordinating chelating units create a nonadentate binding interior in the wrapping motion. The latter readily encapsulates Ln(III) ion shielding it against intrusion of solvent molecules (e.g., H_2O) into its first coordination sphere.

Inherently, 8-hydroxyquinoline possesses a bidentate binding site. As it is ascertained in previous investigations, a bidentate as well as a tetradentate coordination mode is not really appropriate to specifically bind lanthanide(III) ions in a 3 : 1 ligand to metal ratio. Therefore, the attachment of different donor functions (for instance, imino or amido groups) into the 2-position of the oxine core leads to the expansion of its binding potential as a tridentate ligand unit.

3.4.1. Imino and Hydrazone Group Containing Tridentate Ligands

Acyclic Schiff bases are a versatile and well-studied class of ligands easily accessible by simple condensation of appropriate formyl and amine components usually in an excellent yield. The plethora of the coordination compounds, particularly lanthanide complexes or multimetallic 3d-4f and 4f-4f systems, based on the compartmental Schiff base derivatives was thoroughly reviewed by *Vigato*.[127] The simple strategy for the construction of dinuclear triple stranded helicates, based on bis-imine type ligands (for example, bis-pyridylimine or bis-imidazolimine) and transition metals (Ni^{2+}, Fe^{2+}, Ru^{2+}) excluding multistep covalent synthesis was proposed by *Hannon*.[128] But until now, the discrete lanthanide-containing assemblies with Schiff base-based receptors were mostly limited to the safe macrocyclic

[127] P. A. Vigato, S. Tamburini, *Coord. Chem. Rev.* **2004**, *248*, 1717.
[128] (a) G. I. Pascu, A. S. G. Hotze, C. Snchez-Cano, B. M. Kariuki, M. J. Hannon, *Angew. Chem*. **2007**, *119*, 4452. (b) F. Tuna, M. R. Lees, G. J. Clarson, M. J. Hannon, *Chem. Eur. J*. **2004**, *10,* 5737.

nests, in which the binding segments are preorganized for the insertion of particular lanthanides or selective recognition of d- and f-block elements. The tuning of intermetallic separation was achieved in the range from 3.81 Å to 10.89 Å.[129]

In order to introduce Schiff base coordination principles into the design of lanthanide(III) helicates, preliminary studies on the model systems had to be carried out. Two (**24**-H_2) and three (**25**-H_3) imine binding sites as well as oxime function (**23**-H) are attained in a one-step condensation reaction with 8-hydroxyquinoline-2-carboxaldehyde **16a**. The attempts of complexation with these tridentate ligands did not lead to the well-defined structures; all following crystallization experiments failed.

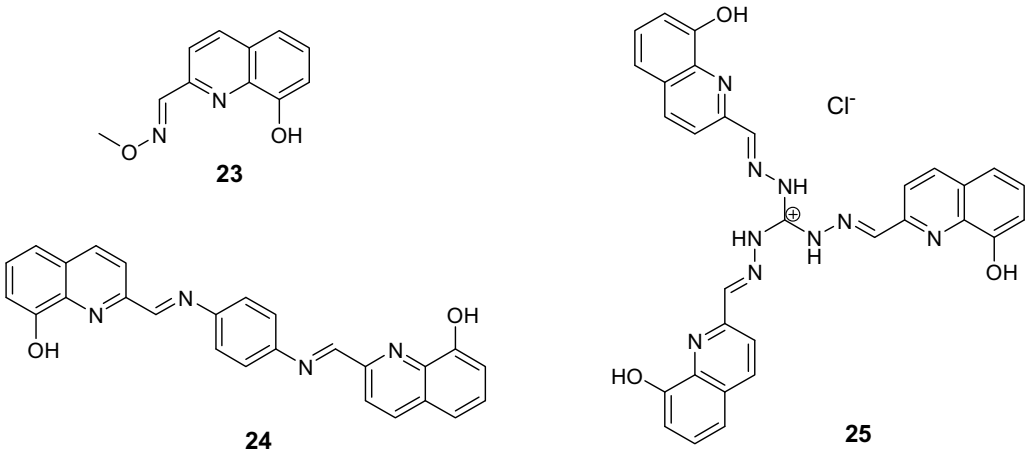


Figure 30. Tridentate oxime (**23**-H), imine (**24**-H_2), and hydrazone (**25**-H_3) ligands.

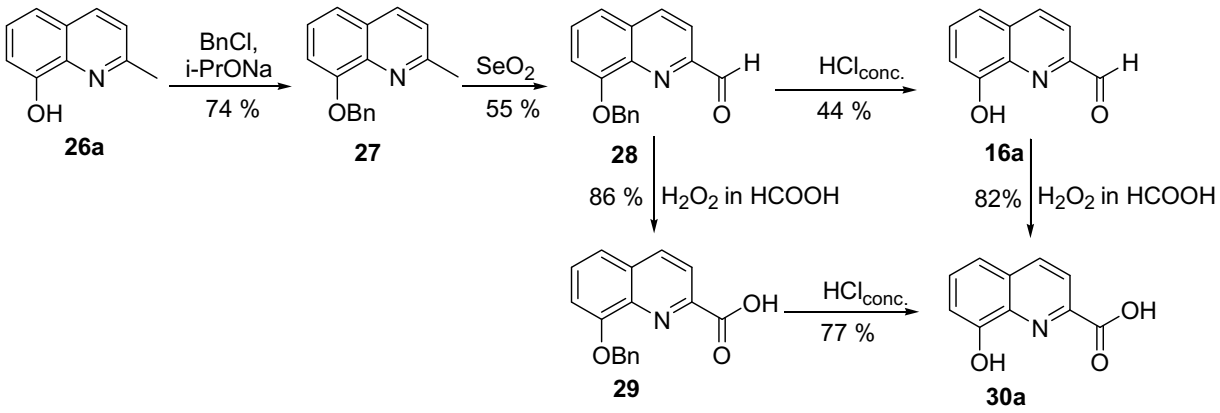
The correction in the ligand-metal affinity can be easily realized by tuning softness / hardness of the donor functions and/or optimization of steric / structural factors. The amide-coupling reaction of acid with an appropriate amine is a common strategy to functionalize quinolines in the 2-position. Thus, a proper choice of suitable carboxylic acids must be provided.

3.4.2. Synthesis of Quinoline Precursors for the Tridentate Building Blocks

3.4.2.1. On the way to 8-hydroxyquinoline-2-carboxylic acid

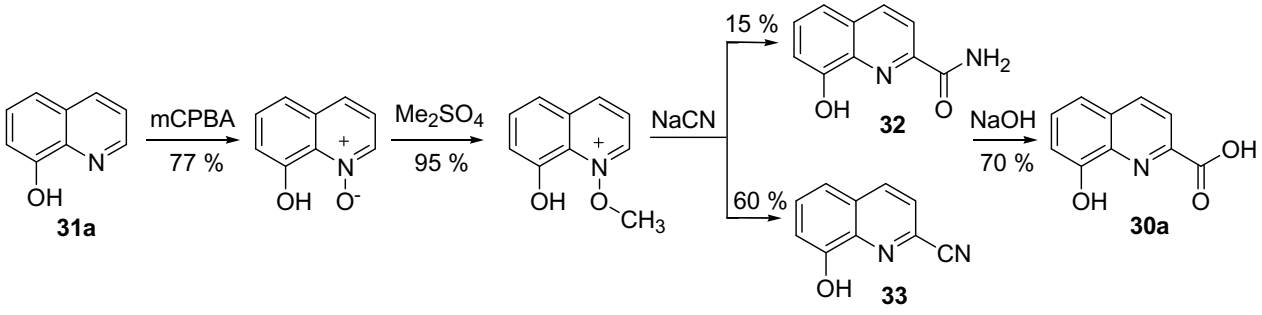
The reaction sequence in Scheme 5 represents a synthetic approach to the large scale preparation of 8-hydroxyquinoline-2-carboxylic acid (**30a**). Although the protocol proved to be time-consuming, generality and convenience make it especially useful for producing the

[129] K. Ariga, T. Kunitake, *Supramolecular Chemistry – Fundamentals and Applications*, Springer-Verlag Berlin Heidelberg **2006**.



Scheme 5. Synthetic routes for the preparation of 8-hydroxyquinoline-2-carboxaldehyde (**16a**) and 2-carboxylic acid (**30a**).

unsubstituted aldehyde (**16a**).[130] The deprotection step,[119] usually being an obstacle due to low yields (44 %), can be circumvented by the prior oxidative transformation of the benzyloxyquinoline aldehyde **28** to the protected acid **29**. The following ether cleavage proceeds smoothly leading to the **30a** in good yield (77 %) due to much simplified workup procedure. The effective method for oxidation of aromatic aldehydes to the corresponding carboxylic acids using H_2O_2 in formic acid, reported by *Dodd*,[131] can be applied in the present case to the aldehydes **16a** and **28** as well as the substituted derivatives thereof (*vide infra*). The need of a reliable and compact synthetic procedure for the preparation of 8-hydroxyquinoline-2-carboxylic acid **30a** was a driving force to reconsider once more the original protocol described by *Krasavin*[132] and essentially modified by *Shrader*[133] (Scheme 6).



Scheme 6. Synthesis of 8-hydroxyquinoline-2-carboxylic acid (**30a**) and related nitrile (**32**) and amide (**33**) compounds starting from 8-hydroxyquinoline (**31a**).

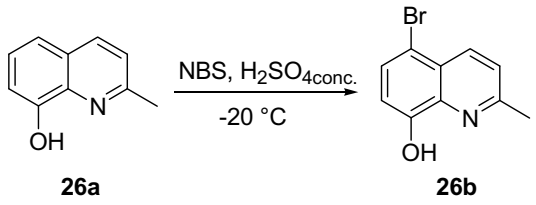
[130] E. G. Petkova, R. D. Lampeka, M. V. Gorichko, K. V. Domasevitch, *Polyhedron* **2001***, 20*, 747.
[131] R. H. Dodd, M. Le Hyaric, *Synthesis* **1993**, 295.
[132] I. A. Krasavin, V. M. Dziomko, Y. P. Radin, *Metody Policheniya Khim. Reactivov i Preparatov* **1965**, *13,* 94.
[133] (a) W. D. Shrader, J. Celebuski, S. J. Kline, D. Johnson, *Tetrahedron Lett*., **1988**, *29*, 1351. (b) C. R. Clark, R. W. Hay, *J. Chem. Soc. Dalton Trans.* **1974**, 2148. (c) R. W. Hay, C. R. Clark, *J. Chem. Soc. Dalton Trans.* **1976**, 1866.

Although this pathway is not ideal, especially regarding the specific purification details of the intermediates and high toxicity of reagents, it opens opportunities to design new building blocks stemming from the unique accessibility of carboxamide (**32**) and nitrile (**33**) derivatives.

3.4.2.2. Bromination of the quinoline core

In seeking further methods for the modification of the quinoline scaffold, the introduction of halogen substituents was envisaged as an opportunity to additionally affect the electronic structure of potential ligands.

The bromination of quinaldine **26a** using NBS furnishes the desired 5-bromocompound **26b** in 88 % yield (Scheme 7). To avoid the along formation of dibromo derivative **26c** the reaction conditions must be carefully followed.[134]



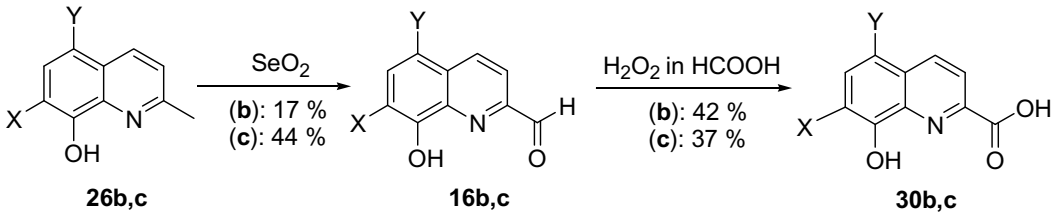
26a **26b**

Scheme 7. Bromination of quinaldine.

The endeavour of straightforward oxidation of **26b,c** to the corresponding acids **30b,c** failed, despite a variety of involved oxidation agents ($K_2Cr_2O_7$, CrO_3, $KMnO_4$, H_2NSO_3H in aq $NaClO_2$, SeO_2 in pyridine).[135]

Therefore, a two-step oxidation protocol (quinaldine - aldehyde - acid) was elaborated (Scheme 8). The treatment of the commercially available 5,7-dibromoquinaldine **26c** or previously synthesised 5-bromoquinaldine **26b** with selenium dioxide in 1,4-dioxane furnishes aldehydes **16c** and **16b** in low to moderate yields due to a number of side-products and a laborious purification procedure. However, the possibility to obtain different aldehydes, interesting precursors for the supramolecular building blocks, to some extent compensates the drawbacks of handling of SeO_2.

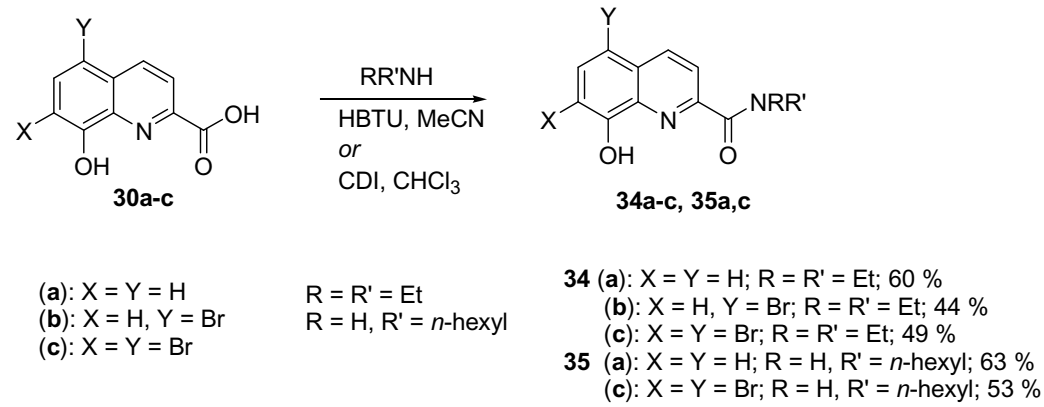
[134] W. D. Brown, A. H. Gouliaev, *Synthesis* **2002**, *1*, 83.
[135] (a) C. Caris, P. Baret, J.-L. Pierre, G. Serratrice, *Tetrahedron*, **1996**, *52*, 4659. (b) C. Piguet, J.-C. G. Bünzli, G. Bernardinelli, G. Hopfgartner, A. F. Williams, *J. Am. Chem. Soc*. **1993**, *115*, 8197.



Scheme 8. The oxidation procedure for the preparation of bromo substituted carboxylic acids **30b,c.**

3.4.2.3. Amidation reaction

Unpretentiousness of the quinoline based carboxylic acids to the coupling reagents (2-(1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate HBTU, carbonyl diimidazole CDI, or dicyclohehylcarbodiimide DCC) used in the amidation reaction allows to access a wide range of amidoquinolinate ligands. The amide coupling reactions of unsubstituted **30a** and substituted acids **30b** and **30c** with *N,N*-diethylamine or *n*-hexylamine proceed smoothly in moderate yields (Scheme 9).



Scheme 9. Synthesis of amidoquinolinate ligands **34a-c** and **35a,c.**

As an option, the bromination of amidoquinolinate **35a** with Br_2 under mild conditions (stirring in CH_2Cl_2 / MeOH solvent mixture at rt) was attempted yielding **35c** in 72 % yield. This reaction did not find real application since the synthetic procedure described above starting from the dibrominated quinaldine **26c** seems to be more effective and shorter.

3.4.2.4. Solid state structures and conformational considerations

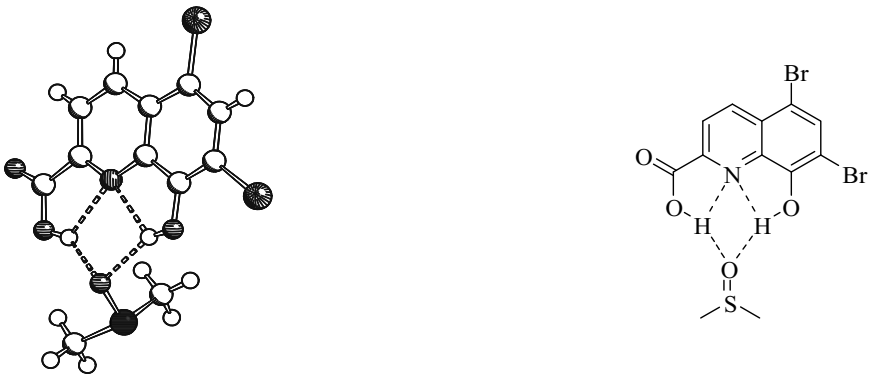


Figure 31. X-ray structure of **30c** · DMSO.

Yellow weakly diffracting crystals of the DMSO adduct of 5,7-dibromo-8-hydroxyquinoline-2-carboxylic acid **30c** suitable for X-ray crystallographic analysis were obtained from DMSO / MeCN solution. The molecular structure (Figure 31) shows the orientation of the two acidic protons (phenol and carboxylic acid) towards the front of the molecule. This is induced by intramolecular hydrogen bridging to the pyridine nitrogen atom. Thus, the hydrogen atoms are ideally predisposed to host a hydrogen bond acceptor - in the present case DMSO molecule - owing to the tweezer type interaction. This observation of intramolecular bonding is an outset for the development in the field of anion recognition and is of interest for the optimization of anion receptors based on quinoline backbone.

Colourless X-ray quality crystals of the 5,7-dibromo-8-hydroxyquinoline carboxamide **34c**-H were obtained by slow evaporation of the CH_2Cl_2 solution on air. The molecular structure is depicted in Figure 32 and represents similar conformational features as were found for the corresponding acid. The phenolic proton points towards the inner molecular front due to hydrogen bonding to the pyridine nitrogen. The amide oxygen is forced out of the quinoline binding site and stabilized in this position owing to the probable hydrogen interactions of the CH_3 protons of the ethyl unit with the nitrogen donor. However, minor disorder affects the two peripheral ethyl groups preventing the observation of the bridging between one of ethyl groups and the pyridine moiety.

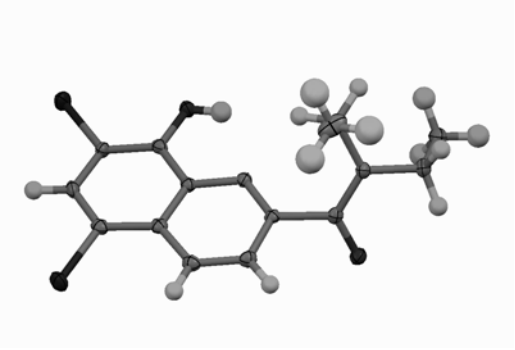


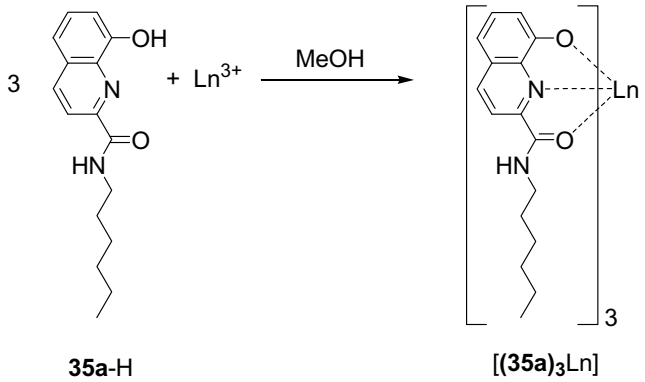
Figure 32. The structure of the carboxylic acid amide **34c**-H.

3.4.3. Coordination Studies with Tridentate Amidoquinolinate Ligands

3.4.3.1. The molecular structure of a holmium(III) complex

Recently the solid state structure of the 2-amido substituted 8-hydroxyquinoline **35a**-H was reported by *Albrecht*. The compound crystallizes as a single stranded helix and is packed in polymeric array by hydrogen bonding.[136]

This ligand is a useful model system to provide an insight into the coordination ability of tridentate amidoquinolinates with regard to lanthanide(III) ions. The lanthanide(III) complexes were prepared by reaction of **35a**-H with lanthanide(III) salts in a 3 : 1 ligand to metal ratio in the presence of K_2CO_3 as base (Scheme 10). The crystallographic information was of primary necessity in order to confirm the structural expectations. Only the holmium complex was obtained in form of X-ray quality single crystals by vapour diffusion of Et_2O into a methanolic solution. The preliminary molecular structure exhibits nine coordination at the central Ho^{3+} ion which is contributed by three tridentate ligand strands wrapped around the metal atom in a helical arrangement. Importantly, no solvent molecules are bound to the holmium(III) (Figure 33).



Scheme 10. Synthesis of the lanthanide(III) complexes of the ligand **35a**-H.

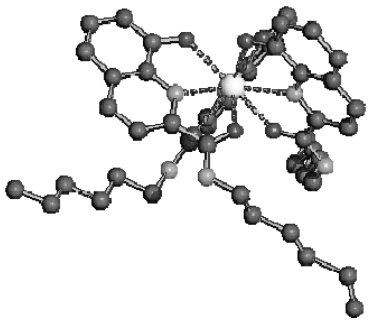


Figure 33. The structure of the [Ho(**35a**)$_3$] complex.

With the aim to gain spectroscopical sense of luminescent lanthanide(III) complexes two further related projects stem from this model study:

- the introduction of halogen atoms in the quinolinate scaffold and the replacement of the N-H unit of carboxamide group with an alkyl substituent in order to eliminate X-H (X = C, N, O) high energy vibrational modes;

[136] M. Albrecht, K. Witt, R. Fröhlich, O. Kataeva, *Tetrahedron* **2002**, *58*, 561.

- the extension of the helical motif to the bi-/polytopic receptors in order to approach homo- as well as hetero-bi-/polynuclear helicates.

Considering these issues, a comprehensive approach to the modification of the ligand structure should be developed according to the substitution effect on the spectroscopical properties of the lanthanide(III) complexes.

3.4.3.2. Substitution effect on the luminescence properties

The spectroscopic value of lanthanides(III) incorporated in a specific coordination environment can be estimated by the combination of three phenomenological intensity parameters Ω_λ (λ = 2, 4, 6) representing Judd-Ofelt theory. The Ω_2-parameter describes the hypersensitivity and is attributed to the tuning of polarizability of the coordinative bonds between the donor functions of the ligand and the central metal ion. An increase of covalency contribution results in the corresponding increase of this parameter. On the other hand, the high symmetry of the coordination surrounding at the lanthanide(III) center leads to its decrease. The rigidity of the ligand environment defines the parameters Ω_4 and Ω_6, which have an inconsiderable impact on the overall relative luminescence intensity. *Van Deun* observed the effect of halogen substitution on the Ω_2 value and ascribed it to the changes in the electronic structure upon bromination or chlorination (the mesomeric donating effect of *ortho*- and *para*-orienting substituents induces the increase of a covalent dominant). Moreover, the replacement of aromatic C-H with heavy halogen atoms lowers stretching frequencies and suppresses non-radiative relaxation processes.[75]

The elegant way to design an "ideal" ligand for the optimum sensitization of the lanthanide(III) emission, particularly in the NIR region, by multiple aromatic C-F substitution was proposed by *Pikramenou*. The fully fluorinated imidodiphosphinate ligand in assembly with lanthanide ions forms a safe triple-stranded shell around emitting center precluding any solvatation effects during complexation and provides maximal possible sensitization of lanthanide(III)-centered luminescence. Hence, the remarkably enhanced quantum yields with unprecedented lifetimes were detected for NIR emitters. The highest value was observed for the corresponding Yb^{3+} complex, which is half the value of the Yb^{3+} radiative lifetime.[137]

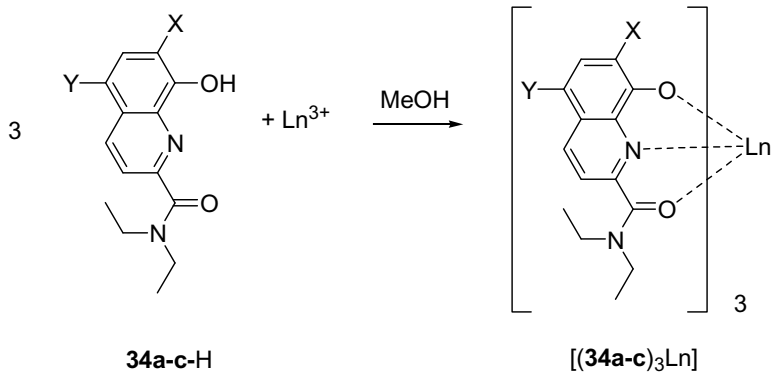
Besides the photophysical sense addressed in novel lanthanide complexes, the heteroatoms grafted into an aryl fragment create the opportunity to develop ligand systems by appropriate cross-coupling reactions.

[137] P. B. Glover, A. P. Bassett, P. Nockemann, B. M. Kariuku, R. Van Deun, Z. Pikramenou, *Chem. Eur. J.* **2007**, *13*, 6308.

3.4.3.3. Systematic solution, crystallographic, and photophysical studies on the luminescent lanthanide(III) complexes of amidoquinolinate ligands

Synthesis and solid state determination of the complexes

The complexes were prepared by reaction of the ligands **34a-c**-H with hydrated lanthanide salts $LaCl_3$, $EuCl_3$, and $NdCl_3$ as well as $Yb(SO_3CF_3)_3$ and $Er(SO_3CF_3)_3$ in a 3 : 1 ligand to metal ratio in the presence of K_2CO_3 as base (Scheme 11).



Scheme 11. Synthesis of the complexes [Ln(**34a-c**)$_3$], where Ln = La, Eu, Nd, Er, Yb.

The excellent solubility in organic solvents allows the extraction of the neutral LnL_3 species from the concomitant side-products and inorganic components. Often in ESI MS, the peak corresponding to the $[LnL_2]^+$ complex can be also observed along with a characteristic peak of LnL_3 species. Therefore, elemental analysis is the most reliable method to confirm the solitude and analytical purity of the target compound.

In order to get more understanding about the structural features of the complexes in the solid state, X-ray quality crystals of erbium [Er(**34a**)$_3$] (from THF / chloroform / Et_2O solvent system) and ytterbium [Yb(**34c**)$_3$] (from DMF solution) compounds were obtained (Figure 34). As expected, in the [Er(**34a**)$_3$] complex the ligand coordinates in a tridentate manner with separations Er-O_{quin} = 2.313(3), 2.329(3), 2.347(3) Å, Er-N = 2.494(4), 2.500(4), 2.484(4) Å, and Er-O_{amide} = 2.415(3), 2.424(4), 2.431(4) Å. The three ligand strands are arranged around the metal center in a helical fashion, resulting in a nine coordination at the erbium(III) ion. In the isolated crystals only the *syn* isomer was found, while in solution of the pure [Er(**34a**)$_3$] complex, the presence of both isomers - *syn* and *anti* - is expected. In the solid state the compound is stabilized in the *syn*-form by the potassium cation of $K(SO_3CF_3)$ which is coordinated to the three phenolate oxygen atoms of the (**34a**)$^-$ ligands in [Er(**34**)$_3$]. Thus, the complex itself performs as a tridentate ligand for potassium.

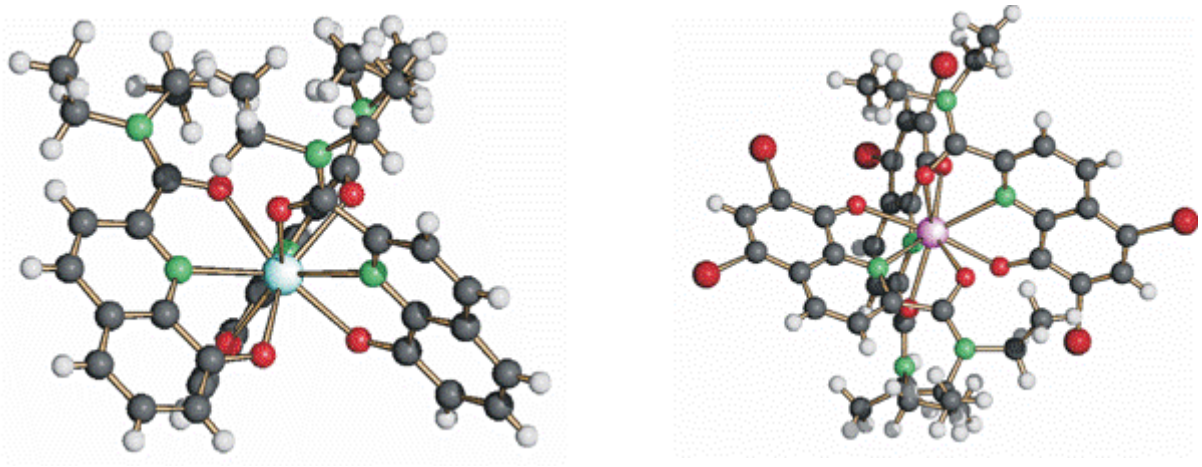


Figure 34. The molecular structure of the [Er(**34a**)$_3$] (left; Er: blue) and [Yb(**34c**)$_3$] (right; Yb: purple) complexes.

The inversion of related pairs of K^+ and triflate ions links the [Er(**34a**)$_3$] moieties to form a large centrosymmetric dimer. In contrast to the erbium complex, [Yb(**34c**)$_3$] crystallized as *anti* isomer. The coordination environment of the Yb^{3+} ion is comprised of the two parallel oriented chelating ligands with bond lengths Yb-O_{quin} = 2.344(9) and 2.284(9) Å, Yb-N = 2.484(11) and 2.455(11) Å, and Yb-O_{amide} = 2.363(9) and 2.415(10) Å and one antiparallel ligand strand with bond lengths Yb-O_{quin} = 2.363(9) Å, Yb-N = 2.437(11) Å, and Yb-O_{amide} = 2.376(9) Å.

Coordination studies in solution

In order to get knowledge about the solution structure of the complexes, NMR measurements with diamagnetic [La(**34c**)$_3$] were performed by J. Klankermayer in CD_2Cl_2. The broad resonance signals observed by ^{1}H NMR at room temperature getting sharper upon cooling of the sample to 235 K. Finally, the five sets of aromatic signals can be distinguished for the ligand (**34c**)$^-$ consequently arising in ten sets of resonances for protons of the ethyl groups. The assignment of coupling patterns was enabled due to a low-temperature COSY NMR experiment. Resonances for two ethyl groups without diastereotopic protons at δ = 3.42 (CH_2), 1.18 (CH_3); 3.59 (CH_2), 1.24 (CH_3) are resulting from the free ligand **34c**-H since they correspond to resonances occurring in the NMR spectrum of **34c**-H. Six of the remaining eight sets of signals (δ = 2.31 CH_2, 0.43 CH_3, and 3.83 CH_2, 1.48 CH_3; 3.22/2.82 CH_2, 0.63 CH_3; 3.83/3.49 CH_2, 1.38 CH_3; 3.74/3.59 CH_2, 1.42 CH_3; 3.01/2.83 CH_2, 0.57 CH_3; 3.38/3.21 CH_2, 0.92 CH_3; 3.83/3.42 CH_2, 1.25 CH_3) are assigned to the diastereotopic methylene protons. These NMR observations suggest inequivalence of the four different types of ligands in the *syn* and *anti* isomers of [La(**34c**)$_3$] induced by chirality at the complexes. The *syn*

isomer possesses C_3 symmetry and generates only one set of signals, while the unsymmetrical *anti* isomer (C_1) results in three sets. Statistically, a 1 : 3 *syn* : *anti* ratio for the complex isomers is expected. Indeed, it matches the detected relative intensities of the resonances from the inequivalent ligand units.

Photophysical investigations in solid state

Solid phase photophysical investigations were performed by F. Gumy and J.-C. G. Bünzli for the [Ln(**34c**)$_3$] complexes (Ln = La, Eu, Er, Nd, Yb) at 295, 77, and 10 K.[138] All three lanthanum complexes display emission spectra with broad bands of a similar shape and a maximum at 650 nm (295 K) or 630 nm (77 K) upon excitation at 277, 370, or 522 nm. These wavelengths are attributed to the absorption bands of the coordinated ligands. The quantum yield of the ligand-centred fluorescence is determined to be Q = 0.44(5) % for [La(**34c**)$_3$]. No triplet state emission could be recorded. A similar situation is monitored for the Eu(III) complexes, no metal-centred emission being observed, while the singlet state emission is quite weak. The lack of Eu-centred emission is explained by the low energy of the quinoline ligand triple state and its inability to transfer energy to populate the emissive states of the Eu^{3+} centre.

Interestingly, a 8-hydroxyquinoline based podate reported by *Comby* seems to be suitable for the sensitization of europium-centered luminescence (Figure 10, **8**).[76b,c] The strongly withdrawing sulphonate groups, introduced in the 5-positions of four of the quinolinate chromophores in order to provide water solubility of the complexes, are also responsible for the heavy atom effect which somewhat influences the efficiency of ISC. The observed absolute quantum yield is low Q^{Yb}_L = 0.02 % (determined in water). Two reasons for that should be considered:

1) ΔE ($^1\pi\pi^*$ - $^3\pi\pi^*$) in the **Tsox** is too large (6600 cm^{-1}) compared to the optimum value (5000 cm^{-1}); in such cases the residual fluorescence from the ligand is usually detected;
2) ΔE ($^1\pi\pi^*$ - $^5D_0$) in the **Tsox** is too small (~ 1480 cm^{-1}) compared to the optimal value (2500 - 3500 cm^{-1}); in such cases the temperature-dependent nonradiative decay and energy back transfer can take place. In parallel, the efficient sensitization of NIR lanthanide(III)-centered luminescence was shown.

[138] All luminescence decays were single exponential functions, l_{exc} = 355 nm, l_{an} = 1059 (Nd), 1518 (Er), 979 and 1018 nm (Yb).

In order to get a deeper comprehensive picture about ET processes on quinolines, further photophysical studies were extended to the NIR emitting Nd^{3+}, Er^{3+}, Yb^{3+}. The effective energy transfer from the ligands to the metals and NIR luminescence were detected for all nine complexes, whose excitation spectra closely match the ligand absorption spectra. High-resolution low-temperature spectra exhibit the characteristic ligand-field splitting of the emitting and ground levels.

In these spectroscopic studies the room temperature data were collected (Figure 35), and the effect of bromination on the quantum yields of the metal-centred luminescence and lifetimes of the excited states was deduced (Table 3). All of the excitation spectra are similar, with a broad band ranging from 250 to 570 nm and displaying two main maxima at *ca.* 370 and 520 nm. All three neodymium(III) complexes demonstrate well emissive attitudes upon excitation in the UV or visible (355-488 nm). Typical emission bands for the $^2F_{3/2} \rightarrow {}^4I_{11/2}$, $^2F_{3/2} \rightarrow {}^4I_{13/2}$, and $^2F_{3/2} \rightarrow {}^4I_{9/2}$ transitions are monitored. The quantum yields of the metal-centred luminescence upon ligand excitation, Q^{Nd}_L, increase in the row Nd(**34a**)$_3$ < Nd(**34b**)$_3$ < Nd(**34c**)$_3$. The presence of two bromine atoms leads to a total improvement of the Q^{Nd}_L value by a factor of approximately 2.9. This could be attributed to the "heavy atom effect" of the bromine substituent which seems to be additive upon successive introduction of bromine atoms in the quinoline backbone (enhancement factors are 1.6 and 1.7, respectively). In parallel, the increase of Nd($^2F_{3/2}$) lifetimes by a slightly larger factor (4-fold) is consistent with the trend observed for quantum yields and indicates a decrease in the non-radiative deactivation pathways. The erbium(III) complexes display the typical $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition centred at 1.54 μm. Similarly to the Nd(III) compounds, the quantum yields Q^{Er}_L increase in the series Er(**34a**)$_3$ < Er(**34b**)$_3$ < Er(**34c**)$_3$ by a factor of approximately 2.8, while a 3.5-fold increase of the Er($^4I_{13/2}$) lifetime is observed. The ytterbium(III) complexes display the characteristic $^2F_{5/2} \rightarrow {}^7F_{7/2}$ emission at around 980 nm.

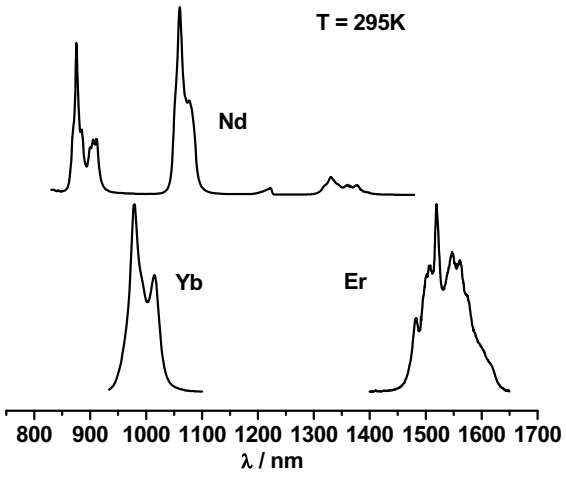


Figure 35. High-resolution emission spectra of solid samples of [Ln(**34c**)$_3$] under ligand excitation at 370 nm.

Table 3. Results of the solid phase photophysical measurements for complexes Ln(**34a-c**)$_3$ at room temperature. Quantum yields $Q^{Ln}{}_L$ [%, excitation in the range 350-400 nm] as well as lifetimes τ [μs, excitation at 355 nm] of the excited states for the NIR emission are listed.

Ligand **L**		Nd**L**$_3$	Er**L**$_3$	Yb**L**$_3$
34a	Q [%]	0.14(2)	0.012(1)	0.56(5)
	τ [μs]	0.39(1)	1.15(2)	11.1(1)
34b	Q [%]	*0.23(4)**		0.60(6)
	τ [μs]	*0.69(2)**	**	10.5(1)
34c	Q [%]	0.40(2)	0.033(5)	1.40(25)
	τ [μs]	1.57(10)	4.05(5)	20.6(2)

* Analysis shows eight water molecules per complex;
** no correct analysis for [Er(**34b**)$_3$] (Q = 0.021(1) %, τ = 2.30(1) μs).

The largest quantum yield, up to $Q^{Yb}{}_L$ = 1.40 %, was detected for [Yb(**34c**)$_3$], but no substantial improvement of the $Q^{Yb}{}_L$ was found when a single bromine atom is introduced. The overall 2.5-fold enhancement is entirely due to the addition of the second bromine and, in parallel, the Yb($^2F_{5/2}$) lifetime is lengthened by the same factor. The yellow side product, which was additionally isolated from reaction of **34c**-H with Yb(SO$_3$CF$_3$)$_3$ and could be recognized from its solubility exclusively in MeOH or DMF, has a significantly larger quantum yield ($Q^{Yb}{}_L$ = 2.24 %, τ = 29.0 μs). However, the nature of this complex is still under investigation (the elemental analysis indicates the composition [Yb(**34c**)(SO$_3$CF$_3$)$_2$]).

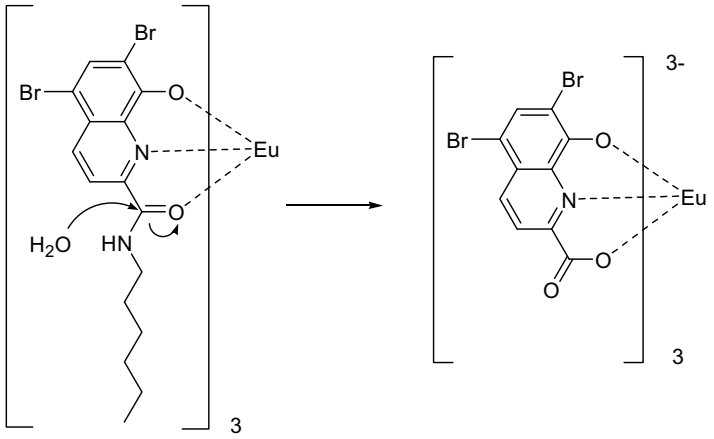
In summary, ligands derived from 8-hydroxyquinoline demonstrated their applicability for the preparation of monometallic tris-coordination compounds in a simple complexation step. Moreover, they confirmed the status of excellent sensitizers of the NIR-luminescence from trivalent lanthanide ions (Nd, Er, Yb). The introduction of halogen substituents into the ligand moiety showed to be an efficient tool for the improvement of luminescence characteristics. It should be pointed out, that the complexes can even be excited in the visible (up to 550-570 nm), which is particularly valuable for potential applications (e.g., *in vivo*).

3.4.3.4. Incidents provoked by Lewis acids in solution

However, not always the complexation with amide group containing ligands leads to an isolation of the target species; some specific processes can take place in the solution under acidic conditions provoked by lanthanide ions. For a long time, the lanthanide(III) complexes were appreciated as catalysts for hydrolysis of phosphodiesters, especially di- and

polymetallic systems attracted much attention due to their more efficient performance enabling simultaneous activation of several steps of the catalytic cycle.[139]

An unusual outcome of the complexation was observed for the **35c**-H. In this particular case the hydrolytic cleavage of the ligand amide function might have occurred in the bound state and was promoted by the deshielding effect of coordinated Eu^{3+} cation. The latter makes the carbonyl group electrophilic enough for an attack by water initiating the irreversible amide hydrolysis to the carboxylate **30c** (Scheme 12).



[Eu(**35c**)$_3$] [Eu(**30c**)$_3$]$^{3-}$

Scheme 12. Amide hydrolysis occurring in the europium(III) complex.

A large 3-fold negative charge is partially neutralized by a potassium cation, which seems to be bound in the complex structure. Analogously to the [La(**34c**)$_3$] complex, two isomers of the europium compound [Eu(**30c**)$_3$]$^{3-}$ and minor amounts of free dibromoacid **30c**-H_2 give rise to five sets of ligand signals which appear in the NMR spectrum with intensities matching a statistical 1 : 3 ratio. ESI MS showed the corresponding peak at m/z = 1227.6 with a correct isotopic distribution for [Eu(**30c**)$_3$]$^{3-}$ species. These observations suggest, that the pronounced affinity of the negatively charged carboxylate ligands to the lanthanide(III) can become a driving force in the complex formation ignoring the secondary electrostatic repulsions, if the other participants - like alternative metal ions - are absent in the competition for thermodynamic preferences. The stability of this europium(III) complex possessing a relatively high negative charge opens perspectives in the design of water-friendly luminescent probes.

[139] (a) B. F. Baker, H. Khalili, N. Wei, J. R. Morrow, *J. Am. Chem. Soc*. **1997**, *19*, 99323. (b) R. Häner, D. Hüsken, J. Hall, *Chimia* **2000**, *54*, 569. (c) N. H. Williams, B. Takasaki, M. Wall, J. Chin, *Acc. Chem. Res*. **1999**, *32*, 485. (d) P. Gomez-Tagle, A. K. Yatsimirsky, *Inorg. Chem*. **2001**, *40*, 3786.

An example of inadequate behavior of tridentate quinolinate ligands containing carboxylate unit is observed in case of monobrominated acid **30b**-H_2 which was employed in the coordination study with Eu^{3+} in the presence of a base K_2CO_3. The product was analyzed by means of negative ESI MS revealing only two peaks at m/z = 685.5 and 1521.8, attributed to the complexes of compositions $[Eu(\mathbf{30b})_2]^-$ and $[Eu_3(\mathbf{30b})_4]^+$, respectively. Surprisingly, the ^1H NMR spectrum recorded at rt for paramagnetic europium compounds is well-structured allowing to distinguish 24 sets of signals, which can be assigned to two kinds of species present in solution, thus, confirming suggested monomeric and trimeric structures. In the former (monomeric) case additional coligands can interact with the metal center filling up the vacant coordination positions. In the second case, the charge of formed agglomerate is probably neutralized by a chloride counteranion. Only the X-ray diffraction analysis could elucidate the situation in molecular structure, but unfortunately, no crystallographic data was obtained for this complex.

The discrepancy in the outcome of reactions suggests that the quinoline based carboxylic acids are not effective and reliable tridentate ligands for the coordination of lanthanides. The high negative charge created at the metal center upon complexation can destabilize the molecular structure becoming a deleterious factor for the planning of coordination strategy.

3.4.3.5. Zinc complex as an example of the coordination behavior of the tridentate quinolinate ligands with respect to the d-elements

Before implementing the coordination studies on the amide group containing quinoline ligands towards the heterodimetallic complexes, which comprise at least one p- or d-metal center with octahedral geometry, it was of interest to examine the binding mode of simple 2-amidoquinolinates in the presence of zinc(II). The latter is spectroscopically inactive and is usually used as a structural organizer due to its poor stereochemical preferences. The bidentate amide- and urea-substituted quinolinol ligands were already involved in the coordination chemistry with zinc demonstrating high binding affinities and

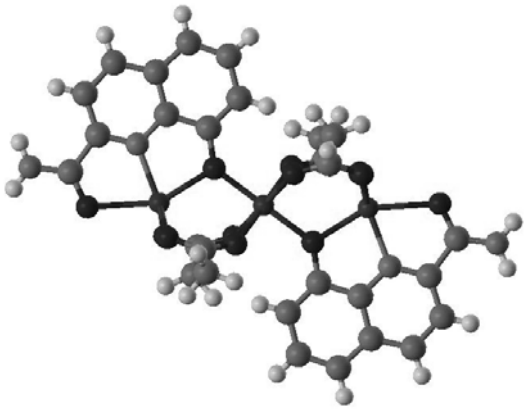


Figure 36. The molecular structure of the trinuclear complex $[Zn_3(\mathbf{32})_2](OAc)_4$

stability of the formed helicate-type complexes.[140] The tridentate ligand **32**-H afforded the trinuclear compound $[Zn_3(\mathbf{32})_2](OAc)_4$ in the reaction with $Zn(OAc)_2$. Each of two complexed ligands is bound to two of three metal centers providing tetradentate coordination at the terminal zinc ions and hexadentate surrounding at the central metal. The bridging phenolate functions and four participating acetates (two of them are coordinated in a monodentate manner, the other two connect neighbouring zinc ions in a bidentate fashion) provide the tetragonal bipyramidal geometry of the central complex fragment. The peripheral zinc ions adopt a tetrahedral structure. This model compound introduces d-elements in the coordination chemistry of tridentate quinolines.

In summary, the coordination and photophysical studies on simpler monometallic complexes based on the quinolinate ligands are a prerequisite to the successful design and preparation of the extended polymetallic systems. Ligand modification is gained by introducing halogen substituents into the quinoline core or/and by altering the donor functions fitted in the 2-position of the chromophore, offering the opportunity to affect spectroscopical properties of the lanthanide(III) complexes.

3.5. Dimetallic Helicates: Synthesis, Characterization, Properties

3.5.1. Synthesis of Sequential Ligands

An upsurge of interest in the design and elaboration of luminescent lanthanide-containing probes for biomedical applications and electrooptics requires the development of polymetallic functional edifies. The combination of several luminescent or magnetic centers along a single system implies the selective recognition of specific metal ions by predisposed binding sites. Unfortunately, the demand of suitable ligands for these coordination purposes, particularly, sequential ones, is by far not covered due to a lack of adequate synthetic pathways.

The strategy developed by *Williams* and *Piguet* relies on the modified double Phillips coupling reaction as a key synthetic step yielding benzimidazole - pyridine ligand systems (Figure 5, **5**).[141] A brief survey of the literature convinces one, that at the moment the above-mentioned protocol can be considered as the most reasonable way to access the unsymmetrical and polytopic ligand strands comprising tridentate domains, although it suffers from a number of intermediates and requires large synthetic efforts.

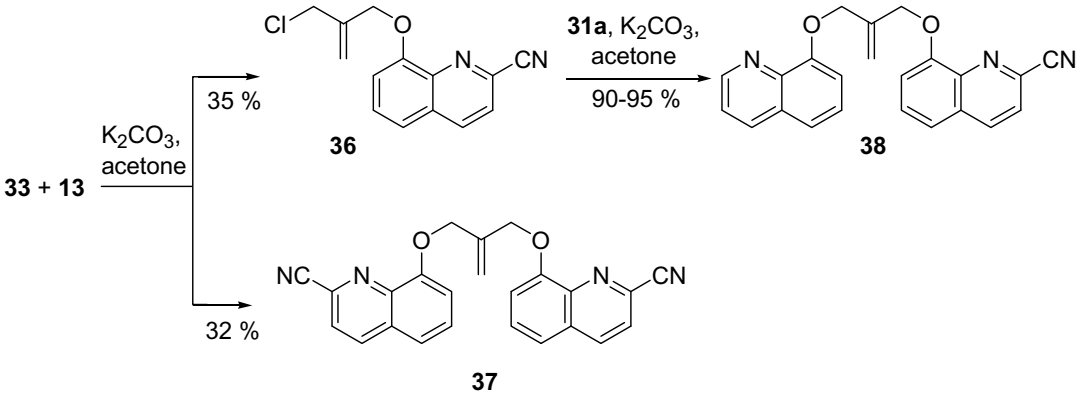
[140] (a) M. Albrecht, K. Witt, P. Weis, E. Wegelius, R. Fröhlich, *Inorg. Chim. Acta* **2002**, 25. (b) M. Albrecht, K. Witt, H. Röttele, R. Fröhlich, *Chem. Commun*. **2001**, 1330.

[141] (a) A. W. Addison, P. J. Burke, *J. Heterocycl. Chem*. **1981**, *18*, 803. (b) C. Piguet, B. Bocquet, E. Müller, A. F. Williams, *Helv. Chim. Acta* **1989**, *72*, 323.

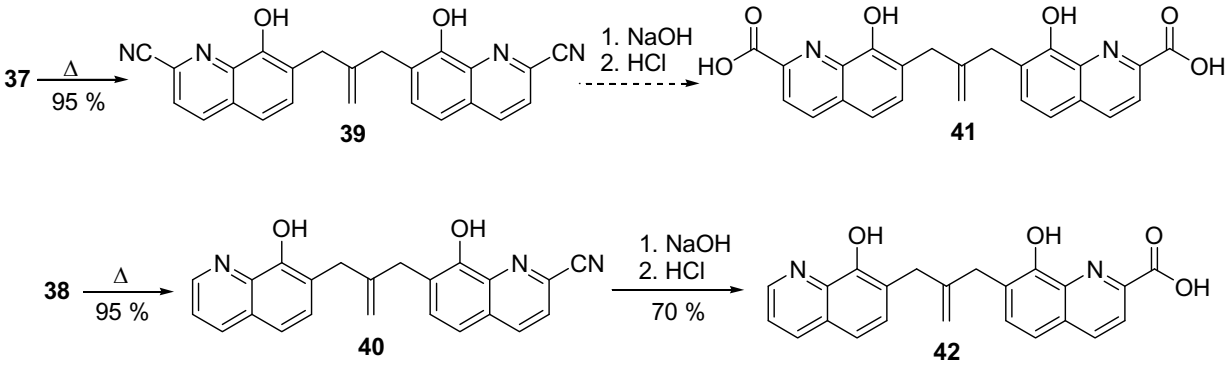
Having 8-hydroxyquinolines in hand and having comprehensively experienced the vast potential and advantageous applicability of the Hiratani method as an ideal option to extend the helicate motif over a longer sequence of binding sites, the scope of new receptors was anticipated.

The exceptional feature of the tandem-double-Claisen synthetic transformation is the possibility to successively bridge unsymmetrical quinolinol moieties by simultaneous establishment of isobutenylidene spacer in 7-positions of both compartments. The engagement of such segmental ligand systems in a self-assembly event should provide well-defined molecular architectures for pursuing certain metal-metal separations in order to enable their intramolecular communication.

A four step procedure conceived for the providing of preparative amounts of 8-hydroxyquinoline-2-carboxylic acid **30a** was interrupted on the third stage offering entry to the 2-nitrilo- **33** and 2-carboxamido-8-hydroxyquinolines **32**. Next, the compound **33** was involved in a Williamson ether synthesis with an excess of 3-chloro-2-chloromethyl-propene **13** in the presence of K_2CO_3 to furnish a mixture of mono- **36** and diether **37** in 38 and 32 % yield, respectively (Scheme 13). The separated mono-ether **36** is envisaged to be an anchor in the construction of a number of reaction sequences. In the present case it was first coupled with 8-hydroxyquinoline **31a** to deliver the unsymmetrical compound **38** which was then thermally rearranged to afford the ligand **40** containing linked bi- and tridentate domains. The symmetric bis-ether **37** also underwent the double-Claisen transformation with almost quantitative conversion furnishing bis-nitrilo compound **39.** Both bis(8-hydroxyquinoline) derivatives **39** and **40** were treated with aqueous NaOH leading in the case of mono-nitrile **40** to the desired acid **42** as hydrolysis product; unfortunately, the expected bis-acid **41** was not isolated in pure form probably due to its extremely low solubility (Scheme 14).



Scheme 13. Preparation of the ether derivatives **36-38** based on the 2-nitriloquinolinol.



Scheme 14. Preparation of the isobutenylidene-bridged symmetric **41**-H_4 and unsymmetric **42**-H_3 carboxylic acids.

3.5.2. A Dinuclear Double-Stranded Zinc Complex

The first synthetic attempt to obtain dimetallic Zn/La triple stranded helicate-type complex by reaction of the monoacid **42**-H_3 with $Zn(OAc)_2$ and $LaCl_3$ in the presence of Rb_2CO_3 as base and potential template failed. The ^{1}H NMR spectum of the yellow solid material was not informative, exhibiting only an intricate mixture of undefined species. This product was used in the crystallization experiment which surprisingly yielded single yellow-orange crystals of X-ray quality. The molecular structure represents the dianion $[(\mathbf{42})_2Zn_2]^{2-}$ and is depicted in Figure 37 (left). Two ligands **42** are wrapped around two zinc(II) ions in an anti-parallel fashion (Figure 37, right) providing the bidentate as well as a tridentate coordination of each metal center by a quinolinate and a quinolinate-2-carboxylate units.[142]

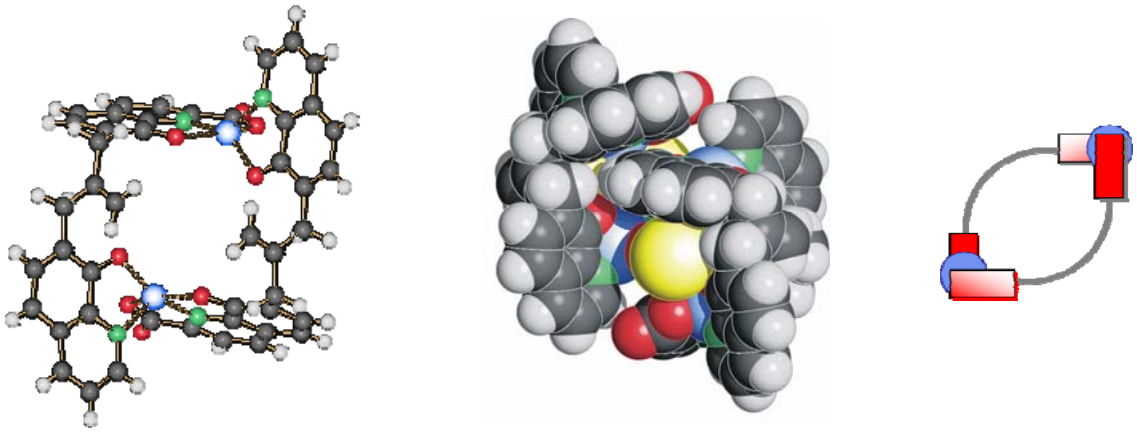


Figure 37. View of the molecular structure of the dianion $[(\mathbf{42})_2Zn_2]^{2-}$ (left), intertwined packing of the dimer (center), and schematic representation of the head-to-tail parallel arrangement of ligands (right); (Zn: blue, Rb: yellow).

[142] C. Piguet, G. Hopfgartner, A. F. Williams, J.-C. G. Bünzli, *J. Chem. Soc., Chem. Commun.* **1995**, 491.

The terminal carboxylate groups are firmly bound to the metal centers precluding the penetration of any solvent molecules, e.g., H_2O, into the first coordination sphere. Thus, the zinc(II) ions adopt a distorted trigonal-bipyramidal geometry. Due to a helical arrangement of the dinuclear $Rb_2[(\mathbf{42})_2Zn_2]$ complex it forms a dimeric structure in the solid phase as is shown in Figure 37 (center). Two rubidium cations, which were thought to perform as templates for helication, are now bound in the interior organized by the bent ligands. They neutralize a negative charge induced by triply deprotonated ligands and stabilize the overall molecular structure.

On the basis of these crystallographic results it can be concluded, that the 6-fold negative charge at the lanthanide(III) center, arising from three phenolate anions in addition to three carboxylates, is unfavorable. Probably the strong repulsion effect forces the crystallization of the more thermodynamically correct species from the complex mixture in solution. Thus, the observed pentacoordination environment at the zinc ions is more likely.

The described incident can also be assigned to the uncontrollable speciation in solution when instead of the desired major component of a "dynamic combinatorial library" the crystallization of a minor, but less soluble, candidate occurs, although very often it is not in agreement with thermodynamic parameters responsible for the equilibrium in solution.[143]

Hereby, it was of interest to reproduce the outcome of this experiment but in a planned way. The reaction of the ligand **42**-H_3 with $Zn(OAc)_2$ in stoichiometric amounts in the presence of Rb_2CO_3 or K_2CO_3 yielded the orange product which in the ^1H NMR spectrum showed only one set of ligand signals ascribed to the quantitatively coordinated ligand **42.**

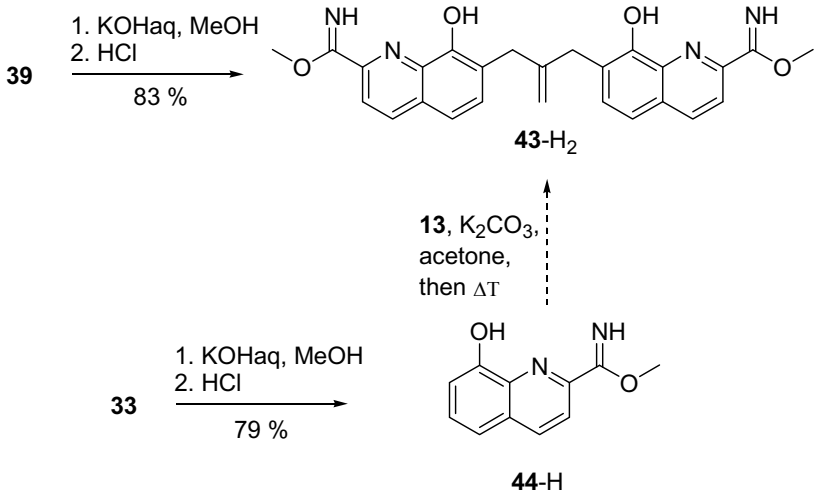
The solid state investigations in the latter example, in association with former solution observations of the europium complex of the ligand **30b**-H_2, prompt to postulate that carboxylic acids derived from 8-hydroxyquinolines are not predisposed to perform as programmed ligands for organization of lanthanide(III) ions in well-defined molecular architectures.

If this hypothesis is correct then the replacement of negatively charged carboxylates possessing a strongly pronounced binding ability by a neutral donor functionality should revolutionize the coordination situation due to the essential perturbations in affinity to the lanthanide(III) ions.

[143] J.-M. Lehn, *Chem. Eur. J.* **1999**, *5*, 2455.

3.5.3. Synthesis of bis-Imidate Ligand and its Ytterbium Complex

As a continuation of the synthetic transformations implementing the nitrile function of the bis(8-hydroxyquinoline) derivative **39**, the procedure discovered by *Nef* in 1895 in his work with cyanogen[144] and then further developed towards the diversity of the alkyl and aryl nitrilo derivatives, was envisaged to be appropriate for the preparation of quinoline imidates. Although the formation of the hydrochloride salt of alkyl imidates was reported by *Pinner* already in 1892, they were not isolated as individual compounds.[145] The addition of lower alcohols to nitriles is alkoxide-catalyzed and usually proceeds in high yields. The treatment of the derivative **39** with aqueous KOH in methanol afforded bis-imidate **43**-H_2 which alternatively might be accessed via Hiratani method employing mono-imidate **44**-H (Scheme 15).



Scheme 15. Synthesis of the bis-imidate ligand **43**-H_2.

The compound **43**-H_2 possesses extremely low solubility. The latter can be caused by additional hydrogen bonding between the C=NH unit and pyridine donor nitrogen leading to the exceptional stabilization of the structure. But in the presence of base, e.g. K_2CO_3, the hydrogen bridging is broken and deprotonated ligand can participate in complexation studies. Unfortunately, NMR spectra of diamagnetic complexes with this ligand did not clarify the solution situation, therefore the crystallization experiments were performed to obtain the information about the binding mode of the ligand in solid state. The ytterbium complex was prepared by reaction of the bis-imidate, $Yb(OTf)_3$, and K_2CO_3 in methanol.

[144] J. U. Nef, *Ann*. **1895**, *287*, 265.
[145] (a) A. Pinner, *Die Imidoäther und ihre Derivate*; Oppenheim: Berlin, **1892**. (b) F. C. Schaefer, In *The Chemistry of Cyano Group*; Z. Rappoport, Ed.; Interscience: London, **1970**; Chapter 6.

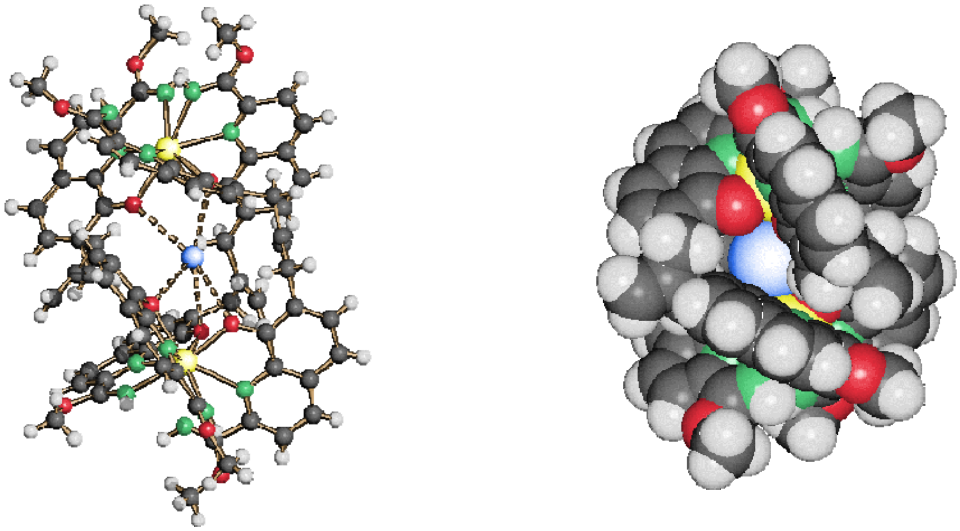


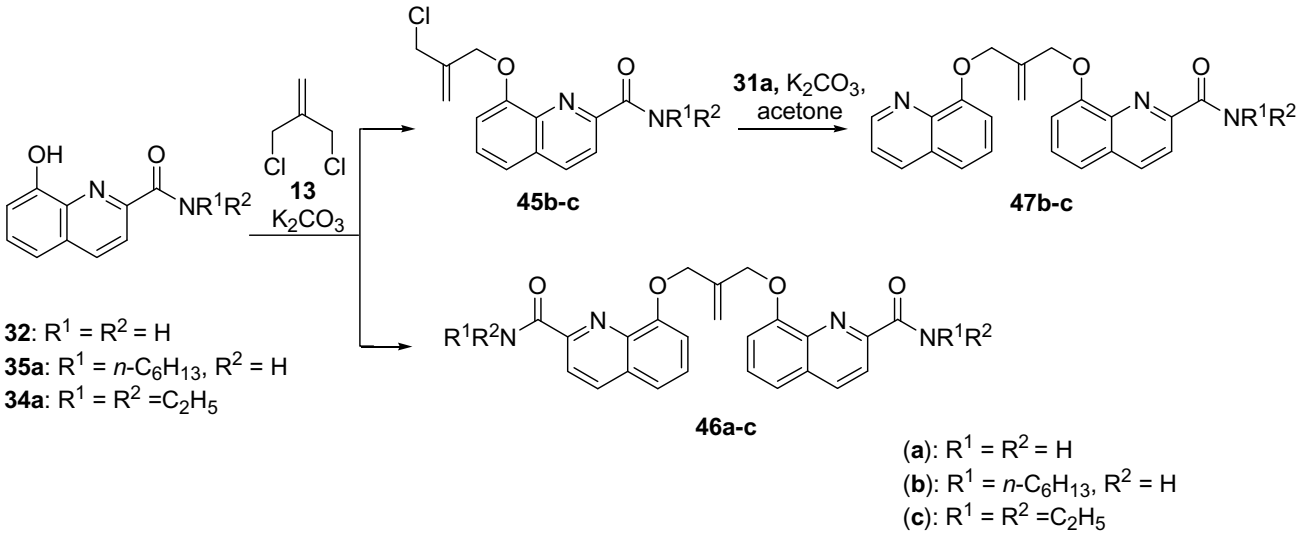
Figure 38. Representation of the $[K(\mathbf{43})_3Yb_2]^+$ complex cation; (Yb: yellow, K: blue).

The product was characterized by ESI MS and elemental analysis evidencing the formation of the compound with a 3 : 2 ligand to metal stoichiometry. X-ray quality crystals of $[K(\mathbf{43})_3Yb_2]OTf$ complex were obtained by vapour diffusion of Et_2O in MeOH / THF solution. A preliminary molecular structure analysis reveals the complex cation formed by three ligand strands wrapped around the C_3 axis which passes through the two ytterbium centers (Figure 38). An unusual π-type coordination of the templating potassium to the vinylic unit of the isobutenylidene spacer of one ligand strand should be pointed out as a rare structural feature observed for this kind of helicates. The binding of imidate function to the ytterbium(III) ion in its protonated form provides a high energy vibration oscillator which weakly interacts with lanthanide(III) excited states depopulating them via radiationless deactivation. In this particular case, the employment of basic reaction conditions is not helpful for the preparation of spectroscopically useful systems. The NH group can be functionalized with the aid of, for example, methylating agents like CH_2N_2. But as an alternative it can be employed in further transformations leading to a variety of the nitrogen - containing heterocycles (*vide infra*).

3.5.4. Synthesis of Ditopic Amidoquinolinate Ligands

The idea of the implementation of alternative carboxamide groups in the periphery of a ditopic receptor can be traced back to the paragraph 3.4.3.3. Based on the encouraging results demonstrated by all three model ligands **34a-c**-H and relying on the reliability of the *Hiratani* protocol, new fields of synthetic and supramolecular research are envisaged.

The synthetic route followed to prepare ligand systems possessing tridentate amide binding sites is adopted from the Paragraph 3.5.1.



Scheme 16. Preparation of the ether derivatives **45b,c, 46a-c,** and **47b,c.**

The three different kinds of amides **35a**-H, **34a**-H, **32**-H derived from primary or secondary amines or possessing an "unsubstituted" NH_2 unit, respectively, were examined. The Williamson ether coupling of **35a**-H, **34a**-H, and **32**-H with 3-chloro-2-chloromethyl-propene **13** results in the formation of mono-ethers **45b-c** as well as diethers **46a-c** by correlating a ratio between reactants (Scheme 16). The reaction of the "unsubstituted" amide **32** with **13** in equimolar amounts furnished the diether **46a** as the only product in 17 % yield. It is assumed, that the mono-ether **45a** was formed, but it could not be isolated after work up. Instead, the products of hydrolysis of the CH_2-Cl bond **48** and **49** were identified by NMR and ESI MS after column chromatography (Figure 39).

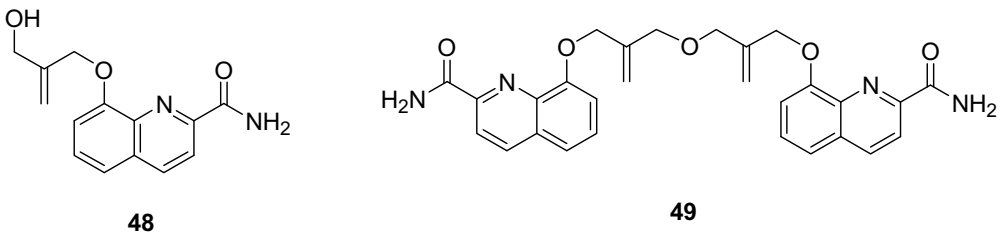
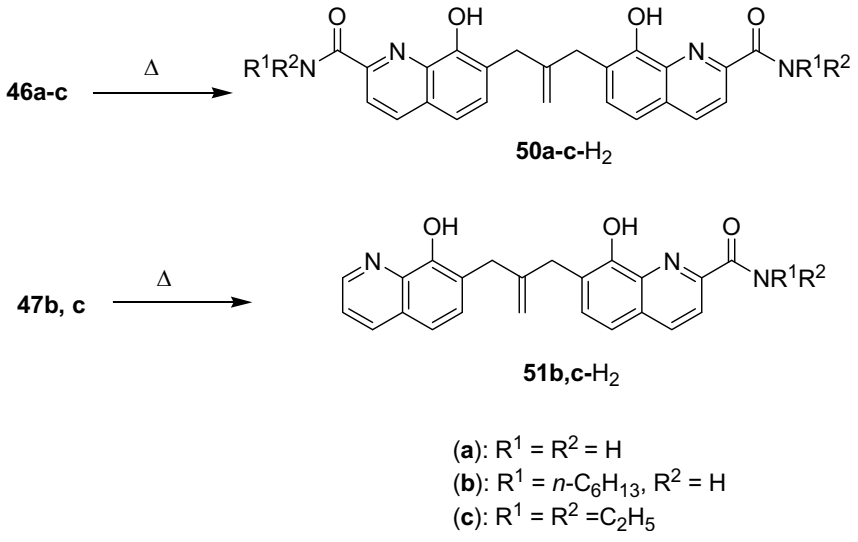


Figure 39. The product of hydrolysis of the mono-ether **45a**.

The same 1 : 1 stoichiometry was applied to the reactants in the case of amides **35a** and **34a** resulting in a mixture of **45b (**28 %) and **46b** (59 %) or **45c** (46 %) and **46c** (41 %), respectively**.** Attempts to optimize the reaction outcome to the formation of a single product

by varying the stoichiometry failed. But in terms of the reaction optimization, the separation procedure was improved to allow the isolation of the individual components of a mixture as precursors for further transformations in order to obtain useful building blocks for supramolecular purposes. The mono-ethers **45b,c** afforded in a successive coupling step with the parent 8-hydroxyquinoline **31a** the unsymmetric diethers **47b** and **47c** in 77 % or 82 % yield, respectively (Scheme 17).

Finally, all homo- (**46a-c**) and hetero-substituted diether compounds (**47b,c**) were converted into isobutenylidene-bridged dihydroxyquinoline derivatives **50a-c** and **51b,c**, respectively. The thermal rearrangement proceeded smoothly within 5-7 h at 170-175 ºC under N_2. The yields of this highly specific step are close to quantitative (88-100%) (Scheme 17). Often the compounds can be involved in the next reaction steps (e.g., complexation) without further purification. Where necessary, the derivatives are obtained in analytically pure form by crystallization or column chromatography.



Scheme 17. Preparation of symmetric (**50a-c**-H_2) and unsymmetric (**51b,c**-H_2) 8-hydroxyquinoline derivatives *via Hiratani*-double-Claisen rearrangement.

X-ray crystallographic structure determination for the ligand **50c**-H_2 suggests a twisted conformation induced by the isobutenylidene unit which connects the two 8-hydroxyquinoline moieties.[146] The intramolecular O-H···N hydrogen bonding motif is typical for 8-hydroxyquinoline systems, but in the present case it additionally bridges an amide oxygen of a neighbouring molecule twisting it out of the plane of the quinoline (Figure 40). This interesting precedent can be explained by the bulkiness of the diethylamide moieties, which

[146] H. Houjou, S. Tsuzuki, Y. Nagawa, K. Hiratani, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 831.

prevents the dimerization of the 8-hydroxyquinoline common for the related unsubstituted derivatives. Moreover, the bridging hydrogen is forced to be off plane of the usually planar 5-membered ring.[147] The comparative 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.

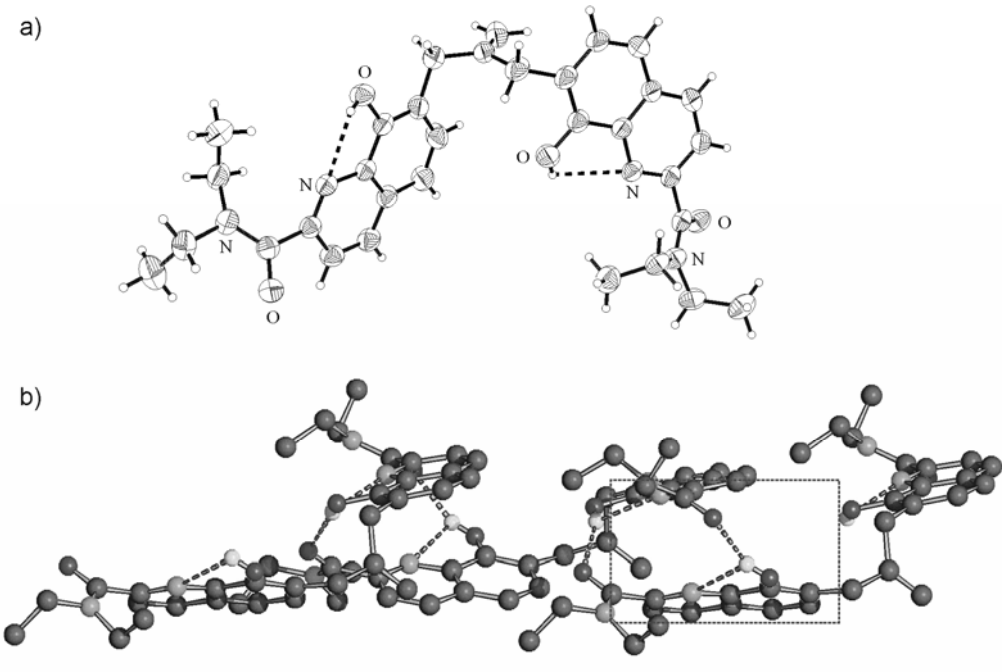
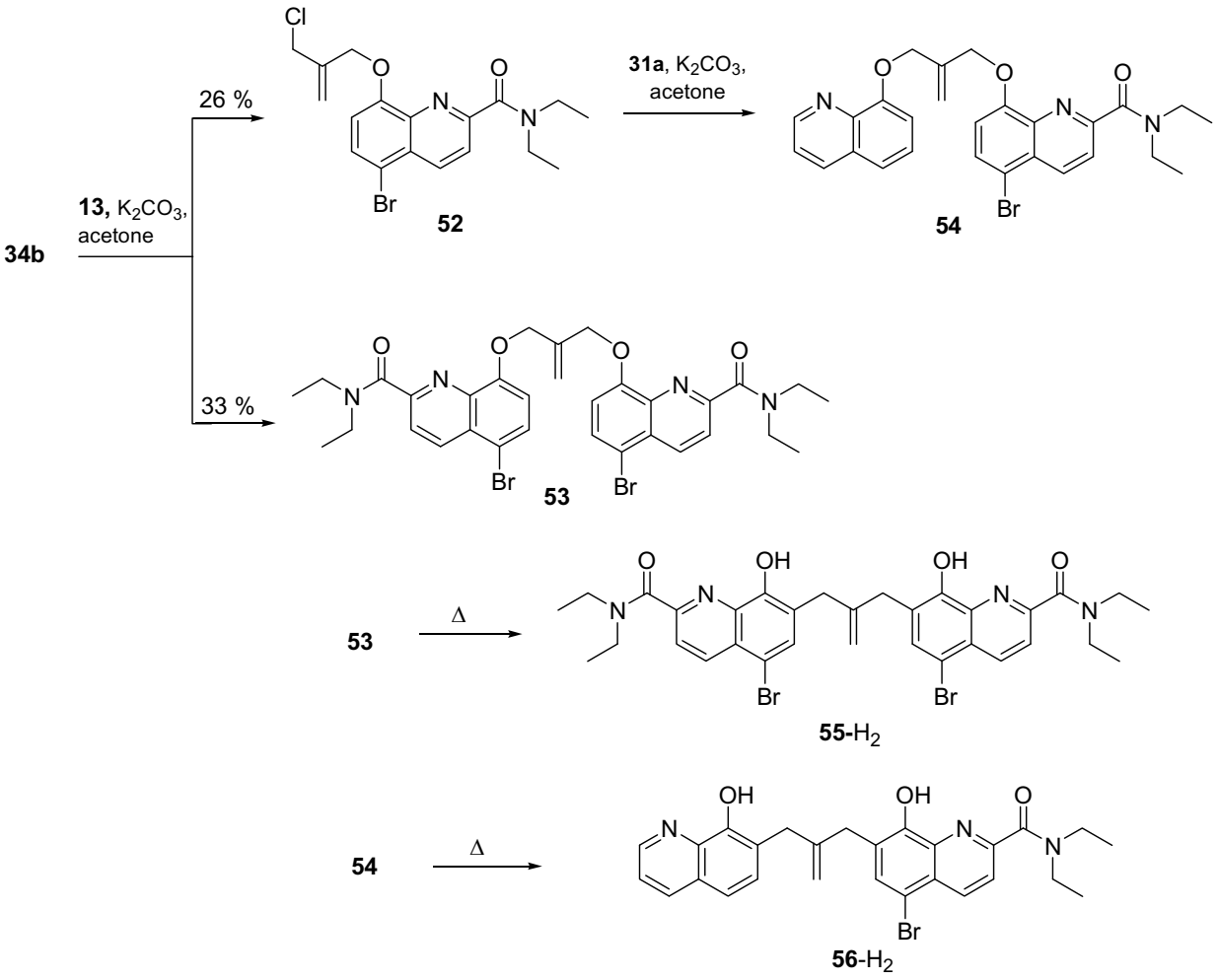


Figure 40. (a) The molecular structure of **50c**-H_2 in the solid state. (b) The polymeric hydrogen bonded structure is shown for three molecules of **50c**-H_2, representing the hydrogen bridged pattern for two adjacent 2-amido-8-hydroxyquinoline units of different molecules; H-atoms except OH are omitted for clarity.

The same reaction sequence (Scheme 16 and 17) was applied to incorporate bromosubstituted tridentate quinolinates into the ligand system. Stemming from the 5-bromo-amidoquinolinate **34b** the corresponding mono- **52** and bis-ether **53** derivatives were obtained, and next, **52** was further coupled with an oxine unit **31a** yielding the hetero compound **54** (Scheme 18). But both homo- **53** and hetero- **54** ethers showed to be much more sensitive to the thermal rearrangement conditions. Only minor rise of temperature in the reaction system followed by neat heating at 130-140 °C under N_2 atmosphere allowed the suppression of product decomposition or formation of a number of undesirable by-products. The conversion provided the target homo- **55**-H_2 and hetero- **56**-H_2 ditopic ligands available for the complexation

[147] P. Roychowdhury, P. N. Das, B. S. Basak, *Acta Crystallogr. Sect. B* **1978**, *34*, 1047.

experiments after utter purification. The overall reaction yields are of satisfactory values of 24 and 14 % for **55**-H_2 and **56**-H_2, respectively.



Scheme 18. Synthesis of the bromosubstituted ditopic amidoquinolinate ligands **55**-H_2 and **56**-H_2.

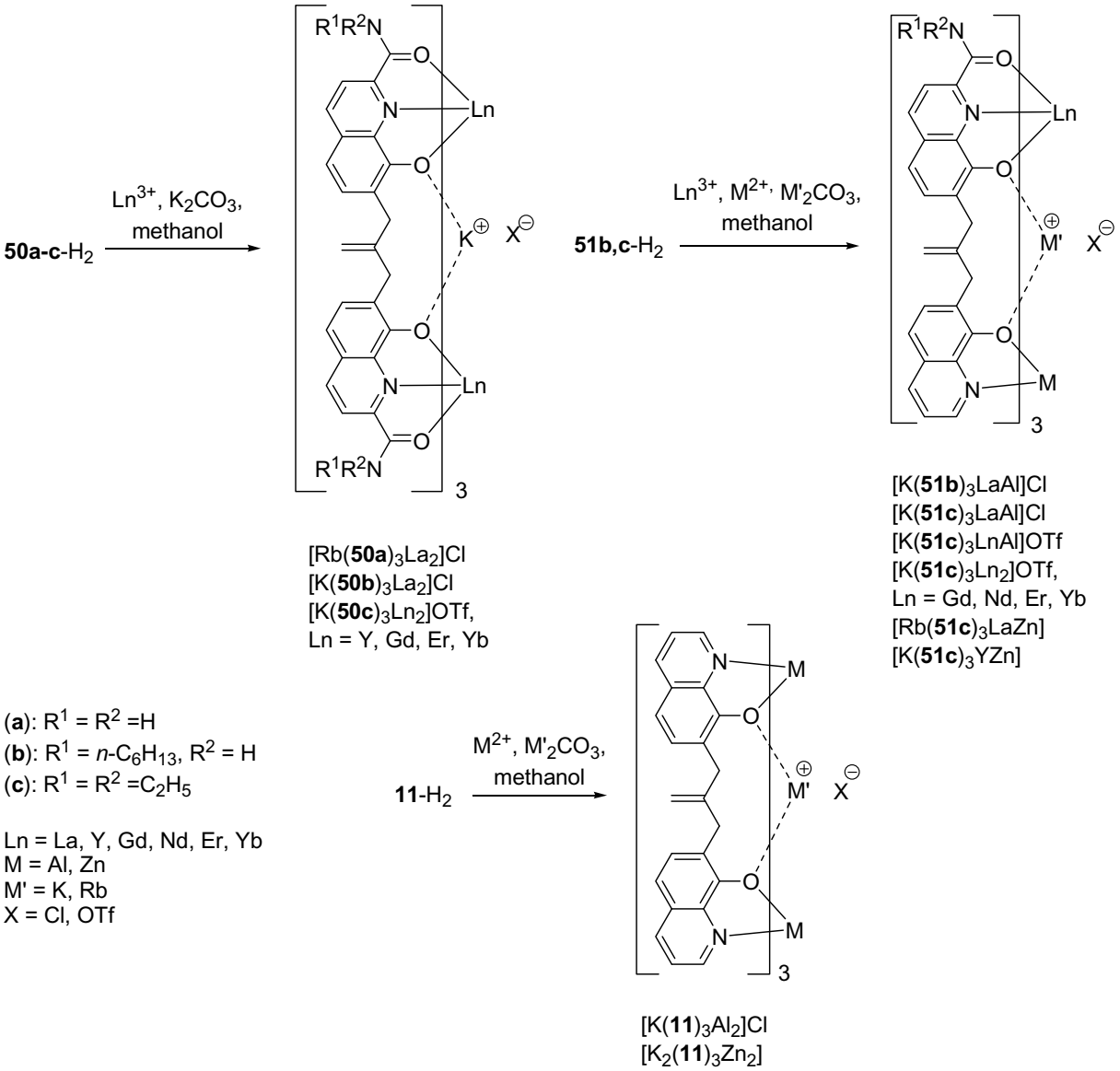
In conclusion, *Hiratani*-double-Claisen rearrangement offers an attractive way to establish a spacer between two hydroxyquinoline moieties with three carbon atoms in the chain. To get a variation of the distance between the two binding sites, it is of interest to introduce bridges of different length and rigidity (*vide infra*).

3.5.5. Coordination Studies on the Homo- and Hetero-Ditopic Amidoquinolinate Ligands towards Lanthanides(III)

The formation of dimetallic triple-stranded complexes with ditopic carboxamide group containing ligands **50a-c**-H_2 and **51b,c**-H_2 was observed by means of ESI MS, elemental analysis, and NMR spectroscopy for diamagnetic compounds.

3.5.5.1. Synthesis of the dimetallic lanthanide(III) complexes

The homodimetallic complexes [Rb(**50a**)$_3$La$_2$]Cl, [K(**50b**)$_3$La$_2$]Cl and [K(**50c**)$_3$Ln$_2$]OTf (Ln = Y, Gd, Yb, Er) were prepared by reaction of the ligands **50a-c**-H_2 and $LaCl_3 \cdot 6\ H_2O$ or Ln(OTf)$_3$, respectively, in a 3 : 2 ligand to metal ratio in the presence of K_2CO_3 or Rb_2CO_3 as base (Scheme 19).



Scheme 19. Preparation of the dimetallic complexes of ligands **50a-c**-H_2, **51b,c**-H_2, and **11**-H_2.

Positive ESI MS spectra clearly evidence the presence of the cations [K(**50b**)$_3$La$_2$]$^+$, [K(**50c**)$_3$Y$_2$]$^+$, [KH(**50c**)$_3$Gd$_2$Cl]$^+$, [KH(**50c**)$_3$Yb$_2$Cl]$^+$, and [KH(**50c**)$_3$Er$_2$Cl]$^+$ at m/z = 2097, 1832, 2006, 2036, and 2026, respectively. The lanthanum(III) complex of ligand **50a**-H_2 appears as cation [H(**50a**)$_3$La$_2$]$^+$ at m/z = 1557.3 in positive ESI MS and as anion [(**50a**)$_3$La$_2$ -

$H]^-$ at m/z = 1555.6 in negative ESI MS. The heterodimetallic complexes [K(**51b,c**)$_3$LaAl]Cl, [K(**51c**)$_3$LnAl]OTf (Ln = Gd, Yb, Nd, Er), [Rb(**51c**)$_3$LaZn], and [K(**51c**)$_3$YZn] were prepared by the reaction of the ligands **51b,c**-H_2, $LaCl_3 \cdot 6\ H_2O$ or $Ln(OTf)_3$, and hydrated $AlCl_3$ or $Zn(OAc)_2 \cdot 2\ H_2O$ in a 3 : 1 : 1 ligand to f-metal to p-/d-metal ratio in the presence of K_2CO_3 or Rb_2CO_3 as base. Positive ESI MS spectra display single peaks at m/z = 1607 for $[K(\mathbf{51b})_3LaAl]^+$, 1523 for $[K(\mathbf{51c})_3LaAl]^+$, 1557 for $[K(\mathbf{51c})_3YbAl]^+$, 1541 for $[K(\mathbf{51c})_3GdAl]^+$, 1528 for $[K(\mathbf{51c})_3NdAl]^+$, 1541 for the $[K(\mathbf{51c})_3ErAl]^+$ cations. The neutral Zn/La and Zn/Y complexes appear as cationic species $\{Rb[Rb(\mathbf{51c})_3LaZn]\}^+$ and $\{H[K(\mathbf{51c})_3YZn]\}^+$ at m/z = 1692 and 1511, respectively.

In most cases the elemental analysis confirmed the analytical purity of the obtained compounds.[148]

3.5.5.2. Solution studies

The well resolved ^1H NMR spectra indicate the high stability of the complexes in solution and allow the observation of the ligand proton shifts as well as diastereotopicity of the methylene protons. The high symmetry of the NMR spectra of complexes is in agreement with the presence of a single helicate species possessing C_3 axis in solution.

As can be seen from Figure 41 the most illustrative behaviour is demonstrated by the protons of methylene units in the benzylic positions and in the hexyl chain, which become diastereotopic upon complexation. In the [K(**50c**)$_3$La$_2$]Cl complex the signals of the spacer methylene protons ***b***, which in case of uncomplexed ligand appear as a singlet at δ = 3.66 ppm, are shifted and split into two doublets at δ =3.79 and 2.04 with a coupling constant J = 13.1 Hz. The triplet of the methylene units ***c*** of the NH-$\underline{CH_2}$-(C_5H_{11}) substituent (δ = 3.47 for the free ligand) generates two broad signals at δ = 2.91 and 2.67 ppm in the spectrum of the complex. The resonances of the vinylic group ***a*** are only slightly affected: δ = 4.45 ppm in case of the complex *versus* δ = 4.57 ppm for the ligand. The significant upfield shift of the aromatic protons up to Δδ = 0.7 ppm is ascribed to the wrap of the ligand strands around metal centers upon complexation. This arranges the quinolinate cores in such a way that the protons of each of them are influenced by π-systems of the neighbouring units causing an anisotropic shift.

[148] [Rb(**50a**)$_3$La$_2$]Cl and [K(**51c**)$_3$YZn] are characterized only by means of ESI MS.

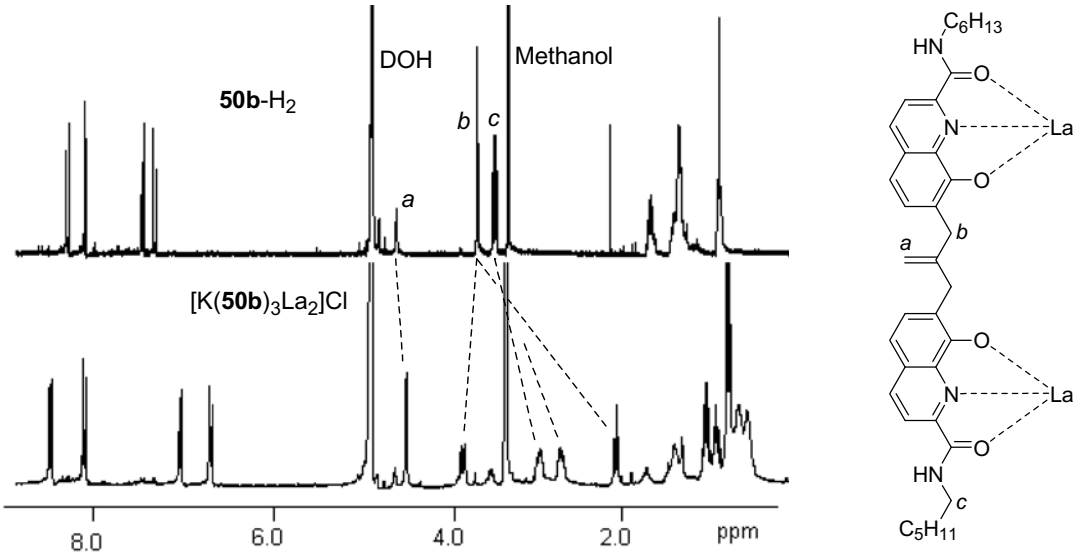


Figure 41. ^{1}H NMR spectra of the ligand **50b**-H_2 and [K(**50b**)$_3$La$_2$]Cl in methanol-d_4.

Compound [K(**50c**)$_3$Y$_2$]OTf could not be isolated in analytically pure form, but the major set of signals in the NMR spectrum corresponds to the desired complex, being the main component present in solution. Additional low-intensity signals are assigned to the minor unidentified species detected in insignificant amounts.

The ^{1}H NMR spectrum of [K(**51b**)$_3$LaAl]Cl is recorded in the strongly coordinating DMSO-d_6 solvent, but nevertheless it is well-structured pointing towards the high stability of the complex and its resistance against dissociation processes that often occur in solution (Figure 42). A single set of aromatic protons indicates the high symmetry (C_3 axis) of the complex originating from the helical wrap at the ligands as a consequence of their organization about two different metals. Based on the observations in spectrum of the [K(**50b**)$_3$La$_2$]Cl complex, the high field shifts of protons of the both quinolinate and amidoquinolinate units in heterodimetallic system can be attributed to the same specific structural features of the ligand environment at the lanthanum and aluminium centers.

The signals of the spacer protons are broadened. This could be explained by interactions of the solvent molecules with templated K^+, which becomes partially solvated and thus labile affecting the protons of the vinylic unit, which is usually involved in coordination to the incorporated cation in the solid state. Therefore the vinylic protons ***a*** are observed as broad singlets at δ = 4.30 and 2.73 ppm in the spectrum of complex, whereas in the ligand spectrum they appear as sharp resonances at δ = 4.74 and 4.73 ppm.

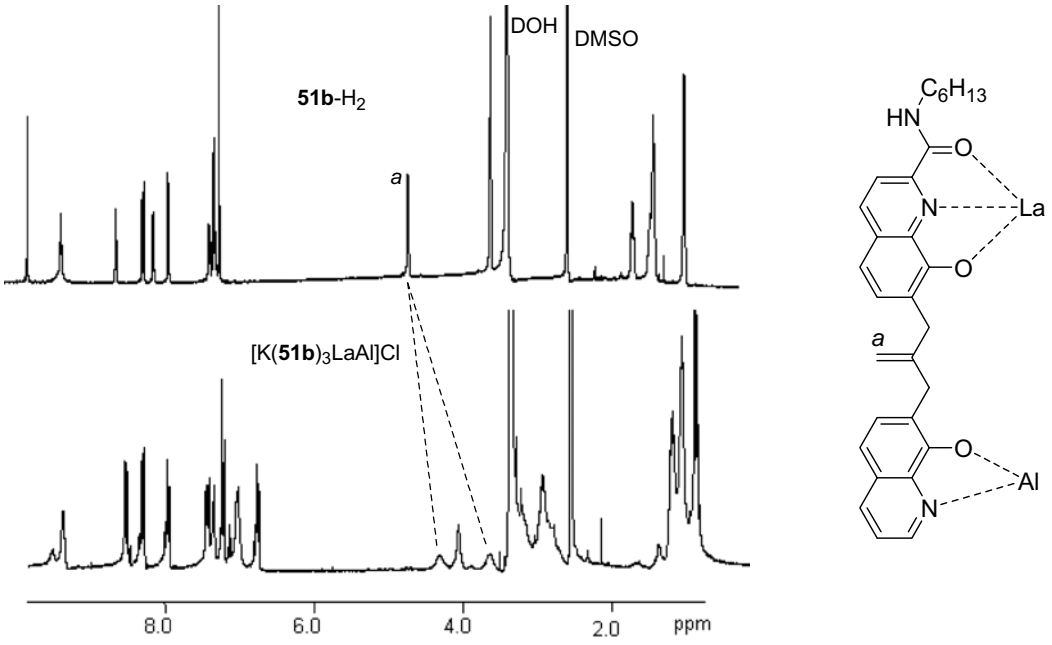


Figure 42. ^{1}H NMR spectra of the ligand **51b**-H_2 and [K(**51b**)$_3$LaAl]Cl in DMSO-d_6.

Before discussing further the NMR behaviour of the unsubstituted 8-hydroxyquinoline upon its binding to the metals, it is useful to analyze the spectra of the prototype ligand **11**-H_2 and its zinc complex as a model.

The range of aluminium complexes based on the bis(8-hydroxyquinoline) was thoroughly studied by *Blau* using NMR spectroscopy and X-ray crystallographic analysis.[111] Zinc complex differs from its aluminium analogues in its anionic nature requiring the presence of additional cations. The alkali metals introduced in the reaction mixture with the carbonate bases (K_2CO_3, Rb_2CO_3 etc.) can readily perform as templates and simultaneously neutralize a charge at the complex. Therefore, it is expected that the proton shifts and the signals splits in NMR spectra will reflect the changes in the electronic structure, not only that of the binding aromatic units, but also of the spacer (Figure 43). For instance, vinylic protons ***a*** of the K_2[(**11**)$_3Zn_2$] complex are shifted upfield by $\Delta\delta$ = 0.34 ppm. The protons of methylene units ***b*** become diastereotopic upon complexation producing two broad signals at δ = 3.46 and 3.12 ppm *versus* a sharp singlet at δ = 3.56 ppm which is observed in the ligand spectrum. The aromatic protons can be easily assigned due to the coupling constants (J) which retain their approximate values in the zinc compound as compared to those for the ligand. Thus, the protons of the pyridine moiety are the most affected: *ortho*-H^2 is anisotropically shifted in complex by $\Delta\delta$ = 1.4 ppm, *meta*-H^3 - by $\Delta\delta$ = 0.27 ppm, and *para*-H^4 - by only $\Delta\delta$ = 0.1 ppm.

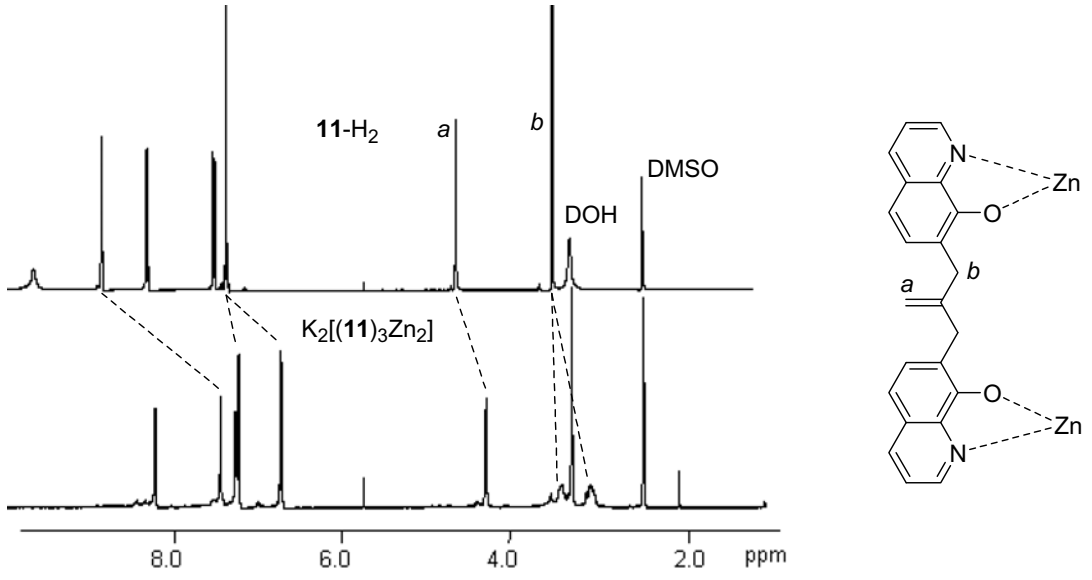


Figure 43. ^{1}H NMR spectra of the ligand **11**-H_2 and $K_2[(\mathbf{11})_3Zn_2]$ in DMSO-d_6.

A singlet with double intensity in the ligand spectrum (δ = 7.37 ppm), attributed to the overlapped phenolate protons H^5 and H^6, is split in the complex spectrum arising in two individual doublets at δ = 7.22 (J = 8.2 Hz) and 6.73 ppm (J = 8.2 Hz). These data could be helpful in the characterization of other complexes comprising a p- or d-metal complex fragment.

The ^{1}H MNR spectra of the La/Zn and La/Al helicates of the compound **51c**-H_2 are comparable and depicted in Figure 44 together with the ligand spectrum. The spectrum of the La/Zn complex proves the quantitative formation of a single species which retains its structure upon redissolving in organic solvents. The La/Al complex exhibits similar behaviour to Rb[(**51c**)$_3$LaZn] in solution, although some overlaps of the signals are observed. The aromatic patterns are well-resolved but too complicated to make reliable assignments and comparison of the shift values. For example, typical anisotropic shift of the *para*-phenolate H^5 protons in the zinc complex reaches Δδ = 0.6 ppm with respect to free ligand, whereas in aluminium complex it is less pronounced and shows Δδ = 0.35 ppm. The upfield shift of *ortho*-protons H^2 of the terminal unsubstituted pyridine moiety is more representative (Δδ = 1.14 ppm for zinc complex) and is ascribed to its spatial position in the close vicinity to two other coordinated ligand aromatics. At the same time, the shift of *para*-protons H^4 of the pyridine side is found to be only Δδ = ~ 0.1 ppm upfield if compared with the ligand. It would seem, that in the complex structure these protons are held away from the influence of the neighbouring π-systems. These assignments are amenable to comparison of the aromatic signals in the spectra of ligand and of complexes due to the coupling constants which remain

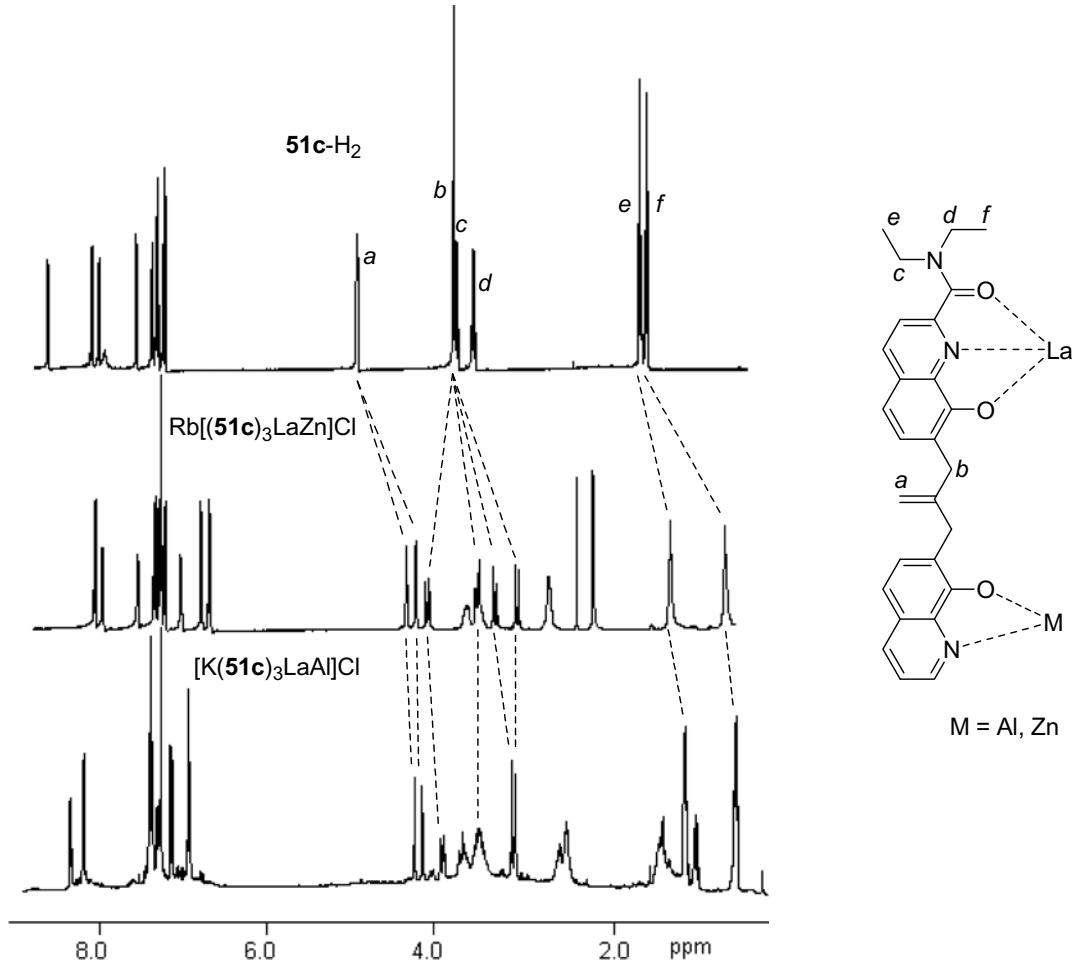


Figure 44. ^{1}H NMR spectra of the ligand **51c**-H_2 and complexes Rb[(**51c**)$_3$LaZn], [K(**51c**)$_3$LaAl]Cl in $CDCl_3$.

similar upon complexation. Unfortunately, for the [K(**51c**)$_3$LaAl]Cl complex this is not the case because the resonances are localized in the very narrow region complicating the resolution.

Remarkable differences are observed for the positioning of the signals of the spacer protons and of protons of ethyl groups of the carboxamide substituents. The resonances of the vinylic unit ***a*** in the ligand spectrum are situated at δ = 4.75 and 4.76 ppm. This minute discrepancy is due to the inequivalence of quinolinate compartments along the ligand. But in the complex the electronic structure of the coordinated units is strongly disturbed, affecting the obvious perturbations in the aliphatic region of the spectrum. Thus, the vinylic protons ***a*** are observed at δ = 4.26 and 4.14 ppm for the Rb[(**51c**)$_3$LaZn] compound and at δ = 4.22 and 4.13 ppm for the [K(**51c**)$_3$LaAl]Cl complex.

The methylene protons of the spacer ***b*** also experience crucial changes in the ligand environment. Due to their diastereotopic nature, the singlet at δ = 3.55 ppm, detected in the

spectrum of free ligand, splits in the heterodimetallic complex into four individual signals: at δ = 4.00 (J = 15.9 Hz), 3.39 (J = 16.5 ppm), 3.17 (J = 16.5 Hz), and 2.90 (J = 15.9 Hz) for the La/Zn complex; at δ = 3.89 (J = 16.8 Hz), 3.73-3.56 (hidden under a multiplet), 3.07 (two overlapping patterns with J = 15.9 Hz) for La/Al complex. The CH_2 units of the ethyl substituents ***c*** and ***d***, observed at δ = 3.48 and 3.25 ppm in the ligand spectrum, also become diastereotopic upon metal coordination and generate four signals in the complex spectra: at δ = 3.51, 3.37, and 2.51 ppm (double intensity) for the La/Zn complex; at δ = 3.73-3.56 and 2.50-2.35 ppm (both signals with double intensities) for the La/Al compound. The methyl protons of complexes ***e*** and ***f*** are shifted upfield compared to the uncoordinated ligand.
The NMR studies of the diamagnetic La/La, Y/Y, La/Zn, and La/Al complexes provide more understanding of the solution behaviour of homo- and hetero-dimetallic compounds. The informative shifts of the aromatic protons in parallel with observation of diastereotopicity of the methylene groups allow to suggest the helicate-type complex structure. But only X-ray diffraction analysis could ratify either the helical or meso-form adopted by the complex.

In order to dissect thermodynamic contributions of self-assembly for dimetallic complexes the spectrophotometric titrations for the ditopic hydroxyquinoline ligand **50c**-H_2 with ytterbium and europium triflates were performed by J. Hamacek in Geneva. The interaction between metal salts and the deprotonated ligand $(\mathbf{50c})^{2-}$ has been quantified in acetonitrile in the absence of templating potassium ions. The obtained cumulative stability constants are listed in Table 4 and show the similar binding affinities of both Yb(III) and Eu(III). The species distribution for the different Yb / ligand ratios is depicted in Figure 45. $[Ln_2(\mathbf{50c})_3]$ proved to be the most stable species in solution. Thus the absence of the templating cation is not detrimental to its formation.

Table 4. Cumulative stability constants (log $ß_{mn}(\sigma)$) for the complexes $[Ln_m(\mathbf{50c})_n]^{3m-2n}$ (acetonitrile, 298 K, M = Eu, Yb).

Species	Eu	Yb
$[Ln(\mathbf{50c})_2]^-$	13.9(2)	13.3(2)
$[Ln(\mathbf{50c})_3]^{3-}$	18.5(3)	18.1(3)
$[Ln_2(\mathbf{50c})_3]$	**26.1(3)**	**25.7(3)**
$[Ln_2(\mathbf{50c})_2]^{2+}$	19.3(2)	19.0(2)

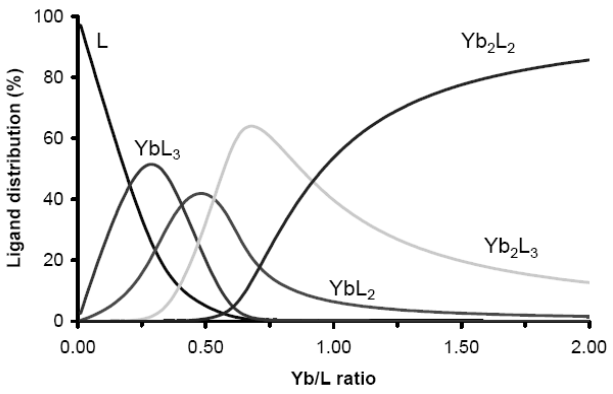


Figure 45. Species distribution in the system homodinuclear ligand **50c** / Yb(III)

3.5.5.3. Solid state determination of a dinuclear ytterbium(III) complex

Single crystals of $[K(\mathbf{50c})_3Yb_2]OTf$ were obtained by vapour diffusion of Et_2O into methanol / THF / chloroform solution. The structure of the cation is depicted in Figure 46 and reveals the helical twist of the ligand strands about the Yb···K···Yb axis (162.6°). The Yb(III) ions are separated by 7.77 Å while the templating potassium ion exhibits distances of 3.91 and 3.95 Å to the metal centers. Each Yb ion is coordinated by three tridentate *syn*-arranged 2-amidoquinolinates. Potassium is incorporated in an unusual manner in the cavity of the complex. It coordinates to three internal oxygen atoms with relatively short contacts of 2.7-2.8 Å. Two longer K···O bonds (3.45 and 3.59 Å) are also detected. However, one "open" front of the cation is directed towards the vinylic unit of one spacer showing the K-C distances of 3.21 and 3.46 Å. Apparently, encapsulation of K^+ in the cavity enforces η^2-binding of the C=C double bond towards the potassium ion.

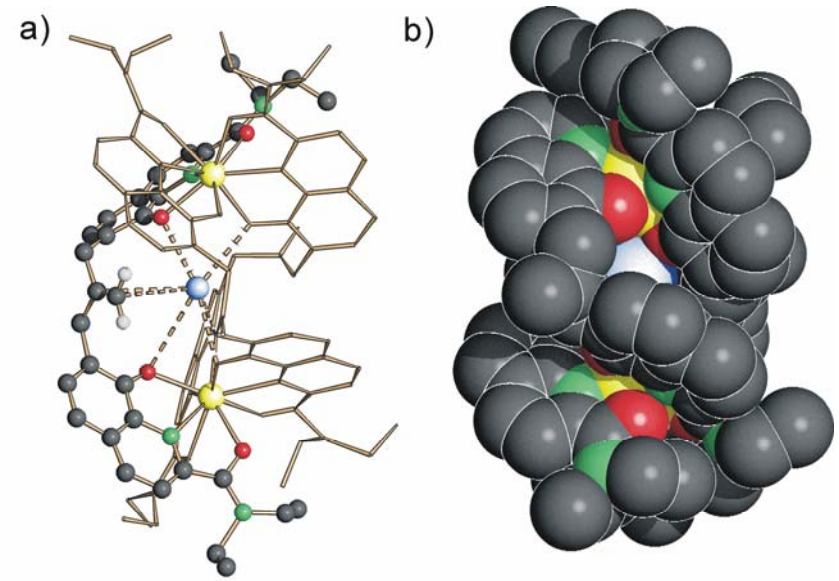


Figure 46. Molecular structure of the cation of $[K(\mathbf{40c})_3Yb_2]OTf$. H-atoms (except the two vinylic H in (a)) as well as triflate and water are omitted for clarity. Yb: yellow, K: blue, N: green; O: red, C: black. (a) The ligand exhibiting an unusual alkene-potassium coordination is shown as ball-and-stick model. (b) Space filling model showing the helical arrangement of the ligands around the Yb···K···Yb axis.

Nine coordination at Yb(III) is insured by the tridenticity of the ligand chelator, perfectly matching the f-element geometries as well as the steric demand of the spacers preventing the penetration of solvent molecules into the inner coordination sphere. Importantly, this Yb/Yb molecular structure represents the shortest metal-metal separation documented for lanthanide helicates to date. The typical distances realized by *Piguet* and *Bünzli* in the related binuclear systems are in the range of 8.8-9.0 Å.[45]

3.5.5.4. Solid-state luminescence studies of dinuclear lanthanide(III) helicates

The spectroscopic features of mononuclear NIR-emitting lanthanide(III) complexes with 2-amidoquinolinate ligands were already elucidated in Chapter 2.4.3.3. The helicate-type compounds described above allow the extension of the photophysical investigations in order to address the emissive properties of the related bimetallic edifies and to establish correlation between the solid state structure and exhibited luminescence. Many studies were dedicated to the preparation and properties of 3d-4f dimetallic systems, in which a transition metal is used to populate the Ln^{3+} exited states by the long-lived emitting levels of the d-donor. Such apparent extension of, for example, NIR luminescence lifetimes should notably improve the efficiency of time-resolved detection. As an alternative to the d-block elements, in this study Al was chosen to be incorporated into p/f dimetallic helicates. Although it doesn't perform itself as emitter, in assembly with quinoline units it furnishes the useful complex fragment **7** well known due to its prominent role in the construction of OLEDs (Figure 9). Therefore it is of interest to learn about energy transfer processes that take place in Al/Ln compounds from the intramolecular inter-quinolines directional communication point of view. The gadolinium(III) samples are studied in order to determine the energy of the triplet states of coordinated ligand since the resonance levels of the Gd^{3+} are located above the quinolinate excited states and consequently, no metal-centered emission can be observed for the Gd/Gd and Gd/Al complexes.[149] In general, the efficiency of the ET from the organic chromophore to the emitting levels of the Ln(III) is proportional to the overlap between the phosphorescence spectrum of the ligand and the absorption spectrum of the lanthanide. If the ET is inefficient, the emission spectrum of the complex will be comparable with the phosphorescence band recorded for the related Gd(III) compound.[150]

Ln/Ln, Ln/Al, and Al/Al (Ln = Gd, Yb) helicates were proposed as objects to get first insight into energy processes that occur upon irradiation of the complex with UV or visible light. NIR/Vis emission spectra of [K(**50c**)$_3$Yb$_2$]OTf, [K(**51c**)$_3$YbAl]OTf, and [K(**11c**)$_3$Al$_2$]Cl are depicted in Figure 47, while relevant parameters for K(**50c**)$_3$Yb$_2$]OTf and [K(**51c**)$_3$YbAl]OTf are listed in Table 5. The dinuclear Al/Al complex exhibits bright green luminescence with a maximum around 535 nm (Figure 47) and quantum yield around 1.25 %, similar to the aluminum trisquinolinate. It originates from electronic $\pi\pi^*$ transitions in the quinolinate ligand.

[149] S. Sato, M. Wada, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1955.
[150] M. Iwamur, Y. Wada, T. Kitamura, N. Nakashima, S. Yanagida, *Phys. Chem. Chem. Phys*. **2000**, *2*, 2291.

Surprisingly, this green emission is not observed in the spectrum of Yb/Al indicating energy transfer from the aluminum quinolinate to the amidoquinolinate moiety of the ligand. The visible luminescence spectra of Gd/Gd, Yb/Yb, Al/Gd, and Al/Yb complexes are very similar upon excitation at 350 nm and exhibit maxima at 610 nm at 77 K or 630 nm at 295 K, with lifetimes of the excited states much shorter than 10 μs. This luminescence is significantly different from the one observed for Al/Al: it is redshifted by nearly 100 nm, much weaker; and is temperature-dependent. The red-centered luminescence is thus attributed either to the fluorescence originating from $^{1}\pi\pi^{*}$ or phosphorescence arising from short-lived $^{3}\pi\pi^{*}$ quinoline excited states, or a mixture of both of those. This can be attributed to the "paramagnetic effect" relying on the presence of heavy paramagnetic Gd^{3+} or Yb^{3+} ions what enhances the ISC from ^{1}S to ^{3}T due to the mixing of the singlet and triplet states.[151] Therefore the red emission observed for Gd and Yb samples has the same nature as the green photoluminescence detected for Al quinolinate but it is much weaker to measure the quantum yields in the visible. However, these studies are focused on the NIR spectroscopy, particularly emissive properties of Yb(III) complexes, and the temperature dependence of the luminescence quantum yields and life times.

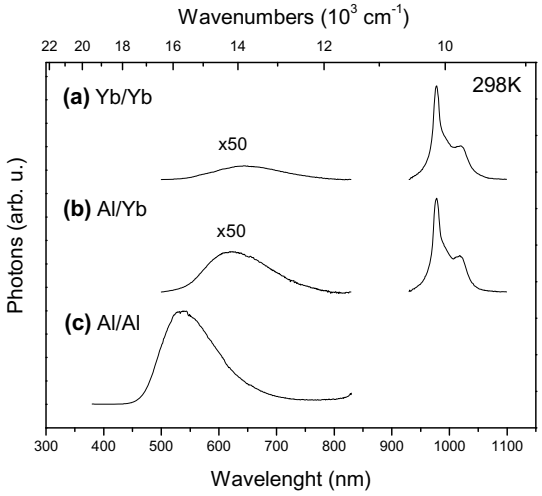


Figure 47. Normalized room temperature emission spectra upon excitation at 350 nm of powders of (a) Yb/Yb, (b) Yb/Al, and (c) Al/Al. The Vis emission spectra of (a) and (b) are multiplied by a factor of 50.

Table 5. Room temperature luminescence lifetimes of Yb^{3+} ($^{2}F_{5/2}$) monitored at 980 nm upon excitation at 355 nm and quantum yields measured in an integration sphere upon excitation at 392 nm of powders of K(**50c**)$_3$Yb$_2$]OTf and [K(**51c**)$_3$YbAl]OTf

	K(**50c**)$_3$Yb$_2$]OTf	[K(**51c**)$_3$YbAl]OTf
$\tau \pm 2\sigma$ (298 K)	18.8 ± 0.1 μs	22.6 ± 0.2 μs
$\tau \pm 2\sigma$ (10 K)	17.4 ± 0.1 μs	19.5 ± 0.1 μs
$\Phi \pm 2\sigma$ (295 K)	1.04 ± 0.07 %	1.17 ± 0.03 %

[151] S. Tobita, M. Arakawa, I. Tanaka, *J. Phys. Chem*. **1984**, *89*, 5649.

The Yb(III) complexes display efficient NIR emission upon UV excitation at 350 nm, arising from the Yb($^2F_{5/2} \rightarrow {}^2F_{7/2}$) transition. The integrated NIR/Vis photon ratios are 90 and 30 for K(**50c**)$_3$Yb$_2$]OTf and [K(**51c**)$_3$YbAl]OTf, respectively. Although the ligands in these complexes are different, the Yb^{3+} excitation and emission spectra are very similar at both 298 and 10 K indicating an alike structural environment for the Yb(III) centers in both helicates. The quantum yield of Yb/Al is about 12% higher with respect to Yb/Yb. The lifetime is consistent with the quantum yields of the heterodinuclear complex [K(**51c**)$_3$YbAl]OTf and shows to be higher by about 16% with respect to the homodinuclear helicate K(**50c**)$_3$Yb$_2$]OTf. The longer luminescence lifetime and larger quantum yield of the Yb/Al compound indicate more efficient energy transfer from the ligand to the emitter, as well as less competitive nonradiative deactivation processes occurring in the heterodinuclear complex with respect to those of Yb/Yb sample. The latter could be ascribed to the probable interactions between the two Yb^{3+} centers of the homodimetallic helicate provoking their susceptibility to each other and enabling the self-quenching processes (reminiscent of the concentration quenching effects).

Surprisingly, for both complexes the emission lifetimes are shorter at cryogenic temperatures than those measured at rt. Normally, at 77 K the deactivation of the triplet state by radiationless processes is minimized and the solvent quenching of ^3T can be neglected; no competition with the ligand fluorescence is expected. A possible explanation of these results could be a different energy transfer mechanism or cooperativity of several energy transfer pathways at 10 and 295 K.

In conclusion, the compounds K(**50c**)$_3$Yb$_2$]OTf and [K(**51c**)$_3$YbAl]OTf display efficient NIR emission, demonstrating the adequate choice of the sensitizing units.

3.6. Catechol / Quinoline Isobutenylidene-Bridged Ligands

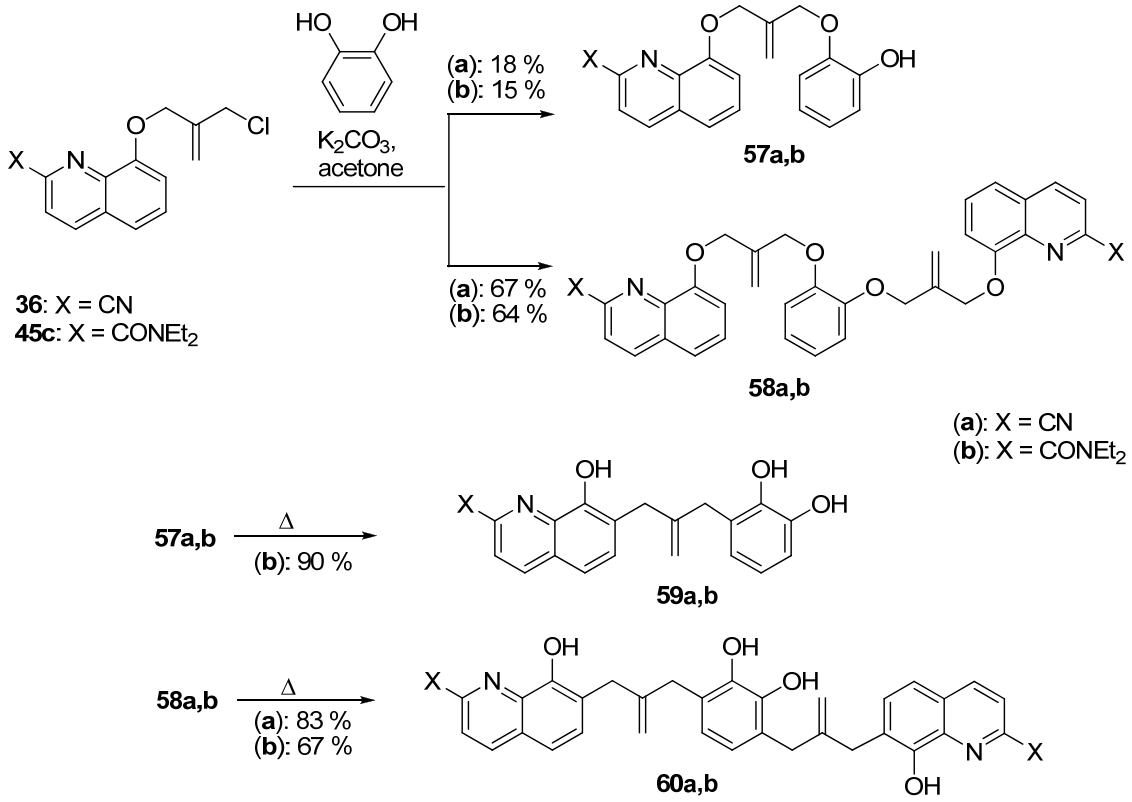
Theoretically, a plethora of appropriate phenols should enable the enormous variety of the bridged diphenols successively attached to the isobutenylidene spacer. For example, the initial procedure for the double-Claisen rearrangement was applied by *Hiratani* to 8-hydroxyquinolines. Shortly thereafter it was extended to the phenol derivatives for the conversion of macrocyclic polyethers to the crownophanes.[152]

With the aim of further advancing the ligand systems, new receptors possessing three binding compartments were envisaged. Referring to the valuable achievements in the exploration of the self-assembly processes on the catechol ligands with pronounced chelating properties in

[152] K. Hiratani, H. Uzawa, K. Kasuga, H. Kambayashi, *Tetrahedron Lett.* **1997**, *38*, 8993.

relation to the hard Lewis acids (Ti^{4+}, MoO_2^{2+}, Al^{3+} etc.),[36a-c] the corresponding structural motif was employed as a connector between two quinolines. Therefore, the central complex fragment will predetermine the charge of the entire helicate and possibly even perform as a structural organizer upon self-assembly. Thus, two lanthanide(III) ions, embedded into from the central one intrinsically different peripheral complex moieties, are safely isolated and not more susceptible to each other, insuring the additivity and adequateness of the exhibited spectroscopic or magnetic properties.

The mono-ethers **36** and **45c** were involved in the successive coupling with catechol providing symmetrical **57a,b** and unsymmetrical **58a,b** heterosubstituted diether compounds (Scheme 20). Their separation by column chromatography, followed by the prolonged thermal rearrangement afforded a series of novel catechol / quinoline ligands possessing a nitrilo group (**59a** and **60a**) or an amide donor function (**59b** and **60b**) in the 2-position of each of the quinolinate moieties.



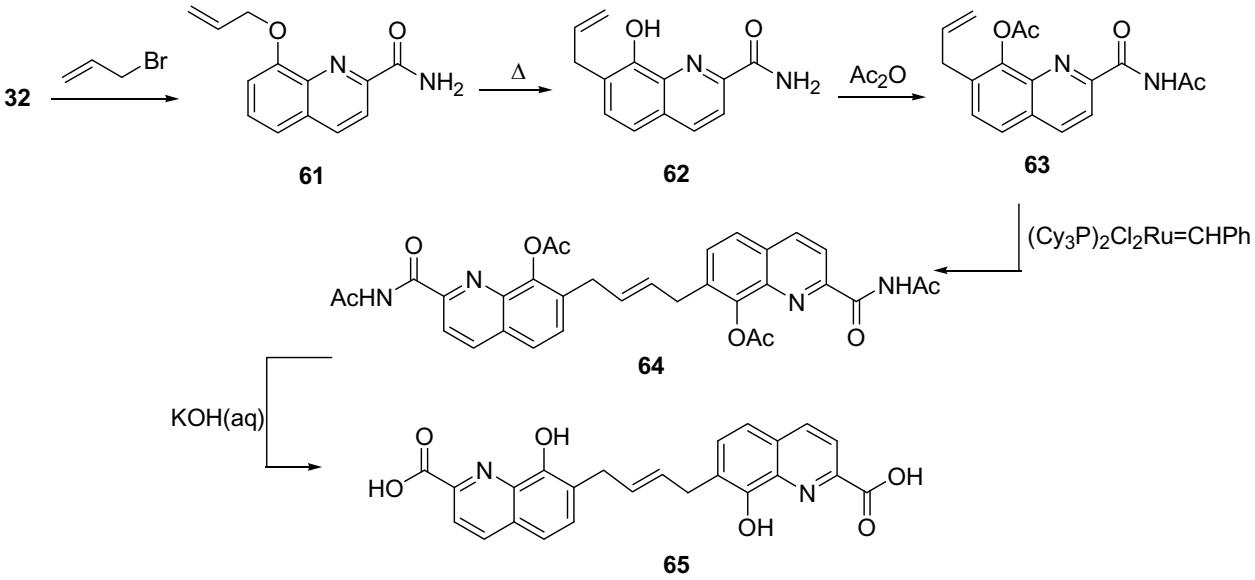
Scheme 20. Synthesis of catechol / quinoline ligands **59a,b** and **60a,b**.

Some complexation experiments were attempted with ligands **59b** and **58b**, lanthanum(III) or ytterbium(III) salt, and $[TiO(Ac)_2]$ taken in 3 : 2 : 1 ligand to f- to d-element ratio in the presence of K_2CO_3 or Rb_2CO_3 as base. But neither were structured NMR spectra of the

complexes recorded, nor were the corresponding peaks observed in ESI MS. The optimization of reaction conditions as well as the precise examination of reagents (for example, testing of different octahedral d-elements for accommodation by the central catecholate nest) is still required to suppress the scrambling processes upon speciation.The derivatives **59a** and **60a** need further transformations before being used as ligands for complexation. The attempts of hydrolysis of these nitrilo compounds under basic conditions failed and no traces of desired acids were evident by NMR spectroscopy or by ESI MS. Therefore, the other options allowing to convert a "passive" CN group into more suitable moieties for coordination studies, e.g. groups with donor functions – amides, imidates and derivatives thereof (oxazolines, oxazines etc.), five or six member heterocycles (oxazoles, oxadiazoles, tetrazoles etc.) have to be developed.

3.7. Claisen Approach to Ditopic Ligands

An alternative strategy to connect identical tridentate 8-hydroxyquinoline units is envisaged by employing a Claisen rearrangement followed by the olefin metathesis "homodimerization". Therefore, an allyl group was attached to 8-hydroxyquinoline-2-carboxamide **32**. The resulting ether **61** underwent Claisen rearrangement at 170 °C under N_2 atmosphere to afford the C-allylated 8-hydroxyquinoline derivative **62** in quantitative yields. Upon treatment of compound **62** with acetic anhydride both the phenolate and the amide units were acetylated (Scheme 21).



Scheme 21. Synthesis of bis-acid **65** *via* Claisen rearrangement - intermolecular tandem olefin metathesis.

"Homodimerization" of **63** by intermolecular metathesis reaction in the presence of Grubbs catalyst (of the "first generation") results in a bis(8-hydroxyquinoline-2-carboxamide) **64** with the *n*-butenylidene spacer connecting the 7-positions of the quinolines. 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);[79b]
2) a single isomer in a yield of 26 %. Only the latter isomerically pure *E*-product **64** was employed in the final transformation.

The assignment of the *Z*- and *E*-isomers was enabled by NMR spectroscopy (measurements performed by J. Klankermayer) using a recently introduced technique.[153] Non-equivalence of the two vinylic protons is observed for those located at an H-C=^{13}C-H unit. ^{3}J (HH) coupling constants of 10.2 Hz or 15.6 Hz are observed for the *Z*- or *E*-isomers of **64**, respectively.

The reaction sequence was completed by hydrolytic cleavage of the acetyl groups at the phenolate functions, accompanied by the simultaneous hydrolysis of the *N*-acetamido substituents upon treatment with aqueous KOH in pyridine to afford the symmetrical bis-8-hydroxyquinoline-2-carboxylic acid derivative **65** in a good yield (64 %).[154]

X-ray quality crystals of the bis-acid **65** were obtained from DMSO / MeCN solvent mixture. Keeping in mind the situation observed for the dibromosubstituted carboxylic acid **30c** it was expected that the DMSO molecule should interact with acceptor functions of the quinolinate binding site.

The molecular structure of **65** can be considered as double reproduction of the DMSO adduct of the compound **30c** with an analogous tweezer-type arrangement of hydrogen atoms oriented to bind O=S donor unit of the guest (S=O···H-O) distances are 2.06 and 1.93 Å. Simultaneously the protons participating in the hydrogen bridging to the pyridine nitrogen exhibit separations N···H-O of

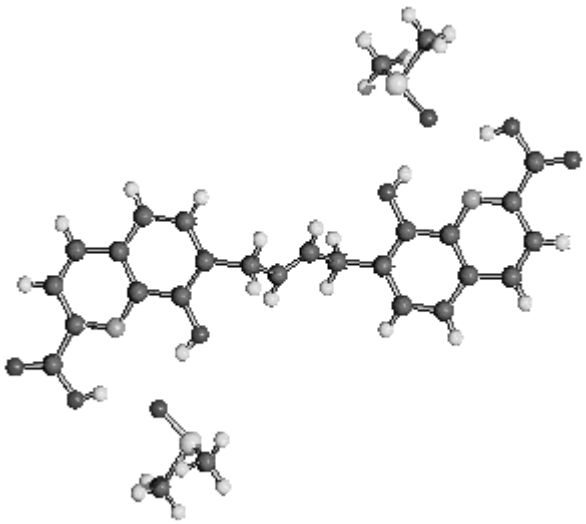


Figure 48. The molecular structure of the DMSO adduct of bis-acid **65**.

[153] (a) B. Radeglia, *J. prakt. Chem.* **1993**, *335*, 291. (b) B. Luy, G. Hauser, A. Kirschning, S. J. Glaser, *Angew. Chem*. **2003**, *115*, 1338; *Angew. Chem. Int. Ed.* **2003**, *42*, 1300.

[154] (a) K. Mekouar, J.-F. Mouscadet, D. Desmaële, F. Subra, H. Leh, D. Savouré, C. Auclair, J. d'Angelo, *J. Med. Chem.* **1998**, *41*, 2846.

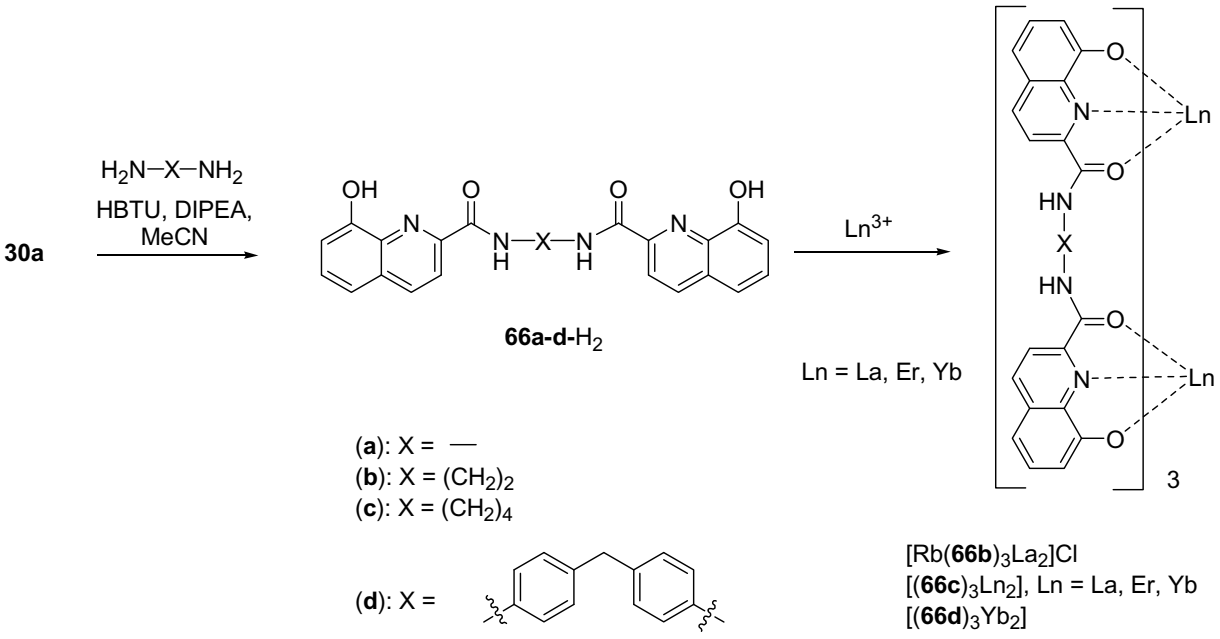
2.16 and 2.28 Å with an angle H-N-H of 83.9 °. The molecular framework adopts a *trans*-conformation with two identical quinolinates related by a center of inversion. The pivotal double bond C=C length is of typical value (1.29 Å).

The introduction of negatively charged carboxylates, which possess high affinity to the later Ln(III) ions, in the terminal positions of oxine cores should affect the Ln^{3+} - ligand bond strength leading to the stabilization of charged helicate complexes possibly even in water.[155]

3.8. Bis-Amide-Bridged Ligands and Homodinuclear Helicates. Amide / Imine Ligands

3.8.1. Synthesis of Ligands and Complexes

The control of the size and stereochemistry of helicate macromolecules can be realized by systematic tuning of the length, rigidity, and conformation of the spacer between two binding sites. The simplest synthetic strategy implies the introduction of the bis-amide bridging unit by single-step condensation of 2 equiv. of carboxylic acid **30a** with 1 equiv. of appropriate aliphatic or aromatic bis-amine (Scheme 22). The effortless work-up procedure and satisfying yields allow for the scaling up of the amide preparation.



Scheme 22. Synthesis of bis-amide-bridged quinoline ligands **66a-d**-H_2 and dimetallic complexes based on them.

The findings reported not long ago by *Albrecht* concerning obeying the chirality features at the complexes by altering the number of CH_2 units in the spacer[27b,34] were applied to the bis-

[155] (a) M. Elhabiri, R. Scopelliti, J.-C. G. Bünzli, C. Piguet, *J. Am. Chem. Soc.* **1999**, *121*, 10747. (b) Y. V. Korovin, N. V. Rusakova, *J. Fluorescence* **2002**, *12*, 159.

amidoquinolinate ligands. Therefore, it was expected that ethyl and butyl units in the linker would induce a helical twist at the ligand upon complexation. The participation of the template should have provided the charge at the helicate apparently improving the solubility and facilitating the ESI MS measurements. The shortest hydrazide spacer might preclude the templating effect still generating helication. The ligand pattern with a semirigid diphenylmethane spacer has an arguable nature as it possesses two stereo-controlling units - rigid aromatic and flexible methylene contact with corresponding C_2 axis and σ-plane symmetry elements. Interestingly, both conformational versions, meso - helicate *versus* chiral helicate, were realized for the bis-catecholimine[36a,b] and bis-imidazolimine, as well as pyridylimine ligand,[128] respectively.

The complexes were prepared by reaction of the ligands **66b-d**-H_2 with lanthanide(III) salts in the 3 : 2 ligand to metal ratio in the presence of base M_2CO_3 (M = K, Rb, Cs) (Scheme 22). Surprisingly, no influence of size of the cation template on the chemical shifts of the ligand protons was detected by NMR spectroscopy. Moreover, the difficulties and often even impossibility to obtain a molecular peak with a reasonable intensity in ESI MS convince of the absence of a plausible charge at the complex. The formation of neutral helicates without the typically incorporated template in the interior could be only evidenced by elemental analysis.

3.8.2. NMR Observations

Unfortunately, the critically low solubility of the compounds does not allow to perform two-dimensional NMR investigations, but the ^{1}H NMR spectra of the diamagnetic lanthanum(III) complexes with ligands **66b**-H_2 and **66c**-H_2 proved to be well-structured and quite informative.

The proton spectrum of the complex [(**66c**)$_3$La$_2$] exhibits only one set of quinolinate signals in agreement with the highly symmetric arrangement adopted by the coordinated ligand (Figure 49). This means that the complex in solution retains its helical conformation which it possesses in the solid state. The ***g*** protons of the methylene units are diastereotopic and produce two broadened peaks which are shifted to high field and appear at δ = 3.04 and 2.85 ppm. The ***h*** protons of the central methylene units are only slightly affected and situated at δ = 1.40 *versus* 1.72 ppm for the free ligand pointing towards very weak interstrand interactions or even their absence. The large upfield shifts for aromatic protons are typical features of the quinolinate ligands involved in helication. The deshielding effect of the metal center in a complex fragment is expected to be decisive for the interpretation of the perturbations in NMR spectra. But anisotropic shifts seem to be dominating for the helicate-type complexes. It

originates from the twist provoked during organization of the ligand strands about a C_3-axis passing the two lanthanum centers. As a consequence, the quinolinate π-rings are sloped and susceptible to each other. Therefore, the ***a*** and ***c*** protons of the phenolate moiety are found out of the usual aromatic region at δ = 6.30 and 6.81 ppm, respectively.

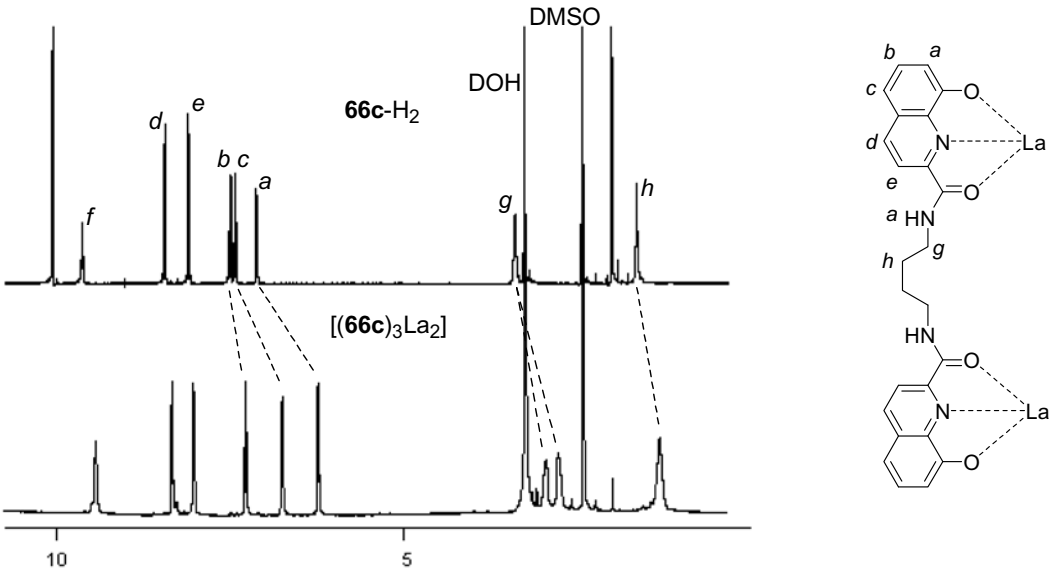


Figure 49. Comparison of ^{1}H NMR spectra of ligand **66c**-H_2 and complex [(**66c**)$_3$La$_2$].

These interpretations are well suited for the [Rb(**66b**)$_3$La$_2$]Cl complex, although according to the molecular peak at m/z = 1649 in the positive ESI MS and the calculated composition proposed by elemental analysis the rubidium templating is suspected (Figure 50). Owing to the shorter spacer between the two complex compartments the helicate structure might be somewhat compressed resulting in a more pronounced tilt of the coordinated ligands at the central lanthanum(III) ion, and subsequently amplifying the anisotropic shifts.

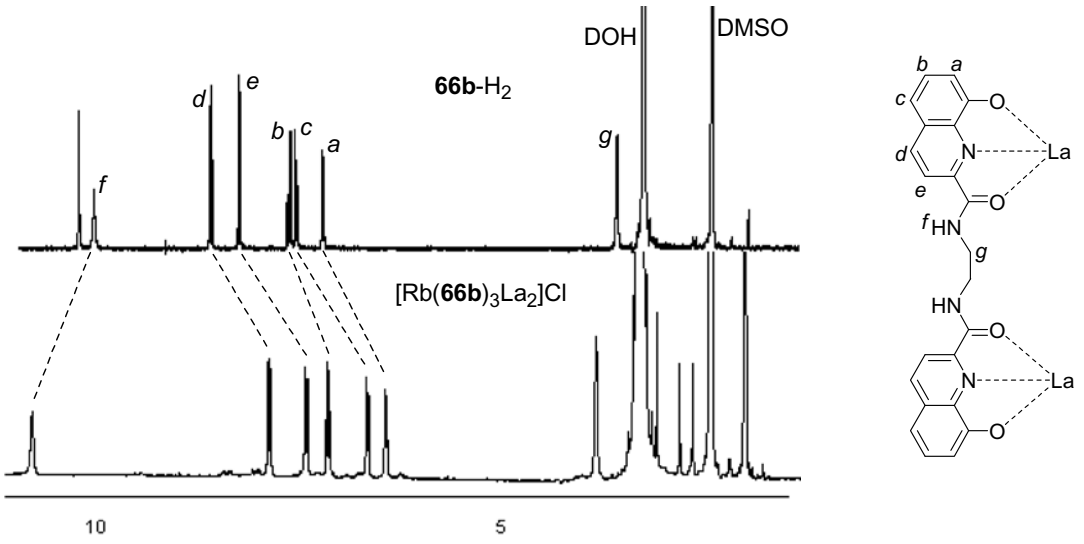


Figure 50. Comparison of ^{1}H NMR spectra of ligand **66b**-H_2 and complex [Rb(**66b**)$_3$La$_2$]Cl.

Thus, the protons of the pyridine side ***d*** and ***e*** are especially affected and shifted upfield for $\Delta\delta$ = 1.6-1.7 ppm in comparison to the uncoordinated ligand **66b**-H_2. Protons of the phenolate moiety ***a*** and ***c*** are detected at δ = 6.50 and 6.73 ppm versus δ = 7.16 and 7.47 ppm recorded for the free ligand.

Interestingly, deshielding effect of the coordinated metal is finally observed for the resonances ***f*** of the NH pattern shifted for almost $\Delta\delta$ = 1 ppm to the lower field in the complex spectrum.

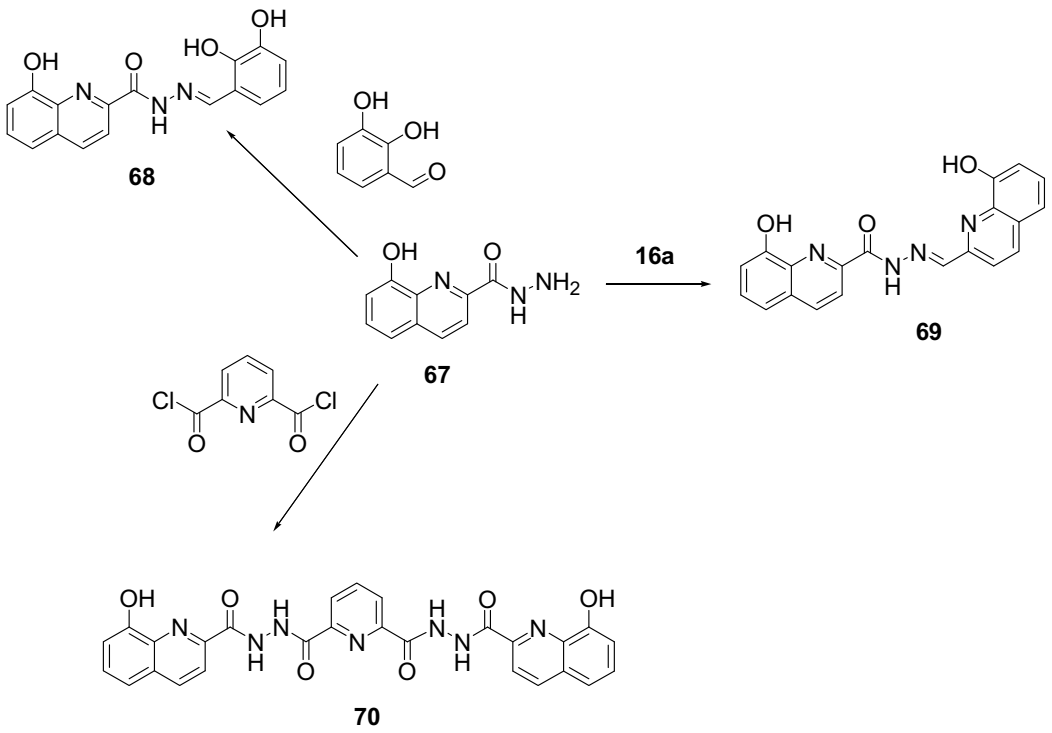
The complexation with ligands **66a**-H_2 and **66d**-H_2 did not furnish well defined NMR spectra and thus did not enable any signal assignments and structural interpretations.

The hydrazide derivative **66a**-H_2 is thought to be a suitable precursor for the establishment of the 1,3,4-oxadiazole linker between two quinolinate binding sites. Good thermal stability and electron-deficiency of the 1,3,4-oxadiazole component make it especially attractive as electron transport material.[105a,156] The felicitous combination of the electronic properties of both heterocycles - peripheral oxine and central oxadiazole in association with the coordination preferences of the quinolinol unit towards aluminium or lanthanides, represent an endeavour to design multifunctional ligands for OLED applications.[157]

3.8.3. Sequential Amide - Imine Ligands

In the present case, the typical procedure for amidation uses carboxylic acid **30a** and diamine compounds in a 2 : 1 ratio in the presence of HBTU as coupling agent in dry MeCN at rt. The conversion is limited to approximately 60-70 % after two days. The attempts to adjust the stoichiometry of reactants by increasing the excess of the diamine component in order to selectively obtain the product of mono-amidation with a terminal amino group available for further coupling, were successful only in case of hydrazine hydrate. While the reaction of acid with N_2H_4 at a 1 : 1 stoichiometry furnished the desired hydrazide derivative **67** as a single compound, the coupling with other diamines yielded only a mixture of mono- and bis-amides which were identified by MS and NMR, but not isolated as independent products due to the complex separation procedure. Due to the grafted amine unit, the new substrate can be next employed in either an imine condensation or an amide coupling to provide different binding sites along the single receptor (Scheme 24). Thus, imino-amido quinoline / catechol systems represent a new family of hetero-bis-tridentate **69** or bi-/ tridentate **68** ligands for various coordination purposes.

[156] N. J. Lundin, A. G. Blackman, K. G. Gordon, D. L. Officer, *Angew. Chem*. **2006**, *118*, 2644.
[157] G. Huges, M. R. Bryce, *J. Mater. Chem*. **2005**, *12*, 94.

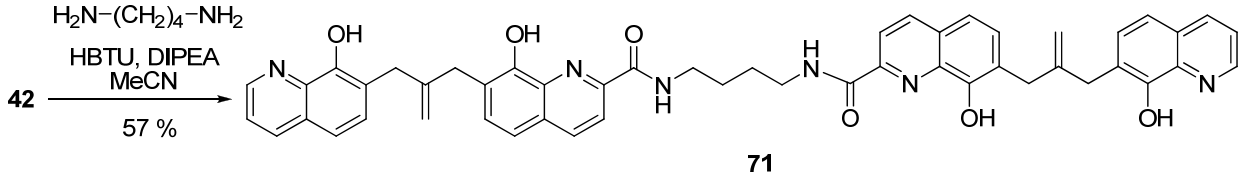


Scheme 23. Ligand perspectives emerging from the hydrazide derivative **67**.

The ligand **70** is of special interest since it possesses three different tridentate compartments - two identical terminal amidoquinolinates and a central 1,5-diamidopyridine moiety. Next, the extension of the bridging motif between quinolinates and pyridine units should facilitate the conformational work upon wrapping the ends when coordination to the metal centers proceeds. The different nature of the binding sites is foreseen as an important aspect in the recognition of specific lanthanide(III) ions during the self-assembly of f-f' helicates.

3.8.4. Towards Polytopic Ligand System

Finally, the preparation of a tetratopic ligand system, initially envisaged as one of the destination points in the ligand design, was enabled due to the reaction sequences depicted in Schemes 14 and 15. The previously characterized carboxylic acid **42** is a suitable component for the amidation reaction, which, depending on the kind of functionalities involved in the coupling bis-amine compound, provides the opportunity to modify the central fragments of the receptor (Scheme 24). The *n*-butylene spacer between the two identical structural compartments is an efficient tool to connect two terminal quinolinates and two central amidoquinolinates into one symmetrical semirigid receptor **71**.



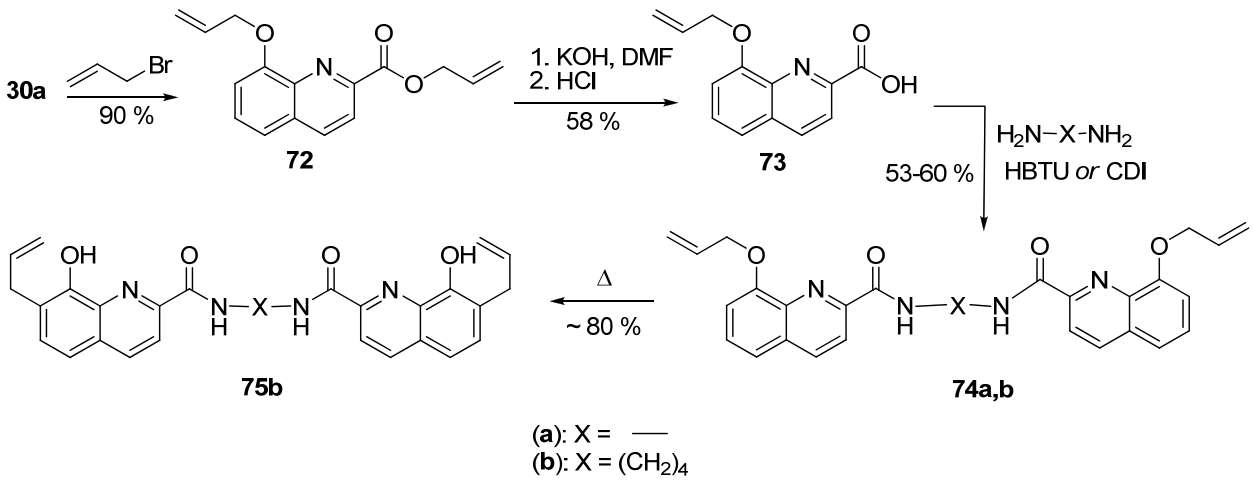
Scheme 24. Preparation of the tetratopic ligand **71**.

Thus, the combination of the bidentate and tridentate binding sites should allow the simultaneous recognition of p-, d-, and f- block elements leading to the triple-stranded tetranuclear helicates. To some extent the latter can be considered as the duplication of the heterometallic helical motif, well-studied and thoroughly represented in the paragraph 3.5, by introducing flexible *n*-butylene linkers. The self-assembly process is expected to be template-mediated referring to the results obtained for the simpler isobutenylidene-bridged systems. Additionally, the templation is attractive as the source of charge at the complex.

3.8.5. C7-Allylated bis-Amide-Bridged Ligands

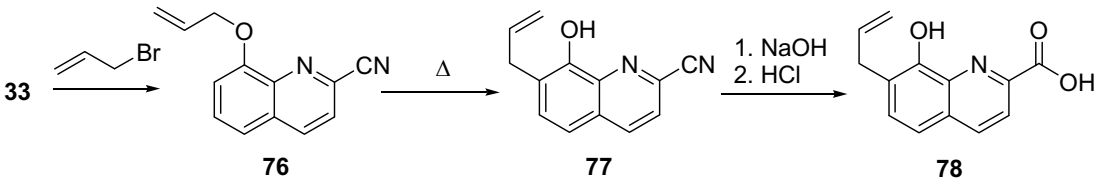
The extremely low solubility of the bis-quinolinate ligand systems is an appalling drawback for the complexation purposes since it hampers the dynamic processes in the self-organizing reaction mixture and leads to the rapid isolation of undesired insoluble components as major products.

Attachment of alkyl / allyl chains at the outside of the quinolinate core in such a manner that its coordination mode is not affected or sterically hindered is suggested as an option to overcome the solubility challenge and yet preserving the receptor design. Therefore, the treatment of 8-hydroxyquinoline-2-carboxylic acid **30a** with an excess of allyl bromide provided the bis-allylated derivative **72** which in the saponification step furnished the corresponding allyl ether of the carboxylic acid **73**. Thus the compound is predisposed for the amidation reaction and, in parallel, is readily suitable for the Claisen rearrangement. The coupling reactions with hydrazine hydrate or 1,4-diaminobutane, experienced already with unsubstituted carboxylic acid **30a,** were now conducted with its allyl ether analogue **73** under similar conditions with HBTU or with CDI as an alternative coupling agent (Scheme 25). The purification by column chromatography afforded the diether compounds **74a** and **74b. 74b** was thermally converted in good yield to the 7C-allylated bis-amidoquinolinate ligand **75b** which exhibits satisfying solubility in organic solvents. Alternatively, the 2-nitrilo-8-hydroxyquinoline **33** is used as an initial participant in the synthetic Scheme 27.



Scheme 25. Synthesis of more soluble bis-amide-bridged quinoline derivatives**.**

In this procedure, the ester cleavage step, usually considered as deleterious in sense of the overall reaction yield, is omitted and the acid **78** is achieved by hydrolysis of its nitrilo derivative **77** under basic conditions. The thermal rearrangement is suggested to be optimal prior to the hydrolysis stage since it results in the about quantitative conversion of ether compound **76** yielding the the 7C-allylated cyano derivative **77.** The latter can be used for the next transformations without further purification. The final acid **78** opens opportunities to access a new family of the related soluble amides, esters and many other derivatives. Moreover, the allyl appendant is especially attractive in view of the "dimerization" reaction by means of intermolecular metathesis promising a reliable entry to the homo-polytopic ligand homologues.



Scheme 26. Synthesis of the 7C-allylated carboxylic acid **78**.

3.9. Expansion of the Aromatic System of Quinolines by Introduction of Additional Heterocycles

3.9.1. A Failure in the Synthesis of Tetrazines

An important issue which has to be taken into account in the ligand design is the energy of target luminescent levels. It means, that in case of NIR emitting lanthanide(III) ions the organic "antenna" absorbing light at longer wave lengths is an appropriate coordination

sensitizer of the metal-centered luminescence. The low energy ligand systems are of growing interest since they propose some advantageous points:

- the lower power and correspondingly energy saving source is required for the stimulation of the photon in visible (~ 500 nm) what is especially valuable in the optoelectronic devices;
- the employment of the lanthanide complexes as bioprobes for the investigation of deeper tissues exclude the application of UV and most of visible light for the excitation or detection of luminescence, since it is not penetrable the biological tissues.

Only few reports, concerning the preparation and spectroscopic studies of the complexes with ligands possessing relatively long wavelength absorption maxima, are encountered in the literature. The implication of dyes which are structurally similar to the xanthene moiety - fluorescein, eosin, fluorexen - connected to the terphenyl unit through a *ß*-alanine spacer provided a low energy chromophore with an absorption window of 500-550 nm.[158] The distance between Ln^{3+} emitting center and corresponding xanthene pendant has been established in the range of 6.1-6.2 Å thus facilitating energy transfer from a dye chromophore to the luminophore resulting in the efficient sensitization of the NIR metal-centered emission.
Similar achievements were demonstrated by *Shavaleev* with simpler tetrazine-based ligands. This nitrogen-enriched heterocycle provides a moderately intense chromophore and moreover, it possesses specific coordination properties, particularly towards rare-earths.[159] The 3,6-disubstituted-1,2,4,5-tetrazine moiety is quite popular and efficient electronic spacer in the various dinuclear and polynuclear systems.[160] Its properties originate from the low lying π^* orbital responsible for the pronounced π accepting characteristics which, in turn, enable the excellent electronic communication between the incorporated metals. Tetrazine derivatives, particularly in the combination with ancillary molecular framework, are mainly utilized in developing diruthenium systems.[161] The interest to these low energy chromophores as potential lanthanide coordinators is only awaking.

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[158] (a) G. A. Hebbink, L. Grave, L. A. Woldering, D. N. Reinhoudt, F. C. J. M. van Veggel, *J. Phys. Chem. A* **2003**, *107*, 2483. (b) M. P. O. Wolbers, F. C. J. M. van Veggel, F. G. A. Peters, E. S. E. Beelen, J. W. Hofstraat, F. A. J. Geurts, D. N. Reinhoudt, *Chem. Eur. J.* **1998**, *4*, 772. (c) M. H. V. Werts, J. W. Verhoeven, J. W. Hofstraat, *J. Chem. Soc., Perkin Trans*. *2*, **2000**, 422. (d) J. W. Hofstraat, M. P. Oude, M. P. O. Wolbers, F. C. J. M. van Veggel, D. Reinhoudt, M. H. V. Wert, J. W. Verhoeven, *J. Fluoresc*. **1998**, *8*, 301.
[159] N M. Shavaleev, S. J. A. Pope, Z. R. Bell, S. Faulkner, M. Ward, *J. Chem. Soc., Dalton Trans.* **2003**, *808*.
[160] W. Kaim, *Coord. Chem. Rev*. **2002**, *230*, 127.
[161] (a) S. Patra, B. Sarkar, S. Maji, J. Fiedler, F. A. Urbanos, R. Jimenez-Aparicio, W. Kaim, G. K. Lahiri, *Chem. Eur. J*. **2006**, *12*, 489. (b) S. Chellamma, M. Liebermann, *Inorg. Chem*. **2001**, *4*0, 3177. (c) A. Singh, N. Singh, D. S. Pandey, *J. Organomet. Chem.* **2002**, *642*, 48. (d) B. Sarkar, R. H. Laye, B. Mondal, S. Chakraborty, R. L. Paul, J. C. Jeffery, V. G. Puranik, M. D. Ward, G. K. Lahiri, *J. Chem. Soc., Dalton Trans*. **2002**, 2097.

The introduction of the tetrazine bridging motif in the bis-(8-hydroxyquinoline) ligands was anticipated as an attractive effortless step in the elaboration of bis-tridentate receptors where possibly different oxidation states, +2 / +3, of lanthanide ions may be tuned trough electron- or hole-transfer mechanism.

The standard two step synthetic procedure involves the reaction of the nitrilo compound **33** with hydrazine hydrate yielding the 1,4-dihydro-1,2,4,5-tetrazine derivative which is prone to oxidize in the presence of NO gas or even oxygen. But already the purification of the product from the first reaction stage by column chromatography using acetone / CH_2Cl_2 as a solvent system for elution resulted in two fractions:

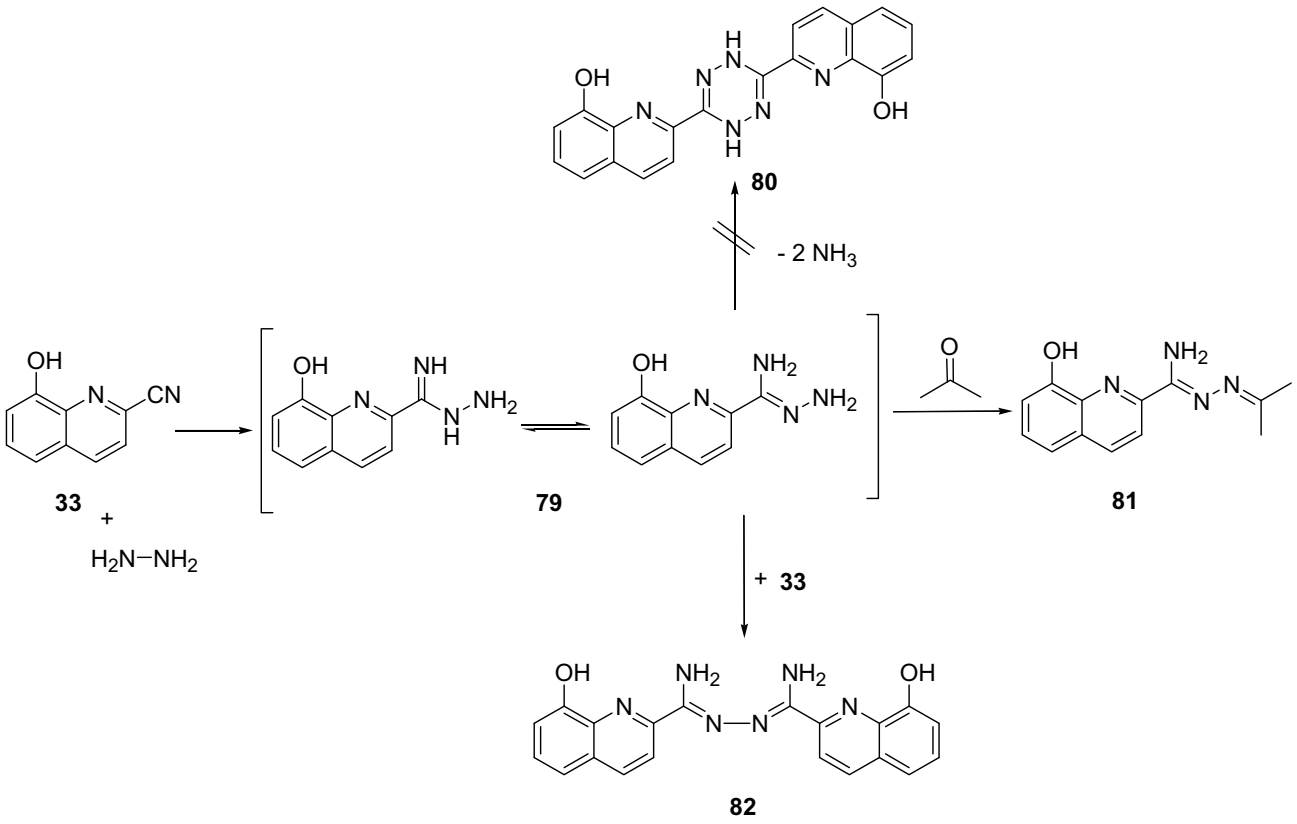
1) a yellow crystalline product **81** which was identified by X-ray diffraction analysis;
2) a dark-yellow solid **82** which was characterized by ESI MS and ^{1}H-NMR.

The product from the second fraction showed the molecular peak at m/z = 373.1 (100 %) in the positive ESI MS and a signal at m/z = 371.3 (100 %) in the negative ESI MS. The ^{1}H NMR spectrum exhibits the symmetric pattern with one set of quinolinate aromatic signals and large broad resonance in the middle field which is ascribed to the NH_2 protons. These observations indicate the presence of the 1,4-diaminohydrazine **82** arising as the stable product from the nucleophilic addition of hydrazide **79** to the nitrile **33**.

This unexpected outcome can be easily explained as shown in Scheme 28.

Initially the addition of the hydrazine to the nitrile function of the quinolinate derivative **33** leads to the formation of the amidrazone **79**.[162] The latter is supposed to undergo dimerizing cycloaddition affording 1,4-dihydro-1,2,4,5-tetrazine **80**. But instead of the desired product compounds **81** and **82** were isolated from the reaction mixture in 24 % and 19 % yield, respectively. The reason for that is the high activity of amidrazone **79** which can be readily involved in condensation with a carbonyl component yielding the corresponding acetone-hydrazone **81**. This took place upon purification of the crude reaction residue by column chromatography eluting with acetone / CH_2Cl_2.

[162] (a) J. F. Geldard, F. Lions, *J. Org. Chem.* **1965**, *30*, 318. (b) T. Eicher, S. Hauptmann, *The Chemistry of Heterocycles*, Wiley-VCH, Verlag GmbH & Co. KGaA, **2003**.



Scheme 28. Formation of **81** and **82**.

X-Ray quality crystals of the acetone-hydrazone **81** were obtained from CH_2Cl_2. The molecular structure of **81** exhibits a helical arrangement of two polymeric strands which are fixed by means of multiple hydrogen bonding that takes place in the inner rim of the helix. Additionally, interstrand π-π stacking interactions maintain the overall architecture (Figure 51). Quite common tweezer-type hydrogen bridging engages a pivotal nitrogen donor of the pyridine moiety and two hydrogen acceptors - of the phenolate unit ($H_{phen}\cdots N_{pyrid}$ 2.33 Å) and of the amino group of the ligand side arm ($N_{pyrid}\cdots H_{amin}$ 2.26 Å), displaying an angle of 79°. Thus, the ligand conjugated chain adopts a stretched conformation. The deviation from coplanarity of the quinolinate plane is described by the dihedral angle between ligand aromatic and C=N-N plane resulting in 153°. The double-helix structure allows insignificant π-π stacking overlap between the aromatic moieties of each ligand strand with the interplanar distance of 3.6 Å. A significant contribution to the stabilization of helix structure is provided by interstrand hydrogen bridging between the pyridine nitrogen and both CH_3 units of the neighbouring ligand terminus and a NH_2 group of the related side chain resulting in separation values of 2.35 Å for the $C\text{-}H\cdots N_{pyrid}$ unit and 3.19 Å for the $N\text{-}H\cdots N_{pyrid}$ pattern. Simultaneously, the hydrogen of the phenyl O-H interacts with the *syn*-positioned hydrazo-nitrogen of the consecutive ligand ($O\text{-}H_{phen}\cdots N$ 1.97 Å) which is extra fixed by the

intramolecular hydrogen bonding to the H acceptors of one of the NH_2 units (N-H_{amin}···N 2.34 Å).

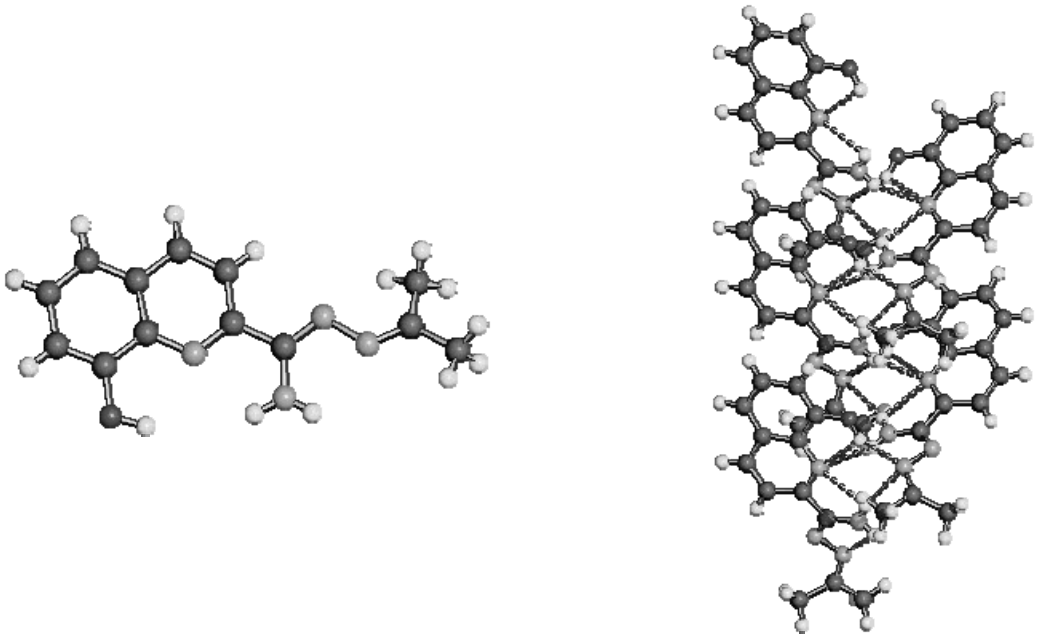


Figure 51. Molecular structure of the hydrazide derivative **81** (left) and a double helix generated by **81** in a self-assembly step (right).

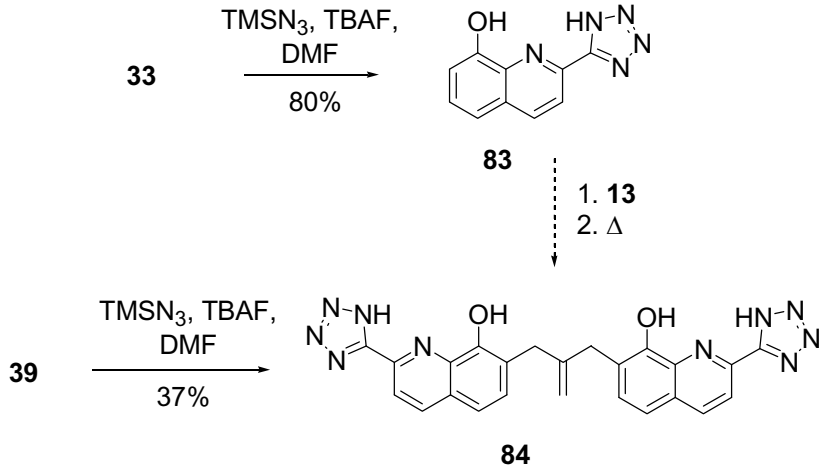
Thus, the felicitous combination of the donor functionalities and hydrogen acceptors provokes the non-covalent propagation of the ligand helical motif over the long polymeric structure. The helical mode of the self-assembly of the conformationally stabile unnatural polymeric arrays maintained by hydrogen bonds is of especial interest in the field of peptidomimetics.[163]

3.9.2. Synthesis of Tetrazole Derivatives

A variety of accessible nitrogen containing heterocycles allows the modification of the ligand system, depending on the available precursor. The scope of the transformations involving organic nitrile substrates motivated us to switch to the five-member heterocycles, thus altering the number of nitrogen atoms or introducing other heteroatoms, for example oxygen. The tetrazoles have attracted much attention due to great perspectives in pharmaceutical applications as metabolically stable carboxylic acid surrogates. Moreover, they are widely used as precursors for the construction of more complicated and complex nitrogen-containing heterocycles. The innovative methodologies still rely on the formal [2+3] cycloaddition of azides and nitriles,[164] but in contrast to the classical protocols, the presence of toxic metals

[163] (a) D. J. Hill, M. J. Mio, R. B. Prince, T. S. Hughes, J. S. Moor, *Chem. Soc. Rev*. **2001**, *101*, 3219. (b) V. Berl, I. Huc, R. G. Khoury, J.-M. Lehn, *Chem. Eur. J*. **2001**, *7*, 13.
[164] A review: S. Wittenberger, *J. Org. Prep. Proc. Int*. **1994**, *26*, 499.

and expensive reagents is avoided. Also, harsh reaction conditions, moisture sensitivity, and the danger associated with the formation of explosive hydrazoic acids are not limiting factors anymore.[165] Employment of the non metallic catalyst TBAF and $TMSN_3$ as the azide source simplifies the reaction from the synthetic point of view.[166] On the other hand, accessibility of mono- and bis-nitrilo quinoline derivatives like **33** and **39** allows the extension of the ligand system to the bis-tetrazole compounds **83** and **84** (Scheme 29).



Scheme 29. Synthesis of tetrazole derivatives **83** and **84**.

The simple workup procedure completes the cycloaddition step with moderate to high yield. The *Hiratani* method would offer an alternative pathway for the preparation of **84** starting from **83**. The product **84** possesses low solubility, which is notably improved in the presence of base pointing to the probable presence of hydrogen bonding. The latter stabilizes the tetrazole / quinoline structure in the solid state.

Unfortunately, the attempts to involve the new ligands **83** and **84** in complexation experiments with lanthanides(III) failed. No traces of products were identified by NMR spectroscopy or by ESI MS. The reason for that could be inadequate reaction conditions applied in the complexation step or the incompatibility of the reactants participating in the thermodynamic processes. But, the 8-hydroxyquinoline ligands containing the tetrazole unit remain in the focus of attention since they represent a new class of low-energy receptors with a rigid tridentate binding domain.

[165] (a) Z. P. Demko, K. B. Sharpless, *J. Org. Chem*. **2001**, *66*, 7945. (b) F. Himo, Z. P. Demko, L. Noodleman, K. B. Sharpless, *J. Am. Chem. Soc*. **2002**, *124*, 12210.
[166] D. Amantini, R. Bellegia, F. Fringuelli, F. Pizzo, L. Vaccaro, *J. Org. Chem*. **2004**, *69*, 2896.

3.9.3. Approaching Oxazoline Ligands

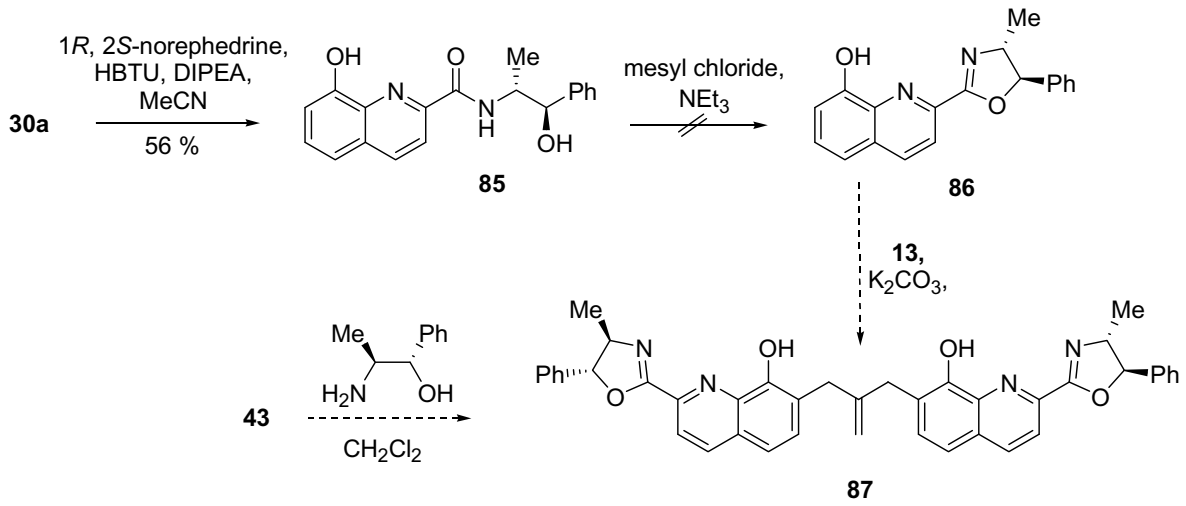
The novel trend in the design of the multifunctional ligands suitable for supramolecular purposes and simultaneously applicable, for example, in asymmetric catalysis became inspiring force for implication of the oxazoline motif in the design of the quinolinate ligands. The success of the bis-oxazolines (box) as supramolecular building blocks[167] and chiral catalysts[168] and the triumph of the pyridine-2,6-bis(oxazolines) (pybox) as tridentate ligands for the rhodium complexes, famous due to their enormous reactivity and the excellent chiral control,[169] explain the synthetic tendency towards elaboration of the new ligands and study of their coordination behaviour with lanthanides.[170] The catalysts derived from the pybox ligands and a set of rare earth(III) triflates have been examined for efficiency in the asymmetric Diels-Alder and Mukaiyama-Michael reactions, 1,3-dipolar cycloaddition,[171] and in the synthesis of the homopropargylic alcohols[172] showing reasonable rationalization of the reaction outcome up to 99 % ee. Recently *Williams* reported the preparation of the enantiopure silver double-stranded helicates and more complicated trinuclear species with pybox ligands.[173]

In general, there are several common synthetic protocols for the preparation of the pybox derivatives starting from the carboxylic acids or related derivatives. The imidate route is found to be the most convenient and efficient, implying a one step conversion upon treatment with the appropriate aminoalcohol. The simplicity of the reductive transformation of the *ß*-amino-esters to the enantiopure 3-aminopropan-1-ols provides useful substrates to approach pyboxazine ligands.[174] Recently, *Davenport* reported the synthesis of chiral imidazoline ligands, prepared from the aromatic imidates and C_1 symmetric diamines, and their application in the asymmetric catalysis of Diels-Alder reaction.[175] Compound **43,** discussed in paragraph 3.5.2, comprises two imidate units positioned at the termini of the ligand. The cyclization reaction should proceed gently under reflux in low temperature boiling organic solvents yielding bis-oxazoline derivatives of 8-hydroxyquinoline ligand **87** possessing two

[167] M. Gómez, G. Muller, M. Rocamora, *Coord. Chem. Rev*. **1999**, *193-195*, 769.
[168] K. A. Jørgensen, M. Johannsen, S. Yao, H. Audrain, J. Thornauge, *Acc. Chem. Res*. **1999**, *32*, 605.
[169] (a) H. Nishiyama, H. Sakaguchi, T. Nakamura, M. Horihata, M. Kondo, K. Itoh, *Organometallics* **1989**, *8*, 846. (b) G. Disimoni, G. Faita, P. Quadrelli, *Chem. Rev*. **2003**, *103*, 3119.
[170] H. C. Aspinal, *Chem. Rev*. **2002**, *102*, 1807.
[171] G. Disimoni, G. Faita, M. Guala, A. Laurenti, M. Mella, *Chem. Eur. J*. **2005**, *11*, 3816.
[172] D. A. Evans, Z. K. Sweeney, T. Rovis, J. S. Tedrow, *J. Am. Chem. Soc.* **2001**, *123*, 12095.
[173] C. Provent, E. Rivara-Minten, S. Hewage, G. Brunner, A. F. Williams, *Chem. Eur. J*. **1999**, *5*, 3487.
[174] M. N. Tse, S. Bhor, M. Klawonn, G. Anilkumar, H. Jiao, C. Döbler, A. Spannenberg, W. Mägerlein, H. Hugl, M. Beller, *Chem. Eur. J*. **2006**, *12*, 1855.
[175] A. J. Davenport, D. L. Davies, J. Fawcett, D. R. Russell, *J. Organometal. Chem*. **2006**, 3445.

separate binding sites suitable for the coordination of rare-earths (Scheme 30). The coordination compounds of such ligands open opportunities for producing chiral helicates. This project is in progress at the moment.

The alternative pathway for the preparation of oxazoline ligands like **86**, proposed by *Denmark*[176] involves the amide coupling reaction with *ß*-amino alcohols followed by the ring cyclization in the presence of mesyl chloride and large excess of triethylamine (Scheme 30). But as expected, upon treatment with mesyl chloride the phenolate moiety of **85** was also functionalized; the attempts to cleave the mesyl ester group failed.



Scheme 30. Proposed methods for the synthesis of bis-oxazole derivatives.

Thus, the latter method showed to be disadvantageous due to a more prolonged reaction sequence and requiring the unfavourable deprotection step.

3.9.4. Substituted Quinolines in Cross-Coupling Reactions

In the light of optical spectroscopy, the presence of heterocyclic substituents is much more important in the 5-/ 7- or 4-positions of the quinolinate ligands. Thus, the control and the correlation of the HOMO or LUMO levels are enabled by introducing appropriate electron donating or electron withdrawing groups into the phenolate or the pyridine moiety, respectively. The illustrative studies, reported by *Anzenbacher*, showed how the tactful handling of the 5-position allows the efficient tuning of red-green-blue emission of tris(5-aryl-8-quinolinolate)Al(III) complexes. The latter acted as convincing driving force to extend this strategy to the related lanthanide(III) systems. Furthermore, the attachment of additional aromatic moieties at the quinoline core enlarges the chromophoric system, theoretically

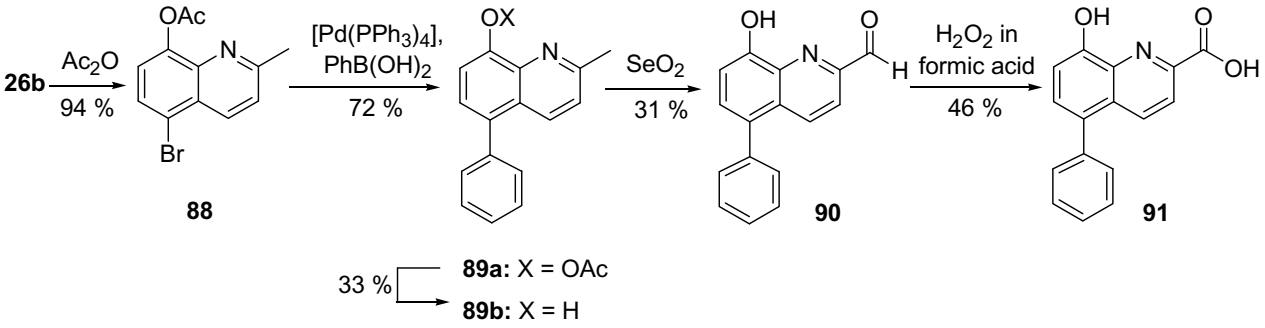
[176] S. E. Denmark, N. Nakajima, O. J.-C. Nicaise, A.-M. Faucher, J. P. Edwards, *J. Org. Chem*. **1995**, *60*, 4884.

improving its light absorption properties. The tilt angle between adjacent aryls modulates their electronic interactions; in turn, the size of π-overlap is responsible for the emission wavelength.[108]

Another field of interest to the 5-substituted quinolinoles, explored by *Nakano*, deals with a phenomenon of axial chirality arising from the rotational barrier about the pivotal bond. This is especially attractive in the context of coordination chemistry.[177]

A common and well proven way to introduce a phenyl group into the quinolinate scaffold is the Suzuki cross-coupling reaction of quinolinol halides with phenylboronic acid. The synthesis in the Scheme 31 starts with 5-bromo-8-hydroxyquinaldine **26b** which was previously used for the preparation of the monosubstituted carboxylic acid **30b** and its corresponding amide **34b.** Now it is converted to the acylated intermediate **88** which is next coupled with the phenyl boronic acid in the presence of K_2CO_3 as base in 1,4-dioxane. This solvent allows running the reaction at temperatures up to 100 °C and thus ensures the full conversion of **88**. After workup, the crude product was applied to flash chromatography furnishing two fractions: first containing a mixture of **89b** and its acylated substrate **89a**; and the second consisting of only **89b**. This unexpected outcome can be explained by the instability of the acyl group under strongly basic reaction conditions. Somewhat similar protocols for cross-coupling with quinoline derivatives reported by *Anzenbacher*[178] and *Nakano*[179] proposed the use of a benzyl ether compound in the coupling step. Although it is hydrolytically stable but the deprotection of the phenolate moiety (for example, by hydrogenolysis) is required resulting in moderate 40-60 % yields. As an option to the benzyl group, *tert*-butyldimethylsilyl TBDMS protection was used for the related 8-hydroxyquinoline systems by *Babudri* et al.[180] The TBDMS can be easily removed by the treatment of quinoline derivative with NaOH, but the initial ether is obtained only in 60-70 % yield.

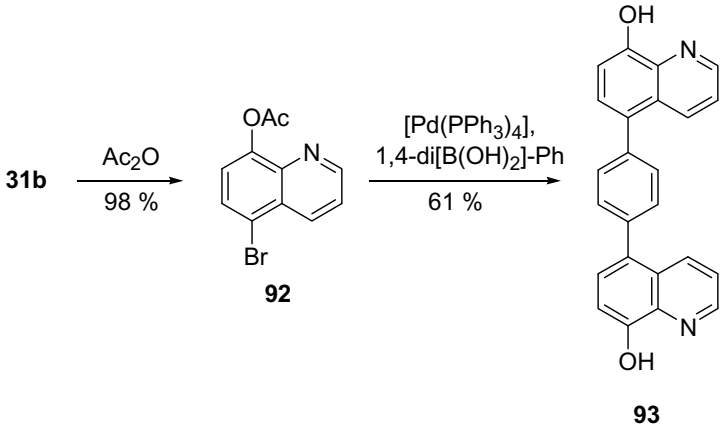
[177] Y. Nakano, Y. Yoshikawa, H. Kondo, *J. Am. Chem. Soc*. **1986**, *108*, 7630.
[178] C. Pérez-Bolivar, V. A. Montes, P. Anzenbacher, *Inorg. Chem*. **2006**, *45*, 9610.
[179] Y. Nakano, D. Imai, *Synthesis* **1997**, 1425.
[180] F. Babudri, A. Cardone, C. T. Cioffi, G. M. Farinola, F. Naso, R. Ragni, *Synthesis* **2006**, 1325.



Scheme 31. Introduction of the phenyl group in quinoline ligands.

Thus, the findings desribed above demonstrate that cross-coupling takes place even with less reliable protection. Compound **89b** was treated with SeO_2 in 1,4-dioxane affording the aldehyde **90** which was further oxidized using H_2O_2 in formic acid. 5-Phenylcarboxylic acid **91** is suggested for the preparation of amide derivatives, which additionally can be "dimerized" employing the *Hiratani* procedure.

An alternative method to connect the two 8-hydroxyquinoline units into one molecule applying the Suzuki reaction is shown in Scheme 32. The acylated bromoquinoline **92** reacts with phenyl-1,4-diboronic acid in the presence of the $[Pd(PPh_3)_4]$ catalyst and K_2CO_3 as base under reflux in 1,4-dioxane. The product **93** was isolated in its "free" form as well. The phenyl bridged bis-8-hydroxyquinoline ligands can be used for the preparation of extended aluminium coordination polymer nets, interesting due to the modified spectroscopical properties and thought to be used for the implementation as emissive material in OLEDs fabrication.

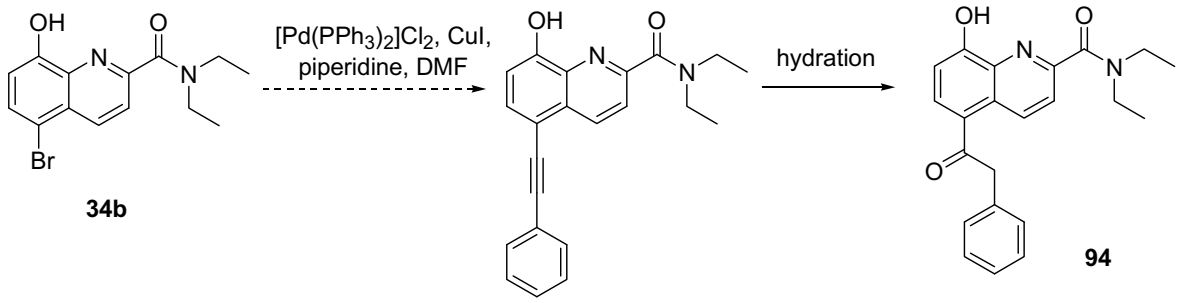


Scheme 32. Synthesis of the phenyl-bridged bis-quinolinol ligands.

In order to get more understanding about the substitution effect on the emission colour tuning in the complexes, an ethynylene unit can be introduced as a spacer between the quinolinate moiety and aryl pendant. This specific linker influences the electronic nature of the ligand providing a high degree of electronic communication between aromatic compartments.

Additionally, the inclusion of the ethynylene group precludes their mutual interaction thus allowing the participation of the *ortho*-substituted aryls in the ligand construction.

The synthetic strategy relies on the Sonogashira palladium-catalyzed cross-coupling reaction between 5-bromo-2-amidoquinoline **34b** with electron-rich ethynylbenzene using a large excess of piperidine which serves as both base and solvent together with DMF (Scheme 33). The reaction proceeded at an elevated temperature (100 °C) for 24 h; during this time the additional portions of ethynylbenzene in piperidine were injected into the reaction mixture to insure maximal conversion of the starting material. The generation of byproducts could not be avoided and the target compound was isolated by means of column chromatography in a low yield of 22 %. The analysis of the ^{1}H NMR spectrum of the product revealed a singlet at δ = 4.38 ppm with a double intensity indicating the formation of the carbonyl compound **94**. EI MS exhibited the related peak of the water adduct at m/z = 362 confirming the NMR determinations. A similar precedent of the triple bond hydration was described by *Anzenbacher*.[181] Upon the cleavage of the Boc protection group in the presence of trifluoroacetic acid (TFA) the TFA salt of the deprotected ligand was formed due to the addition of the former to the triple bond. The hydrolysis of this intermediate resulted in the **94**-type compound. In the present case, the hydration of alkyne might occur on the silica gel column due to the acidic conditions during the entire purification procedure.[182]



Scheme 33. Alkyne hydration in Sonogashira procedure.

3.10. Synthesis of the Quinoline Scaffold: Taking Advantage of MW (Microwave) Irradiation

The quinoline structure is found in many natural products (evolitrine, luotonin F, lavendamycin, mefloquine, bulaquine, montelukast, and probably the most extraordinary and

[181] V. A Montes, R. Pohl, J. Shinar, P. Jr. Anzenbacher, *Chem. Eur. J.* **2006**, *1*2, 4523.
[182] L. Hintermann, A. Labonne, *Synthesis* **2007**, 1121.

versatile *cinchona* alkaloid class).[183] Quinoline systems are important in medical chemistry (treatment of malaria, cancer, asthma, gastric disorder, Alzheimer's disease, inhibition of HIV integrase etc.)[184] and as organocatalysts in asymmetric transformations (the *cinchona* alkaloids quinine, quinidine etc.).[185] But the simple structure of quinoline belies the lack of straightforward routes for the synthesis of its polysubstituted derivatives. The classical methods - Skraup, Doebner-Von Miller, Friedländer, Combes, Conrad, Limpach - generally involve arylamines or ortho-substituted arylamines and a reactive component - carbonyl, alkyne or alkene, and proceed through a cyclodehydration event.[186] Usually they are carried out under extremely harsh reaction conditions resulting in relatively low yields due to side reactions. The modified alternative protocols (Borsche, Niemantowski, Pfitziger etc.) require substitution patterns on the available starting materials, restricting the functionalization of the quinoline. The pyridine ring of quinolines is particularly difficult to access in a substitution step. The 4-position remains the object of preparative aspiration. There are three strategies commonly chosen for this synthetic purpose - Conrad-Limpach, Gould-Jacobs, and Combes reactions,[187] which imply condensation of aniline derivatives with *ß*-ketoesters, *ß*-diketones, or *ß*-ketoaldehydes followed by thermal cyclization of respective enamines or arylaminoacrylates to yield 4-quinolones (well-known due to their antibiotic activity).[188] The reactions proceed at high temperatures (up to 250 °C); mineral oil, diphenyl ether, Dowtherm, or PPA are traditionally used as cyclization medium additionally complicating isolation of the product. An improved protocol clearly is desirable.

4-Aminoquinolines are an important scaffold in the preparation of drugs (chloroquine, tacrine, mefloquine).[189] Most of the synthetic protocols employ S_NAr reaction of 4-haloquinolines (usually chloro) with amine under relatively harsh conditions.[190] Alternatively the procedure,

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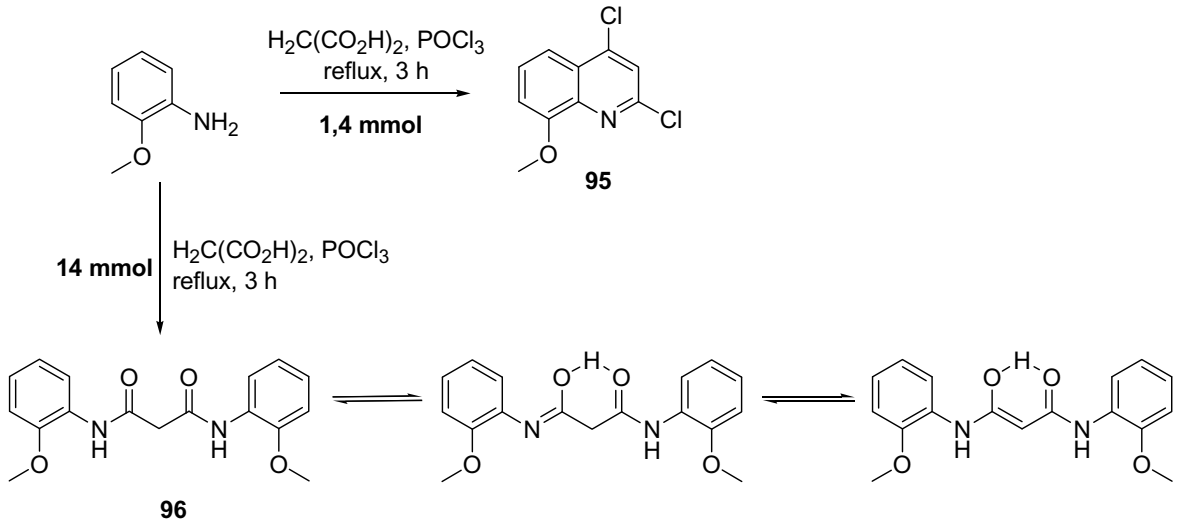
[183] (a) J. P. Michael, *Nat. Prod. Rep.* **2001**, *18*, 543. (b) M. Balasubramanian, J. G. Kelay, In *Comprehensive Heterocyclic Chemistry II*, A. R. Katritzky, C. W. Rees, E. F. V. Scriven, Eds.; Pergamon: Oxford, **1996**, *5*, 245.
[184] J. Polanski, F. Zouhiri, L. Jeanson, D. Desmaële, J. d'Angelo, J.-F. Mouscadet, R. Gieleciak, J. Gasteiger, M. Le Bret, *J. Med. Chem*. **2002**, *45*, 4647.
[185] (a) K. Kacprzak, J. Gawroński, *Synthesis* **2001**, 961. (b) T. P. Yoon, E. N. Jacobsen, *Science* **2003**, *299*, 1691.
[186] (a) M. Abass, *Heterocycles* **2005**, *65*, 901. (b) V. K. Kouznetsov, L. Y. Vargas Méndez, C. M. Meléndez Gómez, *Current Organic Chemisry* **2005**, *9*, 141. (c) G. Jones, In *Comprehensive Heterocyclic Chemistry II*, A. R. Katritzky, C. W. Rees, E. F. V. Scriven, Eds.; Pergamon: Oxford, **1996**, *5*, 505. (d) A. R. Katritzky, C. W. Rees, *Comprehensive Heterocyclic Chemistry*, Pergamon Press, **1984**. (e) L. D. Larsen, D. Kai, *Quinolines*, In *Science of Synthesis*, Georg Thieme Verlag, Stuttgard - New York, **2005**. (f) K. Skraup, *Ber*. **1880**, *13*, 2086, (g) R. H. F. Mansake, M. Kulka, *Org. React*. **1953**, *7*, 59, (h) P. Friedländer, *Ber*. **1882**, *15*, 2572.
[187] (a) R. G. Gould, W. A. Jacobs, *J. Am. Chem. Soc*. **1939**, *61*, 2890. (b) N. D. Heindel, I. S. Bechara, P. D. Kennenwall, J. Molnar, C. J. Ohnmacht, S. M. Lemke, T. F. Lemke, *J. Org. Chem.* **1968**, *11*, 1218. (c) A. Combes, *C. R. Hebd. Sceances Acad. Sci*. **1888**, *106*, 142.
[188] L. A. Mitscher, *Chem. Rev*. **2005**, *105*, 559.
[189] (a) S. C. Turner, T. A. Esbenshade, Y. L. Bennani, A. A. Hancock, *Bioorg. Med. Chem. Lett*. **2003**, *13*, 2131. (b) P. B. Madrid, J. Sherrill, A. P. Liou, J. L. Weismann, J. L. DeRisi, R. Kiplin Guy, *Bioorg. Med. Chem. Lett*. **2005**, *15*, 1015.
[190] A. R. Surrey, H. F. Hammer, *J. Am. Chem. Soc*. **1946**, *68*, 113.

used by *Osborne*[191] for the preparation of 2,4-dimethoxyquinoline in order to reveal its structural inconsistence with montrutanine erroneously proposed by *Ulubelen*,[192] was suggested for the synthesis of the related 8-methoxyderivative **95**. A mixture of *o*-anisidine and malonic acid was treated with $POCl_3$ resulting in 2,4-dichlorosubstituted quinoline **95** in 55 % yield. Surprisingly upon 10-fold scaling up of synthesis the malonamide **96** was isolated as the only product of condensation in 55 % yield (Scheme 34).[193]



Scheme 34. Synthesis of 2,4-dichloro-8-methoxyquinoline **95**.

Thus, a more reliable synthetic methodology is needed to access polysubstituted quinoline derivatives. In this context, a useful cyclization protocol was recently developed by *Zewge*.[194] Eaton's reagent (a mixture of P_2O_5 and $MeSO_3H$) is proposed as an inexpensive and effective promoter for transformation of a variety of aniline derivatives to 4-quinolones in good yields. Conrad-Limpach and Could-Jacobs cyclization methods are thoroughly examined and extended to the preparation of bis-quinolones, thiochromenes, and other heterocycles. However, the relatively long reaction times (2-3 h) arise as disadvantage of the reported method.

The competition in the field of drug preparation requires new improved and simplified strategies for the production of a diversity of quinoline scaffolds, particularly scalable procedures are of interest. Recently MW assisted synthesis of heterocycles has become a

[191] A. G. Osborne, J. F. Warmsley, *J. Nat. Prod.* **1992**, *55*, 589.
[192] A. Ulubelen, *J. Nat. Prod*. **1990**, *53*, 207.
[193] E. Ziegler, K. Gelfert, *Monatsh. Chem.* **1959**, *90*, 822.
[194] D. Zewge, C. Chen, C. Deer, P. G. Dormer, D. L. Hughes, *J. Org. Chem.* **2007**, *72*, 4276.

subject of numerous reviews,[195] focused mostly on the multi-component, multi-step, one-pot, or domino versions. The impressive rate accelerations, remarkably increased yields, mild reaction conditions, and suppressed formation of side-products characterize reactions performed under MW irradiation. The latter corresponds to 0.3-300 GHz frequencies, but chemical reactions are conducted at a frequency of 2.45 MHz. All in all, the microwave phenomenon is attributed to the ability of material to absorb electromagnetic energy and convert it efficiently into heat. But the contribution of different effects - thermal / kinetic (referred to the rapid rise of temperatures when polar substrates are irradiated), specific microwave (include the superheating effect of the solvent, selective heating of more polar component, formation of specific microscopic hotspots - "molecular radiators", avoidance of wall effects), and non-thermal microwave (results from an immediate coupling of electric field with specific molecules in the reaction medium) - should be taken into account if alteration of the reaction outcome is addressed.

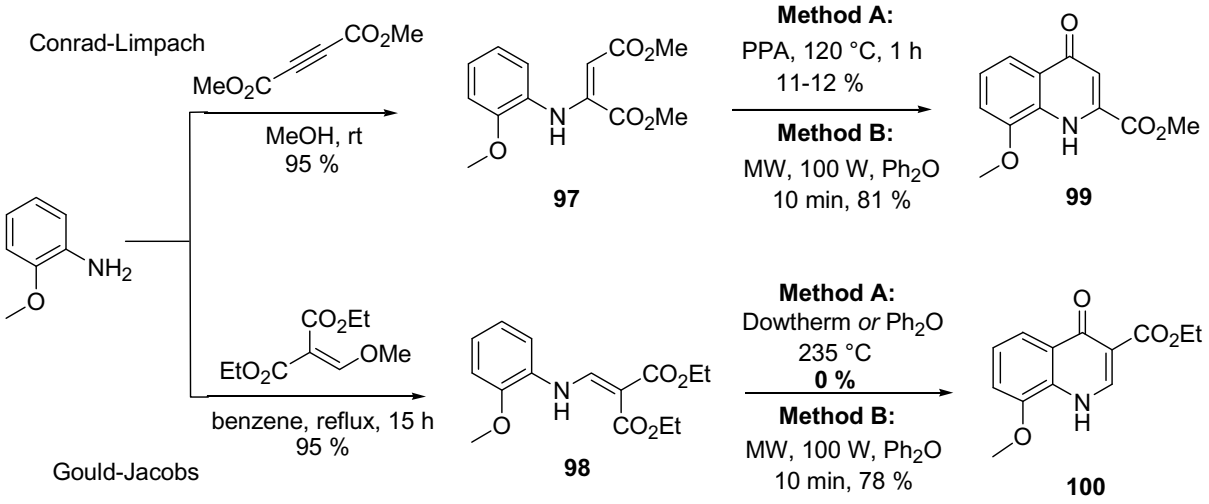
The first reports on the synthesis of substituted quinolines under MW conditions started to appear in the literature only recently (1998[196]-1999[197]). But acidic conditions (PPA,[196] AcOH[198]), solid supports (clays,[197,203] Al_2O_3, SiO_2,[199] bentonite[200]), or metal catalysts ($InCl_3$,[199] *p*-TsOH,[201] $Sc(OTf)_3$,[202] CuBr,[203] $SnCl_2$[204]) remained a crucial requirement for the reaction performance (Skraup[199, 202] and Povarov[205] procedures, Friedländer annulation,[197, 201] Niementowski condensation[206]).

The initial efforts to conduct a cyclization of enamines **97** and **98,** obtained by simple condensation of *o*-anisidine with dimethyl acetylenedicarboxylate (DMAD) or dimethyl methoxymethylenemalonate, respectively, by conventional heating in PPA (at 110 °C) or in Ph_2O (at 235 °C - external temperature) were not encouraging due to very low yield for **99** and total failure for **100** (Scheme 35). These results can be explained in the first case by

[195] (a) P. Lidström, J. Tierney, B. Wathey, J. Westman, *Tetrahedron* **2001**, 57, 9225. (b) A. De la Hoz, Á. Díaz-Ortiz, A. Moreno, *Chem. Soc. Rev*. **2005**, *34*, 164. (c) C. O. Kappe, *Angew. Chem. Int. Ed*. **2004**, *43*, 6250. (d) C. O. Kappe, A. Stadler, *Microwaves in Organic and Medicinal Chemistry*, V. 25, Ed.: R. Mannhold, H. Kubinuyi, G. Folkers, Wiley-VCH Verlag GmbH & Co. KGaA, **2005**.
[196] M. Kidwai, P. Misra, R. Kumar, R. K. Saxena, R. Gupta, S. Bradoo, *Monatsh. Chem*. **1998**, *129*, 961.
[197] G. Sabitha, R. S. Babu, B. V. S. Reddy, J. S. Yadav, *Synth. Commun*. **1999**, *29*, 4403.
[198] A. Perzyna, R. Houssin, D. Barbry, J.-P. Hénichart, *Synlett* **2002**, *12*, 2077.
[199] (a) B. C. Ranu, A. Hajra, U. Jana, *Tetrahedron* **2003**, *59*, 813. (b) B. C. Ranu, A. Hajra, U. Jana, *Tetrahedron Lett*. **2000**, *41*, 531.
[200] L. Găină, C. Cristea, C. Moldovan, D. Porumb, E. Surducan, C. Deleanu, A. Mahamoud, J. Barbe, I. A. Silberg, *Int. J. Mol. Sci.* **2007**, *8,* 70.
[201] C.-S. Jia, Z. Zhang, S.-J. Tu, G.-W. Wang, *Org. Biomol. Chem*. **2006**, *4*, 104.
[202] M. Theoclitou, L. A. Robinson, *Tetrahedron Lett*. **2002**, 43, 3907.
[203] J. S. Yadav, V. S. Reddy, R. S. Rao, V. Naveenkumar, K. Nagaiah, *Synthesis* **2003**, 1610.
[204] M. K. Chaudhuri, S. Hussain, *J. Chem. Sci*. **2006**, *118*, 199.
[205] D. Duvelleroy, C. Perrio, C. Parisel, M.-C. Lasne, *Org. Biomol. Chem*. **2005**, *3*, 3794.
[206] F.-R. Alexandre, A. Berecibar, R. Wrigglesworth, T. Besson, *Tetrahedron* **2003**, *59*, 1413.

solidification of the reaction mixture upon cooling and a complex base / acid extraction procedure leading to significant product losses; in the second case by a long contact time and insufficient rise of internal temperature provided by heating in oil or sand bath.

The beneficial effects of MW irradiation were expected to essentially affect the reaction outcome. The exposure of **97** in Ph_2O (as polar and high microwave absorbing solvent) in a closed vessel at 250 °C for 10 min (100 W) resulted in 81 % conversion to the 2-carboxy-4-quinolone **99**. The even precipitation of product upon addition of *n*-hexane to the reaction mixture allowed the isolation of **99** in acceptable purity. A similar experiment was performed with **98** affording 3-carboxy-4-quinolone **100** in 78 % yield.

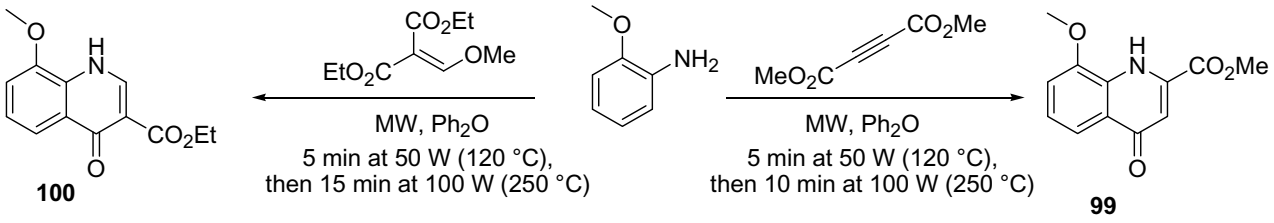


Scheme 35. Synthesis of substituted 4-quinolones under convential heating.

Having successfully established the route for the preparation of 4-quinolones employing *Conrad-Limpach* and *Could-Jacobs* strategies, the optimization of conditions for the MW-assisted cyclizations was attempted.

Standard closed-vessel technology is not ideal in the present case because the volatile by-products like methanol formed upon condensation are not removed from equilibrium. This can cause a decrease of reaction yields especially in the scale-up of the synthesis. Therefore, an open-vessel was used for the 10-fold amount of reactants affording ~ 70 % conversions of **97** and **98** to **99** and **100**, respectively.

Next, a tandem condensation-cyclodehydration sequence was subjected to the microwave dielectric heating (Scheme 36). Thus, **99** and **100** were prepared in a one-pot two-step two-component reaction of *o*-anisidine and DMAD or dimethyl methoxymethylenemalonate, respectively. Reactions proceed smoothly via the internal formation of enamines **97** and **98** which undergo subsequent cyclocondensation resulting in the 4-quinolones **99** and **100**. Yields depending on the applied technology are listed in the Table 6.



Scheme 36. Microwave-promoted two-step one-pot synthesis of 4-quinolones.

Table 6. Reaction yields for the two-step one-pot synthesis of 4-quinolones under closed- and open-vessel conditions.

Condition	Compound	Yield (%)
closed-vessel, 1 mmol	**99**	54
	100	38
open-vessel, 10 mmol	**99**	41
	100	19

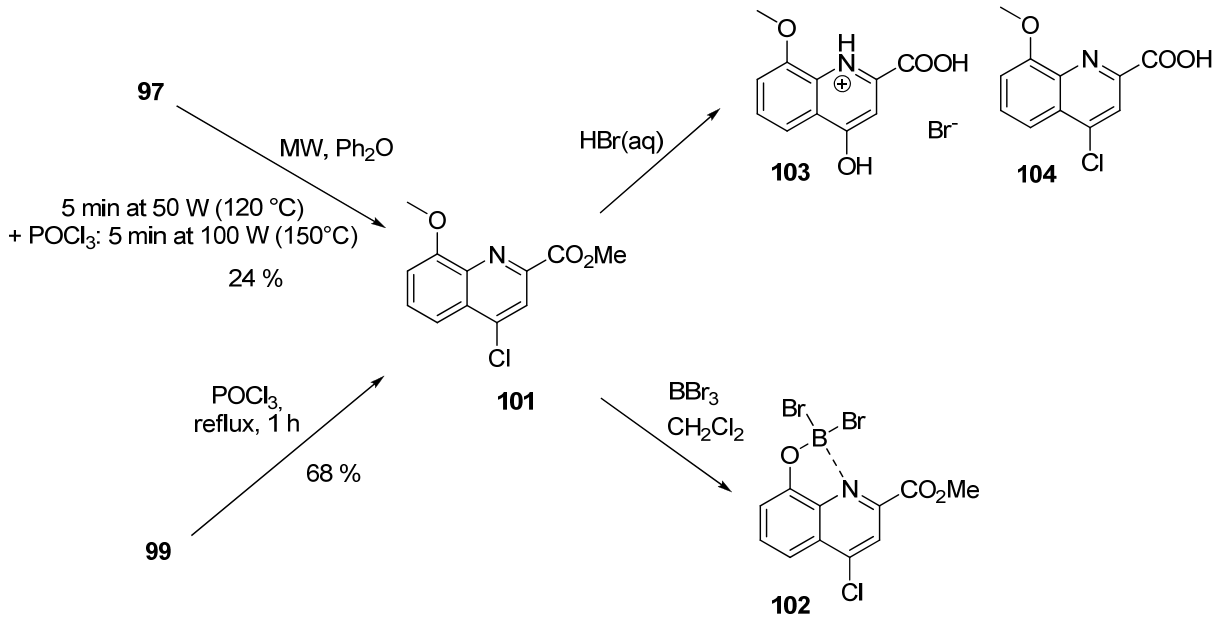
Finally an attempt of simultaneous ring closure followed by chlorination of **97** was carried out under MW irradiation. In this experiment, $POCl_3$ was added in excess to the reaction mixture successively after irradiation of **97** in Ph_2O for 5 min. This system was heated in the sealed vessel at 150 °C (100 W) until a rapid rise of pressure was monitored. After workup and purification by column chromatography 4-chloroquinoline derivative **101** was isolated in low yield (Scheme 37). This reaction represents a two-step cyclization realized in one-pot, although it still requires further improvement of conditions in order to suppress formation of side-products.

In comparison, the *Nakagome* method implies the cyclization of malonate **97** to the chloroquinoline **101** by refluxing it in $POCl_3$ for 18 h resulting in 58 % yield.[207] In parallel, in order to make the chlorination reaction more comprehensive with respect to MW and conventional conditions, the 4-quinolone **99** was treated with phosphorus oxychloride at 100 °C for 1.5 h resulting in **101** with 68 % yield.

In continuation of the reaction sequence, the deprotection of the phenolate moiety of **101** was contemplated as a final step to attain 4-chlorosubstituted methylester of 8-hydroxyquinoline-2-carboxylic acid. However, the reaction of methoxyquinoline derivative **101** with BBr_3 furnished only the stable boronic complex **102**. Thus, **101** was treated with aqueous HBr (48 %). The isolated product exhibited an extremely low solubility and an uncertain set of signals

[207] H. Agui, T. Mitani, M. Nakashita, T. Nakagome, *J. Heterocycl. Chem.* **1971**, *8*, 357.

in ^{1}H NMR. EI MS revealed two peaks at m/z = 238 and 220 which correspond to the methyl ether derivatives of carboxylic acids **103** and **104**. In one of the compounds the chloride is hydrolyzed to the hydroxy group (Scheme 37).



Scheme 37. Synthesis of 4-chlorosubstituted quinolines.

In order to get more understanding of solid state structure of the product single crystals were obtained from DMSO solution. The molecular structure is depicted in Figure 52.

Two inequivalent quinolinate components are held together in an almost opposite manner forming a conglomerate, which is supported by considerable overlap between the coplanar ligand aromatics with a π-π stacking distance in a range of 3.5 Å. One of the quinolinates retains its chloro substituent in the 4-position of the core, which is replaced by a hydroxy group in the second one. The latter quinoline pattern is protonated at the pyridine nitrogen releasing a cationic species, the charge of which is neutralized by the bromine anion incorporated in the molecular cell. The bromine atom is fixed in the structure by means of hydrogen bonding to the water molecule with separation O-H···Br of 2.51 Å. In turn, another hydrogen of H_2O is pointed to the oxygen donor atom of the methoxy group (Me-O···H-O 2.09 Å). Additionally, oxygen of the water molecule also participates in the hydrogen bonding assembly offering its electron pair for bridging to the hydrogen of the carboxylic acid function (O-H···O-H 1.89 Å). A similar situation is observed for the protonated quinolinate compartment. The carboxylic acid hydrogen is involved in the hydrogen bonding to the second water molecule (O-H···O-H 1.75 Å). The carboxylic C=O unit contributes to the bridging to the pyridine proton (N-H···O=C 2.31 Å) and weakly to the water hydrogen (O-H···O=C 2.98 Å), simultaneously. At the same time hydrogen at the pyridine moiety may affect the methoxy group forcing it outwards (N-H···O-Me 2.36 Å).

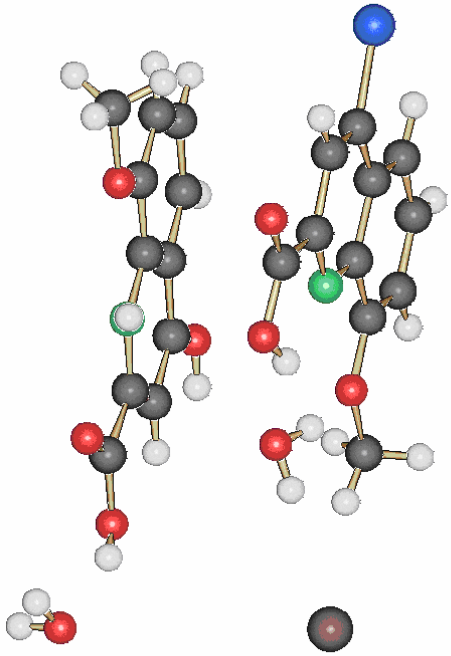
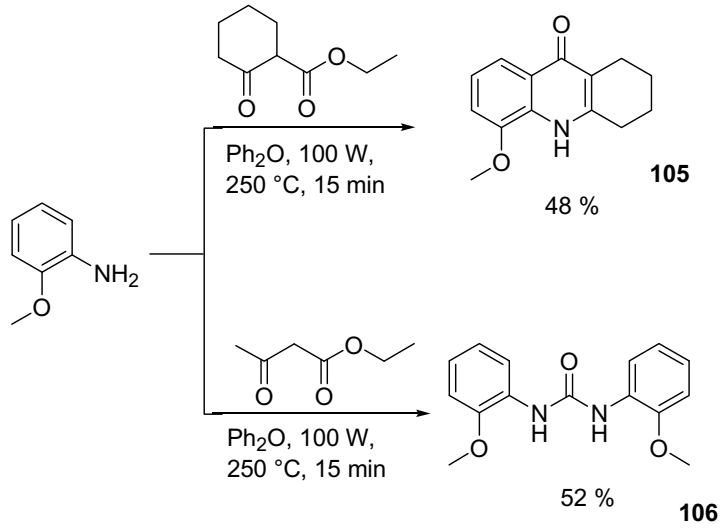


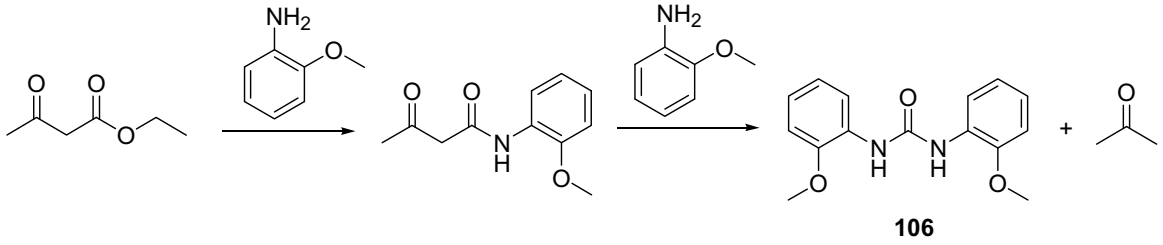
Figure 52. Structure of molecular agglomerate formed by **103** and **104.** (Br: brown, Cl: blue).

The efficiency of the *Conrad-Limpach* method[208] was further examined for *ß*-keto esters under MW irradiation. A standard procedure usually requires a prior preparation of arylaminoacrylates which cyclize when heating in high boiling solvents (Dowterm or Ph_2O). In the present experiment, the isolation of the enamine intermediate was omitted and the reaction of *o*-anisidine with 2-oxocyclohexanecarboxylic acid ethyl ester or ethyl acetoacetate was performed in a sealed vessel under MW conditions (Scheme 38). Surprisingly, only in the former case the desired 4-quinolone derivative **105** was obtained since the latter condensation furnished the *N,N*-diaryl urea **106** (Scheme 39).

[208] Review for *Conrad-Limpach* and *Knorr* syntheses: A. Jones, *Chem. Heterocycl. Compd* **1977**, *32*, 137.



Scheme 38. Examples of *Conrad-Limpach* condensation under MW irradiation.



Scheme 39. Formation of the *N,N*-diaryl urea **106**.

The condensation of arylamines with *ß*-keto esters leads to the ß-keto anilides (*Knorr* procedure) or arylaminoacrylates (*Conrad-Limpach* version) depending on the reaction conditions (temperature, acidity). In the present case, amide formation took place as the result of nucleophilic addition of *o*-anisidine to acetyl acetoacetate. The stabilization of the enol form of *ß*-keto anilide favoured the ketone cleavage which furnished *N,N*-diaryl urea **106**.

To summarize, the mild and efficient protocol for the rapid synthesis of 4-quinolones and derivatives thereof was developed using MW irradiation. Facile cyclization of enamines and arylaminoacrylates as well as one-pot several-step sequential transformations were optimized in terms of reaction rate and time.

4. Summary and Outlook

Fascinating optical properties of the lanthanide(III) ions provide a powerful stimulus for various technological applications. Thus, mono-, bi-, and polymetallic edifies are envisaged as multifunctional systems and are designed to perform as luminescent chemosensors in medical diagnostic and as electroluminescent materials in optoelectronic devices, particularly OLEDs.

In the present study a concept for the preparation of molecular and supramolecular lanthanide(III) containing complex architectures was further developed based on the self-assembly principles. In order to provide suitable supramolecular building blocks, the efficient pathways for the preparation of modified 8-hydroxyquinoline chelate ligands were elaborated. Most of these protocols can be applied to a wide range of substrates, tolerating donor functionalities in 2-position of the quinoline scaffold (imine / hydrazone / carboxylate / carboxamide / imidate / N-containing heterocycle). Furthermore, *Hiratani*-double-Claisen rearrangement was found to be an effective tool to access sequential di- and polytopic segmental receptors enabling selective recognition of p-, d-, and f-elements and their incorporation into discrete helicate-type compounds.

First, monometallic rare-earth(III) complexes were properly characterized, including structural determinations in solid state and speciation in solution. Thus, it was concluded that the expansion of the ligand framework for the tetradentate coordination (**17**-H and **22**-H) does not provide tight chromophore surrounding at the metal center provoking the binding of small coligands, e.g., solvent molecules (Figure 54).

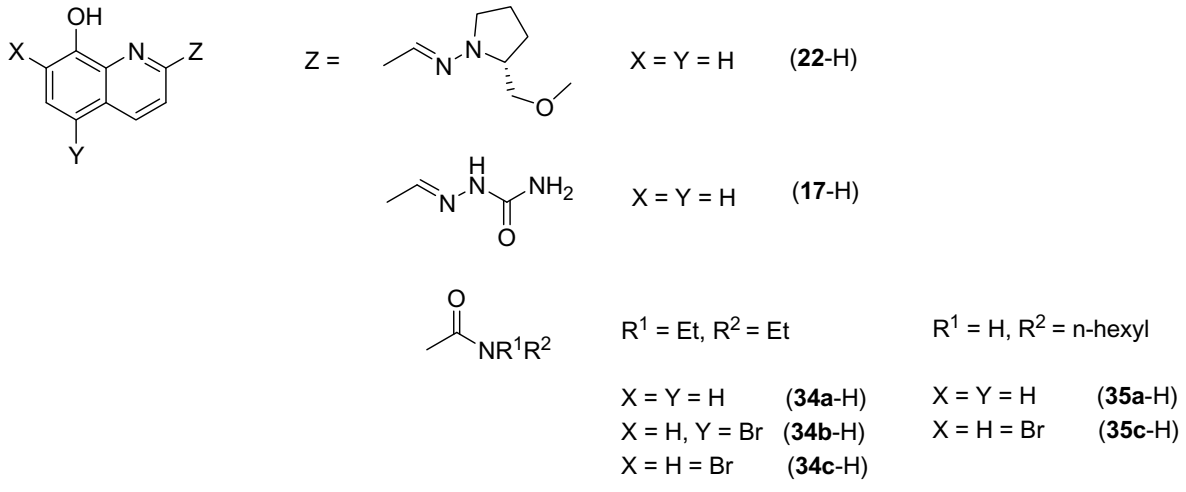
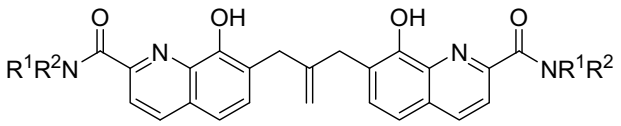


Figure 54. Tetradentate and tridentate ligands.

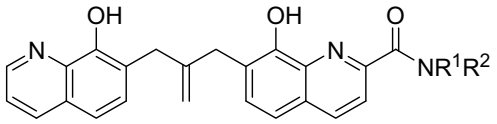
Therefore tridentate amidoquinolinate ligands (**34a-c**-H and **35b,c**-H) were introduced in coordination studies since they furnish triple-stranded complexes in which the potential emitter is safely protected from undesirable external interactions (Figure 54). Finally, the spectroscopic investigations on the solid phase samples were performed to show efficient sensitization of NIR-luminescence from Nd, Er, and Yb complexes. Moreover the effect of bromination was deduced in this study exhibiting the opportunity to remarkably improve luminescence characteristics - quantum yield and life time.

Next, the attention was focused on the dimetallic f-f' and p-/d-f complexes of symmetrical (**50a-c**-H_2) and unsymmetrical (**51b,c**) ligands. Two equivalent tridentate or two different bi- and tridentate binding domains were connected *via* an isobutenylidene spacer within a single receptor (Figure 55).



50a-c-H_2

(**a**): $R^1 = R^2 = H$
(**b**): $R^1 = n\text{-}C_6H_{13}$, $R^2 = H$
(**c**): $R^1 = R^2 = C_2H_5$



51b,c-H_2

Figure 55. Ditopic symmetrical and unsymmetrical ligands.

Thus, octahedral geometries of p- and d-elements as well as tricapped trigonal prismatic environments around the f-metal were addressed upon self-assembly of three ligand strands around the C_3 axis which passes through two metal centers. The speciation in solution was monitored by ^{1}H NMR spectroscopy, ESI MS, and spectrophotometric titration. This unambiguously evidenced the quantitative presence of complexes with a 3 : 2 ligand to f-metal stoichiometry for homo species, and a 3 : 1 : 1 ligand to f- to p-/d-element ratio for hetero compounds. In parallel, the template effect was observed by means of X-ray diffraction analysis as mediator of self-organization processes which occur in solution. The photophysical properties of Yb/Yb and Yb/Al helicates of ligands **50c**-H_2 and **51c**-H_2, respectively, were determined in the solid phase. It was of interest to compare the photoluminescence from monometallic model systems and from extended dimetallic helicates. However the elucidation of the energy transfer processes was considered as a crucial point of the study. The aluminium fragment well-known due to its bright green

emission was introduced as additional chromophoric pendant which was positioned on the certain distance from the Yb luminophore unit. The intrinsic deactivation of the $[Al(8\text{-}Q)_3]$ compartment followed by intramolecular energy transfer to the excited states of the neighbouring lanthanide(III) quencher is mirrored by improvement of the sensitized Yb-centered emission. The latter is described by 12 % higher quantum yields and 16 % longer life times in comparison to those of the Yb/Yb sample. At the same time these results indicate less competitive nonradiative deactivation of the Yb(III) ion of the Yb/Al helicate with respect to the homodinuclear Yb/Yb complex. It could be traced back to the effective intermetallic communication between two Yb(III) ions of one system which become susceptible to each other giving rise to intramolecular self-quenching processes.

Further studies on the heterodimetallic d-/f-helicates are clearly needed to reveal the participation of other donor chromophores in the sensitization of NIR luminescence thus allowing optimization of the complex design and adjustment of the energy flow in the predetermined direction.

Over past time much effort was incorporated in the development of hetero- and polymetallic systems in which the combination of different lanthanide(III) ions possessing particular magnetic or luminescence properties features the multifunctionality of a single probe. The straightforward strategy for the preparation of pure heteronuclear f-f' edifies implies the simultaneous recognition of the lanthanides(III) heteropair. The modification of the ligand termini and/or introduction of various electron-donating/-withdrawing substituents into the quinoline backbone should address the binding affinity to earlier or heavier lanthanides(III) insuring strict selectivity upon complexation. Thus, the electronic structure (covalency, softness / hardness) of the coordination site is amenable to control; simultaneously steric and conformational requirements are affected. In such luminescent helicates the energy migration is modulated by correlation of the ligand/f-/f'-metal excited states. In addition, the kinetically inert stereogenic carbon centers could be grafted into the ligand side arms allowing the increase of the degree of diastereoselectivity upon the complex formation (e.g., **87**).

Generation of linear polymetallic helicates is resorted to the more extended (tri- and tetratopic) 8-hydroxyquinoline based ligands (like **60**, **70**, **71** in Figure 56). Current investigations towards their coordination behaviour imply the rationalization of the self-assembly processes in terms of positive cooperativity.

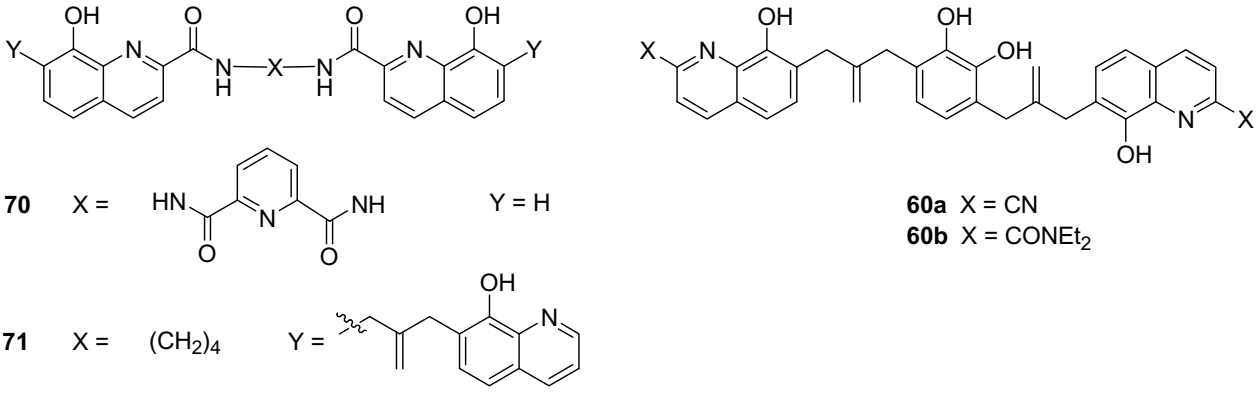


Figure 56. Tri- and tetratopic ligands.

This thesis also contains some studies on the bis-amide bridged quinoline-based symmetrical ligands (**66a-d**-H_2). The low solubility of the complexes complicated their proper characterization. Therefore, the appropriate routes for the derivatization of oxine core were developed aiming the improvement of solubility by attachment of allyl groups via Claisen rearrangement (**75c**).

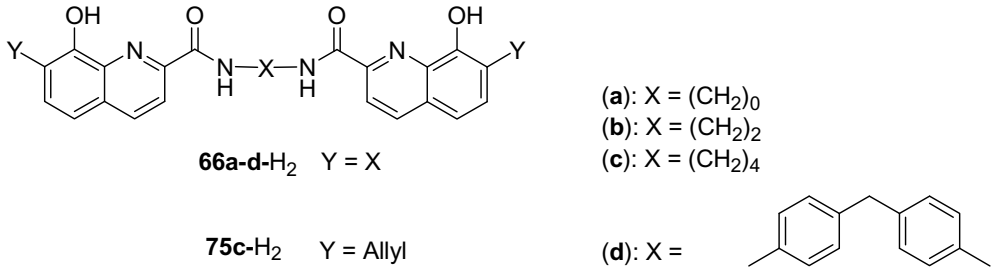


Figure 57. Bis-amide-bridged symmetrical ligands.

As next, the ligand modification should be realized in spectroscopic sense implying the replacement of high energy oscillators - amide N-H and aromatic C-H groups which decrease the overall luminescence efficiency (Figure 58). Furthermore, the rigidity and stereocontrol may be gained by altering the nature of connector between binding domains. Thus, the flexible and chiral spacers are of special interest since they would facilitate conformational rotation upon helication and enantiopurity of the optically active luminescent probes.

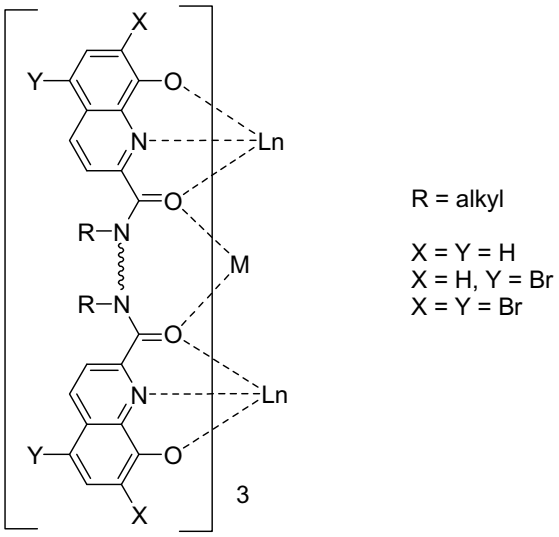


Figure 58. Modification of the ligand structure and complex properties via systematic variation of the linker nature.

Another part of this work was dedicated to the elaboration of low-energy chromophoric systems suitable for the sensitization of the lanthanide(III)-centered NIR luminescence. The tetrazole-containing ligands (**83** and **84**) were prepared and some synthetic strategies for producing tetrazine, oxazole, oxazine comprising receptors were proposed. Improvement of the light absorption capacity of the chromophore could be attained by extension of the ligand conjugated aromatic system (**91**, **93**, **94**). The latter was implemented *via* cross coupling reactions of the halogen substituted quinolines (Figure 59).

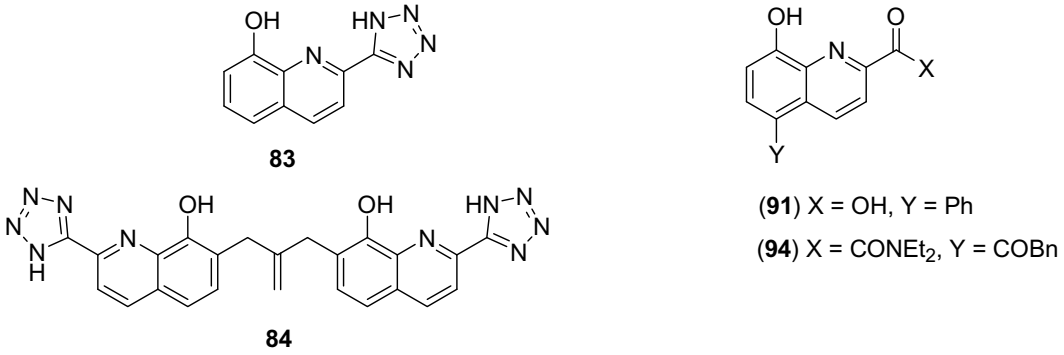


Figure 59. Extension of the ligand aromaticity.

At last, the scope of the cyclization reactions was examined under MW conditions. The *Combes*, *Conrad-Limpach*, *Gould-Jacobs* methods for the preparation of 4-quinolones and substituted quinolines derived thereof were tested under dielectric heating offering an excellent alternative to the traditional procedures. Further studies would be concentrated on

the exploration of various arylamines towards their applicability to the protocols mentioned above.

The whole work was aimed to shed light on the coordination ability of functionalized 8-hydroxyquinoline ligands towards rare-earths(III). An important achievement is the revealing of vital potential of the novel compounds as object for supramolecular purposes. The concept for construction of luminescent helicates is developed emerging from the efficient synergy of self-assembly principles and photochemistry rules invoking the advancing to more responsive and rational systems.

5. Experimental Section

5.1. General Remarks

All synthetic operations described in this experimental part including reactions, work-ups and chromatographic separations were carried out in a well ventilated hood according to the current safety regulations.

Air and moisture sensitive manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques.[209] The glassware employed for the manipulations was oven-dried, and then cooled under a stream of nitrogen. Reagents and solvents were transferred under argon using cannulae or syringes.

5.1.1. Solvents

Solvents for reactions and flash chromatography were dried and purified according to standard techniques.[210] Water was deionised before use. For NMR spectroscopy deuterated solvents were used.

5.1.2. Chemicals

All chemicals employed were purchased from the companies *Sigma-Aldrich*, *Fluka*, *Acros*, *Lancaster*, *ABCR*, *Novabiochem, Strem Chemicals,* and *Merck*, and were used as received unless otherwise stated.

5.1.3. Determination of the Physical Properties of the Synthesized Compounds

5.1.3.1. ^{1}H-NMR Spectroscopy

^{1}H-NMR spectra were recorded either on a *Varian* Gemini 300 spectrometer (300 MHz) or a *Varian* Inova 400 spectrometer (400 MHz). COSY and two dimensional NMR spectra for the assignment of the *E* configuration of **64** using a recently described technique[153] were recorded on a Bruker instrument (600 MHz) at the Institute of Technical and Macromolecular Chemistry RWTH Aachen. Chemical shifts are given in ppm relative to tetramethylsilane (TMS, δ 0.00 ppm). Solvent residual peaks ($CDCl_3$, δ 7.26 ppm; CD_3OD, δ 3.31 ppm; $(CD_3)_2CO$, δ 2.05; $(CD_3)_2SO$, δ 2.50) were used as internal standard. Coupling patterns are

[209] D. F. Shriver, M. D. Drezdzon, *The Manipulation of Air-Sensitive Compounds*, Wiley, Chichester, **1986**.
[210] W. L. F. Armarego, D. D. Perrin, *Purification of Laboratory Chemicals*, Butterworth-Heinemann, Oxford, **1996**.

described by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), br. (broad signal), ps. (pseudo). Coupling constants (J) are given in Herz (Hz).

5.1.3.2. ^{13}C-NMR Spectroscopy

^{13}C-NMR spectra were recorded either on a *Varian* Gemini 300 spectrometer (75 MHz) or on a *Varian* Inova 400 spectrometer (100 MHz). Chemical shifts are given in ppm and were determined by comparison with solvent residual peaks ($CDCl_3$, δ 77.0 ppm; CD_3OD, δ 49.00 ppm; $(CD_3)_2CO$, δ 29.84, δ 206.26; $(CD_3)_2SO$, δ 39.52).

5.1.3.3. IR Spectroscopy

IR spectra were measured on a *Perkin-Elmer* PE 1760 FT spectrometer as KBr pellets or neat (in case of liquid compounds). Only characteristic absorption bands are reported. Absorptions are given in wavenumbers (cm^{-1}).

5.1.3.4. Mass Spectrometry

Mass spectra were recorded on a *Varian* MAT 212 or on a *Finnigan* SSQ 7000 spectrometer with EI (electronic impact) ionization, at 70 eV ionization potential, or CI (chemical ionization), at 100 eV ionization potential. Peaks are listed according to their m/z value. Only signals with highest intensities or characteristic peaks are listed. ESI (electrospray ionization) spectra were recorded on *LCQ Deca XP Plus Thermo Finnigan* mass spectrometer. High resolution mass spectra (HRMS) were recorded on a *Finnigan* MAT 95 spectrometer.

5.1.3.5. Stability constant determination.

Spectrophotometric titrations were performed with J&M diode array spectrometer (TIDAS). All titrations were done in the thermostated glass-jacketed vessels (25.0 ± 0.1 °C). Typically, 20 ml of a deprotonated ligand solution (7×10^{-5} M) was titrated with a Ln(III) solution under an inert atmosphere. After each addition, the absorption spectra were recorded using Hellma optrodes (optical path length 0.5 cm) connected to the spectrometer. Factor analysis and mathematical treatment of the spectrophotometric data were performed with the SPECFIT program. The measurements were performed by Dr. J. Hamacek at the University of Geneva.

5.1.3.6. Photophysical studies

1. Sample handling

The samples have been transferred into quartz capillaries, which were closed with parafilm. The samples have been kept in a (not evacuated) desiccator and were protected from sunlight.

2. Spectroscopy

Room temperature and 77 K emission and excitation spectra have been taken on a Fluorolog FL3-22 spectrometer from Jobin Yvon Horiba. The emitted light in the visible and in the near-infrared range was measured with a room temperature photomultiplier (Jobin Yvon R928P) and with a cooled (-60 °C) photomultiplier (Hamamatsu H9170-75), respectively. In order to measure at 77 K, the quartz capillaries containing the powder samples were immersed in a liquid-nitrogen-filled dewar flask.

Room temperature quantum efficiencies were measured in an integrating sphere, which has been developed by Frédéric Gumy as an accessory to the Fluorolog FL3-22 spectrometer.

High resolution low temperature (10 K) emission and lifetime measurements have been performed upon excitation at 514 nm with an Ar^+ laser (Coherent Innova 90C) and with pulsed excitation at 355 nm from a frequency-tripled Nd^{3+}:YAG laser (Vibrant 355I, 1024 nm, 10 ns, 10 Hz), respectively. The NIR sample luminescence was dispersed at 90° through a single monochromator blazed at 900 nm (Spex 1870). The emitted light was measured with a cooled (-60 °C) photomultiplier (Hamamatsu H9170-75) interfaced with a photon counter (Stanford Research 400) or a multichannel scaler (Standford Research 430) for the continuous wave emission and the lifetime measurements, respectively. Sample cooling was achieved using closed-cycle cryogenic cooling (CTI-Cryogenics).

Excitation spectra have been corrected for the wavelength dependence of the lamp output (power correction) and emission spectra for the instrumental response.

The measurements were performed by J.-C. G. Bünzli, A. Aebischer, and F. Gumy at the EPFL, Lausanne.

5.1.3.7. Elemental analysis

Elemental analyses were performed using a *Heraeus* CHN-O-Rapid instrument.

5.1.3.8. Melting points

Melting points were measured in open glass capillaries with a *Büchi* B-540 apparatus and are uncorrected.

5.1.4. Chromatographic Methods

Preparative column chromatograpy

Purifications by Flash Column Chromatography were carried out in glass columns using *Merck* silica gel 60, particle size 0.040-0.063 mm (230-400 mesh).

Thin layer chromatography (TLC)

Support: TLC aluminum sheets silica gel 60 F_{254} (*Merck*) with a fluorescent indicator.

Detection: exposition to UV-light (λ = 254 nm).

5.1.5. Synthetic Methods

Microwave

The microwave oven used is the model "Discovery" from *CEM GmbH*. The microwave oven was equipped with an IR-sensor for temperature, integrated pressurized air cooling system, pressure sensor and an external fiber optic thermometer.

5.1.6. Compounds Prepared Following Literature Procedures

2-(8-Hydroxyquinolin-7-methylene)-3-(8-hydroxyquinolin-7-yl)-1-propene **11**[81a,152]

3-*n*-Decyl-8-hydroxyquinoline **12**[36d, 211]

5-Bromoquinolin-8-ol **31b** and 5-bromo-2-methylquinolin-8-ol **26b**[212]

8-Hydroxyquinoline-2-carbonitrile **33**, 8-hydroxyquinoline-2-carboxamide **32**, and 8-hydroxyquinoline-2-carboxylic acid **30a**[132, 213]

8-Benzyloxyquinoline-2-carboxaldehyde **28** and 8-hydroxyquinoline-2-carboxaldehyde **16a**[122,130]

5,7-Dibromo-8-hydroxy-2-carboxaldehyde **16c**[214]

2-(*N*-*n*-Hexylcarboxamide)-8-hydroxyquinoline **35a**[136]

2-Butenedioic acid, 2-[(methoxyphenyl)-amino]-, dimethyl ether **97a** and 2-butenedioic acid, 2-[(methoxyphenyl)-amino]-, diethyl ether **97b**[194]

2-[(2-Methoxyphenylamino)methylene]malonic acid diethyl ester **98**[215]

Ethyl (2*E*)-3-(2-methoxyanilino)-2-butenoate or ethyl (2*Z*)-3-(2-methoxyanilino)-2-butenoate[216]

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5.2. General Synthetic Procedures

General procedure for Williamson ether coupling with 3-chloro-2-chloromethyl-propene (GP-1)

K_2CO_3 (5.0 equiv.) and 3-chloro-2-chloromethyl-propene **13** (0.5-1.0 equiv.) were added to the solution of a corresponding 8-hydroxyquinoline derivative (1.0 equiv.) in dry acetone or DMF. The resulting suspension was refluxed in acetone or stirred at 60-90 °C in DMF for 15-60 h. The solvent was evaporated in vacuum; the remaining residue dissolved in CH_2Cl_2 was washed with water and dried over Na_2SO_4. Removal of the solvent under reduced pressure furnished the crude ether compounds mostly as oils, which were either purified by recrystallization or subjected to flash column chromatography.

General procedure for the thermal Claisen rearrangement (GP-2)

The compound was placed in a Schlenk flask; the rearrangement proceeded at 130-180 ºC without a solvent under inert atmosphere of N_2 for 3 - 14 h.

General procedure for the imine condensation (GP-3)

A mixture of 8-hydroxyquinoline-2-carboxaldehyde **16a** (0.20 g, 1.16 mmol, 1.0 equiv.) and appropriate 1,4-diaminobenzene (0.55 equiv.), *O*-methylhydroxylamine (1.1 equiv.), (thio)semicarbazide hydrochloride (1.1 equiv.), SAMP hydrazide **21**[125] (1.1 equiv.) or triaminoguanidinium chloride[217] (0.37 equiv.) was dissolved in MeOH (15 ml) and stirred at rt for 15 h. Reduction in volume on a rotary evaporator resulted in an abundant precipitate, which was collected by filtration, washed with cold MeOH and Et_2O, and then dried in vacuum. If necessary, the product was recrystallized from MeOH, EtOH or DMF.

General procedure for the synthesis of allyloxyquinoline derivatives (GP-4)

To a solution of the 8-hydroxyquinoline-2-carboxylic acid derivative (0.5-1.0 equiv.) in DMF (25 ml), K_2CO_3 (10.0 equiv.) and allylbromide (10.0 equiv.) were added. The suspension was stirred at 90 °C for 15 h. The reaction mixture was cooled to rt, DMF was evaporated under reduced pressure to dryness. The dark brown residue was partitioned between CH_2Cl_2 and water. The organic extract was dried over Na_2SO_4 and concentrated in vacuum. The crude oily product was purified by column chromatography.

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General procedure for the amide coupling (GP-5A)

The carboxylic acid (1.0 equiv.), HBTU (1.2 equiv), and DIPEA (1.1 equiv.) were stirred in MeCN at rt for 30 min. An appropriate amine (1.1 equiv.) or diamine (0.5 equiv.) dissolved or suspended in 2 ml of MeCN was added, and then the mixture was stirred at rt for another 2 d. After removal of the solvent in vacuum, the oily brown residue was dissolved in CH_2Cl_2 (100 ml) and washed with satd. aq NH_4Cl, satd. aq $NaHCO_3$, H_2O, and brine. After drying the organic phase over Na_2SO_4 the solvent was removed under reduced pressure. The crude product was purified by column chromatography or recrystallization.

General procedure for the amide coupling (GP-5B)

A carboxylic acid (1.0 equiv.), HBTU (1.2 equiv), and DIPEA (1.1 equiv.) were stirred in MeCN at rt for 30 min. An appropriate amine (1.1 equiv.) or diamine (0.5 equiv.) dissolved or suspended in 2 ml of MeCN was added, and the mixture was stirred at rt for 2 d. The separated solid was collected by filtration, washed with MeCN, and then purified by recrystallization from MeOH.

General procedure for the two step Williamson ether coupling with 8-hydroxyquinoline (GP-6)

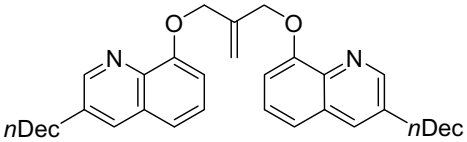
8-Hydroxyquinoline **31a** (2.0 equiv.) and K_2CO_3 (5.0 equiv.) were added to a solution of 8-(2-chloromethyl)allyloxyquinoline derivative (1.0 equiv.) in acetone. The suspension was refluxed for 18 h, cooled to rt; then the solvent was evaporated under reduced pressure. The crude residue was taken up in CH_2Cl_2 (50 ml) and washed once with water. The organic phase was dried over Na_2SO_4. Evaporation of the solvent and purification by column chromatography (EtOAc / *n*-hexane 1:2 → EtOAc) gave an oily colourless product, which was subsequently crystallized from *n*-hexane / CH_2Cl_2 (1:1) or *n*-hexane / acetone (5:1).

General procedure for the Williamson ether coupling with catechol (GP-7)

Catechol (1.0 equiv.) and K_2CO_3 (10.0 equiv.) were added to a solution of 8-(2-chloro-methyl)allyloxyquinoline derivative (1.0 equiv.) in acetone. The suspension was refluxed for 18 h, cooled to rt, and then solvent was 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 over Na_2SO_4. Evaporation of the solvent and purification by column chromatography (EtOAc / *n*-hexane 1:2 → EtOAc) gave colourless oily products.

5.3. Synthesis of Isobutenylidene-Bridged Homoditopic Bidentate Ligands (15-H_2 and 109) and of Aluminium Helicates

8,8'-(2-Methylenepropane-1,3-diyl)bis(oxy)bis(3-decylquinoline) (14)



Prepared according to **GP-1**, starting from 3-*n*-decyl-8-hydroxyquinoline (1.0 g, 3.51 mmol), K_2CO_3 (0.97 g, 7.02 mmol), and 3-chloro-2-chloromethylpropene (0.20 ml, 1.75 mmol) in DMF (30 ml). The mixture was stirred at 70 °C for 60 h. After workup, the black oily residue was subjected to flash chromatography (CH_2Cl_2 / acetone 60:1) to furnish the product as a brownish solid.

Yield: 0.93 g (85 %).

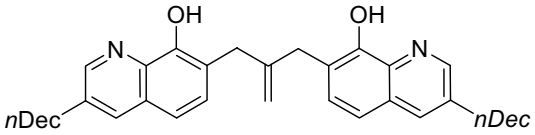
^{1}H NMR (300 MHz, $CDCl_3$, a6072842): δ = 8.71 (d, J = 2.2 Hz, 2 H), 7.77 (d, J = 2.2 Hz, 2 H), 7.24 (d, J = 5.2 Hz, 2 H), 7.23 (d, J = 3.6, 2 H), 6.99 (dd, J = 5.2, 3.6 Hz, 2 H), 5.45 (s, 2 H), 4.99 (s, 4 H), 2.69 (t, J = 7.6 Hz, 4 H), 1.62 (quint, J = 7.5 Hz, 4 H), 1.25 (m, 8 H), 1.17 (m, 20 H), 0.79 (t, J = 6.8 Hz, 6 H).

MS (EI, 70 eV): m/z (%) = 622.5 ($[M]^+$, 4.2), 338.2 ($[M\text{-}C_{19}H_{26}NO]^+$, 100).

IR (KBr): ν 2924, 2854, 1570, 1492, 1463, 1378, 1264, 1180, 1104, 757, 725 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{42}H_{58}N_2O_2 \cdot 0.5\ H_2O$ (631.9): C 79.83, H 9.41, N 4.43; found: C 80.02, H 9.46, N 4.36.

7,7'-(2-Methylenepropane-1,3-diyl)bis(3-*n*-decylquinolin-8-ol) (15-H_2)



Prepared according to **GP-2** (175-180 °C, 7 h), using diether compound **14** (0.90 g, 1.45 mmol). The product was purified by recrystallization from CH_2Cl_2 by slow addition of MeOH to furnish an off-white solid.

Yield: 0.85 g (94 %); mp 75-76 °C.

^{1}H NMR (300 MHz, $CDCl_3$, a6080228): δ = 8.60 (d, J = 2.1 Hz, 2 H), 7.86 (d, J = 2.1 Hz, 2 H), 7.36 (d, J = 8.2 Hz, 2 H), 7.22 (dd, J = 8.2 Hz, 2 H), 4.84 (s, 2 H), 3.64 (s, 4 H), 2.78 (t, J = 7.7 Hz, 4 H), 1.70 (quint, J = 7.7 Hz, 4 H), 1.35 (m, 8 H), 1.26 (m, 20 H), 0.88 (t, J = 7.0 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$, 6080254): δ = 149.5 (C), 149.3 (CH), 147.1 (C), 136.8 (C), 135.4 (C), 134.1 (CH), 130.1 (CH), 127.0 (C), 120.2 (C), 116.7 (CH), 112.4 (CH_2), 36.0 (CH_2), 33.2

(CH_2), 31.9 (CH_2), 31.2 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 22.6 (CH_2), 14.1 (CH_3).

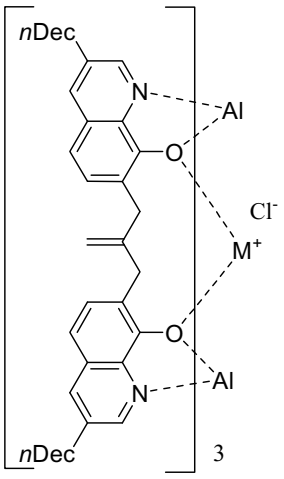
MS (EI, 70 eV): m/z (%) = 622.4 ($[M]^+$, 1.7), 334.2 ($[M\text{-}C_{20}H_{28}NO]^+$, 100).

IR (KBr): ν 3306, 2923, 2851, 1651, 1496, 1471, 1413, 1382, 1288, 1241, 1179, 1098, 899, 775, 725, 660 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{42}H_{58}N_2O_2$ (622.9): C 80.99, H 9.38, N 4.50; found: C 81.15, H 9.33, N 4.54.

General procedure (GP-8) for the synthesis of metalla-cryptates $[M(15)_3Al_2]Cl$

A solution of hydrated $AlCl_3$ (0.031 g, 0.23 mmol, 2.2 equiv.) and a base M_2CO_3 (M = K, Rb, Cs) (0.64 mmol, 6.0 equiv.) or NH_4OAc (0.05 g, 0.64 mmol, 6.0 equiv.) in MeOH / H_2O (4 ml / 1 ml) were added to a solution of ligand **15**-H_2 (0.20 g, 0.32 mmol, 3.0 equiv.) in CH_2Cl_2 (10 ml). The mixture was refluxed for 15 h; the desired complex formed a film which adhered to the reaction flask when the solvent phase was decanted off. The crude product was washed with ice distilled water and MeOH, and then dried in vacuum. The purification either by recrystallization or flash column chromatography resulted in light brown or greenish solids.



$[K(15)_3Al_2]Cl$

Purification by column chromatography (acetone / CH_2Cl_2 1:3) afforded a light brown solid.

Yield: 0.090 g (42 %).

^1H NMR (300 MHz, $CDCl_3$, a7060818): δ = 8.16 (s, 6 H), 7.44 (d, J = 8.2 Hz, 6 H), 7.15 (d, J = 8.2 Hz, 6 H), 6.58 (s, 6 H), 4.30 (s, 6 H), 3.72 (d, J = 17 Hz, 6 H), 3.12 (d, J = 17 Hz, 6 H), 2.53 (t, J = 7.0 Hz, 12 H), 1.41 (m, 12 H), 1.25-1.17, (m, 84 H), 0.88 (t, J = 5.1 Hz, 18 H).

MS (ESI+): m/z (%) = 1991.2 ($\{[K(\mathbf{15})_3Al_2]Cl+H\}^+$, 100).

IR (KBr): ν 2925, 2850, 1588, 1469, 1380, 1340, 1197, 1108, 894, 761, 672, 643 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{126}H_{168}N_6O_6Al_2KCl \cdot H_2O$ (2008.4): C 75.32, H 8.53, N 4.18; found: C 75.19, H 8.41, N 4.01.

$[Rb(15)_3Al_2]Cl$

Purification by recrystallization (acetone / *n*-hexane 1:10) afforded a green solid.

Yield: 0.185 g (84 %).

^{1}H NMR (300 MHz, $CDCl_3$, a5051931): δ = 8.16 (d, J = 1.5 Hz, 6 H), 7.43 (d, J = 8.4 Hz, 6 H), 7.14 (d, J = 8.4 Hz, 6 H), 6.68 (d, J = 1.5 Hz, 6 H), 4.28 (s, 6 H), 3.74 (d, J = 17 Hz, 6 H), 3.11 (d, J = 17 Hz, 6 H), 2.54 (t, J = 7.2 Hz, 12 H), 1.44 (m, 12 H), 1.25, (m, 84 H), 0.89 (t, J = 6.6 Hz, 18 H).

MS (ESI+): m/z (%) = 2038.8 ({[Rb(**15**)$_3$Al$_2$]Cl+H}$^+$, 100).

IR (KBr): ν 2923, 2852, 1648, 1589, 1469, 1382, 1109, 762, 672 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{126}H_{168}N_6O_6Al_2RbCl \cdot H_2O$ (2055.6): C 73.62, H 8.34, N 4.09; found: C 73.54, H 8.52, N 3.77.

[Cs(15)$_3$Al$_2$]Cl

Purification by column chromatography with gradient elution (acetone / CH_2Cl_2 1:3 → 1:1) afforded a light green solid.

Yield: 0.17 g (76 %).

^{1}H NMR (300 MHz, $CDCl_3$, a6072531): δ = 8.17 (d, J = 1.5 Hz, 6 H), 7.43 (d, J = 8.4 Hz, 6 H), 7.13 (d, J = 8.4 Hz, 6 H), 6.91 (d, J = 1.5 Hz, 6 H), 4.31 (s, 6 H), 3.67 (d, J = 17.3 Hz, 6 H), 3.10 (d, J = 17.3 Hz, 6 H), 2.57 (t, J = 7.3 Hz, 12 H), 1.67 (br. s, 12 H), 1.47 (m, 12 H), 1.25-1.17 (m, 72 H), 0.88 (t, J = 6.7 Hz, 18 H).

MS (ESI+): m/z (%) = 2088.1 ({[Cs(**15**)$_3$Al$_2$]Cl+H}$^+$, 100).

IR (KBr): ν 2924, 2852, 1646, 1590, 1470, 1382, 1196, 1107, 895, 763, 672 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{126}H_{168}N_6O_6Al_2CsCl \cdot H_2O$ (2103.1): C 71.98, H 8.15, N 4.00; found: C 71.82, H 8.08, N 3.81.

[(NH$_4$)(15)$_3$Al$_2$]Cl / [(NH$_4$)(15)$_3$Al$_2$](OAc)

Purification by recrystallization (acetone / *n*-hexane 1:10) afforded a greenish solid.

Yield: 0.16 g (72 %).

^{1}H NMR (300 MHz, $CDCl_3$, a7081828): δ = 8.16 (s, 6 H), 7.44 (d, J = 8.4 Hz, 6 H), 7.15 (d, J = 8.4 Hz, 6 H), 6.65 (s, 6 H), 4.30 (s, 6 H), 3.72 (d, J = 17.1 Hz, 6 H), 3.10 (d, J = 17 Hz, 6 H), 2.53 (t, J = 7.4 Hz, 12 H), 1.79 (br. s, 12 H), 1.25 (m, 84 H), 0.88 (t, J = 6.6 Hz, 18 H).

MS (ESI+): m/z (%) = 1970.0 ({[(NH$_4$)(**15**)$_3$Al$_2$]Cl+H}$^+$, 100), 1993.8 ({[(NH$_4$)(**15**)$_3$Al$_2$](OAc)+H}$^+$, 29.6).

IR (KBr): ν 2924, 2853, 1647, 1590, 1469, 1381, 1109, 763 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{126}H_{168}N_6O_6Al_2NH_4CH_3CO_2 \cdot CHCl_3$ (2112.3): C 73.32, H 8.39, N 4.64; found: C 73.44, H 8.06, N 4.17 *or* calcd. (%) for $C_{126}H_{168}N_6O_6Al_2NH_4Cl \cdot CHCl_3$ (2088.2): C 73.00, H 8.35, N 4.69; found: C 73.09, H 8.25, N 4.12.

[(15)$_3$Al$_2$]

Purification by recrystallization (acetone / *n*-hexane 1:10) afforded a brownish solid.

Yield: 0.11 g (51 %).

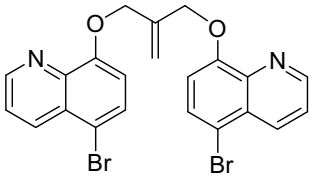
^{1}H NMR (300 MHz, $CDCl_3$, a7081826): δ = 8.63 (s, 6 H), 8.14 (s, 6 H), 7.52 (d, J = 8.4 Hz, 6 H), 7.35 (d, J = 8.4 Hz, 6 H), 4.87 (s, 6 H), 3.65 (s, 12 H), 2.85 (t, J = 7.5 Hz, 12 H), 1.74-1.72 (m, 12 H), 1.26 (m, 84 H), 0.87 (t, J = 3.3 Hz, 18 H).

MS (ESI+): m/z (%) = 1917.0 ({[(**15**)$_3$Al$_2$]+H}$^+$, 100).

IR (KBr): ν 3394, 2924, 2852, 1646, 1588, 1467, 1380, 1107, 764 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{126}H_{168}N_6O_6Al_2 \cdot CHCl_3$ (2036.2): C 74.92, H 8.37, N 4.13; found: C 74.68, H 8.75, N 3.88.

8,8'-(2-Methylenepropane-1,3-diyl)bis(oxy)bis(5-bromoquinoline) (107)



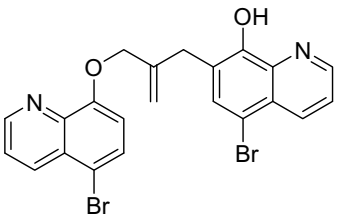
Prepared according to **GP-1,** using 5-bromoquinolin-8-ol **31b** (1.0 g, 4.46 mmol), 3-chloro-2-chloromethyl-propene (0.26 ml, 2.23 mmol), and K_2CO_3 (3.08 g, 22.30 mmol) in dry DMF (30 ml). The mixture was stirred at 60 °C for 15 h. After the usual workup procedure, the residue was chromatographed with gradient elution (EtOAc / *n*-hexane 1:2 → 1:1 → EtOAc) to furnish a grey solid, which was additionally recrystallized from MeOH.

Yield: 0.215 g (19 %).

^{1}H NMR (300 MHz, $CDCl_3$, a5081560): δ = 8.94 (dd, J = 4.2, 1.6 Hz, 2 H), 8.48 (dd, J = 8.7, 1.6 Hz, 2 H), 7.64 (d, J = 8.4 Hz, 2 H), 7.53 (dd, J = 8.7, 4.2 Hz, 2 H), 7.07 (d, J = 8.4 Hz, 2 H), 5.55 (s, 2 H), 5.06 (s, 4 H).

MS (EI, 70 eV): m/z (%) = 500.0 ([M]$^+$, 3.5), 276.0 ([M-C_9H_5BrNO]$^+$, 100).

5-Bromo-7-(2-((5-bromoquinolin-8-yloxy)methyl)allyl)quinolin-8-ol (108)



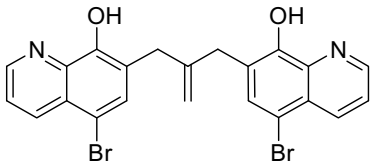
Obtained as a brown solid after incomplete rearrangement of diether **107** (0.15 g, 0.30 mmol) according to **GP-2** (130 °C, 7 h).

Yield: 0.15 g (100 %).

^{1}H NMR (300 MHz, $CDCl_3$, a5080191): δ = 8.90 (dd, J = 4.2, 1.4 Hz, 1 H), 8.85 (dd, J = 4.1, 1.7 Hz, 1 H), 8.49 (dd, J = 8.5, 1.7 Hz, 1 H), 8.42 (dd, J = 8.9, 1.7 Hz, 1 H), 7.93 (s, 1 H), 7.70 (d, J = 8.2 Hz, 1 H), 7.52 (dd, J = 8.5, 4.1 Hz, 1 H), 7.49 (dd, J = 9.0, 4.7 Hz, 1 H), 7.12 (d, J = 8.2 Hz, 1 H), 5.52 (d, J = 1.0 Hz, 1 H), 5.49 (d, J = 0.9 Hz, 1 H), 5.25 (s, 2 H), 5.15 (s, 2 H).

MS (EI, 70 eV): m/z (%) = 501.1 ([M+1]$^+$, 4.3), 276.0 ([M-$C_9H_5N_1O_1Br_1$]$^+$, 100).

7,7'-(2-Methylenepropane-1,3-diyl)bis(5-bromoquinolin-8-ol) (109)



Prepared according to **GP-2** (147 °C, 9 h), using the product of incomplete conversion **108** (0.15 g, 0.30 mmol). Recrystallization from MeOH / CH_2Cl_2 (1:1) gave the product as an off-white solid.

Yield: 0.12 g (78 %); mp 176 °C (decomp.).

^{1}H NMR (300 MHz, DMSO-d_6, a7062748): δ = 8.67 (dd, J = 4.2, 1.5 Hz, 2 H), 8.37 (dd, J = 8.7, 1.5 Hz, 2 H), 7.67 (dd, J = 8.7, 4.2 Hz, 2 H), 7.61 (s, 2 H), 4.78 (s, 2 H), 3.56 (s, 4 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 150.5, 148.8, 148.7, 146.1, 138.7, 134.8, 132.6, 122.8, 122.7, 112.9, 107.9, 35.5.

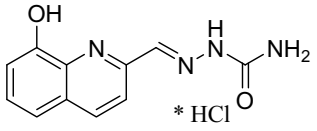
MS (EI, 70 eV): m/z (%) = 499.7 ([M]$^+$, 9.1), 263.9 ([M-$C_{11}H_8BrNO$]$^+$, 100).

IR (KBr): ν 3342, 1589, 1566, 1491, 1459, 1399, 1356, 1301, 1269, 1236, 1198, 1155, 1101, 1049, 917, 792, 718, 626, 561 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{22}H_{16}N_2O_2Br_2$ (500.2): C 52.83, H 3.22, N 5.60; found: C 52.90, H 3.52, N 5.38.

5.4. Tetradentate Ligands for Monomeric and Dimeric Complexes. Preparation of Complex Salts with Semicarbazone and SAMP Hydrazone Ligands (17-20,22)

(*E*)-2-((8-Hydroxyquinolin-2-yl)methylene)hydrazinecarboxamide hydrochlorid (17-H · HCl)



Prepared according to **GP-3**, starting from semicarbazide hydrochloride (0.141 g, 1.27 mmol). After the workup, the product was obtained in pure form.

Yield: 0.31 g (95 %); mp 231 °C (decomp.).

^{1}H NMR (400 MHz, DMSO-d_6, a5040742): δ = 11.22 (s, 1 H), 8.60 (d, J = 9.1 Hz, 2 H), 8.42 (d, J = 9.1 Hz, 1 H), 8.29 (s, 1 H), 7.53 (dd, J = 8.0, 7.4 Hz, 1 H), 7.49 (dd, J = 8.0, 1.5 Hz, 1 H), 7.25 (dd, J = 7.4, 1.5 Hz, 1 H), 6.80 (br. s, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 157.1 (C), 150.6 (C), 150.1 (C), 142.8 (CH), 135.0 (CH), 131.6 (C), 131.2 (CH), 129.4 (C), 119.1 (CH), 115.7 (CH), one CH could not be observed.

MS (EI, 70 eV): m/z (%) = 230.07 ([M]$^+$, 49.9), 186 ([M-$C_{10}H_8NO$]$^+$, 100).

IR (KBr): ν 3363, 3215, 3160, 2958, 1709, 1574, 1506, 1416, 1385, 1179, 1104 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{11}H_{10}O_2N_4 \cdot HCl \cdot H_2O$ (284.5): C 46.41, H 4.60, N 19.68; found C 46.72, H 4.90, N 19.62.

Vapour diffusion of Et_2O into MeOH solution afforded X-ray quality crystals.

General procedure (GP-9) for the preparation of complex salts with semicarbazone ligand 17-H · HCl

Equimolar amounts of hydrated $LnCl_3$ or $Ln(NO_3)_3$, K_2CO_3 (0.02 g, 0.15 mmol), and semicarbazone ligand **17**-H · HCl (0.04 g, 0.15 mmol) were dissolved in MeOH (15 ml) and stirred at rt for 2 d. The solvent was removed under reduced pressure and the complex was isolated by extraction with a MeOH / CH_2Cl_2 solvent mixture.

Yield: 95-97 %.

$[(17)Y(NO_3)_2]_2$

Prepared according to **GP-9**, using $Y(NO_3) \cdot 6\ H_2O$ (0.057 g, 0.15 mmol).

^{1}H NMR (300 MHz, DMSO-d_6, a5011222): δ = 8.44 (d, J = 8.5 Hz, 2 H), 8.33 (s, 2 H), 7.79 (d, J = 8.5 Hz, 2 H), 7.39 (ps. t, J = 7.7 Hz, 2 H), 6.99 (d, J = 7.7 Hz, 2 H), 6.62 (d, J = 7.7 Hz, 2 H).

IR (KBr): ν 3433, 3346, 3240, 1674, 1542, 1502, 1453, 1386, 1331, 1155, 738 cm^{-1}.

X-Ray quality crystals of [(**17**)Y(Cl)$(NO_3)]_2$ were obtained by mixing **17-**H · HCl, $NaHCO_3$, and $Y(NO_3)_3 \cdot 6\ H_2O$ in DMF followed by crystallization by slow diffusion of Et_2O into the resulting solution.

Crystal data for [(**17**)Y(Cl)$(NO_3)]_2$: formula: $[(C_{11}H_9N_4O_2)Y(C_3H_7NO)_2(NO_3)]_2Cl_2 \cdot 2\ C_3H_7NO$; triclinic; code FRO3118; space group Pī (No. 2); a / Å = 10.285(1); b / Å = 11.109(1); c / Å = 13.741(1); α / ° = 68.92(1); β / ° = 68.11(1); γ / ° = 81.10(1); V / $Å^3$ = 1358.9(2); D_c / g cm^{-3} = 1.552; Z = 1; μ / mm^{-1} = 2.302; T / K = 198; $2\theta_{max}$ / ° = 55.82; measd. refl. = 14430; unique refl. = 6462; observed refl. = 5479; R_{int} = 0.056; parameters 328; $R[I \leq 2\sigma(I)]/wR^2$ 0.068/0.193; ρ(min./max) / e $Å^{-3}$ 3.03/-1.40.

$[(17)_2Y][NO_3]$

Prepared according to **GP-9**, except for **17**-H · HCl, K_2CO_3, and $Y(NO_3)_3 \cdot 6\ H_2O$ were used in a 2:2:1 ratio.

^{1}H NMR (300 MHz, DMSO-d_6, a5011221): δ = 8.57 (s, 2 H), 8.53 (d, J = 8.6 Hz, 2 H), 7.90 (d, J = 8.6 Hz, 2 H), 7.31 (t, J = 7.8 Hz, 2 H), 6.99 (d, J = 7.8 Hz, 2 H), 6.36 (d, J = 7.8 Hz, 2 H).

IR (KBr): ν 3341, 3173, 1682, 1656, 1544, 1499, 1446, 1386, 1339, 1153, 835, 739, 490 cm^{-1}.

Pos. FAB MS (3-NBA): m/z = 545 $[(\mathbf{17})_2Y]^+$.

No correct elemental analyses could be obtained for the yttrium(III) complexes. This is probably due to an equilibrium between the 1:1 and 2:1 complexes.

X-Ray quality crystals were obtained from MeOH / Et_2O.

Crystal data for [(**17**)$_2$Y][NO_3]: formula: [($C_{11}H_9N_4O_2$)($C_{11}H_8N_4O_2$)Y] · 3 CH_3OH · $C_4H_{10}O$; monoclinic; code FRO3203; space group $P2_1/n$ (No. 14); a / Å = 16.174(1); b / Å = 11.664(1); c / Å = 18.932(1); α / ° = 90; β / ° = 106.87(1); γ / ° = 90; V / Å^3 = 3412.2(4); D_c / g cm^{-3} = 1.395; Z = 4; μ / mm^{-1} = 1.767; T / K = 198(2); $2\theta_{max}$ / ° = 50.00; measd. refl. = 26738; unique refl. = 5998; observed refl. = 4325; R_{int} = 0.087; parameters 418; $R[I \leq 2\sigma(I)]/wR^2$ 0.058/0.153; ρ(min./max) / e Å^{-3} 1.40/-0.78.

[(17)La(NO_3)$_2$]$_2$

Prepared according to **GP-9**, using La(NO_3)$_2$ · 6 H_2O (0.065 g, 0.15 mmol).

^{1}H NMR (300 MHz, DMSO-d_6, a5012869): δ = 8.37 (d, J = 8.4 Hz, 2 H), 8.35 (s, 2 H), 7.75 (d, J = 8.4 Hz, 2 H), 7.36 (t, J = 7.9 Hz, 2 H), 6.89 (d, J = 7.9 Hz, 2 H), 6.53 (d, J = 7.9 Hz, 2 H).

IR (KBr): ν 3438, 3344, 1668, 1548, 1501, 1450, 1312, 1148, 1092, 837, 731 cm^{-1}.

Elemental analysis: calcd. (%) for ($C_{11}H_9O_8N_6La$)$_2$ · 6 H_2O (1091.8): C 24.19, H 2.77, N 15.39; found C 24.65, H 3.09, N 15.67.

Orange single crystals were obtained by slow evaporation of MeOH solution.

Crystal data for [(**17**)La(NO_3)$_2$]$_2$: formula: [($C_{11}H_9N_4O_2$)La(NO_3)(CH_3OH)$_2$]$_2$(NO_3)$_2$; monoclinic; code FRO3205; space group $P2_1/n$ (No. 14); a / Å = 11.702(1); b / Å = 13.526(1); c / Å = 12.495(1); α / ° = 90; β / ° = 108.70(1); γ / ° = 90; V / Å^3 = 1873.3(3); D_c / g cm^{-3} = 1.972; Z = 2; μ / mm^{-1} = 2.349; T / K = 198(2); $2\theta_{max}$ / ° = 55.84; measd. refl. = 17418; unique refl. = 4476; observed refl. = 3867; R_{int} = 0.044; parameters 273; $R[I \leq 2\sigma(I)]/wR^2$ 0.040/0.103; ρ(min./max) / e Å^{-3} 0.48/-1.10.

H[(17)ErCl_3]

Prepared according to **GP-9**, using ErCl_3 · 6 H_2O (0.067 g, 0.15 mmol) in the absence of base.

IR (KBr): ν 3196, 1662, 1545, 1505, 1455, 1386, 1390, 1335, 1270, 1182, 1159, 1096, 738, 616 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{11}H_{10}O_2N_4ErCl_3$ · 0.5 H_2O · 0.5 CH_3OH (529.26): C 26.12, H 2.48, N 10.59; found C 26.33, H 3.14, N 11.13.

X-Ray quality crystals were obtained from MeOH / Et_2O solvent system.

Crystal data for H[(**17**)$ErCl_3$]: formula: [($C_{11}H_{10}N_4O_2$)$ErCl_3$] · CH_3OH; monoclinic; code FRO3166; space group $P2_1/n$ (No. 14); *a* / Å = 7.982(1); *b* / Å = 19.237(1); *c* / Å = 10.999(1); *α* / ° = 90; *β* / ° = 95.21(1); *γ* / ° = 90; *V* / Å^3 = 1681.9(3); D_c / g cm^{-3} = 2.116; *Z* = 4; *μ* / mm^{-1} = 5.483; T / K = 198(2); $2\theta_{max}$ / ° = 55.74; measd. refl. = 10239; unique refl. = 3995; observed refl. = 3659 R_{int} = 0.051; parameters 227; $R[I \leq 2\sigma(I)]/wR^2$ 0.034/0.092; *ρ*(min./max) / e Å^{-3} 1.46/-2.08.

H[(17)$HoCl_3$]

Prepared according to **GP-9**, using $HoCl_3$ · 6 H_2O (0.066 g, 0.15 mmol) in the absence of base.

IR (KBr): ν 3407, 3140, 1679, 1607, 1569, 1437, 1385, 1334, 1175, 1086, 1004, 848, 755 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{11}H_{10}O_2N_4HoCl_3$ · CH_3OH · 3 H_2O (587.6): C 24.53, H 3.43, N 9.50; found C 24.46, H 3.73, N 9.50.

X-ray quality crystals were obtained from MeOH / Et_2O solvent system.

Crystal data for H[(**17**)$HoCl_3$]: formula: [($C_{11}H_{10}N_4O_2$)$HoCl_3$] · CH_3OH; monoclinic; code FRO3168; space group $P2_1/n$ (No. 14); *a* / Å = 8.001(1); *b* / Å = 19.276(1); *c* / Å = 11.010(1); *α* / ° = 90; *β* / ° = 95.35(1); *γ* / ° = 90; *V* / Å^3 = 1690.6(3); D_c / g cm^{-3} = 2.096; *Z* = 4; *μ* / mm^{-1} = 5.171; T / K = 198(2); $2\theta_{max}$ / ° = 55.76; measd. refl. = 10619; unique refl. = 4012; observed refl. = 3823 R_{int} = 0.053; parameters 219; $R[I \leq 2\sigma(I)]/wR^2$ 0.038/0.103; *ρ*(min./max) / e Å^{-3} 2.53/-2.40.

K[$(17)_2Eu_2(NO_3)_5$]

Prepared according to **GP-9**, using $Eu(NO_3)_3$ · 6 H_2O (0.067 g, 0.15 mmol).

IR (KBr): ν 3427, 1674, 1554, 1505, 1457, 1308, 1155, 1094, 1012, 840, 736 cm^{-1}.

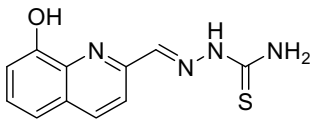
Elemental analysis: calcd. (%) for ($C_{22}H_{18}O_{19}N_{13}Eu_2$)K · 4 H_2O (1183.4): C 22.33, H 2.21, N 15.38; found C 22.06, H 2.26, N 15.11.

Slow diffusion of Et_2O into a DMF solution of components **17**-H · HCl, $NaHCO_3$, $Eu(NO_3)_3$ · 6 H_2O taken in equimolar ratio gave yellow prismatic crystals of H{Eu_2(**17**)$_2(NO_3)_5$}.

Crystal data for [(**17**)$Eu(NO_3)_{2.5}$DMF]: formula: [($C_{11}H_{10}N_4O_2$)Eu]$_2$ Na · 5 NO_3 · 2 C_3H_7NO; tetragonal; code FRO3207; space group $I4_1/a$ (No. 88); *a* / Å =17.752(1); *b* / Å = 17.752(1); *c* / Å = 29.372(1); *α* / ° = 90; *β* / ° = 90; *γ* / ° = 90; *V* / Å^3 = 9256.1(8); D_c / g cm^{-3} = 1.782; *Z* = 8; *μ* / mm^{-1} = 2.786; T / K = 198(2); $2\theta_{max}$ / ° = 55.72; measd. refl. = 35469; unique refl. =

5512; observed refl. = 4081 R_{int} = 0.057; parameters 313; $R[I \leq 2\sigma(I)]/wR^2$ 0.048/0.135; ρ(min./max) / e Å^{-3} 0.61/-0.79.

(*E*)-2-((8-Hydroxyquinolin-2-yl)methylene)hydrazinecarbothioamide (18)



Prepared according to **GP-3**, starting from thiosemicarbazide hydrochloride (0.162 g, 1.27 mmol). The workup procedure was completed by recrystallization of crude product from EtOH to give a pale solid.

Yield: 0.26 g (89 %); mp 254 °C.

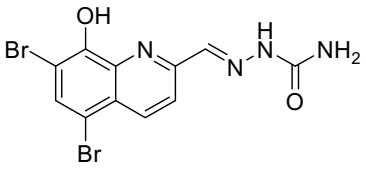
^{1}H NMR (300 MHz, DMSO-d_6, a4122308): δ = 11.85 (br. s, 1 H), 9.85 (s, 1 H), 8.43 Hz (d, J = 8.9 Hz, 1 H), 8.32 (br. s, 1 H), 8.28 (d, J = 8.9 Hz, 1 H), 7.43 (dd, J = 8.1, 7.4 Hz, 1 H), 7.38 (dd, J = 8.2, 1.4 Hz, 1 H), 7.07 (dd, J = 7.4, 1.4 Hz, 1 H).

MS (EI, 70 eV): m/z (%) = 246.03 ([M]$^+$, 100), 186.03 ([M-$CSNH_2$]$^+$, 59.1).

IR (KBr): ν 3386, 3246, 3151, 3024, 2989, 1601, 1537, 1506, 1464, 1328, 1291, 1254, 1110, 1086, 838, 762, 719, 573, 504 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{11}H_{10}N_4OS \cdot 0.5\ H_2O$ (255.3): C 51.75, H 4.34, N 21.95; found: C 51.47, H 4.21, N 21.71.

(*E*)-2-((5,7-Dibromo-8-hydroxyquinolin-2-yl)methylene)hydrazinecarboxamide (19)



A mixture of 5,7-dibromo-8-hydroxycarboxaldehyde **16c** (0.20 g, 0.60 mmol) and semicarbazide hydrochloride (0.074 g, 0.66 mmol) in MeOH was stirred at rt for 16 h. After evaporation of the solvent in vacuum, the crude product was purified by recrystallization from EtOH to furnish a pale solid.

Yield: 0.24 g (95 %); mp 261 °C.

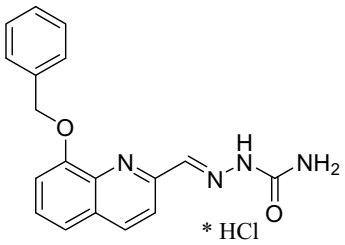
^{1}H NMR (400 MHz, DMSO-d_6, a5061434): δ = 10.92 (s, 1 H), 10.74 (br. s, 1 H), 8.52 (d, J = 8.4 Hz, 1 H), 8.32 (d, J = 8.4 Hz, 1 H), 8.31 (s, 1 H), 8.12 (s, 1 H), 6.82 (br. s, 2 H).

MS (CI, 100 eV): m/z (%) = 389.9 ([M]$^+$, 5.1), 347.9 ([M-$CONH_2$]$^+$, 100).

IR (KBr): ν 3457, 1703, 1577, 1489, 1438, 1350, 1323, 1267, 1164, 1134, 928 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{11}H_8N_4O_2Br_2 \cdot 0.5\ H_2O \cdot 0.5$ MeOH (413.0): C 33.44, H 2.08, N 13.56; found: C 33.23, H 2.86, N 13.20.

(*E*)-2-((8-(Benzyloxy)quinolin-2-yl)methylene)hydrazinecarboxamide (20· HCl)



Prepared according to **GP-3**, but using 8-benzyloxyquinoline-2-carboxaldehyde **28** (0.20 g, 0.76 mmol) instead of 8-hydroxyquinoline-2-carboxaldehyde and semicarbazide hydrochloride (0.093 g, 0.84 mmol) as reactants. After workup, the yellowish product was obtained in pure form.

Yield: 0.26 g (96 %); mp 221 °C.

^{1}H NMR (300 MHz, DMSO-d_6, a7062469): δ = 11.16 (br. s, 1 H), 8.62 Hz (s, 2 H), 8.59 (s, 1 H), 7.50 (m, 10 H), 5.44 (s, 2 H).

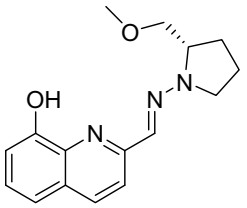
^{13}C NMR (75 MHz, DMSO-d_6): δ = 156.0 (C), 151.9 (C), 151.3 (C), 139.7 (C), 139.6 (C), 136.4 (C), 128.7 (CH), 128.4 (CH), 128.1 (CH), 127.9 (CH), 127.7 (CH), 121.2 (CH), 119.9 (CH), 118.6 (CH), 112.3 (CH), 70.1 (CH_2).

MS (EI, 70 eV): m/z (%) = 320.1 ($[M]^+$, 28.2), 261.1 ($[M\text{-}C_1H_3N_2O_1]^+$, 100).

IR (KBr): ν 3455, 1707, 1593, 1571, 1454, 1379, 1322, 1169, 1094, 973, 951, 845, 771, 510 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{18}H_{16}N_2O_4$ · HCl (356.8): C 60.59, H 4.80, N 15.70; found: C 60.32, H 5.09, N 15.16.

(*S,E*)-2-((2-(Methoxymethyl)pyrrolidin-1-ylimino)methyl)quinolin-8-ol (22-H)



Prepared according to **GP-3**, starting from SAMP **21** (0.165 g, 1.27 mmol, 1.1 equiv.). The crude residue was only washed with Et_2O and dried in vacuum to give the yellowish oily product.

Yield: 0.31 g (94 %).

^{1}H NMR (300 MHz, $CDCl_3$, a5102438): δ = 7.98 (m, 2 H), 7.33 (d, J = 7.4 Hz, 1 H), 7.30 (d, J = 7.4 Hz, 1 H), 7.23 (dd, J = 8.2, 1.5 Hz, 1 H), 7.11 (dd, J = 7.4, 1.5 Hz, 1 H), 3.83 (m, 1 H), 3.68 (dd, J = 9.4, 3.7 Hz, 1 H), 3.55 (dd, J = 9.4, 6.7 Hz, 1 H), 3.46 (m, 1 H), 3.40 (s, 3 H), 3.21 (m, 1 H), 2.00 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.6 (C), 151.8 (C), 137.7 (C), 135.5 (CH), 130.9 (CH), 127.3 (C), 126.4 (CH), 118.0 (CH), 117.7 (CH), 110.0 (CH), 74.3 (CH_2), 62.9 (CH), 59.3 (CH_3), 48.4 (CH_2), 27.0 (CH_2), 22.3 (CH_2).

MS (ESI+): m/z (%) = 286.2 ($[M+H]^+$, 100).

Synthesis of complex [(22)(22-H)YCl$_2$]

The hydrazone ligand **22**-H (0.04 g, 0.14 mmol, 2.0 equiv.) and $YCl_3 \cdot 6\ H_2O$ (0.021 g, 0.07 mmol, 1.0 equiv.) in MeOH (10 ml) were stirred for 15 h in the presence of K_2CO_3 (0.01 g, 0.072 mmol, 1.9 equiv.) at rt. After removing the solvent in vacuum the crude residue was dried in vacuum and extracted with CH_2Cl_2; the evaporation of the solvent under reduced pressure furnished the product as a red powder.

Yield: 0.053 g (100 %).

^{1}H NMR (300 MHz, $CDCl_3$, a5102760): δ = 15.89 (br. s, 1 H), 8.25 (d, J = 8.4 Hz, 1 H), 8.16 (d, J = 8.4 Hz, 1 H), 7.99 (m, 1 H), 7.70 (d, J = 7.8 Hz, 1 H), 7.49 (dd, J = 8.1, 7.8 Hz, 1 H), 7.44-7.28 (m, 5 H), 6.99 (d, J = 8.2 Hz, 1 H), 6.69 (d, J = 7.4 Hz, 1 H), 5.23 (d, J = 9.1 Hz, 1 H), 4.94 (d, J = 6.2 Hz, 1 H), 4.06 (m, 1 H), 3.99 (s, 2 H), 3.85 (m, 2 H), 3.70 (s, 3 H), 3.56 (m, 3 H), 3.41 (s, 3 H), 2.31 (m, 1 H), 2.03 (m, 3 H), 1.71 (m, 2 H), 1.61 (m, 2 H).

MS (ESI+): m/z (%) = 657.4 ([(**22**)(**22**-H)YCl_2 - HCl - Cl]$^+$, 100).

IR (KBr): ν 3851, 3745, 3406, 2929, 2873, 2361, 2338, 1629, 1586, 1527, 1456, 1389, 1323, 1235, 1099, 848, 744, 677, 598 cm^{-1}.

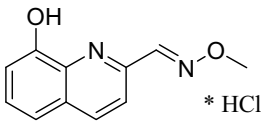
Elemental analysis: calcd. (%) for $C_{32}H_{37}N_6O_4YCl_2 \cdot H_2O \cdot CH_3OH$ (779.5): C 50.84, H 5.56, N 10.78; found: C 51.06, H 5.45, N 11.01.

X-Ray quality crystals of [(**22**)(**22**-H)YCl_2] were obtained by slow evaporation of a concentrated MeCN / $CHCl_3$ solution.

Crystal data for [(**22**)(**22**-H)YCl_2]: formula $C_{32}H_{37}Cl_2N_6O_4Y$, M = 729.49, orange crystal 0.10 x 0.06 x 0.05 mm, a = 15.660(1), b = 12.582(1), c = 17.051(1) Å, β = 104.64(1)°, V = 3250.6(4) Å^3, ρ_{calc} = 1.491 g cm^{-3}, μ = 2.005 mm^{-1}, empirical absorption correction (0.825 ≤ T ≤ 0.906), Z = 4, monoclinic, space group $P2_1$ (No. 4), λ = 0.71073 Å, T = 198 K, ω and φ scans, 12952 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.54 Å^{-1}, 7864 independent (R_{int} = 0.081) and 5566 observed reflections [$I \geq 2\ \sigma(I)$], 815 refined parameters, R = 0.066, wR^2 = 0.113, Flack parameter -0.004(11), max. residual electron density 0.43 (–0.45) e Å^{-3}, hydrogen atom at nitrogen from difference Fourier calculations, others are calculated and refined riding, due to crystal size the analysis is of limited accuracy.

5.5. Tridentate Ligands Containing Oxime, Imine, or Hydrazone Functionalities (23-25)

(*E*)-8-Hydroxyquinoline-2-carboxaldehyde *O*-methyl oxime hydrochloride (23)



Prepared according to **GP-3**, using *O*-methylhydroxylamine hydrochloride (0.106 g, 1.27 mmol). The workup procedure was completed by recrystallization of the crude product from EtOH to give a yellow powder.

Yield: 0.254 g (92 %); mp 201 °C.

^{1}H NMR (400 MHz, DMSO-d_6, a7060807): δ = 8.61 (d, J = 8.6 Hz, 1 H), 8.05 (d, J = 8.6 Hz, 1 H), 8.54 (s, 1 H), 7.58 (dd, J = 8.0, 7.4 Hz, 1 H), 7.53 (dd, J = 8.0, 1.6 Hz, 1 H), 7.37 (dd, J = 7.4, 1.6 Hz, 1 H), 4.05 (s, 3 H).

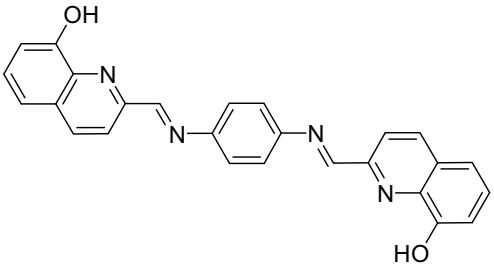
^{13}C NMR (75 MHz, DMSO-d_6): δ = 151.5 (C), 147.8 (C), 146.8 (CH), 140.5 (CH), 134.0 (C), 129.5 (CH), 129.1 (C), 118.0 (CH), 117.8 (CH) 114.1 (CH), 63.8 (CH_3).

MS (EI, 70 eV): m/z (%) = 202.1 ($[M]^+$, 100).

IR (KBr): ν 1627, 1596, 1372, 1039, 975, 950, 840, 773, 571 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{11}H_{10}N_2O_2 \cdot HCl$ (238.7): C 55.36, H 4.65, N 11.74; found: C 55.67, H 4.74, N 11.71.

2,2'-(1*E*,1'*E*)-(1,4-Phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)-diquinolin-8-ol (24)



Prepared according to **GP-3**, starting from 1,4-diaminobenzene (0.069 g, 0.635 mmol). The crude product was recrystallized from DMF / *i*-PrOH to furnish an off-white solid.

Yield: 0.23 g (95 %); mp 231 °C.

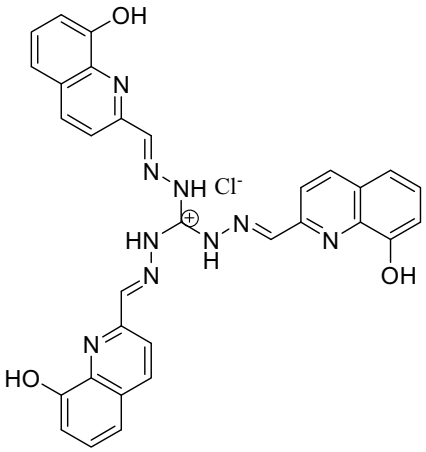
^{1}H NMR (400 MHz, DMSO-d_6, a4100639): δ = 10.01 (s, 2 H), 8.87 (s, 2 H), 8.45 Hz (d, J = 8.5 Hz, 2 H), 8.30 (d, J = 8.5 Hz, 2 H), 7.55 (s, 4 H), 7.54 (dd, J = 8.2, 7.4 Hz, 2 H), 7.48 (dd, J = 8.2, 1.4 Hz, 2 H), 7.19 (dd, J = 7.4, 1.4 Hz, 2 H).

MS (EI, 70 eV): m/z (%) = 418.1 ($[M]^+$, 100), 274.1 ($[M\text{-}C_9H_6N_1O]^+$, 47.3), 248.0 ($[M\text{-}C_{10}H_7N_2O_1]^+$, 50.4).

IR (KBr): ν 1669, 1561, 1505, 1455, 1376, 1329, 1233, 1200, 1166, 1085, 842, 750, 718, 556 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{26}H_{18}N_4O_2$ (418.4): C 74.63, H 4.34, N 13.39; found: C 74.67, H 4.56, N 13.46.

2-((*E*)-(2-(Bis((*E*)-2-ethylidenehydrazinyl)methyl)hydrazono)methyliumquinolin-8-ol) chloride (25)



Prepared according to **GP-3**, starting from triaminoguanidinium chloride[217] (0.059 g, 0.42 mmol). The crude product was recrystallized from DMF / *i*-PrOH to furnish a yellow solid.

Yield: 0.25 g (98 %); mp 214-215 °C.

^{1}H NMR (300 MHz, DMSO-d_6, a5012851): δ = 10.00 (br. s, 3 H), 9.04 (s, 3 H), 8.63 (d, J = 8.7 Hz, 3 H), 8.50 (d, J = 8.7 Hz, 3 H), 7.54 (dd, J = 8.2, 7.4 Hz, 3 H), 7.49 (dd, J = 8.2, 1.5 Hz, 3 H), 7.21 (dd, J = 7.4, 1.5 Hz, 3 H).

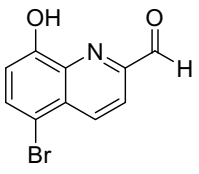
MS (ESI+): m/z (%) = 570.2 ([M-Cl]$^+$, 100).

IR (KBr): ν 1637, 1504, 1464, 1382, 1327, 1234, 1106, 839, 757 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{31}H_{24}N_9O_3Cl \cdot 3\ H_2O$ (660.1): C 56.41, H 4.58, N 19.10; found: C 56.27, H 4.59, N 19.30.

5.6. Bromosubstituted 8-Hydroxyquinoline Building Blocks (16b, 30b,c, 110)

5-Bromo-8-hydroxyquinoline-2-carboxaldehyde (16b)



To a suspension of SeO_2 (5.83 g, 52.5 mmol) in dry 1,4-dioxane (50 ml) 5-bromo-8-hydroxyquinaldine **26b** (10.0 g, 42.0 mmol) in 1,4-dioxane (200 ml) was added in small portions at 80 °C. The mixture was heated at 85 °C for 7 h, and then cooled to rt. The Se remainders were filtered off, solvent was evaporated. Addition of *i*-PrOH to the brown oily residue allowed precipitation of the product, which was collected by filtration, dissolved in EtOAc, and filtered through a pad of Celite®. The solution was concentrated in vacuum to furnish the product as yellow needles. For further purification from Se impurities the aldehyde was filtered trough silica gel using CH_2Cl_2 as an eluent.

Yield: 1.80 g (17 %); mp 202 °C.

^{1}H NMR (300 MHz, $CDCl_3$, a6112289): δ = 10.24 (d, J = 0.9 Hz, 1 H), 8.65 (dd, J = 8.7, 0.9 Hz, 1 H), 8.14 (d, J = 8.7 Hz, 1 H), 7.86 (d, J = 8.2 Hz, 1 H), 7.18 (d, J = 8.2 Hz, 1 H).

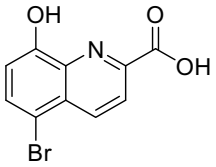
^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.0 (CH), 152.8 (C), 150.4 (C), 137.5 (CH), 134.1 (CH), 129.4 (C), 127.0 (C), 119.0 (CH), 112.0 (CH), 110.0 (C).

MS (EI, 70 eV): m/z (%) = 250.9 ([M]$^+$, 79.5), 220.9 ([M-CO]$^+$, 100).

IR (KBr): ν 3354, 1705, 1620, 1494, 1460, 1370, 1325, 1245, 1187, 901, 836, 778, 615 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{10}H_6NO_2Br$ (251.0): C 47.65, H 2.40, N 5.56; found: C 47.18, H 2.60, N 5.47.

5-Bromo-8-hydroxyquinoline-2-carboxylic acid (30b)



Monobromosubstituted carboxaldehyde **16b** (0.25 g, 0.99 mmol) was suspended in formic acid (5 ml, 0.13 mol) and the suspension was cooled to 0 ºC. Cold hydrogen peroxide (8 ml of 30% solution in water, 0.26 mol) was slowly added; the mixture was warmed up to rt and stirred for 2 d. The reaction mixture was poured into ice water (100 ml), the precipitate was collected by filtration, washed with water, and recrystallized from MeOH to provide the product as a yellow solid.

Yield: 0.115 g (42 %); mp 248 °C.

^{1}H NMR (300 MHz, CD_3OD, a7050335): δ = 8.68 (d, J = 8.8 Hz, 1 H), 8.29 (d, J = 8.8 Hz, 1 H), 7.86 (d, J = 8.2 Hz, 1 H), 7.12 (d, J = 8.2 Hz, 1 H).

^{13}C NMR (75 MHz, CD_3OD): δ = 183.9 (C), 167.1 (C), 155.5 (C), 146.8 (C), 139.3 (C), 138.3 (CH), 134.7 (CH), 130.0 (C), 122.8 (CH), 113.8 (CH).

MS (EI, 70 eV): m/z (%) = 266.9 ([M]$^+$, 72.2), 220.9 ([M-COO]$^+$, 100).

IR (KBr): ν 3602, 1721, 1501, 1467, 1398, 1369, 1326, 1235, 934, 851, 828, 763, 726 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{10}H_6NO_3Br \cdot 0.5\ H_2O$ (277.1): C 43.35, H 2.55, N 5.06; found: C 43.11, H 3.18, N 4.96.

$Eu_X(30b)_Y$

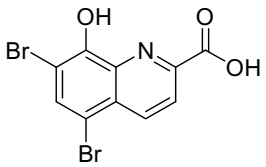
A mixture of carboxylic acid **30b**-H_2 (0.02 g, 0.075 mmol, 3.0 equiv.), K_2CO_3 (0.015 g, 0.11 mmol), and $EuCl_3 \cdot 6\ H_2O$ (0.009 g, 0.025 mmol, 1.0 equiv.) in MeOH (15 ml) was gently refluxed for 15 h. After cooling to rt the solvent was evaporated under reduced pressure. Extraction of the crude product with MeOH / MeCN (1:1 v/v) followed by evaporation of the solvent in vacuum furnished a red solid.

^{1}H NMR (300 MHz, CD_3OD, a5102733): δ = 9.09 (d, J = 8.9 Hz, 2 H), 8.47 (d, J = 8.9 Hz, 2 H), 8.22 (d, J = 8.7 Hz, 2 H), 7.00 (d, J = 8.4 Hz, 1 H), 6.87 (d, J = 8.7 Hz, 2 H), 6.87 (d, J = 8.4 Hz, 2 H), 6.32 (d, J = 8.9 Hz, 1 H), 6.23 (d, J = 8.4 Hz, 2 H), 6.16 (d, J = 8.4 Hz, 1 H),

5.41 (d, J = 8.9 Hz, 2 H), 5.05 (d, J = 8.9 Hz, 1 H), 4.80 (d, J = 8.9 Hz, 2 H), 4.29 (d, J = 8.4 Hz, 2 H), 4.23 (d, J = 8.4 Hz, 2 H).

MS (ESI-): m/z (%) = 685.5 ([Eu(**30b**)$_2$]$^-$, 56.0), 1521.8 ([Eu$_3$(**30b**)$_4$]$^-$, 100).

5,7-Dibromo-8-hydroxyquinoline-2-carboxylic acid (30c)



Prepared according to the procedure described above for monobromosubstituted carboxylic acid **30b**, starting from 5,7-dibromo-8-hydroxyquinoline-2-carboxaldehyde **16c** (0.25 g, 0.72 mmol).

Yield: 0.096 g (37 %); mp 265 °C.

^{1}H NMR (400 MHz, DMSO-d6, a6110701): δ = 13.04 (br. s, 1 H), 11.11 (br. s, 1 H), 8.59 (d, J = 8.8 Hz, 1 H), 8.28 (d, J = 8.8 Hz, 1 H), 8.18 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d$_6$): δ = 163.7 (C), 150.7 (C), 145.1 (C), 137.3 (CH), 136.3 (C), 135.0 (CH), 127.1 (C), 121.2 (CH), 108.3 (C), 105.0 (C).

MS (EI, 70 eV): m/z (%) = 346.9 ([M]$^+$, 63.2), 328.9 ([M-OH+1]$^+$, 100), 300.9 ([M-COOH+1]$^+$, 83.5).

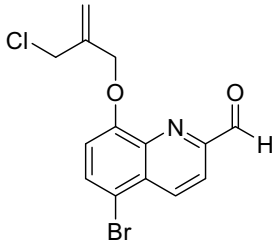
IR (KBr): ν 3309, 1706, 1613, 1572, 1451, 1376, 1245, 1194, 936, 839 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{10}H_5NO_3Br_2 \cdot CH_3OH$ (379.0): C 34.86, H 2.39, N 3.70; found: C 35.09, H 2.68, N 4.08.

X-Ray quality crystals were obtained from DMSO.

Crystal data for **30c**: formula $(C_{10}H_5NO_3Br_2)(SC_2H_6O)$: F_w = 425.10, plate, 0.20 × 0.10 × 0.04 mm^3, triclinic, space group *P*-1 a = 8.6570(17) Å, b = 10.524(2) Å, c = 17.694(4) Å, α = 96.72(3)°, β = 102.80(3)°, γ = 109.81(3)°, V = 1446.1(5) Å^3, Z = 4, D_c = 1.952 g.cm^{-3}, F_{000} = 832, MoKα radiation, λ = 0.71073 Å, μ = 5,761 mm^{-1}, T = 173(2) K, $2\theta_{max}$ = 55.0°, 12587 reflections collected, 3638 unique (R_{int} = 0.1006), 2158 with $I_o > 2\sigma(I_o)$. Solved using SHELXS, and refined with SHELX-97,[21] full-matrix least squares on F^2, 392 parameters, 492 restraints, GoF = 1.128, R_1 = 0.1800, wR_2 = 0.2391 (all reflections), 1.24<Δρ<-1.24 eÅ^{-3}.

5-Bromo-8-(2-(chloromethyl)allyloxy)quinoline-2-carboxaldehyde (110)



A mixture of monobrominated carboxaldehyde **16b** (0.037 g, 0.15 mmol, 1.0 equiv.) and finely powdered KOH (8 mg, 0.15 mmol, 1.0 equiv.) was stirred in MeOH (20 ml) at rt for 30 min. 3-Chloro-2-chloromethyl-propene (0.018 g, 0.017 ml, 0.15 mmol, 1.0 equiv.) in MeOH (2 ml) was slowly added and the resulting mixture was refluxed for 10 h. The solvent was removed under reduced pressure. The crude

residue was taken in Et_2O (25 ml), washed with 10 % NaOH (5 ml), H_2O, and brine. The organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuum and the product was purified by column chromatography (CH_2Cl_2, R_f = 0.70).

Yield: 0.017 g (34 %).

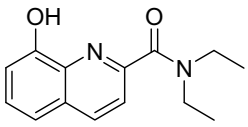
^{1}H NMR (300 MHz, $CDCl_3$, a5080138): δ = 10.29 (s, 1 H), 8.67 (d, J = 8.6 Hz, 1 H), 8.16 (d, J = 8.6 Hz, 1 H), 7.87 (d, J = 8.4 Hz, 1 H), 7.11 (d, J = 8.4 Hz, 1 H), 5.50 (d, J = 5.2 Hz, 2 H), 4.98 (s, 2 H), 4.32 (s, 2 H).

MS (EI, 70 eV): m/z (%) = 341.0 ($[M]^+$, 15.0), 304.0 ($[M\text{-}Cl]^+$, 100).

5.7. Tridentate Carboxamide Containing Ligands (34a-c, 35c, and 86) and their Mononuclear Complexes

_N,N_-Diethyl-8-hydroxyquinoline-2-carboxamide (34a-H)

Prepared according to **GP-5A**, starting from 8-hydroxyquinoline-2-carboxylic acid **30a** (1.0 g, 5.29 mmol), HBTU (2.41 g, 6.35 mmol), DIPEA (0.75 g, 1.0 ml, 5.80 mmol), and $HNEt_2$ (0.39 g, 0.55 ml, 5.33 mmol) in 50 ml of MeCN. The crude product was purified by column chromatography (EtOAc / *n*-hexane 1:4) to furnish the product as a colourless crystalline solid.



Yield: 0.77 g, (60 %); mp 104 °C.

^{1}H NMR (300 MHz, $CDCl_3$, a6032347): 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).

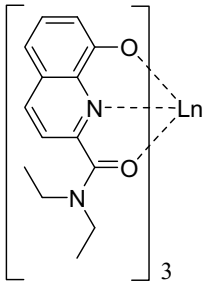
^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.9 (C), 151.9 (C), 151.8 (C), 136.8 (CH), 136.0 (C), 128.2 (CH), 127.8 (C), 120.5 (CH), 117.5 (CH), 110.5 (CH), 42.8 (CH_2), 39.7 (CH_2), 14.1 (CH_3), 12.4 (CH_3).

MS (EI, 70 eV): m/z (%) = 244.1 ($[M]^+$, 32.4), 145.0 ($[M\text{-}CONEt_2+1]^+$, 40.0), 72.1 ($[M\text{-}C_{10}H_6NO_2]^+$, 100).

IR (KBr): ν 3316, 2978, 1618, 1567, 1489, 1459, 1320, 1207, 1185, 1161, 850, 759 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{14}H_{16}N_2O_2$ (244.3): C 68.83, H 6.60, N 11.47; found: C 68.99, H 6.62, N 11.93.

General procedure (GP-10) for the preparation of mononuclear complexes with amido-quinolinate ligand 34a-H



A mixture of ligand **34a**-H (0.10 g, 0.41 mmol, 3.0 equiv.), K_2CO_3 (0.06 g, 0.43 mmol), and corresponding $Ln(OTf)_3$ or hydrated $LnCl_3$ (1.0 equiv.) in MeOH (15 ml) was stirred at 55 °C for 8 h, and then at rt for another 12 h. The resulting red solution was evaporated under reduced pressure. The residue was redissolved in CH_2Cl_2 and filtered from inorganic salts or insoluble species if such were formed during complexation. The CH_2Cl_2 solution was concentrated under reduced pressure to a minimum and *n*-hexane was added dropwise to allow even precipitation of the product. The solvent was cautiously decanted and the product was dried in vacuum to afford a typically red or orange powder.

La(34a)$_3$

Prepared according to **GP-10**, using $LaCl_3 \cdot 7\ H_2O$ (0.0507 g, 0.136 mmol).

Yield: 0.118 g (100 %).

^{1}H NMR (400 MHz, $CDCl_3$, a6030223): δ = 8.08 (d, J = 8.2 Hz, 3 H), δ = 7.37 (dd, J = 8.5, 8.1 Hz, 6 H), 6.77 (d, J = 7.8 Hz, 3 H), 6.66 (d, J = 7.9 Hz, 3 H), 3.63 (q, J = 7.0 Hz, 3 H), 3.27 (q, J = 7.0 Hz, 3 H), 2.46 (br. s, 3 H), 2.29 (br. s, 3 H), 1.32 (t, J = 7.0 Hz, 3 H), 1.25 (t, J = 7.0 Hz, 3 H), 1.11 (br. s, 6 H), 0.34 (br. s, 6 H).

MS (ESI+): m/z (%) = 907.1 ([La(**34a**)$_3$+K]$^+$, 100), 625.3 ([La(**34a**)$_2$+H], 9.0).

IR (KBr): ν 3426, 2971, 2934, 2874, 1627, 1440, 1097, 838, 745 cm^{-1}.

Elemental analysis: calc. (%) for $C_{42}H_{45}N_6O_6La \cdot H_2O$ (868.8): C 56.89, H 5.34, N 9.48; found: C 56.60, H 4.85, N 9.67.

Eu(34a)$_3$

Prepared according to **GP-10**, using $EuCl_3 \cdot 6\ H_2O$ (0.050 g, 0.136 mmol).

Yield: 0.126 g (100 %).

MS (ESI+): m/z (%) = 883.0 ([Eu(**34a**)$_3$+H]$^+$, 22.0), 639.5 ([Eu(**34a**)$_2$+H]$^+$, 100.0).

IR (KBr): ν 3442, 1605, 149, 1388,1093 cm^{-1}.

Elemental analysis: calc. (%) for $C_{42}H_{45}N_6O_6Eu \cdot 2.5\ H_2O$ (926.9): C 54.43, H 5.44, N 9.07; found: C 54.43, H 5.22, N 9.31.

Nd(34a)$_3$

Prepared according to **GP-10**, using $NdCl_3 \cdot 6\ H_2O$ (0.049 g, 0.136 mmol).

Yield: 0.085 g (71 %).

MS (ESI+): m/z (%) = 910.0 ([Nd(**34a**)$_3$+K]$^+$, 40.0), 627.8 ([Nd(**34a**)$_2$+K], 100).

IR (KBr): ν 3430, 2972, 2935, 1592, 1441, 1356, 1305, 1102, 841, 742 cm^{-1}.

Elemental analysis: calc. (%) for $C_{42}H_{45}N_6O_6Nd$ (874.1): C 57.71, H 5.19, N 9.61; found: C 58.23, H 5.88, N 9.60.

Er(34a)$_3$

Prepared according to **GP-10**, using Er(OTf)$_3$ (0.084 g, 0.136 mmol).

Yield: 0.058 g (45 %).

MS (ESI+): m/z (%) = 936.1 ([Er(**34a**)$_3$+K]$^+$, 6.0), 654.4 ([Er(**34a**)$_2$+H], 100).

IR (KBr): ν 3433, 2972, 1594, 1444, 1307, 1101, 841, 745 cm^{-1}.

Elemental analysis: calc. (%) for $C_{42}H_{45}N_6O_6Er \cdot 3\ H_2O$ (951.15): C 53.04 H 5.40, N 8.84; found: C 52.75, H 5.17, N 9.38.

An X-ray structural analysis of Er(**34a**)$_3$ · K(SO_3CF_3) · ether · chloroform has been obtained after crystallizing the crude product from THF / Et_2O / $CHCl_3$.

Crystal data for $(C_{14}H_{15}N_2O_2)_3Er \cdot (CF_3SO_3)K \cdot C_4H_{10}O \cdot CHCl_3$, M = 1278.76, triclinic, space group $P\bar{1}$ (No. 12), a = 13.531(1), b = 15.467(1), c = 15.721(1) Å, α = 115.44(1), β = 110.20(1), γ = 91.18(1)°, V = 2732.4(3) Å^3, D_c = 1.554 g cm^{-3}, μ = 1.866 mm^{-1}, Z = 2, λ = 0.71073 Å, T = 223(2) K, 25206 reflections collected (±h, ±k, ±l), [($sin\theta$)/λ] = 0.59 Å^{-1}, 9457 independent (R_{int} = 0.067) and 7647 observed reflections [$I \geq 2\sigma(I)$], 666 refined parameters, R = 0.046, wR^2 = 0.115, CCDC data collection.

Yb(34a)$_3$

Prepared according to **GP-10**, using Yb(OTf)$_3$ (0.085 g, 0.136 mmol).

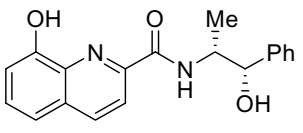
Yield: 0.129 g (100 %).

MS (ESI+): m/z (%) = 942.2 ([Yb(**34a**)$_3$+K]$^+$, 100), 660.4 ([Yb(**34a**)$_2$+H], 100).

IR (KBr): ν 3431, 2972, 1595, 1445, 1354, 1309, 1273, 1103, 845, 746 cm^{-1}.

Elemental analysis: calc. (%) for $C_{42}H_{45}N_6O_6Yb \cdot 2.5\ H_2O$ (947.9): C 53.22, H 5.32, N 8.87; found: C 53.66, H 5.52, N 8.38.

8-Hydroxy-*N*-[(1*R*,2*S*)-1-hydroxy-1-phenylpropan-2-yl]quinoline-2-carboxamide (86)



Prepared according to **GP-5A**, starting from 8-hydroxyquinoline-2-carboxylic acid **30a** (0.20 g, 1.06 mmol), HBTU (0.48 g, 1.27 mmol), DIPEA (0.15 g, 0.20 ml, 1.16 mmol), and (1*R*, 2*S*)-

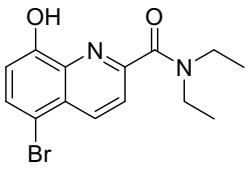
norephedrine (0.175 g, 1.16 mmol) in MeCN (25 ml). The crude product was purified by column chromatography (CH_2Cl_2) to furnish a pale orange solid.

Yield: 0.19 g (56 %).

^{1}H NMR (300 MHz, $CDCl_3$, a6101505): δ = 8.49 (d, J = 8.8 Hz, 1 H), 8.29 (d, J = 8.5 Hz, 1 H), 8.25 (d, J = 8.5 Hz, 1 H), 7.50 (dd, J = 8.2, 7.7 Hz, 1 H), 7.42-7.27 (m, 6 H), 7.19 (dd, J = 7.7, 1.1 Hz, 1 H), 5.06 (d, J = 2.5 Hz, 1 H), 4.61-4.53 (m, 1 H), 3.88 (br. s, 1 H), 1.15 (d, J = 7.1 Hz, 3 H).

MS (EI, 70 eV): m/z (%) = 322.1 ($[M]^+$, 4.0), 215.1 ($[M\text{-}PhCHOH]^+$, 100).

5-Bromo-*N,N*-diethyl-8-hydroxyquinoline-2-carboxamide (34b-H)



Prepared according to **GP-5A**, starting from monobrominated carboxylic acid **30b** (0.50 g, 1.87 mmol), HBTU (0.85 g, 2.24 mmol), DIPEA (0.26 g, 0.35 ml, 2.05 mmol), and $HNEt_2$ (0.15 g, 0.215 ml, 2.05 mmol). After the usual workup, the crude product was purified by column chromatography (EtOAc / *n*-hexane 1:4) to afford a colourless crystalline solid.

Yield: 0.264 g (44 %); mp 86 °C.

^{1}H NMR (400 MHz, $CDCl_3$, a6031698): δ = 8.44 (d, J = 8.7 Hz, 1 H), 8.07 (br. s, 1 H), 7.72 (d, J = 8.7 Hz, 1 H), 7.65 (d, J = 8.2 Hz, 1 H), 7.02 (d, J = 8.2 Hz, 1 H), 3.59 (q, J = 7.0 Hz, 2 H), 3.31 (q, J = 7.0 Hz, 2 H), 1.27 (t, J = 7.0 Hz, 3 H), 1.17 (t, J = 7.0 Hz, 3 H).

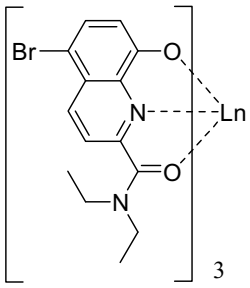
^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6 (C), 152.9 (C), 152.1 (C), 137.0 (C), 136.8 (CH), 131.7 (CH), 127.1 (C), 122.1 (CH), 111.6 (CH), 109.7 (C), 43.2 (CH_2), 40.1 (CH_2), 14.5 (CH_3), 12.8 (CH_3).

MS (EI, 70 eV): m/z (%) = 322.1 ($[M]^+$, 9.2), 223.0 ($[M\text{-}CONEt_2+H]^+$, 12.7), 72.2 ($[M\text{-}C_{10}H_5BrNO_2]^+$, 100).

IR (KBr): ν 2975, 2931, 1620, 1487, 1454, 1364, 1309, 1239, 1200, 1098, 1069, 824, 539 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{14}H_{15}N_2O_2Br$ (322.0): C 52.03, H 4.68, N 8.67; found: C 51.85, H 4.68, N 8.85.

General procedure (GP-11) for the preparation of mononuclear complexes with monobromosubstituted amidoquinolinate ligand 34b-H



GP-11 is similar to **GP-10** described for analogous complexes with **34a**-H, using alternative ligand **34b**-H (0.10 g, 0.31 mmol, 3.0 equiv.), K_2CO_3 (0.06 g, 0.43 mmol), and corresponding $Ln(OTf)_3$ or hydrated $LnCl_3$ (1.0 equiv.).

La(34b)$_3$

Prepared according to **GP-11**, using $LaCl_3 \cdot 7\ H_2O$ (0.038 g, 0.103 mmol).

Yield: 0.116 g (100 %).

MS (ESI+): m/z (%) = 1144.8 ([La(**34b**)$_3$+K]$^+$, 100), 783.1 ([La(**34b**)$_2$+H], 62.0).

IR (KBr): ν 2971, 2361, 2336, 1591, 1435, 1343, 1305, 1077, 935, 829, 739, 557 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{42}H_{42}N_6O_6Br_3La \cdot H_2O$ (1120.2): C 44.90, H 3.95, N 7.48; found: C 44.79, H 4.90, N 7.49.

Eu(34b)$_3$

Prepared according to **GP-11**, using $EuCl_3 \cdot 6\ H_2O$ (0.050 g, 0.103 mmol).

Yield: 0.080 g (66 %).

MS (ESI+): m/z (%) = 1118.5 ([Eu(**34b**)$_3$+H]$^+$, 40.0), 797.1 ([Eu(**34b**)$_2$+H], 100).

IR (KBr): ν 3429, 1590, 1436, 1345, 1307, 1080, 941, 830, 744 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{42}H_{42}N_6O_6Br_3Eu \cdot 3\ H_2O$ (1169.3): C 43.02, H 4.13, N 7.17; found: C 43.06, H 3.87, N 6.99.

[Nd(34b)$_2$]Cl

Prepared according to **GP-11**, using $NdCl_3 \cdot 6\ H_2O$ (0.037 g, 0.103 mmol).

Yield: 0.098 g (68 %).

MS (ESI+): m/z (%) = 788.0 ([Nd(**34b**)$_2$+H]$^+$, 16.0).

Elemental analysis: calcd. (%) for $C_{28}H_{28}N_4O_4Br_2NdCl \cdot 8\ H_2O$ (930.2): C 40.20, H 4.66, N 6.70; found C 39.99, H 4.21, N 6.39.

IR (KBr): ν 3450, 3267, 2968, 1589, 1435, 1343, 1308, 1079, 939, 827, 737 cm^{-1}.

Er(34b)$_3$

Prepared according to **GP-11**, using $Er(OTf)_3$ (0.064 g, 0.103 mmol).

Yield calcd. on M_W (M_W = 1130.6 g mol^{-1}): 0.10 g (87 %).

MS (ESI+): m/z (%) = 1172.0 ([Er(**34b**)$_3$+K]$^+$, 100).

IR (KBr): ν 3453, 2362, 2340, 1591, 1440, 1348, 1267, 1169, 1034, 646 cm^{-1}.

No correct elemental analyses could be obtained for the erbium(III) complex.

Yb(34b)$_3$

Prepared according to **GP-11**, using Yb(OTf)$_3$ (0.050 g, 0.103 mmol).

Yield: 0.11 g (92 %).

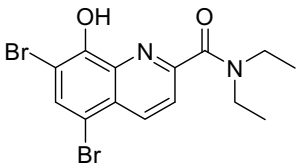
MS (ESI+): m/z (%) = 1178.0 ([Yb(**34b**)$_3$+K]$^+$, 100), 818.4 ([Yb(**34b**)$_2$+H]$^+$, 36.0).

IR (KBr): ν 3439, 2972, 2930, 1598,1441, 1348, 1078, 941,823,749, 643 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{42}H_{42}N_6O_6Br_3Yb \cdot H_2O$ (1154.3): C 43.58, H 3.83, N 7.26; found: C 43.50, H 4.14, N 7.17.

5,7-Dibromo-*N*,*N*-diethyl-8-hydroxyquinoline-2-carboxamide (34c-H)

Prepared according to **GP-5A**, starting from dibrominated carboxylic acid **30c** (0.50 g, 1.44 mmol), HBTU (0.656 g, 1.73 mmol), DIPEA (0.205 g, 0.272 ml, 1.58 mmol), and $HNEt_2$ (0.116 g, 0.166 ml, 1.58 mmol). The crude product was purified by column chromatography (EtOAc / *n*-hexane 1:4) to yield a colourless crystalline solid.



Yield: 0.284 g (49 %); mp 154 °C.

^{1}H NMR (400 MHz, $CDCl_3$, a6031012): δ = 8.47 (br. s, 1 H), 7.57 (d, J = 8.5 Hz, 1 H), 7.87 (s, 1 H), 7.73 (d, J = 8.5 Hz, 1 H), 3.60 (q, J = 7.2 Hz, 2 H), 3.31 (q, J = 7.1 Hz, 2 H), 1.30 (t, J = 7.2 Hz, 3 H), 1.20 (t, J = 7.1 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2 (C), 153.6 (C), 149.6 (C), 137.1 (CH), 136.7 (C), 134.5 (CH), 126.2 (C), 122.2 (CH), 110.2 (C), 105.0 (C), 43.3 (CH_2), 40.3 (CH_2), 14.7 (CH_3), 13.0 (CH_3).

MS (EI, 70 eV): m/z (%) = 401.9 ([M]$^+$, 10.2), 302.8 ([M-$CONEt_2$+H]$^+$, 14.6), 72.2 ([M-$C_{10}H_4Br_2NO_2$]$^+$, 100).

IR (KBr): ν 2936, 1612, 1443, 1313, 1217, 1106, 931, 580 cm^{-1}.

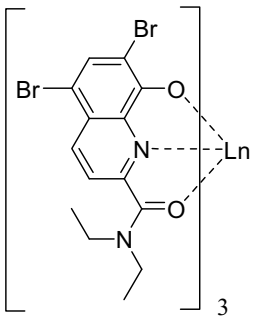
Elemental analysis: calcd. (%) for $C_{14}H_{14}N_2O_2Br_2$ (402.1): C 41.82, H 3.51, N 6.97; found: C 41.75, H 4.05, N 6.96.

X-Ray quality crystals were obtained from CH_2Cl_2 / *n*-hexane solution.

Crystal data for **34c**: formula $C_{14}H_{14}Br_2N_2O_2$; code ext027; Nonius KappaCCD diffractometer (MoKα, 0.71073 Å); colourless, 0.40 × 0.20 × 0.10 mm^3; M = 402.09: monoclinic, space group $P2_1/c$; 173 K; a = 11.448(2) Å, b = 13.676(3) Å, c = 9.878(2) Å; α = 90°, β = 104.26(3)°, γ = 90°; V / Å^3 =

1498.9(5); Z = 4; μ = 5.410 mm^{-1}; D_c / g cm^{-3} = 1.782; refl. for cell refinement = 1361 (θ range 2.5 to 27.5°), indep. refl. 3249 (R_{int} = 0.0545), refl. with $F^2>2\sigma$2187; final R indices [$F^2>2\sigma$] R1 = 0.0465, wR2 = 0.0747; largest diff. peak and hole 0.51 and –0.76 e $Å^{-3}$.

General procedure (GP-12) for the preparation of mononuclear complexes with dibromosubstituted amidoquinolinate ligand 34c-H



GP-12 is similar to **GP-10** described for analogous complexes with **34a**-H, using the alternative ligand **34c**-H (0.10 g, 0.25 mmol, 3.0 equiv.), K_2CO_3 (0.05 g, 0.36 mmol), and corresponding $Ln(OTf)_3$ or hydrated $LnCl_3$ (1.0 equiv.).

La(34c)$_3$

Prepared according to **GP-12**, using $LaCl_3 \cdot 7\ H_2O$ (0.031 g, 0.083 mmol).

Yield: 0.056 g (49 %).

^{1}H NMR (600 MHz, CD_2Cl_2, 235 K): δ = 8.50 (br. s, 1 H), 8.60 (d, J = 9 Hz, 1 H), 8.46 (d, J = 11.4 Hz, 1 H), 8.44 (s, 1 H), 8.43 (d, J = 9.6 Hz, 1 H), 7.93 (d, J = 11.4 Hz, 1 H), 7.91 (d, J = 11.4 Hz, 1 H), 7.90 (s, 1 H), 7.73 (s, 1 H), 7.72 (s, 2 H), 7.64 (m, 4 H), 7.59 (d, J = 9 Hz, 1 H), 3.83 (m, 4 H), 3.74 (m, 1 H), 3.59 (3 H), 3.49 (m, 1 H), 3.42 (m, 3 H), 3.38 (m, 1 H), 3.22 (m, 1 H), 3.21 (m, 1 H), 3.01 (m, 1 H), 2.83 (m, 1 H), 2.82 (m, 1 H), 2.31 (m, 2 H), 1.48 (t, J = 7.2 Hz, 3 H), 1.42 (t, J = 7.2 Hz, 3 H), 1.38 (t, J = 7.2 Hz, 3 H), 1.25 (t, J = 7.2 Hz, 3 H), 1.24 (br. s, 3 H), 1.18 (br. s, 3 H), 0.92 (br. s, 3 H), 0.63 (t, J = 6.6 Hz, 3 H), 0.57 (br. s, 3 H), 0.43 (t, J = 6.6 Hz, 3 H).

MS (ESI+): m/z (%) = 1342.3 ([La(**34c**)$_3$+H]$^+$, 6.0), 941.4 ([La(**34c**)$_2$]$^+$, 100).

IR (KBr): ν 3399, 2970, 2929, 1602, 1535, 1436, 1356, 1305, 1105, 944, 841, 669 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{42}H_{39}N_6O_6Br_6La \cdot 2\ H_2O$ (1377.9): C 36.60, H 3.14, N 6.10; found: C 36.85, H 3.53, N 6.08.

Eu(34c)$_3$

Prepared according to **GP-12**, using $EuCl_3 \cdot 6\ H_2O$ (0.030 g, 0.083 mmol).

Yield: 0.092 g (82 %).

MS (ESI+): m/z (%) = 1394.6 ([Eu(**34c**)$_3$+K]$^+$, 100).

IR (KBr): ν 2970, 2933, 1597, 1538, 1436, 1349, 1309, 1281, 1127, 1102, 945, 744, 669 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{42}H_{39}N_6O_6Br_6Eu$: C 37.22, H 2.90, N 6.20; found: C 37.03, H 3.40, N 6.05.

[Nd(34c)$_2$]Cl

Prepared according to **GP-12**, using $NdCl_3 \cdot 6\ H_2O$ (0.030 g, 0.083 mmol).

Yield: 0.107 g (94 %).

MS (ESI+): m/z (%) = 1385.9 ([Nd(**34c**)$_3$+K]$^+$, 100).

IR (KBr): ν 3435, 2972, 1595, 1540, 1432, 1349, 1103, 943, 744, 667 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{42}H_{39}N_6O_6Br_6Nd \cdot MeOH$ (1379.2): C 37.44, H 3.14, N 6.09; found: C 37.69, H 3.72, N 6.51.

Er(34c)$_3$

Prepared according to **GP-12**, using $Er(OTf)_3$ (0.051 g, 0.083 mmol).

Yield: 0.10 g (90 %).

MS (ESI+): m/z (%) = 1409.7 ([Er(**34c**)$_3$+K]$^+$, 100), 1371.4 ([Er(**34c**)$_3$+H]$^+$, 72.0), 970.1 ([Er(**34c**)$_2$+H], 94.0).

IR (KBr): ν 2360, 2338, 1601, 1542, 1442, 1354, 947 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{42}H_{39}N_6O_6Br_6Er$ (1370.26): C 36.81, H 2.87, N 6.13; found: C 36.54, H 3.05, N 6.08.

Yb(34c)$_3$

Prepared according to **GP-12**, using $Yb(OTf)_3$ (0.051 g, 0.083 mmol). The yellow side product formed during complexation was recognized by its insolubility in CH_2Cl_2. It was collected by filtration and additionally recrystallized from MeOH.

Yield: 0.11 g (75 %).

MS (ESI+): m/z (%) = 1414.0 ([Yb(**34c**)$_3$+K]$^+$, 100).

IR (KBr): ν 1638, 1262, 1174, 1034, 648, 521 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{42}H_{39}N_6O_6Br_6Yb \cdot 3\ H_2O$ (1154.3): C 35.27, H 3.17, N 5.88; found: C 35.05, H 3.08, N 5.69.

Crystal data for Yb(**34c**)$_3$: $(C_{14}H_{13}N_2O_2Br_2)_3Yb$, M = 1376.29, orthorhombic, space group *P*ccn (No. 56), a = 27.425(1), b = 15.739(1), c = 23.156(1) Å, V = 9995.1(8) Å^3, D_c = 1.829 g cm^{-3}, μ = 6.717 mm^{-1}, Z = 8, λ = 0.71073 Å, T = 223(2) K, 55638 reflections collected (±h, ±k, ±l), [($sin\theta$)/λ] = 0.59 Å^{-1}, 8818 independent (R_{int} = 0.134) and 5437 observed reflections [$I \geq 2\sigma(I)$], 556 refined parameters, R = 0.077, wR^2 = 0.228, CCDC data collection.

Characterization of the side product Yb(34c)(O$_3$SCF$_3$)$_2$

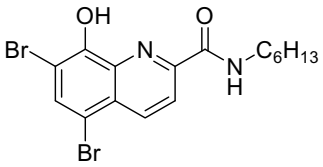
Yield: 0.037 g (16 %).

MS (ESI+): m/z (%) = 722.2 ([Yb(**34c**)(OTf)]$^+$, 16.0).

Elemental analysis: calcd. (%) for $C_{14}H_{13}N_2O_2Br_2Yb(O_3SCF_3)_2 \cdot 3\ H_2O$ (926.17): C 20.75, H 2.07, N 3.02; found C 20.54, H 2.08, N 2.65.

IR (KBr): ν 2973, 2365, 1597, 1546, 1433, 1355, 1265, 1155, 1031, 948, 646 cm^{-1}.

5,7-Dibromo-*N*-hexyl-8-hydroxyquinoline-2-carboxamide (35c-H)



Prepared according to **GP-5B**, starting from 5,7-dibromo-substituted carboxylic acid **30c** (0.50 g, 1.44 mmol), HBTU (0.656 g, 1.73 mmol), DIPEA (0.205 g, 0.272 ml, 1.58 mmol), and *n*-hexylamine (0.16 g, 0.21 ml, 1.59 mmol). The crude product was purified by recrystallization from MeOH / $CHCl_3$ to yield an orange solid.

Yield: 0.33 g (53 %); mp 196 °C.

^{1}H NMR (300 MHz, CD_3OD, a5111134): δ = 8.44 (d, J = 8.7 Hz, 1 H), 8.22 (d, J = 8.7 Hz, 1 H), 7.88 (s, 1 H), 2.86 (t, J = 7.7 Hz, 2 H), 1.58 (quint, J = 7.8 Hz, 2 H), 1.26 (m, 6 H), 0.83 (t, J = 6.7 Hz, 3 H).

^{13}C NMR (75 MHz, CD_3OD, a7062468): δ = 171.4 (C), 154.4 (C), 153.6 (C), 139.5(C), 137.4 (CH), 135.7 (CH), 128.5 (C), 123.7 (CH), 109.8 (C) 105.7 (C), 40.8 (CH_2), 32.4 (CH_2), 28.6 (CH_2), 27.2 (CH_2), 23.5 (CH_2), 14.3 (CH_3).

MS (EI, 70 eV): m/z (%) = 429.9 ($[M]^+$, 1.7), 346.9 ($[M\text{-}C_6H_{13}\text{+}1]^+$, 71.4), 300.9 ($[M\text{-}CONHC_6H_{13}]^+$, 100).

IR (KBr): ν 3254, 2955, 2926, 1643, 1507, 1446, 1393, 1363, 1294, 1206, 1176, 927, 801, 685, 660, 600 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{16}H_{18}N_2O_2Br_2 \cdot H_2O$ (448.1): C 42.88, H 4.50, N 6.25; found: C 42.90, H 4.52, N 6.39.

Synthesis and characterization of Eu complex with ligand 35c-H

A mixture of ligand **35c**-H (0.02 g, 0.046 mmol, 3.0 equiv.), $EuCl_3 \cdot 6\ H_2O$ (5.7 mg, 0.016 mmol, 1.0 equiv.), and K_2CO_3 (0.015 g, 0.11 mmol) in MeOH (15 ml) was refluxed for 15 h. The solution was evaporated under reduced pressure; the crude residue was redissolved in MeOH and filtered from inorganic salts. The solvent was removed under reduced pressure to furnish the product as a red solid.

Yield: 100 %

^{1}H NMR (300 MHz, CD_3OD, a5111741): δ = 9.20 (d, J = 8.4 Hz, 1 H), 8.83 (d, J = 8.7 Hz, 1 H), 8.43 (d, J = 8.7 Hz, 1 H), 8.25 (d, J = 8.7 Hz, 1 H), 8.20 (d, J = 8.7 Hz, 1 H), 7.88 (s, 1 H),

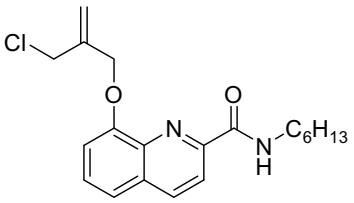
7.21 (d, J = 8.7 Hz, 1 H), 6.97 (d, J = 8.4 Hz, 1 H), 6.54 (s, 1 H), 6.48 (s, 1 H), 6.19 (d, J = 8.7 Hz, 1 H), 5.88 (d, J = 8.4 Hz, 1 H), 5.74 (d, J = 8.4 Hz, 1 H), 4.53 (s, 1 H), 4.47 (s, 1 H).
MS (ESI-): m/z (%) = 1227.6 ([Eu(**30c**)$_3$+K], 1.7), 841.0 ([Eu{(**30c**)$_2$]$^-$, 100).

5.8. Synthesis of Homo- and Heteroditopic Ligands (42-44, 50a-c, 51b,c, 55, 56)

8-(2-(Chloromethyl)allyloxy)-*N*-(*n*-hexyl)quinoline-2-carboxamide (45b) and 8,8'-(2-methylenepropane-1,3-diyl)bis(oxy)di(*N*-(*n*-hexyl)quinoline-2-carboxamide) (46b)

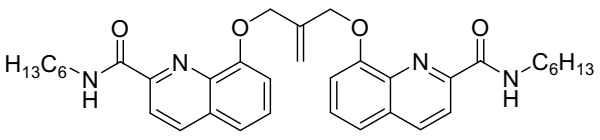
Prepared according to **GP-1**, starting from 2-(*N*-*n*-hexylcarboxamide)-8-hydroxyquinoline **35a** (0.28 g, 1.03 mmol, 1.0 equiv.), K_2CO_3 (0.71 g, 5.14 mmol, 5.0 equiv.), and 3-chloro-2-chloromethyl-propene **13** (0.13 g, 1.03 mmol, 1.0 equiv.) in acetone (50 ml). The resulting suspension was refluxed for 24 h. Separation by flash chromatography (EtOAc / *n*-hexane 1:2) afforded **45b** (R_f = 0.39) and **46b** (R_f = 0.07) as colourless oils.
Yield: **45b**: 0.104 g (28 %) and **46b**: 0.181 g (59 %).

Characterization of 45b:



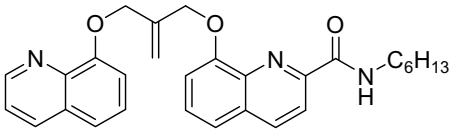
^{1}H NMR (300 MHz, $CDCl_3$, a6080806): δ = 8.36 (br t , J = 5.5 Hz, 1 H), 8.31 Hz (d, J = 8.5 Hz, 1 H), 8.23 (d, J = 8.5, 1 H), 7.46 (m, 2 H), 7.12 (dd, J = 7.2, 1.6 Hz, 1 H), 5.51 (s, 1 H), 5.46 (s, 1 H), 4.88 (s, 2 H), 4.30 (s, 2 H), 3.51 (m, 2 H), 1.66 (m, 2 H), 1.42 (m, 6 H), 0.87 (m, 3 H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.3 (C), 154.2 (C), 148.8 (C), 140.5 (C), 138.6 (C), 137.2 (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).
MS (EI, 70 eV): m/z (%) = 360.2 ([M]$^+$, 17.2), 325.2 ([M-Cl]$^+$, 100).

Characterization of 46b:



^{1}H NMR (300 MHz, $CDCl_3$, a6080807): 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).
^{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).
MS (EI, 70 eV): m/z (%) = 596.7 ([M]$^+$, 2.5), 325.2 ([M-$C_{16}H_{19}N_2O_2$]$^+$, 100).

N-Hexyl-8-(2-((quinolin-8-yloxy)methyl)allyloxy)quinoline-2-carboxamide (47b)



Prepared according to **GP-6**, starting from mono-ether **45b** (0.103 g, 0.29 mmol, 1.0 equiv.), K_2CO_3 (0.20 g, 1.44 mmol, 5.0 equiv.), and 8-hydroxyquinoline **31a** (0.083 g, 0.57 mmol, 2.0 equiv.) in acetone (25 ml). The purified oily colourless product was subsequently crystallized from *n*-hexane / CH_2Cl_2 (1:1) to furnish a waxy solid.

Yield: 0.103 g (77 %).

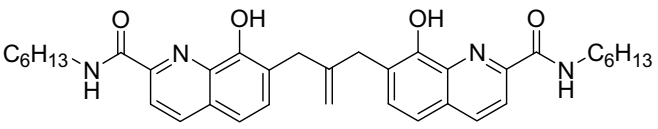
^{1}H NMR (300 MHz, $CDCl_3$, a6081484): δ = 8.86 (dd, J = 4.2, 1.7 Hz, 1 H), 8.33 (br. t, J = 5.7 Hz, 1 H), 8.25 Hz (d, J = 8.6 Hz, 1 H), 8.16 (d, J = 8.6 Hz, 1 H), 8.04 (dd, J = 8.1, 1.7 Hz, 1 H), 7.34 (m, 5 H), 7.14 (dd, J = 5.7, 3.2 Hz, 1 H), 7.07 (dd, J = 6.9, 1.9 Hz, 1 H), 5.54 (s, 1 H), 5.50 (s, 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).

^{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).

MS (EI, 70 eV): m/z (%) = 469.2 ($[M]^+$, 9.3), 325.2 ($[M\text{-}C_9H_6NO]^+$, 84.5), 198.1 ($[M\text{-}C_{16}H_{19}N_2O_2]^+$, 100).

Elemental analysis: calcd. (%) for $C_{29}H_{31}N_3O_3$ (469.6): C 74.18, H 6.65, N 8.95; found: C 74.23, H 6.82, N 8.67.

7,7'-(2-Methylenepropane-1,3-diyl)bis(*N*-hexyl-8-hydroxyquinoline-2-carboxamide) (50b-H_2)



Prepared according to **GP-2**, starting from diether **46b** (0.15 g, 0.25 mmol). The glass-like slightly yellow crude residue was purified by column chromatography (EtOAc / *n*-hexane 1:1) to afford a pale crystalline solid.

Yield: 0.132 g (88 %); mp 112-115 °C.

^{1}H NMR (300 MHz, $CDCl_3$, a6081011): δ = 8.28 (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).

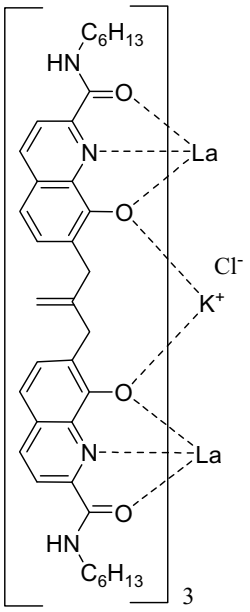
^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.6 (C), 149.8 (C), 147.6 (C), 146.5 (C), 137.1 (CH), 136.3 (C), 131.4 (CH), 128.1 (C), 122.21 (C), 118.8 (CH), 117.2 (CH), 112.9 (CH_2), 39.8 (CH_2), 36.1 (CH_2), 31.4 (CH_2), 29.6 (CH_2), 26.6 (CH_2), 22.4 (CH_2), 13.9 (CH_3).

IR (KBr): ν 3291, 2927, 2857, 1653, 1542, 1505, 1450, 1231, 1181, 1087, 858, 725, 665 cm^{-1}.

MS (EI, 70 eV): m/z (%) = 596.2 ([M]$^+$, 2.7), 311.1 ([M-$C_{17}H_{21}N_2O_2$]$^+$, 100).

Elemental analysis: calcd. for $C_{36}H_{44}N_4O_4$ (596.8): C 72.46, H 7.43, N 9.39; found: C 72.04, H 7.88, N 8.95.

Synthesis and characterization of homodinuclear helicate-type complex [K(50b)$_3$La$_2$]Cl



To ligand **50b**-H_2 (0.04 g, 0.067 mmol, 3.0 equiv.) in CH_2Cl_2 (10 ml) $LaCl_3 \cdot 6\ H_2O$ (0.017 g, 0.045 mmol, 2.0 equiv.) and K_2CO_3 (0.02 g, 0.14 mmol) in MeOH / H_2O (4 ml / 1 ml) were added. The resulting mixture was refluxed for 8 h, and then stirred at rt for another 12 h. The solution was concentrated under reduced pressure and applied to a Sephadex LH-20 column eluting with MeOH. The first fraction containing the desired product was evaporated in vacuum to furnish a red solid.

Yield: 0.022 g (41 %).

^{1}H NMR (300 MHz, CD_3OD, a5090289): δ = 8.51 (d, J = 8.7 Hz, 6 H), 8.12 (d, J = 8.7 Hz, 6 H), 7.02 (d, J = 8.4 Hz, 6 H), 6.67 (d, J = 8.4 Hz, 6 H), 4.45 (s, 6 H), 3.79 (d, J = 13.0 Hz, 6 H), 2.94-2.88 (m, 6 H), 2.70-2.64 (m, 6 H), 2.04 (d, J = 13.0 Hz, 6 H) 1.44-1.28 (m, 12 H), 1.00 (ps. quint, J = 7.3 Hz, 12 H), 0.90-0.84 (m, 12 H), 0.75 (t, J = 7.3 Hz, 18 H), 0.64-0.52 (m, 18 H).

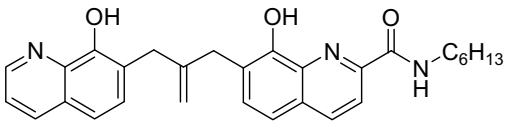
MS (ESI+): m/z (%) = 2137.2 ([(**50b**)$_3$$La_2$KCl+H]$^+$, 8.3).

MS (ESI-): m/z (%) = 2097.3 ([(**50b**)$_3$$La_2$+Cl]$^-$, 15.6).

IR (KBr): ν 2928, 2858, 1633, 1557, 1505, 1441, 1376, 1198, 1107, 852, 739 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{108}H_{126}O_{12}N_{12}La_2KCl \cdot 2\ CHCl_3$ (2375.3): C 55.62, H 5.43, N 7.08; found: C 55.38, H 5.54, N 7.02.

8-Hydroxy-7-[2-(8-hydroxyquinolin-7-ylmethyl)-allyl]quinoline-2-carboxylic acid hexyl-amide (51b-H_2)



Prepared according to **GP-2**, starting from the hetero-substituted ether **47b** (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 colourless crystalline solid.

Yield: 0.075 g (94 %); mp 57-64 °C.

^{1}H NMR (300 MHz, $CDCl_3$, a6092542): 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).

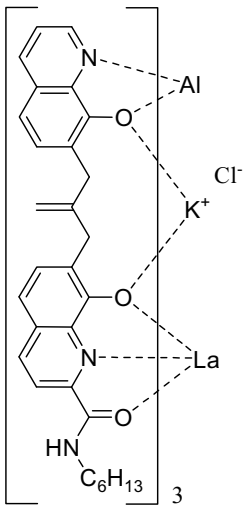
^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.2 (C), 149.5 (C), 148.0 (C), 147.7 (CH), 146.6 (C), 138.1 (C), 137.3 (CH), 136.3 (C), 135.9 (CH), 131.6 (CH), 129.9 (CH), 128.3 (C), 127.1 (C), 122.5 (C), 121.1 (CH), 121.0 (C), 119.1 (CH), 117.4 (CH), 117.1 (CH), 112.9 (CH_2), 39.8 (CH_2), 36.1 (CH_2), 36.1 (CH_2), 31.5 (CH_2), 29.7 (CH_2), 26.7 (CH_2), 22.5 (CH_2), 14.0 (CH_3), one quaternary C atom could not be observed.

IR (KBr): ν 3305, 2925, 2856, 1651, 1542, 1504, 1453, 1372, 1233, 1179, 1089, 894, 827, 667 cm^{-1}.

MS (EI, 70 eV): m/z (%) = 469.2 ($[M]^+$, 10.7), 311.1 ($[M\text{-}C_{10}H_8NO]^+$, 81.6), 184.1 ($[M\text{-}C_{17}H_{21}N_2O_2]^+$, 100).

Elemental analysis: calcd. (%) for $C_{29}H_{31}N_3O_3$ (469.6): C 74.18, H 6.65, N 8.95; found: C 74.23, H 6.82, N 8.67.

Synthesis and characterization of heterodinuclear helicate-type complex [K(51b)$_3$LaAl]Cl



A mixture of ligand **51b-H_2** (0.04 g, 0.085 mmol, 3.0 equiv.), K_2CO_3 (0.02 g, 0.14 mmol), $LaCl_3 \cdot 7\ H_2O$ (0.011 g, 0.028 mmol, 1.0 equiv.), and hydrated $AlCl_3$ (0.004 g, 0.031 mmol, 1.1 equiv.) was stirred in MeOH (15 ml) at 55 °C for 8 h, and then at rt for another 12 h. Solvent was removed under reduced pressure. The residue was redissolved in MeOH / THF and filtered from insoluble inorganic salts. The solution was concentrated in vacuum to a minimum until the product started to precipitate. It was filtered off, washed with Et_2O, and dried in vacuum to furnish a red

powder.

Yield: 0.058 g (86 %).

^{1}H NMR (300 MHz, DMSO-d_6, a7032345): δ = 9.44 (br. s, 3 H), 8.59 (d, J = 8.2 Hz, 3 H), 8.35 (d, J = 8.6 Hz, 3 H), 8.01 (d, J = 8.6 Hz, 3 H), 7.48 (dd, J = 8.2, 5.0 Hz, 3 H), 7.39 (d, J = 8.4 Hz, 3 H), 7.25 (d, J = 8.4 Hz, 3 H), 7.08-7.05 (m, 6 H), 6.78 (d, J = 8.2 Hz, 3 H), 4.04 (br. s, 3 H), 3.18-2.73 (m, 21 H), 1.14-1.09 (m, 12 H), 1.00-0.97 (m, 12 H), 0.79 (t, J = 7.3 Hz, 9 H).

MS (ESI+): m/z (%) = 1606.8 ([(**51b**)$_3$LaAlK]$^+$, 64.0).

IR (KBr): ν 2928, 2858, 1633, 1557, 1505, 1441, 1376, 1198, 1107, 852, 739 cm^{-1}.

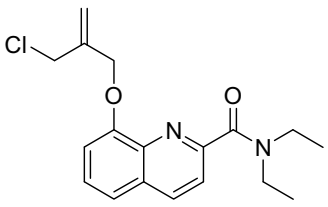
Elemental analysis: calcd. (%) for $C_{87}H_{87}O_9N_9LaAlKCl \cdot H_2O$ (2375.3): C 62.90, H 5.40, N 7.59; found: C 62.35, H 5.57, N 7.81.

8-(2-(Chloromethyl)allyloxy)-*N,N*-(diethyl)quinoline-2-carboxamide (45c) and 8,8'-(2-methylenepropane-1,3-diyl)bis(oxy)di(*N,N*-(diethyl)quinoline-2-carboxamide) (46c)

Prepared according to **GP-1**, by reaction of 2-amidoquinolinate (**34a**) (0.775 g, 3.0 mmol) with 3-chloro-2-chloromethyl-propene (0.40 g, 3.17 mmol) in acetone (50 ml) in the presence of K_2CO_3 (2.19 g, 15.85 mmol). **45c** as a colourless oil (R_f = 0.89) and **46c (**R_f = 0.49**)** as a sticky white solid were separated by column chromatography (EtOAc / *n*-hexane 1:1).

Yield: **45c:** 0.486 g (46 %) and **46c:** 0.352 g (41 %); mp 62 °C.

Characterization of 45c:

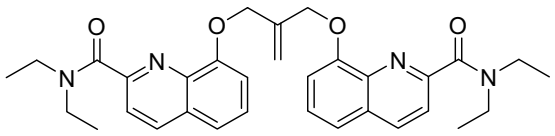


^{1}H NMR (300 MHz, $CDCl_3$, a6080229): δ = 8.18 (d, J = 8.5 Hz, 1 H), 7.77 (d, J = 8.5 Hz, 1 H), 7.46 (t, J = 8.0 Hz, 1 H), 7.25 (dd, J = 8.0, 1.3 Hz, 1 H), 7.11 (dd, J = 8.0, 1.3 Hz, 1 H), 5.43 (s, 1 H), 5.42 (s, 1 H) 4.88 (s, 2 H), 4.27 (s, 2 H), 3.59 (q, J = 7.1 Hz, 2 H), 3.53 (q, J = 7.1 Hz, 2 H), 1.29 (t, J = 7.1 Hz, 3 H), 1.28 (t, J = 7.1 Hz, 3 H).

^{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), 127.3 (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).

MS (EI, 70 eV): m/z (%) = 332.1 ([M]$^+$, 15.8), 261.0 ([M-NEt_2]$^+$, 100), 233.0 ([M-$CONEt_2$]$^+$, 76.5).

Characterization of 46c:



^{1}H NMR (300 MHz, $CDCl_3$, a6080407): 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).

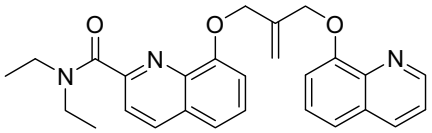
^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.4 (C), 154.5 (C), 153.1 (C), 139.5 (C), 138.4 (C), 136.6 (CH), 129.1 (C), 127.4 (CH), 121.2 (CH), 119.7 (CH), 116.3 (CH_2), 110.3 (CH), 69.4 (CH_2), 43.4 (CH_2), 40.5 (CH_2), 14.4 (CH_3), 12.7 (CH_3).

IR (KBr): ν 3488, 2968, 2932, 1628, 1563, 1477, 1378, 1319, 1256, 1209, 1104, 840, 756 cm^{-1}.

MS (EI, 70 eV): m/z (%) = 540.3 ($[M]^+$, 10.6), 369.1 ($[M\text{-}NEt_2\text{-}CONEt_2]^+$, 52.4), 341.1 ($[M\text{-}2CONEt_2]^+$, 56.7), 297.1 ($[M\text{-}C_{14}H_{15}N_2O_2]^+$, 100).

Elemental analysis: calcd. (%) for $C_{32}H_{36}N_4O_4$ (540.7): C 71.09, H 6.71, N 10.36; found: C 71.10, H 6.97, N 9.95.

***N,N*-Diethyl-8-(2-((quinolin-8-yloxy)methyl)allyloxy)quinoline-2-carboxamide (47c)**



Obtained according to **GP-6**, by reaction of mono-ether **45c** (0.48 g, 1.44 mmol) with 8-hydroxyquinoline **31a** (0.42 g, 2.90 mmol) in acetone (50 ml) in the presence of K_2CO_3 (1.0 g, 7.20 mmol). The purified oily colourless product was crystallized from *n*-hexane / CH_2Cl_2 (1:1).

Yield: 0.53 g (82 %); mp 117 °C.

^{1}H NMR (300 MHz, $CDCl_3$, a6080875): 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).

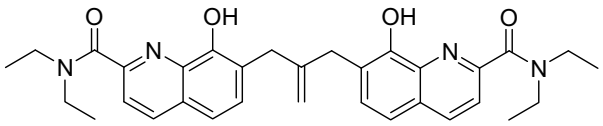
^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.3 (C), 154.3 (C), 153.9 (C), 153.0 (C), 149.0 (CH), 140.1 (C), 139.3 (C), 138.3 (C), 136.5 (CH), 135.6 (CH), 129.2 (C), 129.0 (C), 127.3 (CH), 126.4 (CH), 121.3 (CH), 121.0 (CH), 119.8 (CH), 119.6 (CH), 116.1 (CH_2), 110.2 (CH), 109.8 (CH), 69.4 (CH_2), 69.2 (CH_2), 43.3 (CH_2), 40.4 (CH_2), 14.3 (CH_3), 12.6 (CH_3).

IR (KBr): ν 2928, 1617, 1465, 1373, 1316, 1254, 1103, 755 cm^{-1}.

MS (EI, 70 eV): m/z (%) = 441.2 ($[M]^+$, 5.9), 297.1 ($[M\text{-}C_9H_6NO]^+$, 78.4), 198.1 ($[M\text{-}C_{14}H_{15}N_2O_2]^+$, 100).

Elemental analysis: calcd. (%) for $C_{27}H_{27}N_3O_3$ (441.5): C 73.45, H 6.16, N 9.52; found: C 73.19, H 6.30, N 9.24.

7,7'-(2-Methylenepropane-1,3-diyl)bis(N,N-diethyl-8-hydroxyquinoline-2-carboxamide) (50c-H_2)



Prepared according to **GP-2**, using homodiether **46c** (0.30 g, 0.55 mmol). The brown oily crude product was purified by column chromatography with gradient elution (EtOAc / *n*-hexane 1:2 → 1:1 → 1:0) to afford a colourless crystalline solid.

Yield: 0.282 g (94 %); mp 106 °C.

^{1}H NMR (300 MHz, $CDCl_3$, a6080805): 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).

^{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).

MS (EI, 70 eV): m/z (%) = 540.2 ($[M]^+$, 7.4), 283.1 ($[M\text{-}C_{15}H_{17}N_2O_2]^+$, 100).

HRMS Calcd for ($C_{32}H_{36}N_4O_4$): 540.27366; found: 540.27374.

IR (KBr): ν 2936, 2877, 1611, 1483, 1444, 1375, 1108, 845 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{32}H_{36}N_4O_4$ (540.3): C 71.09, H 6.71, N 10.36; found: C 70.83, H 7.08, N 10.04.

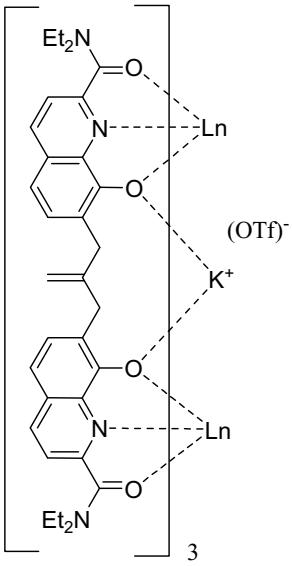
X-Ray quality crystals were obtained from CH_2Cl_2 / *n*-hexane solution.

X-Ray crystal structure analysis for **50c**-H_2: formula $C_{32}H_{36}N_4O_4$, M = 540.65, colourless crystal 0.25 x 0.25 x 0.25 mm, a = 25.2787(9), b = 8.5927(2), c = 13.3004(4) Å, V = 2889.01(15) $Å^3$, ρ_{calc} = 1.243 g cm^{-3}, μ = 0.666 mm^{-1}, empirical absorption correction (0.851 ≤ T ≤ 0.851), Z = 4, orthorhombic, space group $Pna2_1$ (No. 33), λ = 1.54178 Å, T = 223 K, ω and φ scans, 19293 reflections collected (±h, ±k, ±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[218], absorption correction Denzo,[219] structure solution SHELXS-97,[220] structure refinement SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997), graphics XP (BrukerAXS, 2000) and SCHAKAL (E. Keller, Universität Freiburg, 1997).

General procedure (GP-13) for the preparation of homodinuclear helicates [K(50c)$_3$Ln$_2$]OTf

A mixture of ligand **50c**-H_2 (0.04 g, 0.074 mmol, 3.0 equiv.), K_2CO_3 (~ 3.0 equiv.), and Ln(OTf)$_3$ (2.0 equiv.) was stirred in MeOH (15 ml) for 8 h at 55 °C (below bp of MeOH), and then at rt for another 12 h. Solvent was evaporated under reduced pressure. The red residue was redissolved in $CHCl_3$ and filtered from insoluble inorganic components or other unidentified complex species. The $CHCl_3$ solution was concentrated in vacuum to a minimum, *n*-hexane was added dropwise to allow even precipitation of the product.



[K(50c)$_3$Y$_2$]OTf

Prepared according to **GP-13**, using Y(OTf)$_3$ (0.0264 g, 0.06 mmol) and K_2CO_3 (0.01 g, 0.074 mmol).

Yield calcd. on M_W of the complex (M_W = 1981 g mol^{-1}): 0.025 g (51 %).

^{1}H NMR (300 MHz, $CDCl_3$, a5091539): δ = 8.05 (d, J = 8.6 Hz, 6 H), 7.38 (d, J = 8.6 Hz, 6 H), 7.02 (d, J = 8.2 Hz, 6 H),6.60 (d, J = 8.2 Hz, 6 H), 4.16 (s, 6 H), 3.65 (s, 6 H), 3.63 (d, J = 7.2 Hz, 3 H), 3.40 (d, J = 7.2 Hz, 3 H), 2.93 (m, 3 H), 2.72 (m, 3 H), 2.51 (m, 6 H), 1.10 (br. s, 9 H), 0.11 (br. s, 9 H). Significant amounts of side-products are observed in NMR spectrum.

MS (ESI+): m/z (%) = 1831.6 ([Y$_2$(**50c**)$_3$+K]$^+$, 100).

IR (KBr): ν 3433, 2362, 2341, 1629, 1553, 1447, 1350, 1255, 947 cm^{-1}.

An analytically pure sample could not be obtained.

[218] Z. Otwinowski, W. Minor, *Methods in Enzymology* **1997**, *276*, 307.
[219] Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Cryst.* **2003**, *A59*, 228.
[220] G. M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467.

[K(50c)$_3$Gd$_2$]OTf

Prepared according to **GP-13**, using Gd(OTf)$_3$ (0.030 g, 0.06 mmol) and K_2CO_3 (0.01 g, 0.074 mmol).

Yield: 0.033 g (63 %).

MS (ESI+): m/z (%) = 2005.6 ({[K(**50c**)$_3$Gd$_2$]OTf+H}$^+$, 16.8).

IR (KBr): ν 2977, 1586, 1539, 1442, 1358, 1282, 1153, 1106, 1032, 738, 640 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{96}H_{102}N_{12}O_{12}Gd_2KCF_3SO_3 \cdot H_2O$ (2136.6): C 54.53, H 4.91, N 7.87; found: C 54.29, H 5.43, N 7.72.

[K(50c)$_3$Yb$_2$]OTf

Prepared according to **GP-13**, using Yb(OTf)$_3$ (0.031 g, 0.06 mmol) and K_2CO_3 (0.01 g, 0.074 mmol).

Yield: 0.032 g (61 %).

MS: (ESI+): m/z (%) = 2036.1 ({[K(**50c**)$_3$Y$_2$]OTf+H}$^+$, 15.4).

IR (KBr): ν 2975, 1588, 1542, 1444, 1360, 1310, 1279, 1148, 1105, 1031, 740, 639 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{96}H_{102}N_{12}O_{12}Yb_2K_1CF_3SO_3$ (2150.2): C 54.18, H 4.78, N 7.82; found: C 54.16, H 4.99, N 7.66.

Single crystals were obtained from MeOH / THF / $CHCl_3$ / Et_2O.

Crystal data for [K(**50c**)$_3$Yb$_2$]OTf : formula $[K(C_{32}H_{34}N_4O_4)_3Yb_2] \cdot CF_3SO_3 \cdot H_2O \cdot$ ½ MeCN, M = 2188.69, red crystal 0.10 x 0.10 x 0.06 mm, a = 15.831(1), b = 24.262(1), c = 26.818(2) Å, β = 91.52(1)°, V = 10296.9(11) Å^3, D_c = 1.412 g cm^{-3}, μ = 1.938 mm^{-1}, empirical absorption correction (0.830 ≤ T ≤ 0.893), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ= 0.71073 Å, T = 198 K, ω and φ scans, 35448 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.54 Å^{-1}, 13431 independent (R_{int} = 0.180) and 5398 observed reflections [$I \geq 2\ \sigma(I)$], 557 refined parameters, R = 0.140, wR^2 = 0.387, max. residual electron density 1.46 (-0.79) e Å^{-3}, hydrogen atoms are calculated and refined riding.

Data set was collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction SORTAV (R.H. Blessing, *Acta Cryst.* **1995**, *A51*, 33-37; R.H. Blessing, *J. Appl. Cryst.* **1997**, *30*, 421-426), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997), graphics XP (BrukerAXS, 2000).

[K(50c)$_3$Er$_2$]OTf

Prepared according to **GP-13**, using Er(OTf)$_3$ (0.030 g, 0.06 mmol) K_2CO_3 (0.01 g, 0.074 mmol).

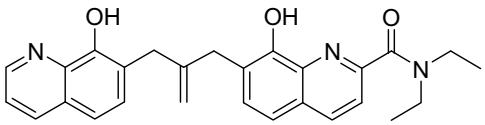
Yield: 0.036 g (66 %).

MS (ESI+): m/z (%) = 1988.8 ([Er$_2$(**50c**)$_3$+K]$^+$, 1.5).

IR (KBr): ν 1588, 1541, 1444, 1359, 1311, 1279, 1151, 1105, 1031, 846, 741 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{96}H_{102}N_{12}O_{12}Er_2KCF_3SO_3 \cdot 3\ H_2O$ (2192.6): C 53.13, H 4.96, N 7.67; found: C 53.00, H 4.68, N 7.47.

***N,N*-Diethyl-8-hydroxy-7-(2-((8-hydroxyquinolin-7-yl)methyl)allyl)quinoline-2-carboxamide (51c-H$_2$)**



Prepared according to **GP-2**, using hetero substituted ether **47c** (0.50 g, 1.13 mmol). The purification of the brown crude product by column chromatography with gradient elution (EtOAc / *n*-hexane 1:2 → EtOAc) provided the product as a white crystalline solid.

Yield: 0.485 g (97 %); mp 65-66 ºC.

^{1}H NMR (300 MHz, $CDCl_3$, a6081087): 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 (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).

^{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).

IR (KBr): ν 3382, 3323, 2925, 1615, 1463, 1463, 1374, 1207, 1089, 882, 830, 777, 663 cm^{-1}.

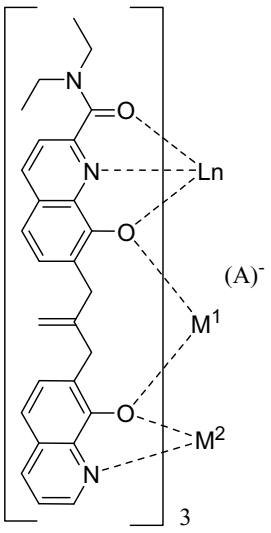
MS (EI, 70 eV): m/z (%) = 441.1 ([M]$^+$, 20.9), 283.1 ([M-$C_{10}H_8NO$]$^+$, 74.4), 184.0 ([M-$C_{15}H_{17}N_2O_2$]$^+$, 100).

HRMS calcd. for $C_{27}H_{27}N_3O_3$: 441.20524; found: 441.20543.

Elemental analysis: calcd. (%) for $C_{27}H_{27}N_3O_3$ (441.2): C 73.45, H 6.16, N 9.52; found: C 74.09, H 6.51, N 9.27.

General procedure (GP-14) for the preparation of heterodinuclear helicates $M^1[LnM^2(51c)_3A]$

A mixture of ligand **51c**-H_2 (0.04 g, 0.09 mmol, 3.0 equiv.), a base M_2CO_3 (M = K or Rb) (~ 2.0 equiv.), $Ln(OTf)_3$ (1.0 equiv.) or $LaCl_3 \cdot 7\ H_2O$ (1.0 equiv.) and hydrated $AlCl_3$ (1.1 equiv.) or $Zn(OAc)_2$ (1.0 equiv.) was stirred in MeOH (15 ml) at 55 °C for 8 h, and then at rt for another 12 h. Solvent was evaporated under reduced pressure. The red residue was dissolved in $CHCl_3$ and filtered from insoluble species. The $CHCl_3$ solution was concentrated in vacuum to a minimum, *n*-hexane was added dropwise to allow even precipitation of the product.



$[Rb(51c)_3LaZn]$ (M^1 = Rb, M^2 = Zn, A = 0)

Prepared according to **GP-14**, using $LaCl_3 \cdot 7\ H_2O$ (11 mg, 0.03 mmol), $Zn(OAc)_2$ (7 mg, 0.03 mmol), and Rb_2CO_3 (20 mg, 0.06 mmol).

Yield: 0.032 g (63 %).

^{1}H NMR (400 MHz, $CDCl_3$, a5093001): δ = 8.08 (d, J = 8.5 Hz, 3 H), 7.98 (dd, J = 8.0, 1.4 Hz, 3 H), 7.55 (dd, J = 4.4, 1.4 Hz, 3 H), 7.34 (d, J = 8.2 Hz, 3 H), 7.28 (d, J = 8.5 Hz, 3 H), 7.22 (d, J = 8.2 Hz, 3 H), 7.02 (dd, J = 8.0, 4.4 Hz, 3 H), 6.77 (d, J = 8.0 Hz, 3 H), 6.67 (d, J = 8.2 Hz, 3 H), 4.26 (s, 3 H), 4.14 (s, 3 H), 4.00 (d, J = 15.9 Hz, 3 H), 3.51 (m, 3 H), 3.39 (d, J = 16.5 Hz, 3 H), 3.37 (m, 3 H), 3.17 (d, J = 16.5 Hz, 3 H), 2.90 (d, J = 15.9 Hz, 3 H), 2.51 (d, J = 6.4 Hz, 6 H), 1.02 (br. s, 9 H), 0.35 (br. s, 9 H).

MS (ESI+): m/z (%) = 1692.3 ($[LaZn(\mathbf{51c})_3Rb_2]^+$, 100).

IR (KBr): ν 2974, 1627, 1449, 1373, 1314, 1206, 1109, 848 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{81}H_{75}N_9O_9LaZnRb \cdot H_2O$ (1644.3): C 59.17, H 4.84, N 7.67; found: C 59.15, H 5.00, N 7.17.

$[K(51c)_3LaAl]Cl$ (M^1 = K, M^2 = Al, A = Cl)

Prepared according to **GP-14**, using $LaCl_3 \cdot 7\ H_2O$ (11 mg, 0.03 mmol), $AlCl_3$ (4.4 mg, 0.033 mmol), and K_2CO_3 (10 mg, 0.07 mmol).

Yield: 0.042 g (88 %).

^{1}H NMR (400 MHz, $CDCl_3$, a7070209): δ = 8.34 (d, J = 8.7 Hz, 3 H), 8.19 (dd, J = 8.5 Hz, 3 H), 7.38 (m, 9 H), 7.29 (dd, J = 8.2, 4.0 Hz, 3 H), 7.13 (d, J = 8.5 Hz, 3 H), 6.93 (d, J = 8.0 Hz, 3 H), 6.91 (d, J = 4.1 Hz, 3 H), 4.22 (s, 3 H), 4.13 (s, 3 H), 3.89 (d, J = 16.8 Hz, 3 H),

3.71 (d, J = 16.8 Hz, 3 H), 3.46 (m, 6 H), 3.07 (d, J = 16.8 Hz, 6 H), 2.48 (m, 3 H), 2.37 (m, 3 H), 0.88 (t, J = 6.7 Hz, 9 H), 0.39 (t, J = 6.8 Hz, 9 H).

MS (ESI+): m/z (%) = 1523.4 ([LaAl(**51c**)$_3$K]$^+$, 100).

IR (KBr): ν 2974, 2932, 1625, 1499, 1462, 1379, 1317, 1111, 833, 803, 760, 677, 572, cm^{-1}.

Elemental analysis: calcd. (%) for $C_{81}H_{75}N_9O_9LaAlKCl \cdot 2\ H_2O$ (1593.4): C 61.00, H 4.99, N 7.90; found: C 60.92, H 5.28, N 7.73.

[K(51c)$_3$GdAl]OTf (M^1 = K, M^2 = Al, A = Cl)

Prepared according to **GP-14**, using $Gd(OTf)_3$ (18.3 mg, 0.03 mmol), $AlCl_3$ (4.4 mg, 0.033 mmol), and K_2CO_3 (10 mg, 0.07 mmol).

Yield: 0.038 g (74 %).

MS (ESI+): m/z (%) = 1541.0 ([GdAl(**51c**)$_3$K]$^+$, 100).

IR (KBr): ν 2977, 1585, 1500, 1463, 1378, 1314, 1279, 1154, 1110, 1030, 742, 739, 642, 573 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{81}H_{75}N_9O_9GdAlKCF_3SO_3$ (1690.0): C 57.41, H 5.04, N 6.93; found: C 57.34, H 4.86, N 7.34.

[K(51c)$_3$YbAl]OTf (M^1 = K, M^2 = Al, A = Cl)

Prepared according to **GP-14**, using $Yb(OTf)_3$ (19 mg, 0.03 mmol), $AlCl_3$ (4.4 mg, 0.033 mmol), and K_2CO_3 (10 mg, 0.07 mmol).

Yield: 0.041 g (79 %).

MS (ESI+): m/z (%) = 1556.9 ([YbAl(**51c**)$_3$K]$^+$, 100).

IR (KBr): 2971, 1586, 1540, 1463, 1378, 1314, 1275, 1150, 1109, 1030, 762, 740, 678, 639 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{81}H_{75}N_9O_9YbAlKCF_3SO_3$ (1706.7): C 57.71, H 4.43, N 7.39; found: C 57.81, H 4.88, N 7.44.

[K(51c)$_3$ErAl]OTf (M^1 = K, M^2 = Al, A = Cl)

Prepared according to **GP-14**, using $Er(OTf)_3$ (19 mg, 0.03 mmol), $AlCl_3$ (4.4 mg, 0.033 mmol), and K_2CO_3 (10 mg, 0.07 mmol).

Yield: 0.043 g (83 %).

MS (ESI+): m/z (%) = 1541.0 ([ErAl(**51c**)$_3$K]$^+$, 100).

IR (KBr): ν 1590, 1503, 1463, 1379, 1278, 1109, 1031, 831, 744, 680, 641 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{81}H_{75}N_9O_9ErAlKCF_3SO_3$ (1700.9): C 57.90, H 4.44, N 7.41; found: C 58.45, H 5.06, N 7.09.

[K(51c)$_3$NdAl]OTf (M^1 = K, M^2 = Al, A = Cl)

Prepared according to **GP-14**, using $Nd(OTf)_3$ (17.9 mg, 0.03 mmol), $AlCl_3$ (4.4 mg, 0.033 mmol), and K_2CO_3 (10 mg, 0.07 mmol).

Yield: 0.049 g (80 %).

MS (ESI+): m/z (%) = 1527.9 ([NdAl(**51c**)$_3$K]$^+$, 100).

IR (KBr): ν 1583, 1538, 1465, 1442, 1377, 1278, 1155, 1110, 1031, 764, 737, 641 cm^{-1}.

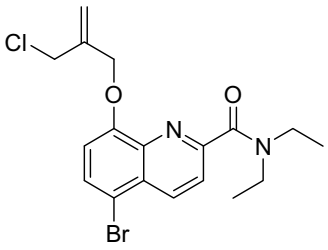
Elemental analysis: calcd. (%) for $C_{81}H_{75}N_9O_9NdAlKCF_3SO_3 \cdot 3\ CHCl_3$ (2036.0): C 50.14, H 3.86, N 6.19; found: C 49.51, H 4.08, N 6.23.

5-Bromo-8-(2-(chloromethyl)allyloxy)quinoline-2-carboxylic acid diethylamide (52) and 8,8'-(2-methylenepropane-1,3-diyl)bis(oxy)bis(5-bromo-*N*,*N*-diethylquinoline-2-carboxamide) (53)

Prepared according to **GP-1**, starting from monobromosubstituted amidoquinolinate **34b** (0.20 g, 0.62 mmol), 3-chloro-2-chloromethyl-propene (0.72 ml, 0.62 mmol), and K_2CO_3 (0.86 g, 6.20 mmol). The reaction mixture in acetone (50 ml) was refluxed for 15 h. After the workup, the crude residue was applied to flash chromatography with gradient elution (EtOAc / *n*-hexane 1:3 → 1:1) which allowed the separation of **52** (R_f = 0.47) and **53** (R_f = 0.11) as colourless oils.

Yield: **52:** 0.067 g (26 %) and **53:** 0.071 g (33 %).

Characterization of 52:

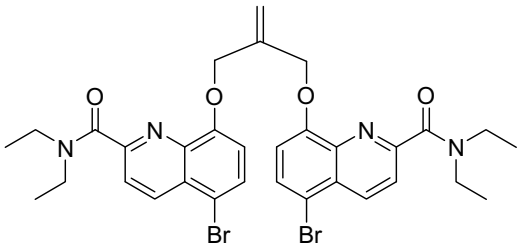


^{1}H NMR (300 MHz, $CDCl_3$, a7072385): δ = 8.55 (d, J = 8.8 Hz, 1 H), 7.89 (d, J = 8.8 Hz, 1 H), 7.74 (d, J = 8.4 Hz, 1 H), 7.01 (d, J = 8.4 Hz, 1 H), 5.43 (s, 2 H), 4.87 (s, 2 H), 4.26 (s, 2 H), 3.61 (q, J = 7.2 Hz, 2 H), 3.52 (q, J = 7.2 Hz, 2 H), 1.30 (t, J = 7.2 Hz, 3 H), 1.29 (t, J = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.4, 154.4, 147.2, 140.1, 136.5, 130.8, 128.2, 125.4, 122.7, 118.1, 110.9, 110.2, 66.1, 45.0, 43.6, 40.8, 14.5, 13.8.

MS (EI, 70 eV): m/z (%) = 411.9 ([M]$^+$, 9.0), 376.9 ([M-Cl]$^+$, 6.9), 340.9 ([M-NEt$_2$+H]$^+$, 29.5), 312.9 ([M-CONEt$_2$+H]$^+$, 20.8), 72.2 ([M-$C_{14}H_{10}BrClN_1O_2$]$^+$, 100).

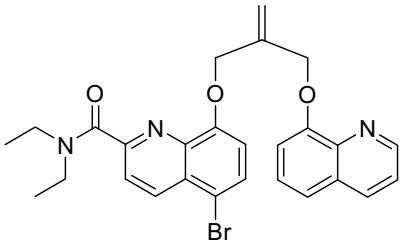
Characterization of 53:



^{1}H NMR (300 MHz, $CDCl_3$, a5093042): δ = 8.56 (d, J = 8.8 Hz, 2 H), 7.85 (d, J = 8.8 Hz, 2 H), 7.71 (d, J = 8.4 Hz, 2 H), 7.06 (d, J = 8.4 Hz, 2 H), 5.52 (s, 2 H), 4.96 (s, 4 H), 3.59 (q, J = 7.1 Hz, 4 H), 3.44 (q, J = 7.1 Hz, 4 H), 1.28 (t, J = 7.1 Hz, 6 H), 1.23 (t, J = 7.1 Hz, 6 H).

MS (EI, 70 eV): m/z (%) = 698.4 ($[M]^+$, 7.9), 596.2 ($[M\text{-}CONEt_2]^+$, 12.1), 375.9 ($[M\text{-}C_{14}H_{14}BrN_2O_2]^+$, 100).

5-Bromo-8-[2-(quinolin-8-yloxymethyl)allyl-oxy]quinoline-2-carboxylic acid *N,N*-diethyl-amide (54)



Prepared according to **GP-6**, by reaction of bromosubstituted mono-ether **52** (0.041 g, 0.10 mmol) with 8-hydroxyquinoline **31a** (0.03 g, 0.21 mmol) in acetone (25 ml) in the presence of K_2CO_3 (0.014 g, 1.0 mmol).

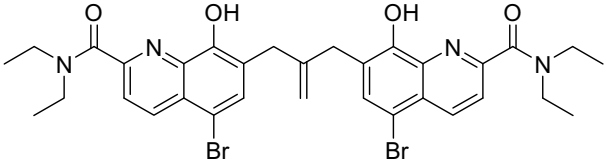
Yield: 0.045 g (87 %).

NMR (300 MHz, $CDCl_3$, a7072348): δ = 8.93 (dd, J = 4.2, 1.7 Hz, 1 H), 8.54 (d, J = 8.7 Hz, 1 H), 8.12 (dd, J = 8.4, 1.7 Hz, 1 H), 7.86 (d, J = 8.7 Hz, 1 H), 7.67 (d, J = 8.4 Hz, 1 H), 7.44-7.37 (m, 3 H), 7.16 (dd, J = 5.2, 1.7 Hz, 1 H), 7.04 (d, J = 8.4 Hz, 1 H), 5.53 (s, 2 H), 5.05 (s, 2 H), 4.98 (s, 2 H), 3.58 (q, J = 7.2 Hz, 2 H), 3.47 (q, J = 6.9 Hz, 2 H), 1.27 (t, J = 7.2 Hz, 3 H), 1.23 (t, J = 6.9 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.9 (C), 154.4 (C), 154.1 (C), 153.7 (C), 149.3 (CH), 140.4 (C), 139.3 (C), 139.2 (C), 136.4 (CH), 135.9 (CH), 130.8 (CH), 129.5 (C), 128.1 (C), 126.6 (CH), 122.5 (CH), 121.6 (CH), 120.1 (CH), 116.7 (CH_2), 112.1 (C), 110.9 (CH), 109.9 (CH), 69.7 (CH_2), 69.5 (CH_2), 43.5 (CH_2), 40.7 (CH_2), 14.5 (CH_3), 12.8 (CH_3).

MS (EI, 70 eV): m/z (%) = 521.1 ($[M]^+$, 4.5), 420.0 ($[M\text{-}CONEt_2]^+$, 4.3), 375.1 ($[M\text{-}C_9H_6N_1O_1]^+$, 35.1), 198.1 ($[M\text{-}C_{14}H_{14}BrN_2O_2]^+$, 100).

7,7'-(2-Methylenepropane-1,3-diyl)bis(5-bromo-*N,N*-diethyl-8-hydroxyquinoline-2-carboxamide) (55)



Prepared according to **GP-2** (145 °C, 7 h), starting from bromosubstituted diether **53** (0.06 g, 0.086 mmol). Purification by

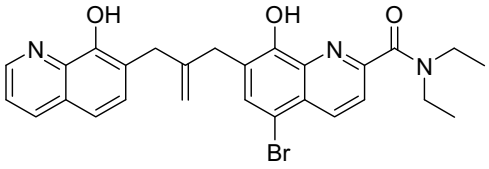
recrystallization from *i*-PrOH afforded a colourless crystalline solid.

Yield: 0.043 (72 %).

^{1}H NMR (400 MHz, $CDCl_3$, a5111607): δ = 8.48 (d, J = 8.6 Hz, 2 H), 8.04 (s, 2 H), 7.72 (d, J = 8.6 Hz, 2 H), 7.65 (s, 2 H), 4.98 (s, 2 H), 3.64 (q, J = 7.1 Hz, 4 H), 3.62 (s, 4 H), 3.38 (q, J = 7.1 Hz, 4 H), 1.33 (t, J = 7.1 Hz, 6 H), 1.23 (t, J = 7.1 Hz, 6 H).

MS (EI, 70 eV): m/z (%) = 698.0 ($[M]^+$, 11.3), 363.0 ($[M\text{-}C_{15}H_{16}BrN_2O_2+H]^+$, 100), 261.7 ($[M\text{-}C_{20}H_{26}BrN_3O_3]^+$, 19.8), 72.2 ($[M\text{-}C_{28}H_{24}Br_2N_3O_2]^+$, 46.0).

5-Bromo-8-hydroxy-7-[2-(8-hydroxyquinolin-7-ylmethyl)allyl]quinoline-2-carboxylic acid diethylamide (56)



Prepared according to **GP-2** (150 °C, 7 h), starting from bromosubstituted hetero-ether **54** (0.04 g, 0.077 mmol). Purification by recrystallization from *i*-PrOH afforded a colourless crystalline solid.

Yield: 0.025 g (62 %).

NMR (400 MHz, $CDCl_3$, a5092630): δ = 8.73 (dd, J = 4.4, 1.6 Hz, 1 H), 8.46 (d, J = 8.8 Hz, 1 H), 8.13 (dd, J = 8.2, 1.6 Hz, 1 H), 8.03 (br. s, 2 H), 7.70 (d, J = 8.5 Hz, 1 H), 7.66 (s, 1 H) 7.40 (dd, J = 8.2, 4.4 Hz, 1 H), 7.39 (d, J = 8.2 Hz, 1 H), 7.27 (d, J = 8.2 Hz, 1 H), 4.94 (s, 1 H), 4.91 (s, 1 H), 3.66 (s, 2 H), 3.64 (q, J = 7.1 Hz, 2 H), 3.63 (s, 2 H), 3.38 (q, J = 7.1 Hz, 2 H), 1.32 (t, J = 7.1 Hz, 3 H), 1.23 (t, J = 7.1 Hz, 3 H).

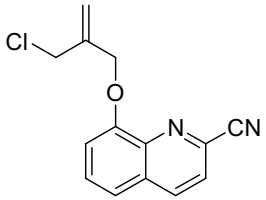
MS (CI, 100 eV): m/z (%) = 520.2 ($[M]^+$, 2.5), 422.3 ($[M\text{-}CONEt_2]^+$, 32.3), 343.2 ($[M\text{-}CONEt_2\text{-}Br]^+$, 100), 184.1 ($[M\text{-}C_{15}H_{16}BrN_2O_2]^+$, 89.4), 74.2 ($[M\text{-}C_{23}H_{16}BrN_2O_3]^+$, 98.4).

8-(2-(Chloromethyl)allyloxy)quinoline-2-carbonitrile (36) and 8,8'-(2-methylene-propane-1,3-diyl)bis(oxy)di(quinoline-2-carbonitrile) (37)

Prepared according to **GP-1**, starting from 8-hydroxyquinoline-2-carbonitrile **33** (1.0 g, 5.88 mmol), K_2CO_3 (8.12 g, 58.8 mmol), and 3-chloro-2-chloromethyl-propene **13** (0.73 g, 0.68 ml, 5.88 mmol), which were refluxed in acetone (50 ml) for 24 h. After the usual workup, the crude residue was applied to flash chromatography (EtOAc / *n*-hexane 1:2) furnishing **36** as colourless crystalline solid (R_f = 0.38) and **37** as a white powder (R_f = 0.13).

Yield: **36:** 0.53 g (35 %); mp 125 °C and **37:** 0.37 g (32 %); mp 204 °C.

Characterization of 36:



^{1}H NMR (400 MHz, $CDCl_3$, a6020705): δ = 8.28 (d, J = 8.4 Hz, 1 H), 7.73 (d, J = 8.4 Hz, 1 H), 7.61 (dd, J = 8.2, 7.9 Hz, 1 H), 7.48 (dd, J = 8.2, 1.0 Hz, 1 H), 7.23 (dd, J = 7.9, 1.0 Hz, 1 H), 5.48 (d, J = 4.2 Hz, 2 H), 4.96 (s, 2 H), 4.32 (s, 2 H).

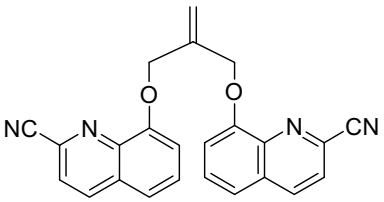
^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.0 (C), 140.3 (C), 138.5 (C), 137.1 (CH), 132.1 (C), 129.7 (CH), 129.7 (C), 123.9 (CH), 119.8 (CH), 117.8 (CH_2), 117.5 (C), 111.1 (CH), 69.0 (CH_2), 45.1 (CH_2).

MS (EI, 70 eV): m/z (%) = 257.9 ($[M]^+$, 12.9), 223.0 ($[M\text{-}Cl]^+$, 100), 208.9 ($[M\text{-}CH_2Cl]^+$, 14.1), 182.9 ($[M\text{-}C_3H_4Cl]^+$, 15.7).

IR (KBr): ν 2235, 1612, 1556, 1499, 1465, 1439, 1380, 1321, 1263, 1211, 1114, 1073, 1020, 976, 931, 842, 758, 655, 504 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{14}H_{11}N_2ClO$ (258.7): C 65.00, H 4.29, N 10.83; found: C 65.11, H 4.46, N 10.82.

Characterization of 37:



^{1}H NMR (300 MHz, $CDCl_3$, 7032767): δ = 8.23 (d, J = 8.4 Hz, 2 H), 7.69 (dd, J = 8.3, 7.9 Hz, 2 H), 7.68 (d, J = 8.4 Hz, 2 H), 7.45 (dd, J = 8.3, 1.2 Hz, 2 H), 7.41 (dd, J = 7.9, 1.2 Hz, 2 H), 5.59 (s, 2 H), 5.09 (s, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.4 (C), 140.5 (C), 138.9 (C), 137.1 (CH), 132.2 (C), 130.3 (CH), 129.8 (C), 123.8 (CH), 119.7 (CH), 117.7 (C), 117.1 (CH_2), 111.6 (CH), 69.9 (CH_2).

MS (EI, 70 eV): m/z (%) = 392.1 ($[M]^+$, 16.1), 223.0 ($[M\text{-}C_2H_5NO]^+$, 100), 183.0 ($[M\text{-}C_{13}H_9N_2O]^+$, 10.9).

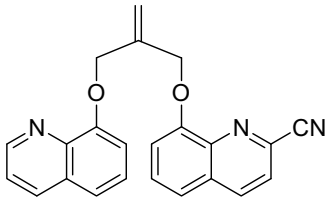
IR (KBr): ν 2230, 1611, 1555, 1500, 1459, 1376, 1321, 1264, 1210, 1102, 978, 926, 835, 750 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{24}H_{16}N_4O_2$ (392.4): C 73.46, H 4.11, N 14.28; found: C 73.53, H 4.46, N 14.28.

8-[2-(Quinolin-8-yloxymethyl)allyloxy]quinoline-2-carbonitrile (38)

Prepared according to **GP-6**, starting from mono-ether **36** (0.50 g, 1.93 mmol), 8-hydroxyquinoline **31a** (0.56 g, 3.86 mmol), and K_2CO_3 (1.34 g, 9.66 mmol). Purification by column chromatography (EtOAc / *n*-hexane 1:2 → EtOAc) furnished a colourless crystalline solid.

Yield: 0.66 g (93 %); mp 157 °C.



^{1}H NMR (400 MHz, $CDCl_3$, a6011338): δ = 8.92 (dd, J = 4.2, 1.8 Hz, 1 H), 8.22 (d, J = 8.3 Hz, 1 H), 8.12 (dd, J = 8.5, 1.8 Hz, 1 H), 7.69 (d, J = 8.3 Hz, 1 H), 7.46 (dd, J = 8.2, 7.7 Hz, 1 H), 7.42 (t, J = 7.9 Hz, 1 H), 7.40-7.36 (m, 3 H), 7.27 (dd, J = 7.9, 1.2 Hz, 1 H), 7.22 (dd, J = 7.9, 1.2 Hz, 1 H), 5.58 (s, 2 H), 5.11 (s, 2 H), 5.05 (s, 2 H).

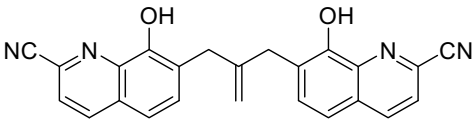
^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.2 (C), 153.8 (C), 149.0 (CH), 140.4 (C), 140.1 (C), 138.9 (C), 137.0 (CH), 135.8 (CH), 132.1 (C), 129.8 (CH), 129.7 (C), 129.3 (C), 126.7 (CH), 123.8 (CH), 121.4 (CH), 119.9 (CH), 119.5 (CH), 117.6 (C), 116.6 (CH_2), 111.2 (CH), 110.0 (CH), 69.7 (CH_2), 69.4 (CH_2).

MS (EI, 70 eV): m/z (%) = 367.0 ($[M]^+$, 6.6), 223.0 ($[M-C_9H_6NO]^+$, 63.1), 198.0 ($[M-C_{10}H_5N_2O]^+$, 100).

IR (KBr): ν 2928, 1612, 1565, 1499, 1460, 1428, 1378, 1317, 1260, 1207, 1181, 1098, 1021, 985, 908, 840, 820, 786, 750, 542, 497, 475 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{23}H_{17}N_3O_2$ (367.4): C 75.19, H 4.66, N 11.44; found: C 74.84, H 5.03, N 11.34.

7,7'-(2-Methylenepropane-1,3-diyl)bis(8-hydroxyquinoline-2-carbonitrile) (39)



Prepared according to **GP-2** (175-180 °C, 4 h), using diether **37** (0.30 g, 0.76 mmol). The product was purified by recrystallization from acetone / CH_2Cl_2 (1:2) to furnish an off-white solid.

Yield: 0.267 (89 %); mp 242-243 °C.

^{1}H NMR (400 MHz, DMSO-d6, a7032794): δ = 10.11 (s, 2 H), 8.54 (d, J = 8.4 Hz, 2 H), 7.96 (d, J = 8.6 Hz, 2 H), 7.55 (d, J = 8.4 Hz, 2 H), 7.48 (d, J = 8.6 Hz, 2 H), 4.70 (s, 2 H), 3.57 (s, 4 H).

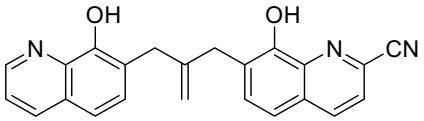
^{13}C NMR (100 MHz, DMSO-d_6): δ = 150.5 (C), 146.4 (C), 138.4 (C), 137.9 (CH), 133.0 (CH), 130.4 (C), 128.1 (C), 124.0 (C), 123.5 (CH), 117.8 (C), 117.3 (CH), 112.5 (CH_2), 35.8 (CH_2).

MS (ESI-): m/z (%) = 391.4 ($[M-1]^-$, 100).

IR (KBr): ν 3421, 1503, 1439, 1400, 1337, 1243, 1088, 897, 848, 783, 723, 567 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{24}H_{16}N_4O_2$ (392.4): C 73.46, H 4.11, N 14.28; found: C 73.48, H 4.13, N 14.14.

8-Hydroxy-7-[2-(8-hydroxyquinolin-7-ylmethyl)allyl]quinoline-2-carbonitrile (40)



Prepared according to **GP-2** (175 °C, 4 h), using hetero-ether **38** (0.50 g, 1.36 mmol). The product was purified by recrystallization from acetone by slow addition of *n*-hexane to furnish a yellowish solid.

Yield: 0.445 g (89 %); mp 156 °C.

^{1}H NMR (300 MHz, $CDCl_3$, a7032766): δ = 8.75 (dd, J = 4.1, 1.6 Hz, 1 H), 8.24 (d, J = 8.4 Hz, 1 H), 8.10 (dd, J = 8.2, 1.6 Hz, 1 H), 7.94 (br. s, 1 H), 7.65 (d, J = 8.5 Hz, 1 H), 7.57 (d, J = 8.5 Hz, 1 H), 7.39 (dd, J = 8.2, 4.1 Hz, 1 H), 7.37 (d, J = 8.5 Hz, 1 H), 7.34 (d, J = 8.5 Hz, 1 H), 7.26 (d, J = 8.5 Hz, 1 H) 4.91 (s, 1 H), 4.86 (s, 1 H), 3.67 (s, 2 H), 3.65 (s, 2 H).

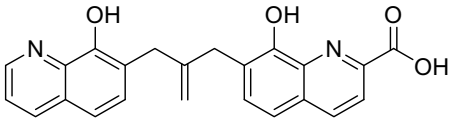
^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.6 (C), 149.5 (C), 147.7 (CH), 146.0 (C), 138.2 (C), 138.1 (C), 137.2 (CH), 135.8 (CH), 133.5 (CH), 130.6 (C), 129.9 (CH), 127.7 (C), 127.1 (C), 123.7 (C), 123.2 (CH), 121.1 (CH), 120.8 (C), 117.4 (C), 117.2 (CH), 117.1 (CH), 113.4 (CH_2), 36.1 (CH_2), 35.9 (CH_2).

MS (EI, 70 eV): m/z (%) = 366.8 ($[M]^+$, 13.4), 208.9 ($[M-C_{10}H_8NO]^+$, 15.0), 183.9 ($[M-C_{12}H_{10}NO]^+$, 63.8), 158.9 ($[M-C_{13}H_9N_2O]^+$, 100).

IR (KBr): ν 3446, 1505, 1444, 1389, 1329, 1176, 1137, 1091, 1050, 900, 830, 673, 581 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{23}H_{17}N_3O_2$ (367.4): C 75.19, H 4.66, N 11.44; found: C 75.03, H 4.83, N 11.35.

8-Hydroxy-7-[2-(8-hydroxyquinolin-7-ylmethyl)allyl]quinoline-2-carboxylic acid (42-H$_3$)



An isobutenylidene-bridged carbonitrile derivative **40** (0.25 g, 0.68 mmol) was dissolved in 3 N NaOH (15 ml). The resulting solution was refluxed for 4 h, cooled to rt, and acidified with 5 N HCl to pH 4-5. The product was collected by filtration, washed with water, and dried in vacuum. The crude product was redissolved in MeOH and applied to a Sephadex LH-20 column (sample weight / bed weight 1:100) eluting with MeOH to afford the product as a yellow crystalline solid.

Yield: 0.187 g (69 %); mp 136 °C.

^{1}H NMR (300 MHz, DMSO-d_6, a5092112): δ = 8.80 (dd, J = 4.1, 1.6 Hz, 1 H), 8.46 (d, J = 8.5 Hz, 1 H), 8.24 (dd, J = 8.2, 1.6 Hz, 1 H), 8.08 (d, J = 8.5 Hz, 1 H), 7.51 (d, J = 8.5 Hz, 1 H), 7.47 (dd, J = 8.2, 4.1 Hz, 1 H), 7.44 (d, J = 8.5 Hz, 1 H), 7.35 (d, J = 8.5 Hz, 1 H), 7.33 (d, J = 8.5 Hz, 1 H), 4.72 (d, J = 6.0 Hz, 2 H), 3.58 (s, 2 H), 3.56 (s, 2 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 165.3 (C), 151.0 (C), 150.2 (C), 148.1 (CH), 147.0 (C), 144.2 (C), 138.2 (CH), 137.7 (CH), 136.4 (C), 136.1 (CH) 132.7 (CH), 129.7 (CH), 128.8 (C), 127.4 (C), 123.1 (C), 121.5 (CH), 121.4 (CH), 119.4 (CH), 117.2 (CH), 117.1 (CH), 112.4 (CH_2), 36.1 (CH_2), 35.9 (CH_2).

MS (ESI+): m/z (%) = 387.2 ($[M+H]^+$, 100), 343.1 ($[M-COO]^+$, 75.3).

IR (KBr): ν 3353, 1743, 1554, 1504, 1456, 1369, 1242, 1088, 826, 665, 476 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{23}H_{18}O_4N_2$ · 2/3 H_2O (398.4): C 69.34, H 4.89, N 7.03; found: C 69.21, H 4.76, N 6.92.

Synthesis of dinuclear helicate-type complexes $K_2[(42)_2Zn_2]$ and $Rb_2[(42)_2Zn_2]$.

To the carboxylic acid **42**-H_3 (0.03 g, 0.078 mmol) in MeOH (15 ml) $Zn(OAc)_2$ (0.017 g, 0.078 mmol) and either K_2CO_3 (0.011 g, 0.08 mmol) or Rb_2CO_3 (0.026 g, 0.08 mmol) were added. The mixture was refluxed for 10 h, and then cooled to rt. The reaction volume was reduced by evaporation under reduced pressure; the abundant orange precipitate was centrifuged, washed with Et_2O, and dried in vacuum.

Characterization of $K_2[(42)_2Zn_2]$

^{1}H NMR (300 MHz, DMSO-d_6, a5092339): δ = 8.45 (d, J = 8.2 Hz, 2 H), 8.34 (m, 2 H), 7.96 (m, 4 H), 7.53 (d, J = 8.2 Hz, 2 H), 7.36 (m, 4 H), 6.92 (m, 4 H), 4.81 (s, 2 H). 4.18 (s, 2 H), the signals of the benzylic protons are hidden under the solvent and water peaks.

MS (ESI+): m/z (%) = 899 ($[M+H]^+$, 100).

Elemental analysis: calcd. (%) for $C_{46}H_{30}O_8N_4Zn_2K_2$ · 5 H_2O: C 51.84, H 3.78, N 5.26; found: C 51.82, H 3.37, N 4.95.

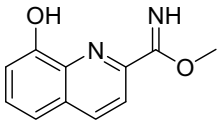
Characterization of $Rb_2[(42)_2Zn_2]$

^{1}H NMR (300 MHz, DMSO-d_6, a6012615): δ = 8.31 (m, 6 H), 7.92 (d, J = 8.2 Hz, 2 H), 7.54 (dd, J = 8.2, 4.7 Hz, 2 H), 7.35 (m, 4 H), 6.85 (m, 4 H), 4.43 (m, 4 H). 3.78 (d, J = 15.3 Hz, 2 H), 3.36 (d, J = 8.7 Hz, 2 H), two further signals are hidden under the water peak.

X-Ray quality crystals were obtained by slow diffusion of Et_2O in MeOH solution of $Rb_2[(\mathbf{42})_2Zn_2]$. *X-ray crystal structure analysis*: formula $Rb_2(CH_3OH)_3$ (H_2O) · $[(C_{23}H_{15}N_2O_4)_2Zn_2]$ · CH_3OH, M = 1214.60, yellow-orange crystal 0.30 x 0.30 x 0.05 mm, a = 12.944(1), b = 13.320(1), c = 15.608(1) Å, α = 101.26(1), β = 107.06(1), γ = 99.84(1)°, V = 2447.2(3) Å^3, ρ_{calc} = 1.648 g cm^{-3}, μ = 0.303 mm^{-1}, empirical absorption correction (0.464 ≤ T ≤ 0.863), Z = 2, triclinic, space group P1bar (No. 2), λ= 0.71073 Å, T = 198 K, ω and φ scans, 25862 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.67 Å^{-1}, 11911 independent (R_{int} =

0.051) and 8202 observed reflections [$I \geq 2\ \sigma(I)$], 656 refined parameters, $R = 0.047$, $wR^2 = 0.100$, max. residual electron density 0.72 (-0.57) e $Å^{-3}$, hydrogen atoms are calculated and refined riding.

Methyl-8-hydroxyquinoline-2-carbimidate (44)



To a solution of 8-hydroxyquinoline-2-carbonitrile (0.20 g, 1.18 mmol) in MeOH (20 ml) 5 ml of 3 N NaOH were added. The deep red solution was refluxed for 2 h, then cooled to rt and neutralized with 5 N HCl. The off-white precipitate was collected by filtration, washed with water, and recrystallized from EtOAc to furnish a colourless crystalline solid. As an alternative, the purification by column chromatography (EtOAc / *n*-hexane 1:6 → EtOAc) allowed the separation of unreacted carbonitrile followed by collecting the desired product.

Yield: 0.188 g (79 %); mp 127 °C.

^{1}H NMR (400 MHz, $CDCl_3$, a7031325): δ = 9.25 (br. s, 1 H), 8.28 (d, J = 8.5 Hz, 1 H), 8.14 (br. s, 1 H), 7.99 (d, J = 8.5 Hz, 1 H), 7.52 (dd, J = 8.2, 7.7 Hz, 1 H), 7.38 (dd, J = 8.2, 1.1 Hz, 1 H), 7.24 (dd, J = 7.7, 1.1 Hz, 1 H), 4.09 (s, 3 H).

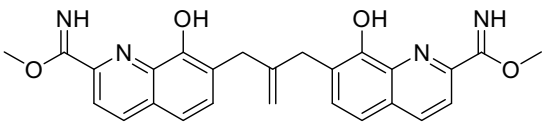
^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.5 (C), 166.5 (C), 152.4 (C), 145.3 (C), 137.7 (CH), 129.1 (CH), 118.9 (CH), 117.7 (CH), 111.0 (CH), 54.3 (CH_3), one quarternary C atom could not be observed.

MS (EI, 70 eV): m/z (%) = 202.0 ($[M]^+$, 70.9), 188.0 ($[M\text{-}CH_3+H]^+$, 100).

IR (KBr): ν 3389, 3196, 1700, 1636, 1566, 1508, 1472, 1390, 1331, 1240, 1204, 1165, 1089, 866, 846, 733, 608, 473 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{11}H_{10}N_2O_2$ (202.2): C 65.34, H 4.98, N 13.85; found: C 64.96, H 4.85, N 13.40.

Dimethyl 7,7'-(2-methylenepropane-1,3-diyl)bis(8-hydroxyquinoline-2-carbimidate) (43-H_2)



Prepared according to the described procedure for monoimidate **44**, starting from bis-carbonitrile **39** (0.40 g, 1.02 mmol). The reflux time was prolonged to 3 h. After workup the crude product was recrystallized from DMF / *i*-PrOH to furnish an off-white solid.

Yield: 0.384 g (83 %); mp 239 °C.

^{1}H NMR (400 MHz, DMSO-d_6, a7033111): δ = 10.28 (s, 2 H), 10.06 (br. s, 2 H), 8.45 (d, J = 8.5 Hz, 2 H), 7.89 (d, J = 8.2 Hz, 2 H), 7.48 (d, J = 8.2 Hz, 2 H), 7.44 (d, J = 8.5 Hz, 2 H), 4.76 (s, 2 H), 3.94 (s, 6 H), 3.60 (s, 4 H).

MS (EI, 70 eV): m/z (%) = 456.1 ($[M]^+$, 11.2), 441.1 ($[M\text{-}CH_3]^+$, 36.6), 241.0 ($[M\text{-}C_{11}H_9N_2O_2\text{-}CH_3+H]^+$, 100).

MS (ESI+): m/z (%) = 479.1 ([M+Na], 100).

IR (KBr): ν 3246, 1648, 1508, 1461, 1369, 1337, 1238, 1214, 1095, 968, 888, 843 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{26}H_{24}N_4O_4$ (456.5): C 68.41, H 5.30, N 12.27; found: C 68.01, H 5.24, N 12.30.

HRMS Calcd. for ($C_{26}H_{24}N_4O_4$): 456.179755; found: 456.179766.

Preparation of dinuclear helicate-type complex [K(43)$_3$Yb$_2$]OTf

A mixture of bis-imidate ligand **43**-H_2 (0.05 g, 0.11 mmol, 3.0 equiv.), K_2CO_3 (0.20 g, 0.14 mmol), and $Yb(OTf)_3$ (0.045 g, 0.07 mmol, 2.0 equiv.) in MeOH (15 ml) was stirred at 60 °C for 15 h. After cooling to rt, the solvent was removed under reduced pressure and the crude residue was redissolved in MeOH / THF, filtered from insoluble inorganic salts, and evaporated in vacuum to afford a red powder.

Yield: 0.065 g (94 %).

MS (ESI+): m/z (%) = 1749.2 ($[Yb_2(\mathbf{43})_3+K]^+$, 63.5), 629.2 ($[Yb_1(\mathbf{43}\text{-}H)_1]^{2+}$, 100).

IR (KBr): ν 3395, 1658, 1454, 1364, 1261, 1166, 1036, 644 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{78}H_{66}N_{12}O_{12}Yb_2KCF_3SO_3$ (1897.7): C 50.00, H 3.51, N 8.86; found: C 49.51, H 3.94, N 8.60.

X-Ray quality crystals were obtained by slow diffusion of Et_2O into MeOH / THF solution.

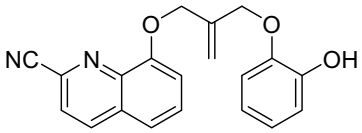
5.9. Isobutenylidene-Bridged Catechol / Quinoline Ligands (59b, 60a,b). Towards Tritopic Ligands

8-[2-(2-Hydroxyphenoxymethyl)allyloxy]quinoline-2-carbonitrile (57a) and 8,8'-(2,2'-(1,2-phenylenebis(oxy))bis(methylene)bis(prop-2-ene-2,1-diyl))bis(oxy)diquinoline-2-carbonitrile (58a)

Prepared according to **GP-7**, starting from 2-carbonitrile mono-ether **36** (0.54 g, 2.09 mmol), catechol (0.115 g, 1.04 mmol), and K_2CO_3 (1.44 g, 10.43 mmol). The crude oily residue was applied to flash chromatography with gradient elution (EtOAc / *n*-hexane 1:6 → 1:3 → 1:1) to furnish unreacted mono-ether **36** (0.040 g, 7.5 %, R_f = 0.24) and the products **57a** (R_f = 0.073) and **58a** (R_f = 0.018) as colourless oils.

Yield: **57a**: 0.125 g (18 %) and **58a**: 0.353 g (67 %).

Characterization of 57a:

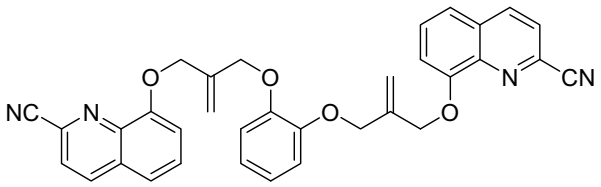


^{1}H NMR (400 MHz, $CDCl_3$, a6021121): δ = 8.27 (d, J = 8.5 Hz, 1 H), 7.73 (d, J = 8.5 Hz, 1 H), 7.59 (dd, J = 8.2, 8.0 Hz, 1 H), 7.47 (dd, J = 8.2, 1.1 Hz, 1 H), 7.18 (dd, J = 8.0, 1.1 Hz, 1 H), 6.98 (dd, J = 7.7, 1.9 Hz, 1 H), 6.93 (dd, J = 7.7, 1.9 Hz, 1 H), 6.88 (d ps. t, J = 7.7, 1.9 Hz, 1 H), 6.82 (d ps. t, J = 7.7, 1.9 Hz, 1 H), 5.85 (s, 1 H), 5.56 (s, 1 H), 5.49 (s, 1 H), 4.90 (s, 2 H), 4.84 (s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.1 (C), 154.0 (C), 148.2 (C), 140.3 (C), 139.4 (C), 137.0 (CH), 132.0 (C), 130.1 (CH), 129.8 (CH), 129.7 (C), 123.7 (CH), 121.6 (CH), 119.5 (CH), 117.6 (C), 116.9 (CH_2),114.3 (CH), 111.4 (CH), 111.1 (CH), 69.6 (CH_2), 69.4 (CH_2).

MS (EI, 70 eV): m/z (%) = 332.2 ($[M]^+$, 21.5), 223.1 ($[M\text{-}C_6H_5O_2]^+$, 100).

Characterization of 58a:

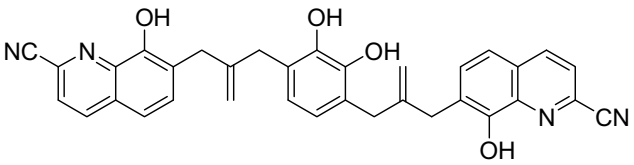


^{1}H NMR (400 MHz, $CDCl_3$, a7072681): δ = 8.19 (d, J = 8.4 Hz, 2 H), 7.65 (d, J = 8.4 Hz, 2 H), 7.50 (dd, J = 8.2, 7.9 Hz, 2 H), 7.37 (dd, J = 8.2, 1.0 Hz, 2 H), 7.14 (dd, J = 7.9, 1.0 Hz, 2 H), 7.00-6.89 (m, 4 H), 5.44 (s, 4 H), 4.95 (s, 4 H), 4.76 (s, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.3 (C), 154.2 (C), 148.4 (C), 140.4 (C), 137.2 (CH), 132.1 (C), 130.0 (CH), 129.8 (C), 123.9 (CH), 121.7 (CH), 119.8 (CH), 117.0 (C), 116.0 (CH_2), 114.5 (CH), 111.2 (CH), 69.8 (CH_2), 69.5 (CH_2).

MS (EI, 70 eV): m/z (%) = 554.1 ($[M]^+$, 2.9), 223.0 ($[M\text{-}C_{20}H_{15}N_2O_3]^+$, 100).

7,7'-(2,2'-(2,3-Dihydroxy-1,4-phenylene)bis(methylene)bis(prop-2-ene-2,1-diyl))bis(8-hydroxyquinoline-2-carbonitrile) (60a)



Prepared according to **GP-2** (175 °C, 10 h), using carbonitrile heteroether derivative **58a** (0.30 g, 0.54 mmol). Purification by flash chromatograpy (EtOAc / *n*-hexane 1:2) furnished a colourless crystalline solid.

Yield: 0.20 g (67 %).

^{1}H NMR (400 MHz, DMSO-d_6, a6030332): δ = 10.17 (br. s, 2 H), 8.56 (d, J = 8.5 Hz, 2 H), 8.14 (br. s, 2 H), 7.97 (d, J = 8.5 Hz, 2 H), 7.51 (d, J = 1.9 Hz, 4 H), 6.52 (s, 2 H), 4.66 (s, 2 H), 4.60 (s, 2 H), 3.52 (s, 4 H), 3.29 (s, 4 H).

^{13}C NMR (75 MHz, DMSO-d_6, a7090640): δ = 150.6, 146.9, 143.4, 138.4, 137.9, 133.0, 130.3, 124.4, 124.36, 123.5, 120.5, 120.47, 117.8, 117.23, 117.21, 36.0, 35.6.

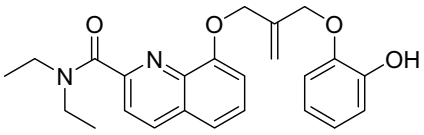
MS (ESI-): m/z (%) = 553.1 ([M-H]$^-$, 100).

8-[2-(2-Hydroxyphenoxymethyl)allyloxy]quinoline-2-carboxylic acid diethylamide (57b) and 8,8'-(2,2'-(1,2-phenylenebis(oxy))bis(methylene)bis(prop-2-ene-2,1-diyl))bis(oxy)-bis(*N,N*-diethylquinoline-2-carboxamide) (58b)

Prepared according to **GP-7**, starting from 2-amidoquinolinate mono-ether **45c** (0.32 g, 0.96 mmol), catechol (0.058 g, 0.48 mmol), and K_2CO_3 (1.33 g, 9.60 mmol). The crude oily residue was applied to flash chromatography (EtOAc / *n*-hexane 1:3) to furnish unreacted **45c** (0.014 g, 4.4 %, R_f = 0.23) and products **57b** (R_f = 0.13) and **58b** (R_f = 0) as colourless oils.

Yield: **57b**: 0.059 g (15 %) and **58b**: 0.217 g (64 %).

Characterization of 57b:

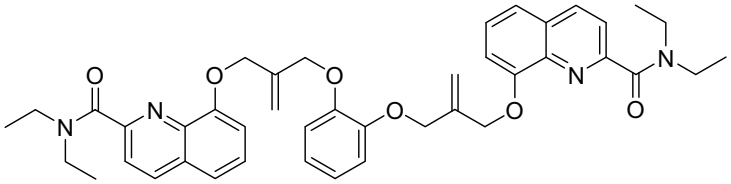


^{1}H NMR (400 MHz, $CDCl_3$, a6081013): δ = 8.21 (d, J = 8.5 Hz, 1 H), 7.75 (d, J = 8.5 Hz, 1 H), 7.47 (dd, J = 8.2, 7.4 Hz, 1 H), 7.43 (dd, J = 8.2, 1.4 Hz, 1 H), 7.11 (dd, J = 7.4, 1.4 Hz, 1 H), 6.92-6.89 (m, 2 H), 6.86 (d ps. t, J = 7.7, 1.9 Hz, 1 H), 6.78 (d ps. t, J = 7.7, 1.9 Hz, 1 H), 5.96 (s, 1 H), 5.52 (s, 1 H), 5.44 (s, 1 H), 4.90 (s, 2 H), 4.80 (s, 2 H), 3.57 (q, J = 7.1 Hz, 2 H), 3.49 (q, J = 7.1 Hz, 2 H), 1.27 (t, J = 7.1 Hz, 3 H), 1.23 (t, J = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.4 (C), 154.4 (C), 153.3 (C), 146.3 (C), 145.5 (C), 139.7 (C), 138.5 (C), 136.7 (CH), 129.2 (C), 127.4 (CH), 122.0 (CH), 121.3 (CH), 120.0 (CH), 119.9 (CH), 117.3 (CH_2), 115.1 (CH), 113.0 (CH), 110.4 (CH), 69.9 (CH_2), 43.4 (CH_2), 40.5 (CH_2), 14.4 (CH_3), 12.8 (CH_3).

MS (EI, 70 eV): m/z (%) = 406.2 ([M]$^+$, 49.1), 297.1 ([M-$C_6H_5O_2$]$^+$, 58.8), 72.2 ([M-$C_{20}H_{16}N_2O_4$]$^+$, 100).

Characterization of 58b:

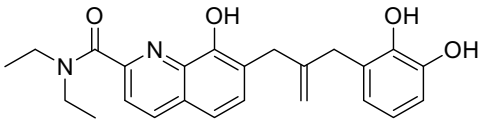


^{1}H NMR (400 MHz, $CDCl_3$, a6081068): δ = 8.17 (d, J = 8.5 Hz, 2 H), 7.76 (d, J = 8.5 Hz, 2 H), 7.38 (dd, J = 8.2, 7.4 Hz, 2 H), 7.34 (dd, J = 8.2, 1.6 Hz, 2 H), 7.08 (dd, J = 7.4, 1.6 Hz, 2 H), 6.95-6.92 (m, 2 H), 6.89-6.86 (m, 2 H), 5.44 (s, 4 H), 4.92 (s, 4 H), 4.75 (s, 4 H), 3.58 (q, J = 7.1 Hz, 4 H), 3.49 (q, J = 7.1 Hz, 4 H), 1.27 (t, J = 7.1 Hz, 6 H), 1.24 (t, J = 7.1 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.4 (C), 154.5 (C), 153.1 (C), 148.5 (C), 139.9 (C), 138.4 (C), 136.6 (CH), 129.2 (C), 127.4 (CH), 121.5 (CH), 121.3 (CH), 119.6 (CH), 115.7 (CH_2), 114.3 (CH), 110.1 (CH), 69.7 (CH_2), 69.3 (CH_2), 43.4 (CH_2), 40.6 (CH_2), 14.4 (CH_3), 12.8 (CH_3).

MS (EI, 70 eV): m/z (%) = 702.5 ($[M]^+$, 3.4), 602.3 ($[M-C_5H_{10}N_1O_1]^+$, 8.4), 459.2 ($[M-C_{14}H_{15}N_2O_2]^+$, 10.2), 297.1 ($[M-C_{14}H_{23}N_2O_4]^+$, 100).

7-[2-(2,3-Dihydroxybenzyl)allyl]-8-hydroxyquinoline-2-carboxylic acid diethylamide (59b)



Prepared according to **GP-2** (170 °C, 7 h), using heteroether **57b** (0.05 g, 0.12 mmol). The brown oily crude product was dissolved in EtOAc and filtered over Celite®. The solution volume was reduced in vacuum to a minimum and washed with *n*-hexane to furnish a colourless oil.

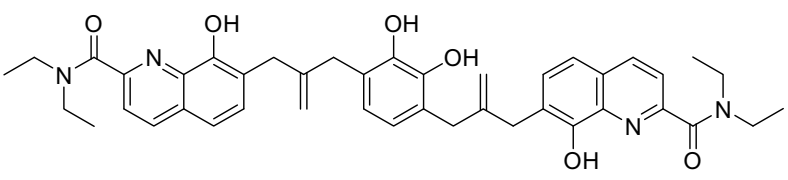
Yield: 0.045 g (90 %).

^{1}H NMR (300 MHz, $CDCl_3$, a7071011): δ = 8.21 (d, J = 8.2 Hz, 1 H), 7.63 (d, J = 8.2 Hz, 1 H), 7.39 (d, J = 8.5 Hz, 1 H), 7.32 (d, J = 8.5 Hz, 1 H), 6.75 (dd, J = 7.7, 1.9 Hz, 1 H), 6.70 (dd, J = 7.7, 7.4 Hz, 1 H), 6.22 (dd, J = 7.4, 1.9 Hz, 1 H), 4.90 (s, 2 H), 3.65 (q, J = 7.1 Hz, 2 H) , 3.60 (s, 2 H), 3.41 (s, 2 H), 3.40 (q, J = 7.1 Hz, 2 H), 1.33 (t, J = 7.1 Hz, 3 H), 1.26 Hz (t, J = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.5 (C), 151.8 (C), 149.3 (C), 146.6 (CH), 144.3 (C), 142.2 (C), 137.1 (CH), 136.2 (C), 131.0 (CH), 126.9 (C), 125.6 (C), 122.1 (C), 122.0 (CH), 120.2 (C), 120.1 (CH), 117.4 (CH), 113.4 (CH), 112.8 (CH_2), 43.4 (CH_2), 40.4 (CH_2), 37.1 (CH_2), 36.2 (CH_2), 14.6 (CH_3), 12.9 (CH_3).

MS (EI, 70 eV): m/z (%) = 406.1 ($[M]^+$, 90.1), 283.1 ($[M-C_7H_7O_2]^+$, 100), 258.1 ($[M-C_9H_9O_2]^+$, 33.9), 72.2 ($[M-C_{20}H_{16}N_2O_4]^+$, 58.3).

7,7'-(2,2'-(2,3-Dihydroxy-1,4-phenylene)bis(methylene)bis(prop-2-ene-2,1-diyl))bis(*N*,*N*-diethyl-8-hydroxyquinoline-2-carboxamide) (60b)



Prepared according to **GP-2** (175 °C, 12 h), using heteroether **58b** (0.20 g, 0.28 mmol). The crude brown oily product was dissolved

in EtOAc and filtered over Celite®. The solution volume was reduced in vacuum and washed with *n*-hexane to furnish a colourless oil.

Yield: 0.166 g (83 %).

^{1}H NMR (300 MHz, $CDCl_3$, a6042429): δ = 8.22 (d, J = 8.4 Hz, 2 H), 7.64 (d, J = 8.4 Hz, 2 H), 7.40 (d, J = 8.5 Hz, 2 H), 7.33 (d, J = 8.5 Hz, 2 H), 6.65 (s, 2 H), 4.89 (s, 4 H), 3.64 (q, J = 7.2 Hz, 4 H), 3.61 (s, 4 H), 3.42 (q, J = 7.2 Hz, 4 H), 3.41 (s, 4 H), 1.32 (t, J = 7.2 Hz, 6 H), 1.24 Hz (t, J = 7.2 Hz, 6 H).

HRMS Calcd for $C_{42}H_{46}N_4O_6$: 702.34173; found: 702.34170.

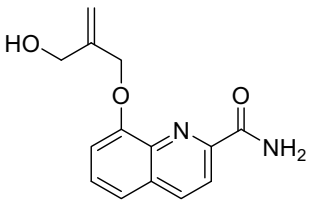
5.10. Claisen and Double-Claisen-Hiratani Approaches to Ditopic Ligands (50a, 65, 75, 78)

8-(2-Hydroxymethylallyloxy)quinoline-2-carboxylic acid amide (48) and 8,8'-(2-methylenepropane-1,3-diyl)bis(oxy)di(quinoline-2-carboxamide) (46a)

Prepared according to **GP-1**, starting from 8-hydroxyquinoline-2-carboxamide **32** (0.50 g, 2.66 mmol), K_2CO_3 (1.84 g, 13.31 mmol), and 3-chloro-2-chloromethyl-propene **13** (0.33 g, 0.306 ml, 2.66 mmol). The reaction mixture in DMF (30 ml) was stirred at 90 °C for 18 h. After workup the crude residue was dissolved in CH_2Cl_2 (30 ml), refluxed for 15-20 min, and then cooled to rt. The precipitate was collected by filtration, washed with CH_2Cl_2, and dried to provide the product as a white powder **46a**. The remaining CH_2Cl_2 solution was evaporated under reduced pressure and residue was applied to column chromatography (EtOAc / *n*-hexane 1:2) to furnish a yellowish sticky solid **48**.

Yield: **48**: 0.09 g (13 %) and **46a**: 0.10 g (17 % yield); mp 203 °C.

Characterization of 48:



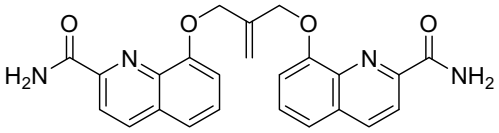
^{1}H NMR (400 MHz, $CDCl_3$, a6103012): δ = 8.34 (d, J = 8.6 Hz, 1 H), 8.28 (d, J = 8.6 Hz, 1 H), 8.19 (br. s, 1 H), 7.54 (dd, J = 8.2, 7.3 Hz, 1 H), 7.49 (dd, J = 8.2, 1.6 Hz, 1 H), 7.14 (dd, J = 7.3, 1.6 Hz, 1 H), 5.08 (br. s, 1 H), 5.34 (s, 2 H), 4.94 (s, 2 H), 4.49 (t, J = 5.8 Hz, 1 H), 4.39 (d, J = 5.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7 (C), 154.0 (C), 148.7 (C), 142.8 (C), 138.7 (C), 137.3 (CH), 130.4 (C), 128.2 (CH), 120.4 (CH), 120.0 (CH), 116.2 (CH_2), 110.6 (CH), 73.3 (CH_2), 65.9 (CH_2).

MS (EI, 70 eV): m/z (%) = 258.0 ($[M]^+$, 29.0), 69.1 ($[M\text{-}C_{11}H_{11}N_2O_2]^+$, 100).

IR (KBr): ν 3554, 3346, 3197, 1678, 1559, 1464, 1405, 1377, 1320, 1256, 1091, 1021, 941, 850, 746, 695 cm^{-1}.

Characterization of 46a:



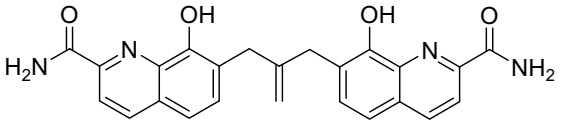
^{1}H NMR (300 MHz, $CDCl_3$, b6100941): δ = 8.30 (d, J = 8.5 Hz, 2 H), 8.26 (d, J = 8.5 Hz, 2 H), 8.12 (br. s, 2 H), 7.50 (dd, J = 8.2, 7.4 Hz, 2 H), 7.45 (dd, J = 8.2, 1.3 Hz, 2 H), 7.21 (dd, J = 7.4, 1.3 Hz, 2 H), 5.63 (s, 2 H), 5.58 (br. s, 2 H), 5.06 (s, 4 H).

MS (EI, 70 eV): m/z (%) = 428.0 ($[M]^+$, 4.1), 241.1 ($[M\text{-}C_{10}H_7N_2O_2]^+$, 100).

IR (KBr): ν 3441, 1696, 1566, 1470, 1375, 1324, 1254, 1099, 753 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{24}H_{20}N_4O_4 \cdot H_2O$ (446.4): C 64.57, H 4.97, N 12.55; found: C 64.36, H 5.12, N 12.47.

7,7'-(2-Methylenepropane-1,3-diyl)bis(8-hydroxyquinoline-2-carboxamide) (50a-H_2)



Prepared according to **GP-2** (180 °C, 7 h), using diether **46a** (0.07 g, 0.16 mmol). The product was purified by recrystallization from DMF by slow addition of *i*-PrOH to afford a white powder.

Yield: 0.076 g (100 %); mp 291 °C (decompos.).

^{1}H NMR (300 MHz, DMSO-d_6, a6103036): 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).

^{13}C NMR (75 MHz, DMSO-d_6): 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.

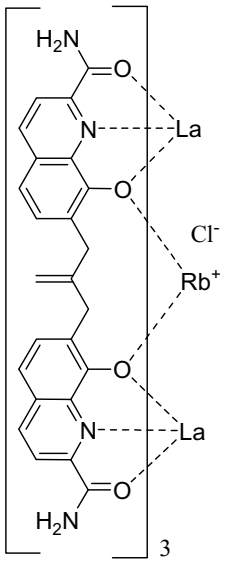
IR (KBr): ν 3445, 3287, 1669, 1572, 1447, 1385, 1327, 1237, 1080, 714, 553 cm^{-1}.

MS (ESI+): m/z (%) = 451.2 ($[M+Na]^+$, 100), 429.3 ($[M+H]^+$, 65.0).

Elemental analysis: calcd. (%) for $C_{24}H_{20}N_4O_4 \cdot 2\ H_2O$ (464.4): C 62.06, H 5.21, N 12.06; found: C 62.27, H 4.96, N 11.67.

Preparation of homodinuclear helicate-type complex $[Rb(50a)_3La_2]Cl$

To the ligand **50a**-H_2 (0.02 g, 0.05 mmol, 3.0 equiv.) in MeOH (15 ml) K_2CO_3 (0.01 g, 0.074 mmol) was added, resulting in a transparent orange solution, to which hydrated $LaCl_3$ (0.0116 g, 0.03 mmol, 2.0 equiv.) was successively added. The reaction mixture was gently refluxed for 15 h, and then cooled to rt. The precipitate was filtered off, washed with chilled water, MeOH, and Et_2O to furnish a red powder.



Yield calcd. on M_W of the complex (M_W = 1677 g mol^{-1}): 0.018 g (69 %).

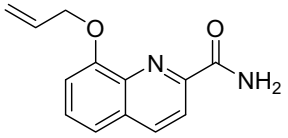
^{1}H NMR (400 MHz, DMSO-d_6, a5101926): δ = 10.05 (s, 2 H), 9.44-8.93 (m, 10 H), 8.49-8.45 (m, 8 H), 8.30-8.12 (m, 12 H), 7.67-7.39 (m, 14 H), 6.95 (d, J = 8.2 Hz, 2 H), 5.55 (s, 1 H), 5.08 (s, 2 H), 4.75-4.66 (m, 6 H), 3.59 (s, 6 H), 3.52 (d, J = 12.7 Hz, 6 H). The spectrum containes the minor resonances of undefined species and ligand.

MS (ESI+): m/z = 1557.3 [La_2(**50a**)$_3$+H]$^+$.

MS (ESI-): m/z = 1555.8 [La_2(**50a**)$_3$-H]$^+$.

An analytically pure sample could not be obtained.

8-Allyloxyquinoline-2-carboxylic acid amide (61)



Prepared according to **GP-4**, starting from 8-hydroxyquinoline-2-carboxamide **32** (0.34 g, 1.80 mmol), allylbromide (2.19 g, 1.56 ml, 18.0 mmol), and K_2CO_3 (2.5 g, 18.0 mmol). The purification by flash chromatography (CH_2Cl_2 / acetone 5:1) afforded a white crystalline solid.

Yield: 0.25 g (88 %); mp 121 °C.

^{1}H NMR (300 MHz, $CDCl_3$, a6080419): 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 = 8.6 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).

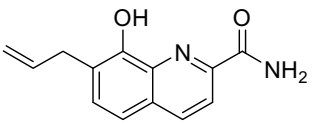
^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.1 (C), 154.1 (C), 147.9 (C), 138.4 (C), 136.9 (CH), 132.6 (CH), 130.2 (C), 128.0 (CH), 119.4 (CH), 119.0 (CH), 117.7 (CH_2), 109.8 (CH), 69.5 (CH_2).

IR (KBr): ν 3426, 1684, 1584, 1464, 1369, 1251, 1086, 990, 504 cm^{-1}.

MS (EI, 70 eV): m/z (%) = 228.0 ([M]$^+$, 58.9), 199.0 ([M-C_2H_5]$^+$, 100).

Elemental analysis: calcd. (%) for $C_{13}H_{12}N_2O_2$ (188.2): 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 (62)



Prepared according to **GP-2** (170 °C, 6 h), using allylether derivative **61** (0.25 g, 1.10 mmol). The product was obtained in pure form as an off-white solid.

Yield: 0.25 g (100 %); mp 198 °C.

^{1}H NMR (300 MHz, CD_3OD, a6081692): 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).

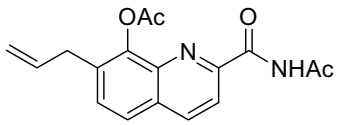
^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.5 (C), 151.8 (C), 148.6 (C), 138.6 (CH), 138.3 (C), 137.7 (CH), 132.5 (CH), 129.9 (C), 124.4 (C), 119.3 (CH), 118.2 (CH), 116.0 (CH_2), 35.0 (CH_2).

IR (KBr): ν 3414, 3307, 3191, 1710, 1672, 1598, 1564, 1509, 1451, 1388, 1234, 1189, 1095, 992, 912, 856 cm^{-1}.

MS (EI, 70 eV): m/z (%) = 228.1 ([M]$^+$, 66.0), 213.0 ([M-CH_3]$^+$, 100).

Elemental analysis: calcd. (%) for $C_{13}H_{12}N_2O_2$ (228.2): C 68.41, H 5.30, N 12.27; found: C 68.82, H 5.20, N 12.20.

2-(Acetylcarbamoyl)-7-allylquinolin-8-yl acetate (63)



A suspension of 7-allyl-8-hydroxyquinoline derivative **62** (0.25 g, 1.10 mmol) in acetic anhydride (30 ml) was refluxed for 15 h. After evaporation of the solvent, the oily residue was suspended in water, neutralized with satd. aq $NaHCO_3$, and extracted with CH_2Cl_2 (3 × 50 ml). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuum before column chromatography (EtOAc / *n*-hexane 1:5) to afford a white crystalline solid.

Yield: 0.29 g (85 %); mp 96 °C.

^{1}H NMR (300 MHz, $CDCl_3$, a6091446): 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).

^{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).

IR (KBr): ν 3308, 1767, 1701, 1468, 1374, 1281, 1198, 865, 748 cm^{-1}.

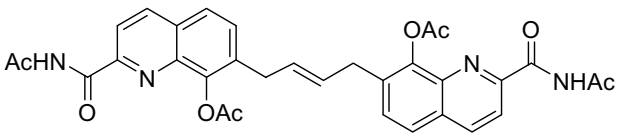
MS (EI, 70 eV): m/z (%) = 312.1 ([M]$^+$, 4.8), 270.1 ([M-Ac+H], 100).

Elemental analysis: calcd. (%) for $C_{17}H_{16}N_2O_4$ (311.3): C 65.38, H 5.16, N 8.97; found: C 65.79, H 5.69, N 9.02.

(*E*)-7,7'-(But-2-ene-1,4-diyl)bis(2-(acetylcarbamoyl)quinoline-8,7-diyl) diacetate (64)

To a solution of 2-(acetyl-carbamoyl)-7-allylquinolin-8-yl acetate **63** (0.25 g, 0.93 mmol, 1 equiv.) in abs. CH_2Cl_2 (5 ml) under inert atmosphere of N_2 benzylidene-

bis(tricyclohexylphosphane)-dichlororuthenium (0.038 g, 0.046 mmol, 0.05 equiv.) in abs. CH_2Cl_2 (5 ml) was added. The mixture



was refluxed for 12 h and then stirred at rt for another 12 h. The solvent was removed in vacuum. The crude product was directly subjected to column chromatography with gradient elution (EtOAc / *n*-hexane 1:2 → 1:1 → 1:0 → MeOH). The fraction with R_f = 0.16 (fraction from EtOAc / *n*-hexane 1:1 → 1:0), which was recrystallized from $CHCl_3$ / MeOH (2:1) furnishing white solid flakes, contained a mixture of *Z*- and *E*-isomers (0.043 g, 18 %). The fraction washed out with MeOH afforded a single compound that was washed with MeOH to give the desired product as a white solid.

Yield: 0.062 g (26 %); mp 268 ºC.

^{1}H NMR (300 MHz, $CDCl_3$, a6110234): 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).

^{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).

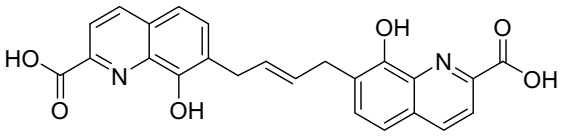
IR (KBr): ν 3312, 1755, 1699, 1472, 1375, 1281, 1213, 1075, 861, 744 cm^{-1}.

MS (EI, 70 eV): m/z (%) = 554.1 ([M–CH_3CO]$^+$, 100).

Elemental analysis: calcd. (%) for $C_{32}H_{28}N_4O_8$ (596.6): C 64.42, H 4.73, N 9.39; found: C 64.19, H 5.09, N 9.24.

(*E*)-7,7'-(But-2-ene-1,4-diyl)bis(8-hydroxyquinoline-2-carboxylic acid) (65)

A solution of 20 % aq KOH (0.5 ml) was added to (*E*)-isomer of **64** (0.05 g, 0.084 mmol) suspended in a mixture of pyridine (2.0 ml) and water (0.5 ml). The reddish solution



was refluxed for 1 h, and then stirred at rt for another 12 h. The mixture was neutralized with diluted HCl until pH 6-7. The precipitate thus formed was filtered off and purified by recrystallization from THF / MeOH (3:1) to furnish an off-white solid.

Yield: 0.023 g (64 %); mp 285 °C (decomp.).

^{1}H NMR (300 MHz, DMSO-d_6, a6122161): 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).

^{13}C NMR (75 MHz, DMSO-d_6): 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.

IR (KBr): ν 3386, 3024, 1669, 1593, 1458, 1375, 1271, 1192, 1157, 1131, 976, 931, 793 cm^{-1}.

MS (ESI+): m/z (%) = 453.2 ([M+Na]$^+$, 100).

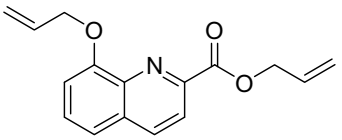
MS (EI, 70 eV): m/z (%) = 430.1 ([M]$^+$, 43.0), 386.0 ([M-COOH+H]$^+$, 41.2), 340.1 ([M-2COOH]$^+$, 22.4), 228.0 ([M-$C_{11}H_8NO_3$]$^+$, 100).

Elemental analysis: calcd. (%) for $C_{24}H_{18}N_2O_6$ (430.4): C 66.97, H 4.22, N 6.51; found: C 67.06, H 4.67, N 7.02.

X-Ray quality crystals were obtained from DMSO / CH_3CN.

Crystal data for **65**: formula $C_{28}H_{30}N_2O_8S_2$; code FRO4299; M = 586.66; monoclinic, space group P21/c (No.14); a = 14.5995(3) Å, b = 5.5275(1) Å, c = 17.5726(4) Å; β = 100.390(1)°; V = 1394.83(5) Å^3; T = 223(2) K; Z = 2; D_{calcd} = 1.397 gcm^{-3}; μ = 21.87 cm^{-1}; *F(000)* = 616; crystal size 0.25 x 0.20 x 0.07 mm; $[(sin\theta)/\lambda]_{max}$ = 0.60 Å^{-1}; reflections collected / unique 10278 / 2448 [*R(int)* = 0.059]; λ = 1.54178 Å; R = 0.0464, wR^2 = 0.1140; CCD data collection.

8-Allyloxyquinoline-2-carboxylic acid allylester (72)



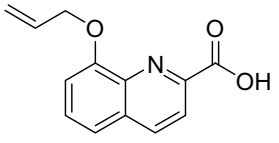
Prepared according to **GP-4**, starting from 8-hydroxyquinoline-2-carboxylic acid **30a** (0.20 g, 1.06 mmol), allylbromide (2.56 g, 1.83 ml, 21.2 mmol), and K_2CO_3 (2.92 g, 2.12 mmol). Purification by column chromatography (acetone / CH_2Cl_2 1:15) afforded a colourless crystalline solid.

Yield: 0.256 g (90 %).

^{1}H NMR (400 MHz, $CDCl_3$, a4110501): δ = 8.20 (d, J = 8.5 Hz, 1 H), 8.14 (d, J = 8.5 Hz, 1 H), 7.47 (dd, J = 8.2, 7.9 Hz, 1 H), 7.37 (dd, J = 8.2, 1.1 Hz, 1 H), 7.06 (dd, J = 7.9, 1.1 Hz, 1 H), 6.19 (ddt, J = 17.3, 10.4, 5.5 Hz, 1 H), 6.08 (ddt, J = 17.3, 10.4, 5.8 Hz, 1 H), 5.49 (dq, J = 17.3, 1.6 Hz, 1 H), 5.43 (dq, J = 17.3, 1.6 Hz, 1 H), 5.31 (dq, J = 10.4, 1.4 Hz, 1 H), 5.27 (dq, J = 10.4, 1.4 Hz, 1 H), 4.90 (dt, J = 5.8, 1.4 Hz, 2 H), 4.80 (dt, J = 5.5, 1.6 Hz, 2 H).

MS (EI, 70 eV): m/z (%) = 268.9 ([M]$^+$, 71.6), 240.7 ([M-C_2H_5]$^+$, 100).

8-Allyloxyquinoline-2-carboxylic acid (73)



To a solution of allylester derivative **72** (0.20 g, 0.743 mmol) in DMF (10 ml) 1 N aq KOH (1 ml) was added. The solution was stirred at 100 °C for 10 h, then cooled to rt and acidified with dild. HCl until pH 4-5.

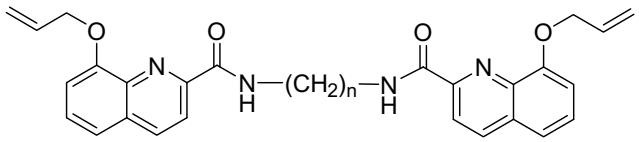
The aqueous phase was extracted with EtOAc; the organic layer was dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave the crude product which was purified by flash column chromatography (EtOAc / *n*-hexane 1:2 → 1:1) resulting in a colourless crystalline solid.

Yield: 0.10 g (58 %).

^{1}H NMR (400 MHz, $CDCl_3$, a5010642): δ = 8.37 Hz (d, J = 8.6 Hz, 1 H), 8.29 (d, J = 8.6 Hz, 1 H), 7.61 (dd, J = 8.2, 8.0 Hz, 1 H), 7.51 (dd, J = 8.2, 1.1 Hz, 1 H), 7.16 (dd, J = 8.0, 1.1 Hz, 1 H), 6.21 (ddt, J = 17.3, 10.4, 5.2 Hz, 1 H), 5.56 (dq, J = 17.3, 1.4 Hz, 1 H), 5.41 (dq, J = 10.4, 1.4 Hz, 1 H), 4.82 (dt, J = 5.2, 1.5 Hz, 2 H).

MS (EI, 70 eV): m/z (%) = 229.0 ($[M]^+$, 39.8), 200.0 ($[M-C_2H_5]^+$, 100), 184.0 ($[M-COOH]^+$, 52.8), 155.0 ($[M-COOH-C_2H_5]^+$, 55.6).

8-(Allyloxy)-*N′*-(8-(allyloxy)quinoline-2-carbonyl)quinoline-2-carbohydrazide (74a, n = 0) and *N,N′*-(butane-1,4-diyl)bis(8-(allyloxy)quinoline-2-carboxamide) (74b, n = 4)



Synthesis and characterization of 74a:

Prepared according to **GP-5**, starting from a carboxylic acid allylether **73** (20 mg, 0.087 mmol), HBTU (40 mg, 0.105 mmol), DIPEA (12 mg, 16 µl, 0.096 mmol), and hydrazine hydrate (2.2 mg, 2 µl, 0.043 mmol) in MeCN (10 ml). The crude product was purified by column chromatography (EtOAc / *n*-hexane 1:1) to furnish colourless crystalline solid.

Yield: 0.012 g (60 %).

^{1}H NMR (300 MHz, DMSO-d_6, a5012169): δ = 8.37 (d, J = 8.7 Hz, 2 H), 8.08 (d, J = 8.7 Hz, 2 H), 7.55 (d, J = 5.7 Hz, 2 H), 7.54 (d, J = 3.2 Hz, 2 H), 7.24 (dd, J = 5.7, 3.2 Hz, 2 H), 6.20 (ddt, J = 17.3, 10.6, 5.4 Hz, 2 H), 5.51 (dq, J = 17.3, 1.5 Hz, 2 H), 5.33 (dq, J = 10.6, 1.5 Hz, 2 H), 4.84 (dt, J = 5.4, 1.5 Hz, 4 H).

MS (EI, 70 eV): m/z (%) = 454.2 ($[M]^+$, 100).

Synthesis and characterization of 74b:

The carboxylic acid allylether **73** (0.042 g, 0.183 mmol) and carbonyl diimidazole (0.033 g, 0.201 mmol) in $CHCl_3$ were refluxed under inert atmosphere of N_2 for 2 h. A solution of 1,4-diaminobutane (0.008 g, 0.009 ml, 0.1 mmol) in 1 ml of $CHCl_3$ was added, and then the

solution was refluxed for additional 2 d. After cooling to rt the organic phase was washed with water and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded crude product which was applied to column chromatography (EtOAc / *n*-hexane 1:1) resulting in a colourless crystalline solid.

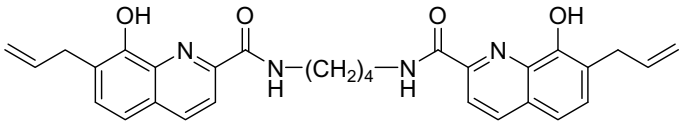
Yield: 0.025 g (53 %).

^{1}H NMR (300 MHz, $CDCl_3$, a5030459): δ = 8.45 Hz (t, J = 5.8 Hz, 2 H), 8.33 (d, J = 8.6 Hz, 2 H), 8.27 (d, J = 8.6 Hz, 2 H), 7.50 (dd, J = 8.3, 7.4 Hz, 2 H), 7.45 (dd, J = 8.3, 1.5 Hz, 2 H), 7.10 (dd, J = 7.4, 1.5 Hz, 2 H), 6.21 (ddt, J = 17.3, 10.6, 5.2 Hz, 2 H), 5.54 (d ps. q, J = 17.3, 1.5 Hz, 2 H), 5.35 (d ps. q, J = 10.6, 1.5 Hz, 2 H), 4.81 (dt, J = 5.2, 1.5 Hz, 4 H), 3.62 (m, 4 H), 1.85 (m, 4 H).

^{13}C NMR (100 MHz, CD_3OD, a7072035): δ = 166.5 (C), 155.0 (C), 149.7 (C), 139.6 (C), 138.6 (CH), 133.7 (CH), 131.7 (C), 129.4 (CH), 121.0 (CH), 120.2 (CH), 118.8 (CH_2), 111.5 (CH), 70.9 (CH_2), 40.3 (CH_2), 27.0 (CH_2).

MS (EI, 70 eV): m/z (%) = 510.2 ($[M]^+$, 100), 495.2 ($[M\text{-}CH_3]^+$, 22.7), 184.1 ($[M\text{-}C_{18}H_{20}N_3O_3]^+$, 45.0).

_N,N'_-(Butane-1,4-diyl)bis(7-allyl-8-hydroxyquinoline-2-carboxamide) (75b)



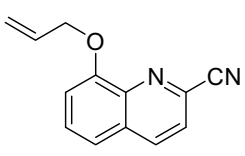
Prepared according to **GP-2** (165 °C, 4 h), using bis-amidoquinolinate derivative **74b** (0.025 g, 0.05 mmol). Purification by recrystallization from CH_2Cl_2 / MeOH afforded the product as a colourless crystalline solid.

Yield: 0.02 g (80 %).

^{1}H NMR (400 MHz, $CDCl_3$, a5030910): δ = 9.10 (t, J = 5.7 Hz, 2 H), 8.91 (s, 2 H), 8.43 (d, J = 8.5 Hz, 2 H), 8.26 (d, J = 8.5 Hz, 2 H), 7.43 (d, J = 8.4 Hz, 2 H), 7.33 (d, J = 8.4 Hz, 2 H), 6.07 (ddt, J = 17.0, 10.0, 6.6 Hz, 2 H), 5.12 (d ps. q, J = 17.0, 1.9 Hz, 2 H), 5.08 (d ps. q, J = 10.0, 1.9 Hz, 2 H), 3.64 (m, 8 H), 1.78 (m, 4 H).

MS (EI, 70 eV): m/z (%) = 510.1 ($[M]^+$, 85.9), 495.2 ($[M\text{-}CH_3]^+$, 35.5), 185.0 ($[M\text{-}C_{18}H_{20}N_3O_3\text{+H}]^+$, 100).

8-Allyloxyquinoline-2-carbonitrile (76)



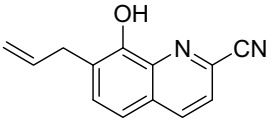
Prepared according to **GP-4**, starting from 8-hydroxyquinoline-2-carbonitrile **33** (0.40 g, 2.35 mmol), allylbromide (2.80 g, 2.0 ml, 23.50 mmol), and K_2CO_3 (3.25 g, 23.50 mmol). Purification by column

chromatography (acetone / CH_2Cl_2 1:10) afforded the product as a colourless crystalline solid.
Yield: 0.45 g (91 %).

^{1}H NMR (300 MHz, $CDCl_3$, a7022137): δ = 8.24 (d, J = 8.7 Hz, 1 H), 7.68 (d, J = 8.7 Hz, 1 H), 7.57 (dd, J = 8.2, 7.9 Hz, 1 H), 7.42 (dd, J = 8.2, 1.0 Hz, 1 H), 7.14 (dd, J = 7.9, 1.0 Hz, 1 H), 6.16 (ddt, J = 17.3, 10.6, 5.2 Hz, 1 H), 5.49 (dq, J = 17.3, 1.5 Hz, 1 H), 5.34 (dq, J = 10.6, 1.5 Hz, 1 H), 4.86 (dt, J = 5.2, 1.5 Hz, 2 H).

MS (EI, 70 eV): m/z (%) = 210.1 ($[M]^+$, 53.0), 181.1 ($[M\text{-}C_2H_5]^+$, 100).

7-Allyl-8-hydroxyquinoline-2-carbonitrile (77)



Prepared according to **GP-3** (170 °C, 5 h), using carbonitrile ether derivative **76** (0.40 g, 1.9 mmol). Purification by recrystallization from *i*-PrOH afforded the product as a yellow crystalline solid.

Yield: 0.376 g, (94 %); mp 187 °C.

^{1}H NMR (300 MHz, $CDCl_3$, a7022352): δ = 8.27 (d, J = 8.4 Hz, 1 H), 7.96 (s, 1 H), 7.67 (d, J = 8.4 Hz, 1 H), 7.54 (d, J = 8.4 Hz, 1 H), 7.37 (d, J = 8.4 Hz, 1 H), 6.05 (ddq, J = 16.8, 10.3, 6.7 Hz, 1 H), 5.15 (d ps. q, J = 16.8, 1.5 Hz, 1 H), 5.11 (d ps. q, J = 10.2, 1.5 Hz, 1 H), 3.65 (dt, J = 6.7, 1.5 Hz, 2 H).

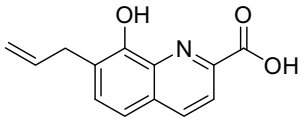
^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.1 (C), 138.1 (C), 137.3 (CH), 135.5 (CH), 133.0 (CH), 130.7 (C), 127.6 (C), 123.9 (C), 123.1 (CH), 117.4 (CH), 117.3 (C), 116.3 (CH_2), 33.8 (CH_2).

MS (EI, 70 eV): m/z (%) = 210.0 ($[M]^+$, 49.8), 194.9 ($[M\text{-}CH_3]^+$, 100).

IR (KBr): ν 3400, 2925, 2237, 1726, 1630, 1505, 1449, 1392, 1329, 1278, 1247, 1211, 1102, 997, 923, 847, 776, 722, 628, 590, 571 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{13}H_{10}N_2O$ (210.2): C 74.27, H 4.79, N 13.33; found: C 74.29.15, H 4.88, N 13.21.

7-Allyl-8-hydroxyquinoline-2-carboxylic acid (78)



7-Allyl-8-hydroxyquinoline derivative **77** (0.30 g, 1.43 mmol) was dissolved in 3 N NaOH (15 ml). The resulting solution was refluxed for 4 h, cooled to rt, and acidified with 5 N HCl to pH 4-5. The precipitate was collected by filtration, washed with water, and recrystallized from MeOH to afford the product as a yellow crystalline solid.

Yield: 0.22 g (67 %); mp 118 °C.

^{1}H NMR (300 MHz, DMSO-d6, a5022733): δ = 8.38 (d, J = 8.4 Hz, 1 H), 8.08 (d, J = 8.4 Hz, 1 H), 7.45 (d, J = 8.5 Hz, 1 H), 7.42 (d, J = 8.5 Hz, 1 H), 6.05 (ddt, J = 17.0, 10.2, 6.5 Hz,

1 H), 5.11 (dd, J = 17.0, 1.9 Hz, 1 H), 5.05 (dd, J = 10.2, 1.9 Hz, 1 H), 3.60 (d, J = 6.5 Hz, 2 H).

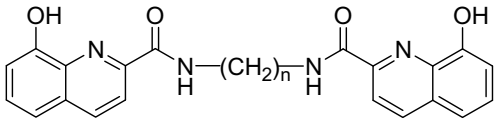
MS (EI, 70 eV): m/z (%) = 229.0 ($[M]^+$, 100), 214.0 ($[M\text{-}CH_3]^+$, 85.0).

IR (KBr): ν 33217, 1730, 1452, 1374, 1244, 1215, 907, 856, 784, 761, 664 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{13}H_{11}NO_3$ (229.2): C 68.11, H 4.84, N 6.11; found: C 67.68, H 4.67, N 6.03.

5.11. Synthesis of bis-Amide Bridged Ligands (66a-d, 71, 111) and Helicate-Type Complexes. Amide / Imine Ligands (68-70)

8-Hydroxy-*N'*-(8-hydroxyquinoline-2-carbonyl)quinoline-2-carbohydrazide (66a-H_2, n = 0); *N,N'*-(ethane-1,2-diyl)bis(8-hydroxyquinoline-2-carboxamide) (66b-H_2, n = 2); *N,N'*-(butane-1,4-diyl)bis(8-hydroxyquinoline-2-carboxamide) (66c-H_2, n = 4)



Prepared according to **GP-5B**, starting from 8-hydroxyquinoline-2-carboxylic acid **30a** (1.0 g, 5.29 mmol), HBTU (2.41 g, 6.35 mmol), DIPEA (0.75 g, 1.0 ml, 5.80 mmol) in MeCN (50 ml), and hydrazine hydrate (**66a,** 0.132 g, 0.128 ml, 2.64 mmol); 1,2-diaminoethane (**66b,** 0.159 g, 0.179 ml, 2.64 mmol); 1,4-diaminobutane (**66c**, 0.233 g, 0.266 ml, 2.64 mmol).

Characterization of 66a:

Yield: 0.52 g (48 %); mp 327 °C.

^{1}H NMR (300 MHz, DMSO-d_6, a5010543): δ = 11.60 (s, 2 H), 10.22 (s, 2 H), 8.60 (d, J = 8.5 Hz, 2 H), 8.20 (d, J = 8.5 Hz, 2 H), 7.63 (dd, J = 8.4, 7.4 Hz, 2 H), 7.55 (dd, J = 8.4, 1.2 Hz, 2 H), 7.23 (dd, J = 7.4, 1.2 Hz, 2 H).

MS (ESI+): m/z (%) = 375.2 ($[M+H]^+$, 100).

IR (KBr): ν 3494, 3426, 1677, 1628, 1500, 1466, 1238, 1189, 1157, 1088, 841, 735, 627 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{20}H_{14}N_4O_4 \cdot 2\ H_2O$ (410.4): C 58.54, H 4.42, N 13.65; found: 58.03, H 4.95, N 13.59.

Characterization of 66b:

Yield: 0.58 g (53 %); mp 305 °C.

^{1}H NMR (300 MHz, DMSO-d_6, a6051851): δ = 10.09 (s, 2 H), 9.91 (br. s, 2 H), 8.52 (d, J = 8.5 Hz, 2 H), 8.17 (d, J = 8.5 Hz, 2 H), 7.57 (dd, J = 8.2, 7.4 Hz, 2 H), 7.49 (dd, J = 8.2, 1.2 Hz, 2 H), 7.16 (dd, J = 7.4, 1.2 Hz, 2 H), 3.65 (d, J = 2.6 Hz, 4 H).

MS (ESI+): m/z (%) = 403.3 ($[M+H]^+$, 100).

IR (KBr): ν 3370, 3426, 1661, 1502, 1461, 1237, 1189, 852, 760, 715 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{22}H_{18}N_4O_4 \cdot 3 / 4\ H_2O$ (415.5): C 63.53, H 4.73, N 13.47; found: 63.66, H 5.12, N 13.38.

Characterization of 66c:

Yield: 0.80 g (66 %); mp 276-277 °C.

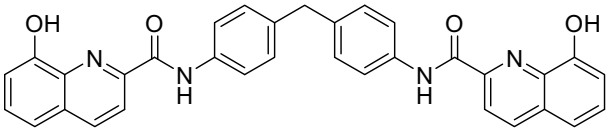
^{1}H NMR (300 MHz, DMSO-d_6, a5012107): δ = 10.09 (s, 2 H), 9.66 (t, J = 6.0 Hz, 2 H), 8.48 (d, J = 8.4 Hz, 2 H), 8.14 (d, J = 8.4 Hz, 2 H), 7.55 (dd, J = 8.2, 7.7 Hz, 2 H), 7.47 (dd, J = 8.2, 1.2 Hz, 2 H), 7.16 (dd, J = 7.7, 1.2 Hz, 2 H), 3.46 (m, 4 H), 1.72 (m, 4 H).

MS (ESI+): m/z (%) = 431.3 ($[M+H]^+$, 100).

IR (KBr): ν 3135, 3052, 1613, 1481, 1389, 1321, 1292, 1160, 1081, 865, 785, 748 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{24}H_{22}N_4O_4 \cdot 1.5\ H_2O$ (457.5): C 63.01, H 5.51, N 12.25; found: 62.92, H 5.55, N 11.94.

_N,N'_-(4,4'-Methylene-bis(4,1-phenylene))bis(8-hydroxyquinoline-2-carboxamide) (66d-H_2)



Prepared according to **GP-5B**, starting from 8-hydroxyquinoline-2-carboxylic acid **30a** (1.0 g, 5.29 mmol), HBTU (2.41 g, 6.35 mmol), DIPEA (0.75 g, 1.0 ml, 5.80 mmol), and 4,4'-diaminodiphenylmethane (0.524 g, 2.64 mmol) in MeCN (50 ml).

Yield: 0.86 g (59 %); mp 301 °C.

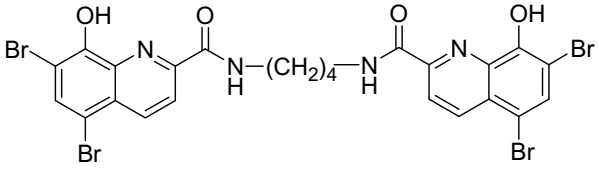
^{1}H NMR (300 MHz, DMSO-d_6, 5030415): δ = 11.15 (s, 2 H), 10.40 (s, 2 H), 8.57 (d, J = 8.7 Hz, 2 H), 8.26 (d, J = 8.7 Hz, 2 H), 7.84 (d, J = 8.4 Hz, 4 H), 7.60 (dd, J = 8.2, 7.7 Hz, 2 H), 7.52 (dd, J = 8.2, 1.2 Hz, 2 H), 7.34 (d, J = 8.4 Hz, 4 H), 7.23 (dd, J = 7.4, 1.2 Hz, 2 H), 3.99 (s, 2 H).

MS (ESI-): m/z (%) = 539.8 ($[M-H]^-$, 100).

IR (KBr): ν 3340, 1681, 1592, 1524, 1463, 1405, 1318, 1237, 1189, 849, 762 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{33}H_{24}N_4O_4 \cdot 0.5\ H_2O$ (549.6): C 72.12, H 4.59, N 10.59; found: 72.57, H 5.07, N 10.29.

***N,N'*-(Butane-1,4-diyl)bis(5,7-dibromo-8-hydroxyquinoline-2-carboxamide) (111)**



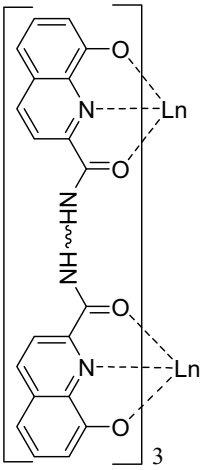
Prepared according to **GP-5B**, starting from dibromosubstituted carboxylic acid **30c** (0.2 g, 0.58 mmol), HBTU (0.26 g, 0.7 mmol), DIPEA (0.082 g, 0.11 ml, 0.63 mmol), and 1,4-diaminobutane (0.025 g, 0.03 ml, 0.29 mmol) in MeCN (15 ml). The product was isolated as a red solid.

Yield: 0.12 g (56 %).

^{1}H NMR (300 MHz, DMSO-d_6, a6052980): δ = 9.66 (t, J = 5.4 Hz, 2 H), 9.54 (d, J = 8.9 Hz, 2 H), 9.28 (d, J = 8.9 Hz, 2 H), 8.13 (s, 2 H), 1.73 (m, 4 H). Resonances of the other two methylene groups of the spacer are hidden under solvent peak.

MS (ESI+): m/z (%) = 747.3 ($[M+H]^+$, 100).

General procedure (GP-15) for the preparation of helicate type complexes with bis-amide-bridged linear homoditopic ligands



To the corresponding ligand **66b-d**-H_2 (3.0 equiv.) in MeOH (15 ml) a base M_2CO_3 (M = Rb, K) was added, resulting in a transparent yellowish solution, to which a $Ln(OTf)_3$ or a hydrated $LnCl_3$ (2.0 equiv.) was successively added. The reaction mixture was gently refluxed for 15 h, and then cooled to rt. The precipitate was filtered off, washed with chilled water, MeOH, and Et_2O to furnish the product.

$[Rb(66b)_3La_2]Cl$

Prepared according to **GP-15**, starting from ligand **66b**-H_2 (0.04 g, 0.10 mmol), Rb_2CO_3 (0.05 g, 0.15 mmol), and $LaCl_3 \cdot 7\ H_2O$ (0.025 g, 0.067 mmol). The desired complex was obtained as a mustard-coloured powder.

Yield: 0.049 g (90 %).

^{1}H NMR (300 MHz, DMSO-d_6, a5111469): δ = 10.85 (br. s, 6 H), 7.94 (d, J = 8.4 Hz, 6 H), 7.49 (d, J = 8.4 Hz, 6 H), 7.12 (dd, J = 7.7, 7.9 Hz, 6 H), 6.73 (d, J = 7.9 Hz, 6 H), 6.50 (d, J = 7.7 Hz, 6 H), 2.73 (s, 6 H), 2.27 (s, 6 H).

Pos. FAB MS (3-NBA): m/z = 1781.6 $[La_2(\mathbf{66b})_3+Rb+H_2O]^+$, 1481.4 $[La_2(\mathbf{66b})_3+H]^+$.

IR (KBr): ν 1635, 1590, 1556, 1499, 1451, 1344, 1306, 1105, 846, 742 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{66}H_{48}O_{12}N_{12}La_2RbCl \cdot 3\ H_2O$ (1653.9): C 47.93, H 3.29, N 10.16; found: C 47.85, H 3.61, N 9.69.

[(66c)$_3$La$_2$]

Prepared according to **GP-15**, starting from ligand **66c**-H_2 (0.04 g, 0.093 mmol), K_2CO_3 (0.02 g, 0.14 mmol), and $LaCl_3 \cdot 7\ H_2O$ (0.023 g, 0.062 mmol). The desired complex was obtained as a deep yellow powder.

Yield: 0.049 g (94 %).

^{1}H NMR (300 MHz, DMSO-d_6, a6081602): δ = 9.44 (br. s, 6 H), 8.39 (d, J = 8.8 Hz, 6 H), 8.06 (d, J = 8.8 Hz, 6 H), 7.33 (t, J = 8.0 Hz, 6 H), 6.81 (d, J = 8.0 Hz, 6 H), 6.30 (d, J = 8.0 Hz, 6 H), 3.04 (br. s, 6 H), 2.85 (br. s, 6 H), 1.40 (br. s, 12 H).

MS (ESI+): m/z (%) = 1585.9 ([La$_2$(**66c**)$_3$+Na]$^+$, 34.0), 1019.1 ([La(**66c**)$_2$+Na]$^+$, 100).

MS (ESI-): m/z (%) = 1597.8 ([La(**66c**)$_3$+Cl]$^-$, 8.0), 1561.1 ([La$_2$(**66c**)$_3$-H]$^-$, 86.0), 995.4 ([La(**66c**)$_2$]$^-$, 69.0).

IR (KBr): ν 1629, 1591, 1552, 1499, 1449, 1374, 1343, 1307, 1104, 845, 741 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{72}H_{60}O_{12}N_{12}La_2 \cdot 7\ H_2O$ (1688.7): C 51.19, H 4.42, N 9.95; found: C 51.25, H 4.57, N 9.79.

[(66c)$_3$Er$_2$]

Prepared according to **GP-15**, starting from ligand **66c**-H_2 (0.04 g, 0.093 mmol), K_2CO_3 (0.02 g, 0.14 mmol), and $Er(OTf)_3$ (0.038 g, 0.062 mmol). The desired complex was obtained as an orange powder.

Yield: 0.050 g (93 %).

MS (ESI+): m/z (%) = 1657.2 ([K(**66c**)$_3$Er$_2$]$^+$, 10.12).

IR (KBr): ν 1633, 1592, 1556, 1500, 1454, 1378, 1350, 1312, 1107, 845, 746 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{72}H_{60}O_{12}N_{12}Er_2 \cdot 7\ H_2O$ (1744.5): C 49.53, H 4.27, N 9.63; found: C 49.11, H 4.25, N 9.53.

[(66c)$_3$Yb$_2$]

Prepared according to **GP-15**, starting from ligand **66c**-H_2 (0.04 g, 0.093 mmol), K_2CO_3 (0.02 g, 0.14 mmol), and $Yb(OTf)_3$ (0.023 g, 0.062 mmol). The desired complex was obtained as a reddish powder.

Yield: 0.050 g (96 %).

MS (ESI+): m/z (%) = 1176.0 ([Yb(**66c**)$_2$Na$_2$]$^+$, 100).

IR (KBr): ν 3389, 3272, 3076, 1633, 1593, 1558, 1500, 1455, 1379, 1351, 1313, 1108, 845, 747 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{72}H_{60}O_{12}N_{12}Yb_2 \cdot 3\ H_2O$ (1685.4): C 51.31, H 3.95, N 9.97; found: C 51.23, H 4.48, N 9.90.

[(66d)$_3$Yb$_2$]

Prepared according to **GP-15**, starting from ligand **66d**-H_2 (0.06 g, 0.11 mmol), K_2CO_3 (0.03 g, 0.22 mmol), and $Yb(OTf)_3$ (0.046 g, 0.074 mmol). The desired complex was obtained as a yellow powder.

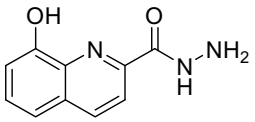
Yield: 0.072 g (95 %).

MS (ESI+): m/z (%) = 1984.0 ([Yb_2(**66d**)$_3$+Na]$^+$, 4.5).

IR (KBr): ν 3375, 1635, 1600, 1543, 1510, 1455, 1416, 1379, 1349, 1314, 1107, 843, 747 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{99}H_{66}O_{12}N_{12}Yb_2 \cdot 5\ H_2O$ (2050.8): C 57.95, H 3.73, N 8.19; found: C 57.91, H 3.98, N 8.07.

8-Hydroxyquinoline-2-carbohydrazide (67)



Prepared according to **GP-5B**, starting from 8-hydroxyquinoline-2-carboxylic acid **30a** (1.0 g, 5.29 mmol), HBTU (2.41 g, 6.35 mmol), DIPEA (0.75 g, 1.0 ml, 5.80 mmol), and hydrazine hydrate (0.291 g, 0.283 ml, 5.82 mmol) in MeCN (50 ml).

Yield: 0.87 g (61 %); mp 251 °C.

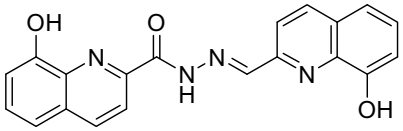
^{1}H NMR (300 MHz, DMSO-d_6, a5012138): δ = 10.76 (br. s, 1 H), 10.12 (s, 1 H), 8.59 (d, J = 8.7 Hz, 1 H), 8.12 (d, J = 8.7 Hz, 1 H), 7.55 (dd, J = 8.2, 7.7 Hz, 1 H), 7.47 (dd, J = 8.2, 1.2 Hz, 1 H), 7.15 (dd, J = 7.7, 1.2 Hz, 1 H), 4.67 (br. s, 2 H)

MS (EI, 70 eV): m/z (%) = 203.0 ([M]$^+$, 100), 144.0 ([M-CONHNH$_2$]$^+$, 50.1).

IR (KBr): ν 3261, 1669, 1570, 1501, 1311, 1237, 1166, 848, 745, 704, 639 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{10}H_9N_3O_2$ (203.2): C 59.11, H 4.46, N 20.68; found: C 58.87, H 4.63, N 20.42.

(*E*)-8-Hydroxy-*N*′-((8-hydroxyquinolin-2-yl)methylene)quinoline-2-carbohydrazide (68)



A mixture of carbohydrazide **67** (0.21 g, 1.04 mmol, 1.0 equiv.) and 8-hydroxyquinoline-2-carboxaldehyde (0.20 g, 1.155 mmol, 1.1 equiv.) in MeOH (25 ml) was stirred at rt for 15 h. The reaction volume was reduced in vacuum to a

minimum until the abundant precipitate separated. It was collected by filtration, washed with cold MeOH and Et_2O to furnish the product as an off-white solid.

Yield: 0.38 g (83 %); mp 288 °C.

^{1}H NMR (300 MHz, DMSO-d_6, a5120842): δ = 12.84 (br. s, 1 H), 10.23 (br. s, 1 H), 9.83 (br. s, 1 H), 8.94 (s, 1 H), 8.61 (d, J = 8.8 Hz, 1 H), 8.41 (d, J = 8.5 Hz, 1 H), 8.28 (d, J = 8.5 Hz, 1 H), 8.18 (d, J = 8.8 Hz, 1 H), 7.64 (dd, J = 8.2, 7.4 Hz, 1 H), 7.56 (dd, J = 8.4, 1.3 Hz, 1 H), 7.50 (dd, J = 8.2, 7.2 Hz, 1 H), 7.46 (dd, J = 8.2, 1.4 Hz, 1 H), 7.36 (dd, J = 7.7, 1.3 Hz, 1 H), 7.17 (dd, J = 7.5, 1.4 Hz, 1 H).

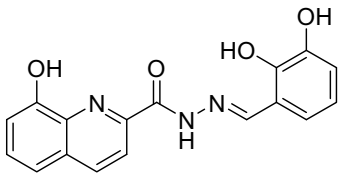
MS (EI, 70 eV): m/z (%) = 358.0 ([M]$^+$, 100), 186.0 ([M-$C_{10}H_8N_2O_1$]$^+$, 95.0).

IR (KBr): ν 3223, 1664, 1533, 1503, 1463, 1330, 1245, 1189, 1156, 843, 743 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{20}H_{14}N_4O_3 \cdot 2\ H_2O$ (394.4): C 60.91, H 4.60, N 14.21; found: C 61.10, H 5.15, N 14.31.

(*E*)-*N'*-(2,3-Dihydroxybenzylidene)-8-hydroxyquinoline-2-carbohydrazide (69)

Prepared according to the procedure described above for **68**, starting from carbohydrazide **67** (0.10 g, 0.49 mmol, 1.0 equiv.) and 2,3-dihydroxybenzaldehyde (0.075 g, 0.54 mmol, 1.1 equiv.).



Yield: 0.152 g (88 %); mp 343 °C (decomp.).

^{1}H NMR (300 MHz, DMSO-d_6, a6080827): δ = 12.67 (br. s, 1 H), 10.81 (br. s, 1 H), 10.18 (br. s, 1 H), 9.35 (br. s, 1 H), 8.81 (s, 1 H), 8.58 (d, J = 8.4 Hz, 1 H), 8.23 (d, J = 8.7 Hz, 1 H), 7.62 (dd, J = 7.9, 7.7 Hz, 1 H), 7.52 (dd, J = 8.4, 1.2 Hz, 1 H), 7.23 (dd, J = 7.4, 1.2 Hz, 1 H), 7.09 (dd, J = 7.7, 1.6 Hz, 1 H), 6.89 (dd, J = 7.9, 1.7 Hz, 1 H), 6.77 (dd, J = 7.9, 7.7 Hz, 1 H).

MS (ESI+): m/z (%) = 324.3 ([M+H]$^+$, 100), 214.2 ([M-$C_6H_5O_2$]$^+$, 2.4).

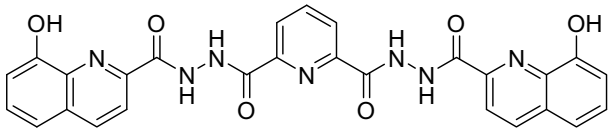
MS (ESI-): m/z (%) = 322.6 ([M-H]$^+$, 100).

IR (KBr): ν 3207, 1669, 1533, 1505, 1463, 1368, 1264, 1236, 1159, 1017, 944, 851, 791, 724, 637, 468 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{17}H_{13}N_3O_4 \cdot 1.5\ H_2O$ (350.3): C 58.28, H 4.60, N 11.99; found: C 57.97, H 4.27, N 11.75.

***N'*2,*N'*6-Bis(8-hydroxyquinoline-2-carbonyl)pyridine-2,6-dicarbohydrazide (70)**

To a solution of carbohydrazide **67** (0.066 g, 0.32 mmol, 2.2 equiv.) in dry 1,4-dioxane (10 ml) 2,6-pyridinedicarbonyl dichloride (0.03 g, 0.147 mmol, 1.0 equiv.) dissolved in 1 ml of 1,4-dioxane, and dry NEt_3 (0.03 g, 0.04 ml, 2.0 equiv.) were added. The mixture was stirred at



rt for 18 h, and then poured into water (20 ml). The suspension was intensively shaken; the precipitate formed was collected by filtration, washed with water, and recrystallized from MeOH to afford an off-white solid.

Yield: 0.06 g (73 %); mp 271 °C.

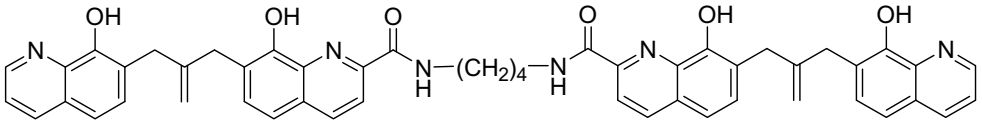
^{1}H NMR (300 MHz, DMSO-d_6, a6101503): δ = 11.59 (s, 2 H), 11.45 (s, 2 H), 10.18 (s, 2 H), 8.59 (d, J = 8.5 Hz, 2 H), 8.40 (d, J = 8.5 Hz, 2 H), 8.34 (dd, J = 8.8, 6.2 Hz, 1 H), 8.19 (d, J = 8.8 Hz, 2 H), 7.62 (t, J = 8.0 Hz, 2 H), 7.53 (d, J = 8.0 Hz, 2 H), 7.22 (d, J = 7.4, 1.2 Hz, 2 H).

MS (ESI+): m/z (%) = 560.4 ([M+Na]$^+$, 100), 1096.8 ([2M+Na]$^+$, 59.0).

IR (KBr): ν 3462, 2922, 2852, 1687, 1639, 1562, 1505, 1470, 1240, 1154, 853, 731, 472 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{27}H_{19}N_7O_6 \cdot 0.5\ H_2O \cdot 0.5\ CH_3OH$ (562.5): C 58.72, H 3.94, N 17.43; found: C 58.30, H 4.14, N 17.08.

_N,N'_-(Butane-1,4-diyl)bis(8-hydroxy-7-(2-((8-hydroxyquinolin-7-yl)methyl)allyl)-quinoline-2-carboxamide) (71)



Prepared according to **GP-5B**, starting from an isobutenylidene-bridged carboxylic acid **42** (0.14 g, 0.36 mmol), HBTU (0.165 g, 0.43 mmol), DIPEA (0.068 ml, 0.40 mmol), and 1,4-diaminobutane (0.016 g, 0.18 mmol).

Yield: 0.085 g (57 %); mp 142 °C.

^{1}H NMR (300 MHz, DMSO-d_6, a7032915): δ = 10.04 (br. s, 2 H), 9.64 (t, J = 6.0 Hz, 2 H), 8.81 (d, J = 4.2 Hz, 2 H), 8.44 (d, J = 8.4 Hz, 2 H), 8.28 (d, J = 8.1 Hz, 2 H), 8.10 (d, J = 8.4 Hz, 2 H), 7.52-7.35 (m, 10 H), 4.72 (s, 2 H), 4.71 (s, 2 H), 3.56 (m, 8 H), 3.45-3.43 (m, 4 H), 1.70 (m, 4 H).

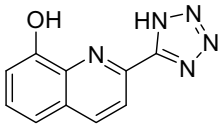
MS (ESI+): m/z (%) = 847.4 ([M+Na]$^+$, 100), 825.4 ([M]$^+$, 12.4).

IR (KBr): ν 3348, 2825, 1737, 1657, 1537, 1453, 1372, 1278, 1238, 1178, 1092, 720, 668 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{50}H_{44}N_6O_6 \cdot H_2O$ (842.9): C 71.24, H 5.50, N 9.97; found: C 71.19, H 5.32, N 10.08.

5.12. Quinolines with Heterocyclic Substituents (81-84, 91, 94)

2-(1*H*-Tetrazol-5-yl)quinolin-8-ol (83)



8-Hydroxyquinoline-2-carbonitrile **33** (0.20 g, 1.18 mmol, 1. 0 equiv.), TBAF · 3 H_2O (0.185 g, 0.59 mmol, 0.5 equiv.), $TMSN_3$ (0.233 ml, 1.76 mmol, 1.5 equiv.), and DMF (1.5 ml) were placed in a Schlenk flask. The resulting mixture was stirred at 90 °C for 15 h under inert atmosphere of N_2, then cooled to rt and transferred to a separatory funnel with 20 ml of EtOAc. TBAF was removed by washing the organic phase with 1 M HCl aqueous solution (3 × 5 ml). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure until the product started to crystallize. After cooling to +4 °C a pale yellow solid was collected by filtration and washed with EtOAc.

Yield: 0.22 g (80 %); mp 271 °C.

^{1}H NMR (300 MHz, DMSO-d_6, a7060849): δ = 9.62 (br. s, 1 H), 8.60 (d, J = 8.7 Hz, 1 H), 8.25 (d, J = 8.7 Hz, 1 H), 7.58 (dd, J = 8.4, 7.3 Hz, 1 H), 7.52 (dd, J = 8.4, 1.5 Hz, 1 H), 7.23 (dd, J = 7.3, 1.5 Hz, 1 H).

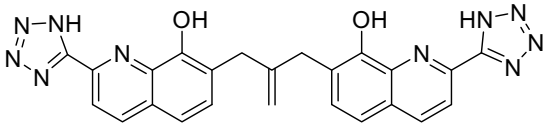
^{13}C NMR (75 MHz, DMSO-d_6): δ = 155.0 (C), 153.0 (C), 140.8 (C), 138.3 (CH), 137.4 (C), 129.5 (CH), 128.9 (C), 119.1 (CH), 117.8 (CH), 111.6 (CH).

MS (ESI-): m/z (%) = 212.1 ([M]$^-$, 100), 184.5 ([M-N_2-H]$^-$, 20.8).

IR (KBr): ν 3414, 3322, 1654, 1626, 1568, 1505, 1470, 1404, 1380, 1317, 1234, 1190, 1162, 1050, 842, 752, 719 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{10}H_7N_5O_1$ · 1/3 DMF (237.5): C 55.61, H 3.96, N 31.45; found: C 55.57, H 4.19, N 31.58.

7,7'-(2-Methylenepropane-1,3-diyl)bis(2-(1*H*-tetrazol-5-yl)-quinolin-8-ol) (84)



Bis-carbonitrile derivative **39** (0.27 g, 0.69 mmol, 1.0 equiv.), TBAF · 3 H_2O (0.217 g, 0.69 mmol, 1.0 equiv.), $TMSN_3$ (0.363 ml, 2.75 mmol, 4.0 equiv.), and DMF (1.5 ml) were placed in a Schlenk flask. The resulting mixture was stirred under an inert atmosphere of N_2 at 100 °C for 24 h, then cooled to rt, and poured cautiously into ice water (25 ml). 1 M HCl (15 ml) was added, and the mixture was stirred for 15 min. The light-brown precipitate was collected by filtration, washed with water, and recrystallized from DMSO / *i*-PrOH to afford an off-white solid.

Yield: 0.137 g (37 %); mp 273 °C.

^{1}H NMR (300 MHz, DMSO-d_6, a6082162): δ = 9.51 (br. s, 2 H), 8.56 (d, J = 8.5 Hz, 2 H), 8.23 (d, J = 8.5 Hz, 2 H), 7.51 (s, 4 H), 4.83 (s, 2 H), 3.63 (s, 4 H).

^{13}C NMR (75 MHz, DMSO-d_6, a7062425): δ = 155.0 (C), 150.2 (C), 146.3 (C), 140.7 (C), 138.0 (CH), 131.4 (CH), 127.3 (C), 125.8 (C), 122.2 (C), 118.3 (CH), 117.1 (CH), 112.7 (CH_2), 34.3 (CH_2).

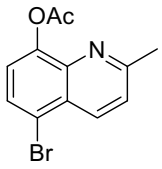
MS (ESI+): m/z (%) = 479.2 ($[M]^+$, 100), 423.2 ($[M-2N_2+H]^+$, 53.9), 395.2 ($[M-2N_3+H]^+$, 83.9).

MS (ESI-): m/z (%) = 477.4 ($[M-H]^-$, 100), 434.6 ($[M-N_3-H]^-$, 49.6).

IR (KBr): ν 3079, 1639, 1570, 1505, 1458, 1399, 1319, 1244, 1185, 1093, 1042, 891, 849, 805, 772, 679 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{24}H_{18}N_{10}O_2 \cdot 0.5$ DMSO $\cdot H_2O$ (535.5): C 56.07, H 4.33, N 26.15; found: C 55.88, H 4.78, N 25.96.

5-Bromo-2-methylquinolin-8-yl acetate (88)



A solution of 5-bromoquinaldine **26b** (1.0 g, 4.2 mmol) in acetic anhydride (15 ml) was refluxed for 15 h. The solvent was evaporated under reduced pressure, the crude residue was taken up in CH_2Cl_2 (50 ml) and washed with satd. aq $NaHCO_3$ (3 × 25 ml). The organic phase was separated, dried over Na_2SO_4, and evaporated in vacuum. The dark oily residue was dissolved in acetone. The slow addition of *n*-hexane into concentrated acetone solution led to the isolation of the product as a colouress crystalline solid.

Yield: 1.10 g (94 %).

^{1}H NMR (400 MHz, $CDCl_3$, a6011337): δ = 8.38 (d, J = 8.8 Hz, 1 H), 7.73 (d, J = 8.0 Hz, 1 H), 7.39 (d, J = 8.8 Hz, 1 H), 7.28 (d, J = 8.0 Hz, 1 H), 2.75 (s, 3 H), 2.51 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.4 (C), 159.9 (C), 146.6 (C), 141.1 (C), 135.5 (CH), 128.6 (CH), 126.8 (C), 123.6 (CH), 121.6 (CH), 118.6 (C), 25.4 (CH_3), 20.9 (CH_3).

MS (EI, 70 eV): m/z (%) = 280.8 ($[M]^+$, 2.5), 238.9 ($[M-Ac+H]^+$, 100).

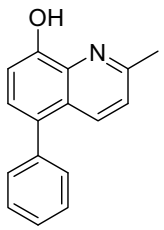
IR (KBr): ν 1766, 1594, 1459, 1430, 1368, 1308, 1191, 1150, 1061, 1008, 885, 825, 788 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{12}H_{10}N_1O_2Br_1$ (280.1): C 51.45, H 3.60, N 5.00; found: C 51.25, H 3.48, N 4.91.

2-Methyl-5-phenylquinolin-8-ol (89b)

A mixture of **88** (1.0 g, 3.57 mmol), phenylboronic acid (0.544 g, 4.46 mmol), 1,4-dioxane (25 ml), and 1 M K_2CO_3 (20 ml) was degassed by bubbling N_2 through the solution for 30

min. Then $Pd(PPh_3)_4$ (0.20 g, 0.18 mmol) was added and the reaction mixture was refluxed under atmosphere of N_2 for 24 h. After cooling to rt, the resulting solution was diluted with H_2O (50 ml) and extracted with Et_2O (3 × 50 ml). The combined organic layers were dried over Na_2SO_4, and then the solvent was evaporated under reduced pressure. The brown oily crude residue was subjected to flash chromatography (CH_2Cl_2 / *n*-hexane 1:1) to furnish a mixture of **89b** and 8-acetoxy-5-phenylquinaldine **89a** (the first fraction), and the product **89b** as an orange powder (the second fraction).



Yield: 0.277 g (33 %).

^{1}H NMR (300 MHz, $CDCl_3$, a7042632): δ = 8.16 (d, J = 8.7 Hz, 1 H), 7.51-7.39 (m, 5 H), 7.37 (d, J = 7.9 Hz, 1 H), 7.27 (d, J = 8.7 Hz, 1 H), 7.21 (d, J = 7.9 Hz, 1 H), 2.74 (s, 3 H).

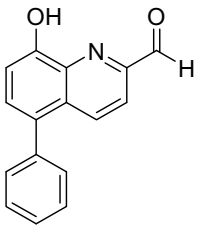
^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.6 (C), 151.1 (C), 139.6 (C), 137.6 (C), 134.6 (CH), 130.6 (C), 130.0 (CH), 128.4 (CH), 127.2 (CH), 127.0 (CH), 124.7 (C), 122.6 (CH), 109.3 (CH), 24.7 (CH_3).

MS (EI, 70 eV): m/z (%) = 235.1 ($[M]^+$, 100).

All data are in agreement with those reported in the literature.[221]

8-Hydroxy-5-phenylquinoline-2-carboxaldehyde (90)

To a suspension of SeO_2 (0.28 g, 2.55 mmol) in dry 1,4-dioxane (20 ml) 5-phenylquinaldine **89b** (0.50 g, 2.13 mmol) in 1,4-dioxane (30 ml) was added in small portions at 80 °C. The mixture was heated at 85 °C for 7 h and then cooled to rt. The Se rests were filtered off and solvent was removed under reduced pressure. The brown oily residue was dissolved in EtOAc and filtered through a pad of Celite®. The solution was evaporated in vacuum furnishing a brownish solid, which was chromatographed (CH_2Cl_2) to afford the product as yellow needles.



Yield: 0.164 g (31 %); mp 128 °C.

^{1}H NMR (300 MHz, $CDCl_3$, a7051425): δ = 10.24 (d, J = 0.7 Hz, 1 H), 8.43 (dd, J = 8.7, 0.7 Hz, 1 H), 8.28 (s, 1 H), 8.01 (d, J = 8.7 Hz, 1 H), 7.60 (d, J = 7.9 Hz, 1 H), 7.54-7.42 (m, 5 H), 7.34 (d, J = 7.9 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.6 (CH), 152.3 (C), 149.8 (C), 138.6 (C), 137.7 (C), 136.1 (CH), 131.3 (C), 131.2 (CH), 130.0 (CH), 128.6 (CH), 128.6 (C), 127.6 (CH), 117.8 (CH), 110.7 (CH).

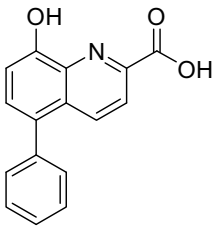
[221] C. Pérez-Bolívar, V. A. Montes, P. Anzenbacher, *Inorg. Chem*. **2006**, *45*, 9610.

MS (EI, 70 eV): m/z (%) = 249.0 ($[M]^+$, 100), 221.0 ($[M\text{-}COH+H]^+$, 5.2).

IR (KBr): ν 1743, 1707, 1474, 1373, 1264, 1220, 1023, 992, 763, 704 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{16}H_{11}N_1O_2$ (249.3): C 77.10, H 4.45, N 5.62; found: C 77.27, H 4.63, N 5.70.

8-Hydroxy-5-phenylquinoline-2-carboxylic acid (91)



Phenyl substituted 2-carboxaldehyde **90** (0.10 g, 0.4 mmol) was suspended in formic acid (3.0 ml, 78.0 mmol) and the suspension was cooled to 0 °C. Cold hydrogen peroxide (4 ml of 30 % solution in water, 0.13 mol) was slowly added. The reaction mixture was kept at +4 °C for 24 h. Then the resulting suspension was poured into ice water (50 ml); the precipitate formed was collected by filtration, washed with cold water, and recrystallized from EtOH providing the product as a yellow solid.

Yield: 0.042 g (46 %); mp 130 °C.

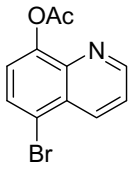
^1H NMR (300 MHz, DMSO-d_6, a7060806): δ = 10.34 (br. s, 1 H), 8.43 (d, J = 8.9 Hz, 1 H), 8.16 (d, J = 8.9 Hz, 1 H), 7.60 (d, J = 7.9 Hz, 1 H), 7.57-7.46 (m, 5 H), 7.30 (d, J = 7.9 Hz, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 165.0 (C), 153.3 (C), 144.2 (C), 138.4 (C), 136.5 (C), 136.2 (CH), 130.9 (CH), 129.8 (CH), 127.7 (CH), 127.6 (C) 127.4 (CH), 120.3 (CH), 111.6 (CH), one quaternary C atom could not be observed.

MS (ESI+): m/z (%) = 266.0 ($[M+H]^+$, 100), 220.1 ($[M\text{-}COOH]^+$, 2.6).

IR (KBr): ν 3056, 1742, 1708, 1571, 1473, 1372, 1220, 1149, 1021, 987, 830, 760, 702 cm^{-1}.

Acetic acid 5-bromoquinolin-8-yl ester (92)



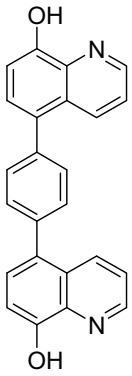
Prepared according to the procedure described for **88** starting from 5-bromoquinoline **31b** (1.0 g, 4.5 mmol).

Yield: 1.10 g (94 %).

^1H NMR (300 MHz, $CDCl_3$, a6092075): δ = 8.93 (dd, J = 4.2, 1.7 Hz, 1 H), 8.54 (dd, J = 8.6, 1.7 Hz, 1 H), 7.82 (d, J = 8.2 Hz, 1 H), 7.55 (dd, J = 8.6, 4.2 Hz, 1 H), 7.34 (d, J = 8.2 Hz, 1 H), 2.51 (s, 3 H).

MS (EI, 70 eV): m/z (%) = 266.3 ($[M]^+$, 4.9), 224.1 ($[M\text{-}Ac+H]^+$, 100).

5,5'-(1,4-Phenylene)diquinolin-8-ol (93)



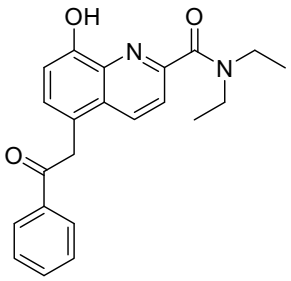
A mixture of **92** (0.2 g, 0.75 mmol), 1,4-benzenediboronic acid (0.062 g, 0.38 mmol), 1,4-dioxane (15 ml), and 1 M K_2CO_3 (2 ml) was degassed by bubbling N_2 through the solution for 30 min. Then $Pd(PPh_3)_4$ (0.026 g, 0.02 mmol) was added and the reaction mixture was refluxed under atmosphere of N_2 for 24 h. After cooling to rt, the resulting solution was diluted with H_2O (25 ml) and extracted with hot Et_2O (3 × 50 ml). The combined organic layers were dried over Na_2SO_4, and then the solvent was evaporated under reduced pressure furnishing a brownish solid.

^{1}H NMR (300 MHz, $CDCl_3$, a6101354): δ = 8.81 (dd, J = 4.2, 1.5 Hz, 2 H), 8.50 (dd, J = 7.2, 1.5 Hz, 2 H), 8.02 (br. s, 2 H), 7.72-7.43 (m, 8 H), 7.08 (d, J = 8.2 Hz, 2 H).

MS (EI, 70 eV): m/z (%) = 365.9 ($[M+H]^+$, 1.20), 277.0 (100).

Compound could not be isolated in analytically pure form.

8-Hydroxy-5-(2-oxo-2-phenylethyl)quinoline-2-carboxylic acid diethylamide (94)



To a solution of bromosubstituted amidoquinolinate **34b** (150 mg, 0.46 mmol), dichlorobis(triphenyl-phosphine)palladium(II) (6.5 mg, 9.3 μmol), and CuI (1 mg, 5.2 μmol) in degassed DMF (10 ml), piperidine (8 ml) and phenylacetylene (24 mg, 0.026 ml, 0.23 mmol) dissolved in piperidine (2 ml) were introduced subsequently under an atmosphere of N_2. After the 2nd and the 4th hour of stirring at 100 °C the same amount of phenylacetylene was added again, and then the resulting mixture was heated for another 20 h. After evaporation of the solvent under reduced pressure, the crude residue was directly applied to column chromatograpy (EtOAc / *n*-hexane 1:2) to afford a yellowish waxy solid.

Yield: 0.037 g (22 %).

^{1}H NMR (300 MHz, $CDCl_3$, a6050569): δ = 9.56 (d, J = 8.9 Hz, 1 H), 8.28 (d, J = 8.2 Hz, 1 H), 7.76 (d, J = 8.9 Hz, 1 H), 7.34-7.26 (m, 5 H), 7.20 (d, J = 8.2 Hz, 1 H), 4.38 (s, 2 H), 3.63 (q, J = 7.2 Hz, 2 H), 3.32 (q, J = 7.2 Hz, 2 H), 1.32 (t, J = 7.2 Hz, 3 H), 1.19 (t, J = 7.2 Hz, 3 H).

MS (EI, 70 eV): m/z (%) = 362.2 ($[M]^+$, 24.3), 271.1 ($[M-C_4H_{10}N_1-H_3O]^+$, 100).

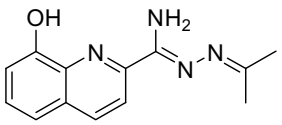
IR (KBr): ν 3453, 2929, 1631, 1475, 1258, 1084, 848, 698 cm^{-1}.

(*Z*)-8-Hydroxy-*N'*-(propan-2-ylidene)quinoline-2-carbohydrazonamide (81) and (*2Z,N'Z*)-*N'*-(amino(8-hydroxyquinolin-2-yl)methylene)-8-hydroxyquinoline-2-carbo-hydrazonamide (82)

To a mixture of 8-hydroxyquinoline-2-carbonitrile **33** (0.50 g, 2.94 mmol) and hydrazine hydrate (0.294 g, 0.285 ml, 5.88 mmol) in EtOH (20 ml), sulfur (0.10 g, 3.12 mmol) was added at rt with stirring. The resulting mixture was refluxed for 3 h, then cooled to rt and concentrated under reduced pressure. The crude residue was chromatographed (acetone / *n*-hexane 1:10) to furnish **81** as yellow needles (first fraction) and **82** as a dark yellow solid (second fraction washed down from the column with acetone as an eluent).

Yield: **81**: 0.171 g (24 %); mp 151 °C; **82**: 0.092 (18 %).

Characterization of 81:



^{1}H NMR (300 MHz, $CDCl_3$, a6051899): δ = 8.44 (d, J = 8.9 Hz, 1 H), 8.18 (d, J = 8.9 Hz, 1 H), 7.92 (s, 1 H), 7.48 (dd, J = 8.2, 7.7 Hz, 1 H), 7.37 (dd, J = 8.2, 1.2 Hz, 1 H), 7.22 (dd, J = 7.7, 1.2 Hz, 1 H), 6.12 (br. s, 2 H), 2.18 (s, 3 H), 2.14 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.1 (C), 152.9 (C), 152.0 (C), 149.2 (C), 136.6 (C), 136.4 (CH), 129.1 (C), 128.3 (CH), 1190.5 (CH), 118.0 (CH), 110.8 (CH), 25.5 (CH_3), 18.3 (CH_3).

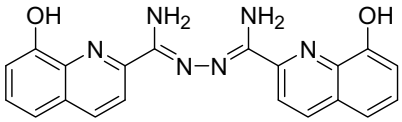
MS (EI, 70 eV): m/z (%) = 242.1 ($[M]^+$, 44.3), 227.1 ($[M\text{-}NH_2+H]^+$, 100).

IR (KBr): ν 3441, 3335, 1628, 1553, 1504, 1463, 1372, 1229, 1182, 843, 753 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{13}H_{14}N_4O$ (242.3): C 64.45, H 5.82, N 23.13; found: C 64.27, H 5.63, N 22.70.

X-Ray quality crystals were obtained from CH_2Cl_2 / acetone. Code FRO3787.

Characterization of 82:



^{1}H NMR (400 MHz, $CDCl_3$, a6042111): δ = 8.32 (d, J = 8.5 Hz, 1 H), 7.73 (d, J = 8.5 Hz, 1 H), 7.64 (dd, J = 8.2, 7.8 Hz, 1 H), 7.42 (dd, J = 8.2, 1.1 Hz, 1 H), 7.30 (dd, J = 7.8, 1.1 Hz, 1 H).

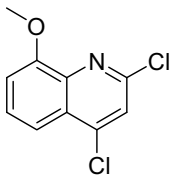
MS (ESI+): m/z (%) = 373.1 ($[M+H]^+$, 100), 356.3 ($[M\text{-}NH_2]^+$, 79.0).

MS (ESI-): m/z (%) = 371.3 ($[M\text{-}H]^+$, 100).

5.13. Synthesis of 4-Substituted Quinolines (95-106, 112)

5.13.1. Dichlorosubstituted Quinolines

2,4-Dichloro-8-methoxyquinoline (95)



Malonic acid (0.148 g, 1.42 mmol) was dissolved in $POCl_3$ (5 ml), and *o*-anisidine (0.22 g, 0.2 ml, 1.77 mmol) was slowly added. The mixture was gently refluxed for 3 h, allowed to cool, poured into ice water (50 ml), and stirred overnight. The solution was neutralized with diluted aq NaOH resulting in the separation of a brownish oil. Decantation of the aqueous phase provided a crude residue, which was washed with water, dissolved in CH_2Cl_2, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure leaving a yellow oil, which was induced to crystallize. Addition of *n*-hexane to the product and prolonged efficient mixing led to the formation of a white powder.

Yield: 0.24 g (60 %); mp 135 °C.

^{1}H NMR (400 MHz, $CDCl_3$, a7080312): δ = 7.76 (dd, J = 8.2, 1.1 Hz, 1 H), 7.57 (dd, J = 8.2, 7.9 Hz, 1 H), 7.56 (s, 1 H), 7.15 (dd, J = 7.9, 1.1 Hz, 1 H), 4.07 (s, 3 H).

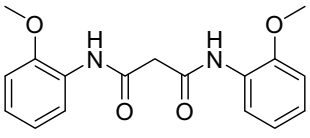
^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.6 (C), 148.7 (C), 144.1 (C), 139.7 (C), 127.9 (CH), 126.2 (C), 122.5 (CH), 115.5 (CH), 109.7 (CH), 56.2 (CH_3).

MS (EI, 70 eV): m/z (%) = 228.0 ($[M]^+$, 64.3), 226.0 (100), 198.0 ($[M\text{-}OMe+H]^+$, 79.2), 162.0 ($[M\text{-}OMe\text{-}Cl]^+$, 55.5).

IR (KBr): ν 3008, 1608, 1560, 1490, 1467, 1437, 1391, 1365, 1285, 1267, 1140, 1102, 1006, 874, 858, 837, 814, 749 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{10}H_7Cl_2NO$ (228.1): C 52.66, H 3.09, N 6.14; found: C 53.00, H 3.46, N 6.32.

***N,N'*-Bis(2-methoxyphenyl)malonamide (96)**



Prepared according to the procedure described above for dichlorosubstituted methoxyquinoline **95**, using 10-fold amounts of starting materials: malonic acid (1.476 g, 14.18 mmol) and *o*-anisidine (2.184 g, 2 ml, 17.73 mmol) in $POCl_3$ (10 ml). The crude product was recrystallized from *n*-hexane to afford a colourless crystalline solid.

Yield: 1.53 g (55 %).

^{1}H NMR (300 MHz, $CDCl_3$, a6101198): δ = 8.80 (br. s, 2 H), 8.35 (dd, J = 7.9, 1.5 Hz, 2 H), 7.07 (dt, J = 7.9, 1.7 Hz, 2 H), 6.96 (dt, J = 7.9, 1.2 Hz, 2 H), 6.89 (dd, J = 7.9, 1.2 Hz, 2 H), 3.90 (s, 6 H), 3.56 (s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.1 (C), 148.4 (C), 127.0 (C), 134.2 (CH), 120.7 (CH), 120.2 (CH), 110.0 (CH), 66.6 (CH_2), 45.4 (CH_3).

MS (EI, 70 eV): m/z (%) = 314.0 ($[M]^+$, 100), 165.0 ($[M-C_8H_8NO_2+H]^+$, 33.4).

All data are in agreement with those reported in the literature.[222]

5.13.2. MW Assisted Synthesis of 4-Quinolones

General procedure for the Conrad-Limpach and Gould-Jacobs cyclizations performed under microwave conditions (GP-16)

Method A. **One-component – one-step procedure:**

An enamine or arylaminoacrylate substrate (1.0 mmol) and Ph_2O (6 ml) were placed in a 10 ml vessel, which was then sealed with a septum, placed into the MW cavity, and locked with the pressure device. Constant MW irradiation of 100 W at 250 °C without air-cooling was used during the entire reaction time (10 min). After cooling to rt, the reaction mixture was diluted with *n*-hexane (150 ml). The brown oil or solid separated rapidly from the solution (with exception of 3-carboxy-4-quinolones **100** where the addition of *n*-hexane even in small amounts led to the spontaneous abundant precipitation of pure product. It was then filtered off and washed only with CH_2Cl_2 and *n*-hexane). The remaining transparent brown solution was poured into another flask and allowed to stay for ~ 1 h. In most of the cases a white solid crystallized on the walls of the flask. The solvent was removed; the product was washed with *n*-hexane and recrystallized from acetone / *n*-hexane to furnish a colourless crystalline solid. The crude brown residue containing the product as well was applied to flash chromatography to afford another portion of the product as a colourless crystalline solid.

Method B. **Two-components – one-step procedure:**

The procedure is in accordance to the one described above in method **A** but using *o*-anisidine (0.123 g, 0.113 ml, 1.0 mmol) and an acetylenedicarboxylate, a methoxymethylenemalonate or a β-dicarbonyl component (1.1 mmol) in Ph_2O (6 ml) as reactants. MW irradiation of 50 W at 120 °C without air-cooling was used during the first 5 min of reaction time, then irradiation power was increased to 100 W at 250 °C for next 10 min (with the exception of 3-carboxy-4-quinolone **100**, when the irradiation time at 100 W was prolonged to 15 min). The workup procedure is analogous to the one described in method **A**.

[222] (a) A. Daubinet, P. T. Kaye, *Synth. Commun*. **2002**, *32*, 3207. (b) H. Nishino, K. Ishida, H. Hashimoto, K. Kurosawa, *Synthesis* **1996**, 888.

Method C. **A "large scale" alternative appropriate for both methods A and B, employing open-vessel technology:**

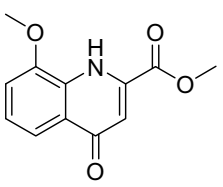
2-Butenedioic acid, 2-[(methoxyphenyl)-amino]-, dimethyl ether (2.65 g, 10.0 mmol), 2-[(2-methoxyphenylamino)methylene]malonic acid diethyl ester[215] (2.93 g, 10.0 mmol) or a mixture of *o*-anisidine (1.23 g, 1.13 ml, 10.0 mmol), dimethyl acetylenedicarboxylate (DMAD) (1.56 g, 1.35 ml, 11.0 mmol) was placed into a 50 ml vessel. Ph_2O (25 ml) was added; the vessel was equipped with an open condensator and placed into the MW cavity. The mixture was irradiated at 50 W and 120 °C without air-cooling for 5 min and at 100 W and 250 °C for another 10 min (with the exception of 3-carboxy-4-quinolone **100**, when the irradiation time at 100 W was prolonged to 20 min). After cooling to rt, the standard workup procedure was applied.

8-Methoxy-4-oxo-1,4-dihydroquinoline-2-carboxylic acid methylester (99) and 8-methoxy-4-oxo-1,4-dihydroquinoline-2-carboxylic acid ethylester (99a)

Prepared according to **GP-16** method **A,** starting from 2-butenedioic acid, 2-[(methoxyphenyl)-amino]-, dimethyl ether (0.265 g, 1.0 mmol) or 2-butenedioic acid, 2-[(methoxyphenyl)-amino]-, diethyl ether (0.293 g, 1.0 mmol) and Ph_2O (6 ml); *or* method **B**, using *o*-anisidine, (0.123 g, 0.113 ml, 1.0 mmol), dimethyl acetylenedicarboxylate (DMAD) (0.156 g, 0.135 ml, 1.1 mmol) or diethyl acetylenedicarboxylate (DEAD) (0.187 g, 0.173 ml, 1.1 mmol) and Ph_2O (6 ml) as reaction components; *or* method **C**, using 2-butenedioic acid, 2-[(methoxyphenyl)-amino]-, dimethyl ether (2.65 g, 10.0 mmol) or a mixture of *o*-anisidine (1.23 g, 1.13 ml, 10.0 mmol) and dimethyl acetylenedicarboxylate (DMAD) (1.56 g, 1.35 ml, 11.0 mmol) in Ph_2O (25 ml). The brown residue was chromatographed (CH_2Cl_2) to afford additional product as a colourless crystalline solid.

Yield: method **A**: 0.19 g (0.017 g , 7 %, were collected after flash chromatography, additional 0.173 g, 64 %, were obtained after recrystallization) (81 % of overall yield); method **B**: 0.126 g (54 %); method **A**/**C**: 1.70 g (0.48 g , 20 %, were collected after flash chromatography, additional 1.22 g, 53 %, were obtained after recrystallization) (73 % of overall yield); method **B**/**C**: 0.88 g (38 %).

Characterization of 99:



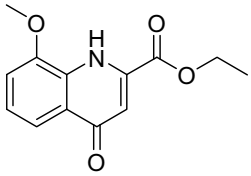
^{1}H NMR (300 MHz, $CDCl_3$, a7080338): δ = 9.41 (br. s, 1 H), 7.88 (dd, J = 8.2, 1.0 Hz, 1 H), 7.28 (dd, J = 8.2, 7.9 Hz, 1 H), 7.08 (dd, J = 7.9, 1.0 Hz, 1 H), 6.97 (s, 1 H), 4.03 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 179.2 (C), 162.0 (C), 148.2 (C), 135.4 (C), 130.2 (C), 126.8 (C), 123.9 (CH), 117.1 (CH), 111.7 (CH), 111.1 (CH), 56.0 (CH_3), 53.6 (CH_3).

MS (EI, 70 eV): m/z (%) = 233.1 ($[M]^+$, 100).

All the data are in agreement with those reported in the literature.[194]

Characterization of 99a:



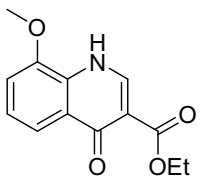
^{1}H NMR (300 MHz, $CDCl_3$, a7080248): δ = 9.40 (br. s, 1 H), 7.85 (dd, J = 8.2, 1.1 Hz, 1 H), 7.25 (dd, J = 8.2, 8.0 Hz, 1 H), 7.05 (dd, J = 8.0, 1.1 Hz, 1 H), 6.96 (s, 1 H), 4.46 (q, J = 7.1 Hz, 2 H), 4.00 (s, 3 H), 1.42 (t, J = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 179.0 (C), 162.3 (C), 148.0 (C), 135.5 (C), 130.0 (C), 126.6 (C), 123.7 (CH), 116.7 (CH), 111.3 (CH), 110.9 (CH), 62.9 (CH_2), 55.9 (CH_3), 13.8 (CH_3).

MS (EI, 70 eV): m/z (%) = 247.1 ($[M]^+$, 100), 171.0 ([M-OEt-OMe], 67.0).

IR (KBr): ν 3398, 1726, 1588, 1531, 1476, 1445, 1370, 1347, 1267, 1230, 1145, 1050, 998, 821, 780, 615 cm^{-1}.

8-Methoxy-4-oxo-1,4-dihydroquinoline-3-carboxylic acid ethylester (100)



Prepared according to **GP-16** method **A,** starting from 2-[(2-methoxy-phenylamino)methylene]malonic acid diethyl ester (0.293 g, 1.0 mmol) and Ph_2O (6 ml); *or* method **B**, using *o*-anisidine (0.123 g, 0.113 ml, 1.0 mmol), diethyl ethoxymethylenemalonate (0.238 g, 0.22 ml, 1.1 mmol) and Ph_2O (6 ml) as reaction components; *or* method **C**, using 2-[(2-methoxyphenyl-amino)methylene]malonic acid diethyl ester (2.93 g, 10.0 mmol) or a mixture of *o*-anisidine (1.23 g, 1.13 ml, 10.0 mmol) and diethyl ethoxymethylenemalonate (2.38 g, 2.20 ml, 11.0 mmol) in Ph_2O (25 ml).

Yield: method **A**: 0.19 g (78 %); method **B**: 0.10 g (41 %); method **A/C**: 1.75 g (71 %); method **B**/**C**: 0.47 g (19 %).

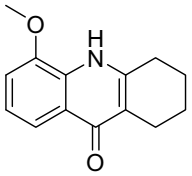
^{1}H NMR (300 MHz, DMSO-d_6, a7011762): δ = 12.09 (br. s, 1 H), 8.43 (d, J = 6.0 Hz, 1 H), 7.71 (dd, J = 7.2, 2.2 Hz, 1 H), 7.34 (dd, J = 7.9, 7.2 Hz, 1 H), 7.30 (dd, J = 7.9, 2.2 Hz, 1 H), 4.21 (q, J = 7.2 Hz, 2 H), 4.01 (s, 3 H), 1.28 (t, J = 7.2 Hz, 3 H).

MS (EI, 70 eV): m/z (%) = 247.0 ($[M]^+$, 86.6), 201.0 ($[M\text{-}OEt\text{-}H]^+$, 100), 171.0 ($[M\text{-}OEt\text{-}OMe]^+$, 53.1).

Elemental analysis: calcd. (%) for $C_{13}H_{13}NO_4$ (247.2): C 63.15, H 5.30, N 5.67; found: C 62.94, H 5.51, N 5.66.

All data are in agreement with those reported in the literature.[215]

5-Methoxy-1,2,3,4-tetrahydroacridin-9(10*H*)-one (105)



Prepared according to **GP-16** method **B,** using 2-oxocyclohexanecarboxylic acid ethyl ester (0.187 g, 0.176 ml, 1.1 mmol). The brown solid residue was purified by flash chromatography (acetone / CH_2Cl_2 1:6) to furnish the product as a colourless crystalline solid.

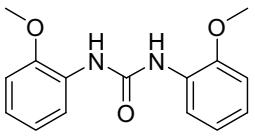
Yield: 0.11 g (48 %).

^{1}H NMR (400 MHz, $CDCl_3$, a7062448): δ = 8.30 (s, 1 H), 7.90 (dd, J = 8.2, 1.0 Hz, 1 H), 7.17 (dd, J = 8.2, 7.9 Hz, 1 H), 6.97 (dd, J = 7.9, 1.0 Hz, 1 H), 3.98 (s, 3 H), 2.68 (dt, J = 17.3, 6.2 Hz, 4 H), 1.90-1.77 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$, a7062747): δ = 177.6 (C), 147.0 (C), 144.8 (C), 129.9 (C), 124.5 (C), 121.9 (CH), 117.9 (C), 117.5 (CH), 109.6 (CH), 55.8 (CH_3), 28.3 (CH_2), 22.2 (CH_2), 21.9 (CH_2), 21.7 (CH_2).

MS (EI, 70 eV): m/z (%) = 229. 2 ($[M]^+$, 96.7), 214.0 ($[M\text{-}OMe]^+$, 55.3).

1,3-Bis(2-methoxyphenyl)urea (106)



Prepared according to **GP-16** method **A**, using the condensation product 3-(2-methoxyphenyl-imino)butyric acid ethyl ester[216] (0.235 g, 1.0 mmol); *or* method **B**, starting from a mixture of *o*-anisidine and ethyl acetoacetate (0.137 g, 0.14 ml, 1.1 mmol). The crude product was purified by flash chromatography (EtOAc / *n*-hexane 1:4) to furnish a colourless crystalline solid.

Yield: method **A**: 0.17 g (62 %); method **B**: 0.14 g (52 %).

^{1}H NMR (400 MHz, $CDCl_3$, a7081824): δ = 8.12 (dd, J = 7.7, 1.9 Hz, 2 H), 7.15 8 (s, 2 H), 7.01 (ddd, J = 7.7, 7.4, 1.9 Hz, 2 H), 6.97 (ddd, J = 7.7, 7.4, 1.9 Hz, 2 H), 6.88 (dd, J = 7.7, 1.9 Hz, 2 H), 3.87 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.4 (C), 148.2 (C), 128.2 (C), 123.0 (CH), 121.3 (CH), 119.8 (CH), 110.2 (CH), 55.9 (CH_3).

MS (EI, 70 eV): m/z (%) = 272.0 ($[M]^+$, 76.0), 123.0 (100).

All the other data are in agreement with those reported in the literature.[223]

5.13.3. Cyclocondensation with Successive / Simultaneous Chlorination

General procedure (GP-17)

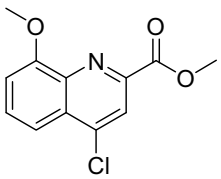
Method A. **MW assisted attempt:**

An enamine substrate (1.0 mmol) and Ph_2O (2 ml) were placed in 10 ml vessel, which was then sealed with a septum, placed into MW cavity, and locked with the pressure device. MW irradiation of 50 W at 120 °C without air-cooling was used during the first 5 min of reaction time. After cooling to rt, $POCl_3$ (3 ml) was added, and then the mixture was irradiated at 100 W and 150 °C for next 5 min, until pressure started to rapidly arise. The resulting mixture was cooled to rt, diluted with water, neutralized with 0.5 M NaOH to pH ~ 5, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4; the solvent was removed in vacuum furnishing black oil, which was applied to flash chromatography (EtOAc / *n*-hexane 1:4) to afford the product as a white powder.

Method B. **Traditional approach with conventional heating:**

A 4-quinolone was heated in $POCl_3$ at 100 °C with stirring for 1.5-2 h. The reaction mixture was allowed to cool to rt and poured into ice water. 2 M NaOH was cautiously added with stirring (a considerable exothermic effect is observed) to adjust the pH to ~ 6. The precipitate was collected by filtration, washed with water, dried in vacuum, and recrystallized from CH_2Cl_2 / *n*-hexane to furnish the product as a white powder.

4-Chloro-8-methoxy-quinoline-2-carboxylic acid methylester (101)



Prepared according to **GP-17** method **A**, using 2-butenedioic acid, 2-[(methoxyphenyl)-amino]-, dimethyl ether (0.265 g, 1.0 mmol); *or* method **B**, using 4-quinolone **99** (1.0 g, 4.29 mmol) and $POCl_3$ (5 ml).

Yield: method **A**: 0.06 g (24 %); method **B**: 0.75 g (68 %); mp 146 °C.

^{1}H NMR (400 MHz, $CDCl_3$, a7073037): δ = 8.32 (s, 1 H), 7.84 (dd, J = 8.5, 1.1 Hz, 1 H), 7.68 (dd, J = 8.5, 8.0 Hz, 1 H), 7.15 (dd, J = 8.0, 1.1 Hz, 1 H), 4.10 (s, 3 H), 4.05 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.0 (C), 156.1 (C), 146.1 (C), 143.7 (C), 140.1 (C), 130.1 (CH), 128.6 (C), 121.8 (CH), 115.4 (CH), 108.9 (CH), 56.3 (CH_3), 53.2 (CH_3).

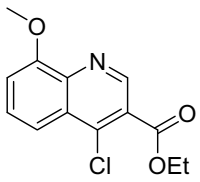
MS (EI, 70 eV): m/z (%) = 251.0 ($[M]^+$, 35.7), 235.9 ($[M\text{-}Me]^+$, 100).

[223] M. C. Etter, Z. Urbañczyk-Lipkowska, M. Zia-Ebrahimi, T. W. Panunto, *J. Am. Chem. Soc.* **1990**, *112*, 8415.

IR (KBr): ν 3094, 1721, 1611, 1557, 1498, 1470, 1448, 1334, 1259, 1204, 1139, 1108, 1009, 969, 896, 819, 784, 747 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{12}H_{10}ClNO_3 \cdot 1/3\ H_2O$ (257.7): C 55.94, H 4.17, N 5.44; found: C 55.70, H 4.10, N 5.56.

4-Chloro-8-methoxyquinoline-3-carboxylic acid ethylester (112)



Prepared according to **GP-16** method **B**, using **100** (0.50 g, 2.02 mmol) in $POCl_3$ (10 ml).

Yield: 0.35 g (65 %).

^1H NMR (400 MHz, $CDCl_3$, a7051402): δ = 9.08 (s, 1 H), 7.82 (dd, J = 8.7, 1.0 Hz, 1 H), 7.48 (dd, J = 8.7, 7.9 Hz, 1 H), 7.06 (dd, J = 7.9, 1.0 Hz, 1 H), 4.42 (q, J = 7.2 Hz, 2 H), 4.01 (s, 3 H), 1.37 (t, J = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.2 (C), 155.1 (C), 148.2 (CH), 142.7 (C), 139.9 (C), 128.2 (CH), 126.9 (C), 123.4 (C), 116.4 (CH), 109.6 (CH), 61.8 (CH_2), 56.0 (CH_3), 13.9 (CH_3).

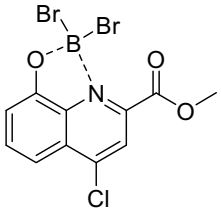
MS (EI, 70 eV): m/z (%) = 264.9 ($[M]^+$, 100), 219.9 ([M-OEt-OMe], 20.2).

IR (KBr): ν 2997, 1710, 1627, 1583, 1544, 1473, 1415, 1376, 1293, 1206, 1171, 1131, 1063, 1008, 773, 621 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{13}H_{12}ClNO_3$ (265.7): C 58.77, H 4.55, N 5.27; found: C 58.59, H 4.86, N 5.22.

All data are in agreement with those reported in the literature.[215]

Methyl-4-chloro-8-(dibromoboryloxy)quinoline-2-carboxylate (102)



To a solution of 4-chlorosubstituted methylester **101** (0.10 g, 0.40 mmol, 1.0 equiv.) in dry CH_2Cl_2 (2 ml) BBr_3 (0.248 g, 0.093 ml, 0.99 mmol, 2.5 equiv.) was added dropwise below -50 °C under inert atmosphere of N_2. After 15 min, the reaction mixture was stirred at rt for 2 h, and then refluxed for another 2 h. The solution was cooled to rt, neutralized to pH ~ 8 with satd. aq $NaHCO_3$, and extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was recrystallized from CH_2Cl_2 to furnish the product as yellow needles.

^1H NMR (400 MHz, $CDCl_3$, a7030814): δ = 8.41 (s, 1 H), 8.12 (dd, J = 8.7, 1.2 Hz, 1 H), 8.01 (dd, J = 8.7, 7.9 Hz, 1 H), 7.55 (dd, J = 7.9, 1.2 Hz, 1 H), 4.15 (s, 3 H),

MS (EI, 70 eV): m/z (%) = 327.9 ($[M-Br]^+$, 100).

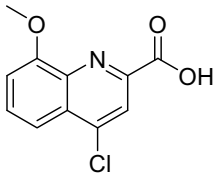
4-Hydroxy-8-methoxyquinoline-2-carboxylic acid (103) and 4-chloro-8-methoxy-quinoline-2-carboxylic acid (104)

Method A is analogous to the described above procedure for **102**, but using 10-fold amounts of starting materials. Neutralization of the reaction mixture and stirring in an ice-water bath for additional 4 h resulted in an abundant precipitate. The crude product was collected by filtration, washed with water and MeOH, and then dried in vacuum to furnish an off-white powder **103/104**. The MeOH fraction was evaporated under reduced pressure until the product started to crystallize. Evaporation was stopped and the mixture was allowed to cool to +4 °C. The formed precipitate was filtered off, washed with Et_2O, and dried to furnish an off-white solid **104**.

Method B: To 4-chlorosubstituted methylester **104** (0.50 g, 1.99 mmol) 25 ml of HBr (48 % in water) were added. The mixture was refluxed for 15 h, then cooled to rt and neutralized with 2 M KOH. The precipitate thus formed was collected, washed with water, cold MeOH and Et_2O, and dried in vacuum to furnish the product **103/104** as an off-white powder.

Characterization of 104:

Yield: 0.061 g (13 %).



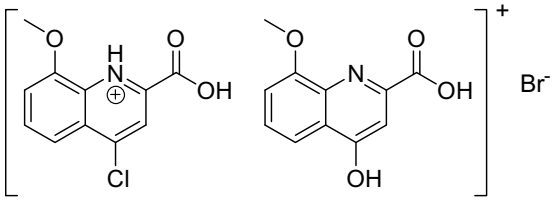
^{1}H NMR (300 MHz, DMSO-d_6, a7040403): δ = 8.23 (s, 1 H), 7.76 (d, J = 3.0 Hz, 1 H), 7.75 (d, J = 5.8 Hz, 1 H), 7.37 (dd, J = 5.8, 3.0 Hz, 1 H), 4.03 (s, 3 H).

MS (EI, 70 eV): m/z (%) = 238.1 ([M]$^+$, 56.2), 161.0 ([M-COOH-OMe]$^+$, 73.3).

Elemental analysis: calcd. (%) for $C_{11}H_8O_3ClN$ (237.6): C 55.60, H 3.39, N 5.89; found: C 55.87, H 3.85, N 6.17.

Characterization of 103/104:

($C_{11}H_8O_3ClN \cdot C_{11}H_9O_4N \cdot HBr \cdot 2\ H_2O$):



Yield: method **A**: 0.65 g (59 %); method **B**: 0.52 g (94 %); mp 262-263 °C

^{1}H NMR (300 MHz, DMSO-d_6, a7032728): δ = 10.70 (br. s, 2 H), 7.55 (d, J = 8.0 Hz, 2 H), 7.30 (dd, J = 8.0, 7.7 Hz, 2 H), 7.14 (d, J = 7.7 Hz, 2 H), 6.90 (br. s, 2 H), 3.17 (s, 3 H). The signal of one CH_3 group is hidden under solvent peak.

MS (ESI+): m/z (%) = 238.1 ([M]$^+$, 45.0), 220.1 ([M+H]$^+$, 100).

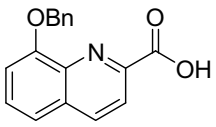
IR (KBr): ν 3344, 1721, 1611, 1577, 1524, 1450, 1372, 1289, 1228, 1164, 1023, 984, 897, 750, 676, 554, 474 cm^{-1}.

X-Ray quality crystals were obtained from DMSO.

Crystal data for the agglomerate ***103/104****:* formula $C_{22}H_{22}BrClN_2O_9$; code FRO4298; M = 573.78; yellow crystal 0.20 x 0.07 x 0.07 mm; monoclinic, space group $P2_1/c$ (No.14); a = 14.8341(3) Å, b = 13.3651(2) Å, c = 13.3864(2) Å, β = 114.592(1)°, Z = 4, λ= 0.71073 Å, T = 223(2) K, V = 2413.25(7) Å^3, ρ_{calc} = 1.579 g cm^{-3}; μ = 1.869 mm^{-1}; 22126 reflections collected ($\pm h$, $\pm k$, $\pm l$), 5757 independent (R_{int} = 0.0695), max. residual electron density ρ = 1.29 (-0.94) e Å^{-3}, empirical absorption correction ($0.706 \leq T \leq 0.88$); $[(sin\theta)/\lambda]_{max}$ = 0.66 Å^{-1}; CCD data collection. Fourier calculations, others are calculated and refined riding, due to crystal size the analysis is of limited accuracy.

5.14. Miscellaneous

Synthesis of 8-benzyloxyquinoline-2-carboxylic acid (29)



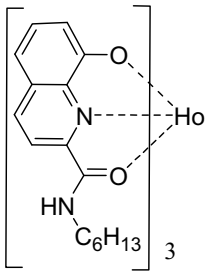
Benzyloxyquinoline-2-carboxaldehyde **28** (0.20 g, 0.76 mmol) was suspended in formic acid (5.0 ml, 0.13 mol) and the suspension was cooled to 0 °C. Cold hydrogen peroxide (7 ml of 30 % solution in water, 0.23 mol) was slowly added. The reaction mixture was kept at +4 °C for 24 h. Then the resulting suspension was poured into ice water (75 ml); the precipitate formed was collected by filtration, washed with cold water, and recrystallized from acetone providing the product as yellow needles.

Yield: 0.18 g (86 %).

^{1}H NMR (400 MHz, $CDCl_3$, a5031005): δ = 8.37 (d, J = 8.4 Hz, 1 H), 8.29 (d, J = 8.4 Hz, 1 H), 7.59 (dd, J = 8.2, 7.8 Hz, 1 H), 7.54-7.35 (m, 6 H), 7.21 (dd, J = 7.8, 0.9 Hz, 1 H), 5.36 (s, 2 H).

MS (EI, 70 eV): m/z (%) = 279.7 ([M]$^+$, 100).

Synthesis and characterization of [(35a)$_3$Ho]



A mixture of 2-(*N*-*n*-hexylcarboxamide)-8-hydroxyquinoline **35a**-H (0.05 g, 0.18 mmol, 3.0 equiv.), $HoCl_3 \cdot 6\ H_2O$ (0.023 g, 0.06 mmol, 1.0 equiv.), and K_2CO_3 (0.025 g, 0.18 mmol, 3.0 equiv.) in MeOH (15 ml) was stirred at rt for 18 h. The yellow solution was evaporated under reduced pressure, the residue was redissolved in CH_2Cl_2 and filtered from remaining inorganic salts. The solution was concentrated in vacuum to a minimum. Upon

dropwise addition of *n*-hexane to the concentrated CH_2Cl_2 solution the product precipitated as a deep yellow solid. The solvent was carefully decanted, leaving the solid product which was dried in vacuum.

Yield: 0.061 (92 %).

MS (ESI+): m/z (%) = 1723.0 ([Ho_2(**35a**)$_5$+K], 18.0), 1413.3 ([Ho_2(**35a**)$_4$], 46.0), 1017.4 ([Ho_2(**35a**)$_3$+K], 39.0), 707.8 ([Ho(**35a**)$_2$]$^+$, 100).

IR (KBr): ν 2928, 2857, 1631, 1593, 1562, 1500, 1455, 1378, 1353, 1309, 1108, 742 cm^{-1}.

Elemental analysis: calcd. (%) for $C_{48}H_{57}O_6N_6 \cdot H_2O \cdot CH_2Cl_2$ (1081.4): C 54.40, H 5.68, N 7.77; found: C 54.65, H 5.80, N 7.85.

X-Ray quality crystals were obtained by slow diffusion of Et_2O in MeOH solution.

Synthesis and characterizatin of [(32)$_2$Zn$_3$](OAc)$_2$

A mixture of 8-hydroxyquinoline-2-carboxamide **32**-H (0.04 g, 0.21 mmol, 2.0 equiv.), K_2CO_3 (0.03 g, 0.22 mmol, 1.0 equiv.), and $Zn(OAc)_2$ (0.07 g, 0.32 mmol, 3.0 equiv.) in MeOH (15 ml) was stirred at rt for 18 h. The solvent was evaporated under reduced pressure to dryness. The residue was redissolved in MeOH / MeCN (1:1 v/v), filtered off from the inorganic salts and allowed to stay on air. The slow evaporation of solvents furnished red cylindric crystals, which were collected and dried in vacuum.

Yield: 0.075 (81 %).

^{1}H NMR (400 MHz, DMSO-d_6, a5122134): δ = 9.41 (br. s, 1 H), 8.28 (d, J = 8.8 Hz, 2 H), 7.99 (d, J = 8.4 Hz, 2 H), 7.52 (br. s, 1 H), 7.40 (t, J = 7.6 Hz, 2 H), 7.09 (d, J = 6.0 Hz, 2 H), 6.90 (d, J = 6.8 Hz, 2 H).

MS (ESI+): m/z (%) = 828.9 ({[(**32**)$_2$Zn$_3$](OAc)$_4$+Na}$^+$, 8.3), 689.2 ({[(**32**)$_2$Zn$_3$](OAc)$_2$}$^+$, 1.9), 565.2 ({[(**32**)$_2$Zn$_2$](OAc)}$^+$, 11.7), 506.2 ({[(**32**)$_2$Zn$_2$]+H}$^+$, 53.9), 439.5 ({[(**32**)$_2$Zn]+H}$^+$, 12.0).

IR (KBr): ν 3392, 1680, 1460, 1363, 1314, 1278, 1111, 847, 749 cm^{-1}.

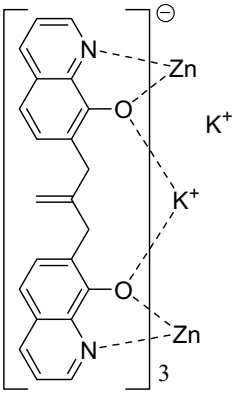
Elemental analysis: calcd. (%) for $C_{28}H_{26}O_{12}N_4Zn_3 \cdot 1.5\ CH_3CN$ (868.2): C 42.88, H 3.54, N 8.87; found: C 43.08, H 4.24, N 8.55.

X-Ray quality crystals were obtained by slow evaporation of MeOH / MeCN solution.

Crystal data for [(**32**)$_2$Zn$_3$](OAc)$_2$: formula $C_{32}H_{44}N_6O_{18}Zn_3$, code ext022; M = 996.84, orange crystal 0.20 x 0.04 x 0.04 mm, a = 8.8529(18) Å, b = 10.781(2) Å, c = 11.960(2) Å, a = 111.36(3)°, β = 92.82(3)°, γ = 103.02(3)°; V = 1024.9(3) Å^3, ρ_{calc} = 1.615 g cm^{-3}, μ = 1.822 mm^{-1}, empirical absorption correction (0.712 ≤ T ≤ 0.9307), Z = 1, triclinic, space group P $\bar{1}$, λ= 0.71073 Å, T = 173(2) K, ω and φ scans, 10667 reflections collected (±h, ±k, ±l), 4392

independent 4392 (R_{int} = 0.0658) and 3044 observed reflections [$I \geq 2\ \sigma(I)$], 288 refined parameters, R = 0.0558, wR^2 = 0.1198, max. residual electron density 0.66 (–0.92) e $Å^{-3}$, hydrogen atom at nitrogen from difference Fourier calculations, others are calculated and refined riding, due to crystal size the analysis is of limited accuracy.

Synthesis and characterization of $[K_2(\mathbf{11})_3Zn_2]$



A mixture of 2-(8-hydroxyquinolin-7-methylene)-3-(8-hydroxyquinolin-7-yl)-1-propene **11**-H_2 (0.04 g, 0.117 mmol, 3.0 equiv.), K_2CO_3 (0.02 g, 0.14 mmol), and $Zn(OAc)_2$.(0.017 g, 0.08 mmol, 2.0 equiv.) in MeOH (15 ml) was stirred at 60 °C for 10 h, and then at rt for another 15 h. The precipitate was filtered off, washed with cold water, cold MeOH, and Et_2O, and dried in vacuum to afford the product as an orange solid.

Yield calcd. on MW (MW = 1229.76 g mol^{-1}): 0.046 g (96 %).

^{1}H NMR (400 MHz, DMSO-d_6, a7030322): δ = 8.20 (dd, J = 8.3, 1.4 Hz, 6 H), 7.44 (dd, J = 4.4, 1.4 Hz, 6 H), 7.26 (d, J = 8.3, 4.4 Hz, 6 H), 7.22 (d, J = 8.2 Hz, 6 H), 6.73 (d, J = 8.2 Hz, 6 H), 4.34 (s, 6 H), 3.41 (br. s, 6 H), 3.12 (br. s, 6 H).

MS (ESI+): m/z (%) = 1154.9 ($[Zn_2(\mathbf{11})_3+3H]^+$, 100), 812.9 ($[Zn_2(\mathbf{11})_2+H]^+$, 40.0).

6. Appendix

6.1. List of Abbreviations

8-HQ	8-hydroxyquinoline
Å	Ångstrom
abs.	absolute
Ac	acetyl
aq	aqueous (solution)
Ar	aromatic substituent
Bn	benzyl
br.	broad (NMR signal)
Bu	butyl
CD	circular dichroism
CDI	carbonyl diimidazole
CPL	circularly polarized luminescence
conc.	concentrated
δ	chemical shift
d	doublet
DCC	*N*,*N'*-dicyclohexylcarbodiimide
DIPEA	diisopropylethylamine, Hünig-Base
DMAD	dimethyl acetylenedicarboxylate
DMF	*N*,*N*-dimethylformamide
DMSO	dimethylsulfoxide
EDG	electron-donating group
ee	enantiomeric excess
EI	electronic impact (in mass spectroscopy)
EL	electroluminescence
equiv.	equivalents
ESI	electrospray ionization mass spectrometry
Et	ethyl
ET	energy transfer
eV	electronvolt
EWG	electron-withdrawing group
FAB	fast atom bombardment

Ph	phenyl
GP	general procedure
h	hours
HBTU	*O*-(1-benzotriazol)-*N,N,N',N'*-tetramethyluroniumhexafluoro-phosphate
*n*Hex	*n*-hexyl
HHH	head-to-head-to-head
HHT	head-to-head-to-tail
HOMO	highest occupied molecular orbital
HRMS	high resolution mass spectroscopy
Hz	Herz
IR	infrared spectroscopy
ISC	intersystem crossing
J	coupling constant (in NMR spectroscopy)
λ	wavelength
L	ligand
LD	laser diode
LUMO	lowest unoccupied molecular orbital
m	multiplet
M	metal ion
M^+	parent molecular ion in mass spectrometry
Me	methyl
min	minute(s)
mol	mole(s)
mp	melting point
MS	mass spectroscopy
Mw	molar mass
MW	microwaves
m/z	mass-to-charge ratio in the mass spectrometry
ν	wave number
nm	nanometer(s)
N	normal (concentration)
NIR	near infrared
NMR	nuclear magnetic resonance (spectroscopy)

OLED	organic light emitting diode
OTf	trifluoromethanesulfonate
PL	photoluminescence
PLED	polymer light emitting diode
PPA	polyphosphoric acid
PVK	poly(*N*-vinylcarbazole)
pybox	2,2-bis(2-oxazolin-2-yl)pyridine
ppm	parts per milion
*i*Pr	*iso*-propyl
ps.	pseudo
q	quartet
quint	quintet
R	organic substituent
R_f	retention factor in chromatography
rac	racemic
rt	room temperature
SAMP	(*S*)-(-)-1-amino-2-(methoxymethyl)-pyrrolidine
SM	small molecule
τ	lifetime
t	triplet
TBAF	tetrabutylammonium fluoride
TBDMS	*t*-butyldimethylsilyl
TFA	trifluoro acetic acid
THF	tetrahydrofurane
TMS	trimethylsilyl
UV	ultravisible
v/v	volume ratio
Φ	luminescence quantum yield

6.2. Acknowledgements

A long way of searching and finding, excitation and disappointments, striving and frustrations is at the end. I would not come so far without the help, support and encouragement who contributed to this work in whatever fashion. I thank all of you for the valuable input in the work done during my PhD time, for the positive influence on the life I lived the last tree years.

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6.3. Curriculum Vitae

Personal information

Birth Date: 9/7/1981	*Birthplace*: Rivne, Ukraine
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Marital status:	Single
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Education

09/1988-09/1998:	High School with honor (specialization Physic), Rivne, Ukraine

Academic Qualification

09/1998-07/2002:	Course of studies in chemistry (majoring in Inorganic Chemistry) at the Chemistry Department of the National Taras Shevchenko University, Kiev, Ukraine. Baccalaureate with honor.
09/2002-06/2003:	Graduation at the Chemistry Department of the National Taras Shevchenko University, Kiev, Ukraine: Degree of Master of Science (with honor). Title: "Coordination chemistry of dinitrones of the aliphatic row and diisoxazolidines on their base".
09/2003-09/2004:	Research work at the Chemistry Department of the National Taras Shevchenko University, Kiev, Ukraine.
10/2004-01/2008:	PhD work at RWTH Aachen, Germany under the supervision of Prof. Dr. Markus Albrecht, working on the coordination chemistry of 8-hydroxyquinoline ligands towards lanthanide(III) metals. Thesis title: "Homo- and Heterodinuclear Luminescent Helicates".