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A Configurationally Stable Chiral Concave Imidazolinium Salt[‡]

Tim Reimers,[a] Christian Näther,[b] and Ulrich Lüning*[a]

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Starting from symmetric bis-*ortho*-alkenyl-substituted aniline **11** and unsymmetric bis-alkenyl-substituted aminonaphthalene **12**, imidazolinium salt **17** has been prepared. Salt **17** was cyclized by ring-closing metathesis, and hydrogenation gave axially chiral N-heterocyclic carbene precursor **19**. The configurational stability of **19** was proven by temperature-dependent NMR studies and also by the use of Λ-BINPHAT as a chiral shift reagent. Compound **19** was also characterized by single-crystal X-ray diffraction.

Introduction

Since Arduengo et al. crystallized an N-heterocyclic carbene (NHC) for the first time in 1991,[1] this class of compounds has gained enormous interest. Because of the high versatility with respect to the NHC core on one hand and to the N-substituents on the other hand, a large number of different NHCs has been synthesized to date. They are widely applied in organocatalysis[2,3] but are also used as ligands for transition metals, resulting in complexes with remarkable new properties.[4] The most famous example might be the second generation Grubbs catalyst used for olefin metathesis.[5,6] Moreover, due to their antimicrobial and antitumor properties, NHC noble metal complexes may have medicinal applicabilities.[7]

Since many biologically active molecules are chiral, there will always be a demand for asymmetric synthesis, and preferentially asymmetric catalysis. Thus, chiral NHCs[8] have been synthesized and investigated in both organocatalysis[2,9–11] and transition-metal catalysis.[12–16] Figure 1 shows some representative examples of chiral NHC precursors with different concepts of chirality: N-Heterocycles **1**–**3** are examples for different types of NHCs, and all of them have N-substituents containing centers of chirality: imidazolinium **1**,[17] triazolium **2**,[18] and imidazolium ions **3**[19] are shown here. Furthermore, there are NHCs with N-substituents containing axial chirality, that is, **6**,[20] as well as planar chirality, that is, **5**.[21] Moreover, carbene precursors containing chiral centers within the N-heterocycle, like imidazolinium salt **4**,[22] were created.

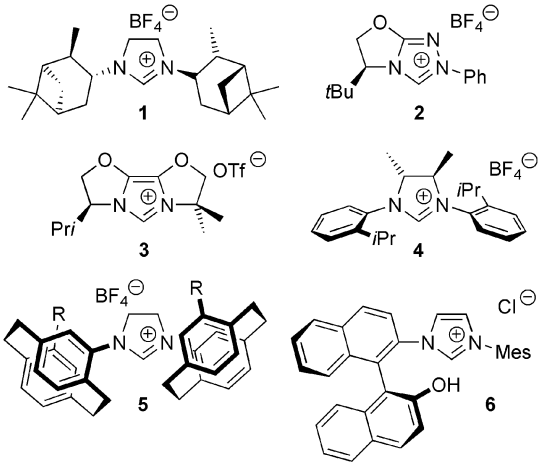
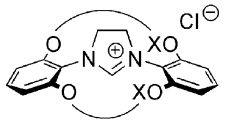


Figure 1. Examples of chiral NHC precursors.

The properties of the NHCs can be influenced by variation of the N-substituents. Especially size and shape of these groups can have a big influence on catalyzed reactions because of their proximity to the reactive carbene unit. By changing the residue R of NHC precursor **5**, for example, both reactivity and stereoselectivity has been tuned.[21]

Another concept of changing the steric properties of an NHC is its incorporation into a concave system. We realized this idea for the first time in 2007 by synthesizing con-



7a : X = $(CH_2)_8$
7b : X = $(CH_2)_{10}$

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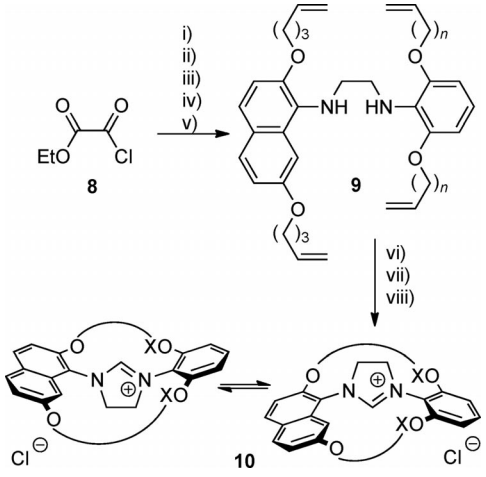
[a] Otto-Diels-Institut für Organische Chemie, Christian-Albrechts-Universität zu Kiel,
Olshausenstraße 40, 24098 Kiel, Germany
Fax: +49-431-8801558
E-mail: luening@oc.uni-kiel.de
[b] Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel,
Olshausenstraße 40, 24098 Kiel, Germany
Fax: +49-431-880-1520
E-mail: cnaether@ac.uni-kiel.de

cave imidazolinium salt **7**.[23] In this NHC precursor, the N-heterocycle is part of a bimacrocycle with two phenyl bridgeheads that are connected by oxyalkyl chains.

Upon deprotonation, the respective NHC was formed and used as an organocatalyst in the reaction of aldehydes with enals.[24] Remarkably, the product distribution depended strongly on the ring size. Whereas smaller bimacrocycle **7a** formed lactones as described for other NHCs, the larger concave NHC derived from **7b** led to the formation of an unexpected hemiacetal. This is proof for the special influence of the concave shape. Interestingly, with shorter alkyl chains, 8 methylene groups in **7a** instead of 10 in **7b**, the formation of a hemiacetal was not observed, nor was a hemiacetal found when standard NHCs such as IMes were used. This fact shows that apparently small changes in the environment of the reactive center can have a big influence on the selectivity of the catalyst.

Moreover, by exchanging one phenyl bridgehead for a naphthalene unit, axially chiral concave bimacrocycle **10** was also prepared (Scheme 1).[25] However, this NHC precursor proved to be configurationally unstable. At room temperature, rotation along the N–C_{Ar} bonds was observed by NMR spectroscopy, which resulted in interconversion of the enantiomers.



Scheme 1. Synthesis of configurationally unstable axially chiral NHC precursors **10**, n = 3, 4; X = $(CH_2)_{n+6}$. Reagents and conditions: (i) Bis(alkenyloxy)aniline, NEt_3, (ii) KOH, (iii) $(COCl)_2$, (iv) bis(alkenyloxy)naphthylamine, (v) $LiAlH_4$, (vi) NH_4Cl, $HC(OEt)_3$, (vii) benzylidenebis(tricyclohexylphosphane)dichlororuthenium, (viii) Pd/C, H_2.

For stabilization of the configuration, rotation along the N–C_{Ar} bonds has to be prevented. This can be realized by installation of stoppers, for example, alkyl substituents, at the backbone of the N-heterocycle. However, the used strategy to build up axially chiral bimacrocyclic NHC precursors **10** (Scheme 1) does not allow this. Reduction of an oxalyl diamide starting material by lithium aluminum hydride leads to methylene-substituted amines and thus cannot introduce substituents in the 4- or 5-position of the imidazolinium ring.

Thus, a new synthetic route had to be found. In 2008, Chung and Grubbs described the synthesis of asymmetric *N*-substituted imidazolinium salts bearing two methyl groups in the 4-position of the N-heterocycle[26] by starting from 2-bromo-2-methylpropionyl bromide (**13**) and anilines.

Results and Discussion

For the construction of an axially chiral NHC related to **10**, two different bridgeheads had to be treated with dibromide **13**. The phenyl bridgehead was introduced by amide formation between **13** and 2,6-bis(pent-4-enyloxy)aniline (**11**). Resulting bromoamide **14** could be isolated in 93% yield. Then, nucleophilic substitution of the remaining bromide with 2,7-bis(pent-4-enyloxy)naphthylamine (**12**) led to aminoamide **15** in 79% yield (Figure 2, Scheme 2).

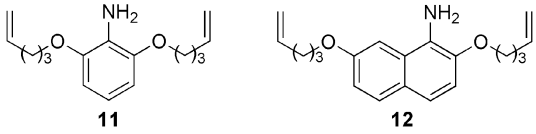


Figure 2. Structures of the arylamines that are used as bridgeheads for the concave bimacrocycles.

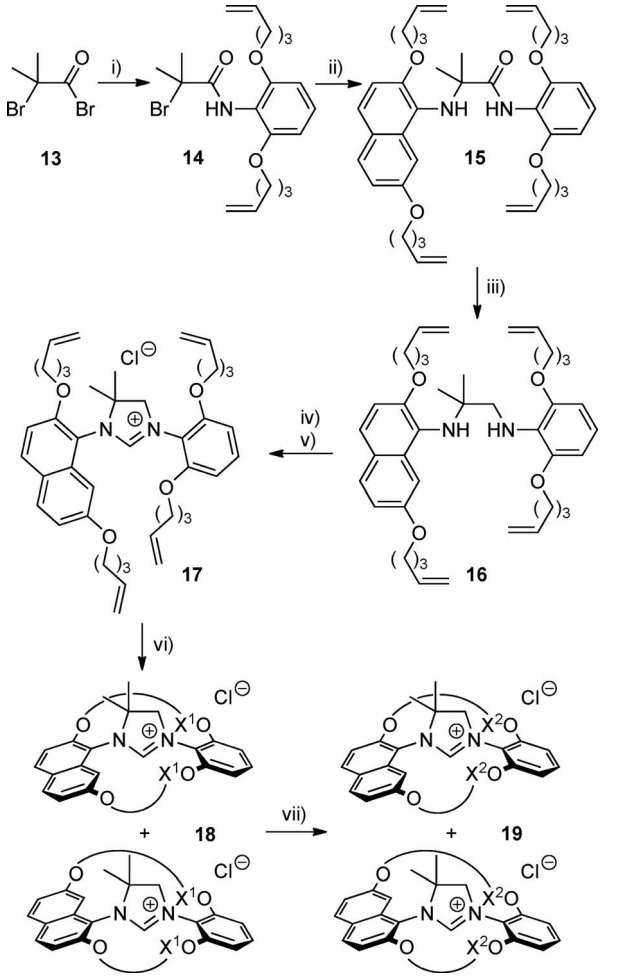
After reduction of amide **15** with lithium aluminum hydride, respective diamine **16** was isolated (80% yield). Treatment with hydrogen chloride dissolved in 1,4-dioxane converted it into the diamino dihydrochloride. After reaction of the salt with triethyl orthoformate at 140 °C, imidazolinium chloride **17** was obtained in 96% yield.

For the generation of bimacrocycle **18**, ring-closing metathesis of **17** with Grubbs first generation catalyst was carried out under high dilution conditions. Because of the two remaining double bonds, a mixture of four *E* and *Z* isomers [(*E*,*E*), (*E*,*Z*), (*Z*,*E*), and (*Z*,*Z*)] was formed in a yield of 88%. Conversion to saturated bimacrocyclic imidazolinium salt **19** was successfully performed by catalytic hydrogenation with palladium on charcoal in 87% yield.

Single crystals were grown from a mixture of $CDCl_3$ and cyclohexane, and the crystal structure (Figure 3) was determined by X-ray structure analysis. A comparison with the crystal structure of related but configurationally unstable chiral macrocycle **10** reveals distinct differences (Figure 4).

Before the two structures can be discussed, **10** and **19** have to be inspected closely: The main change is the introduction of two methyl groups in imidazolinium chloride **19** that do not exist in **10**. Moreover, the alkyl chains of the two bimacrocycles differ by one methylene group [$(CH_2)_8$ in **19**, but $(CH_2)_9$ in **10**]. Furthermore, the crystals were grown in different ways, and **19** crystallized by including one equivalent of chloroform, whereas the crystals of **10** are solvent free.

The most striking differences in the crystal structures are the twists between the aromatic bridgeheads and the N-heterocycle in methylated compound **19** when compared to **10**. The naphthyl ring in **19** is as orthogonal to the imidazolin-



Scheme 2. Synthesis of configurationally stable axially chiral NHC precursor **19**, $X^1 = (CH_2)_3HC{=}CH(CH_2)_3$, $X^2 = (CH_2)_8$. Reagents and conditions: (i) **11**, NEt_3 (93%), (ii) **12**, NaH (79%), (iii) $LiAlH_4$ (80%), (iv) HCl in 1,4-dioxane, (v) $HC(OEt)_3$, [96% over steps (iv) and (v)], (vi) benzylidenebis(tricyclohexylphosphane)dichlororuthenium (88%), (vii) Pd/C, H_2 (87%). Total yield over six steps: 43%.

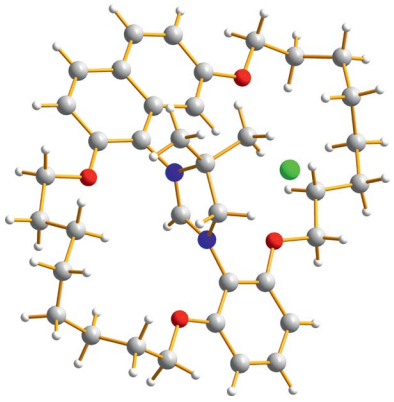


Figure 3. Crystal structure of imidazolinium chloride **19**. Only one enantiomer is shown; the chloroform molecule is omitted for clarity.

ium ring as possible, with the naphthalene unit being bent by ca. 3° out of plane by interaction with the two methyl

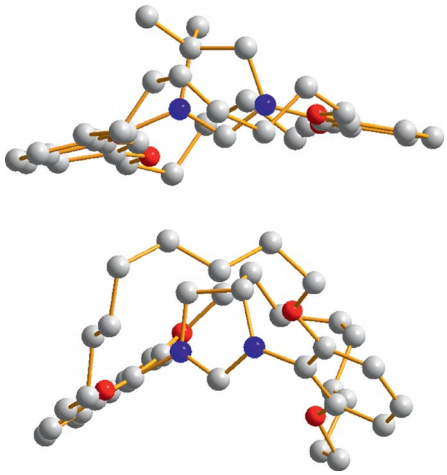


Figure 4. Comparison of the crystal structures of two imidazolinium ions: dimethyl-substituted **19** (top) and unsubstituted **10**[25] (bottom; $n = 4$, see Scheme 1). For clarity, only carbon, nitrogen, and oxygen atoms are shown.

groups. In unmethylated case **10**, there is a twist of ca. 6° out of orthogonality and no distortion of the naphthalene plane is observable.

The other bridgehead, the phenyl ring, is twisted out of orthogonality in both cases, but this twist is much larger in the unmethylated and larger bimacrocycle: 29° in **10** versus ca. 15° in **19**. In **10**, the twist of the two bridgeheads is disrotatory so that the overall "helicity" in the crystals is considerably larger in the wider and unmethylated case **10**. If one is allowed to sum up the twist angles, this sum is ca. 15° for dimethylated **19** but ca. 35° for larger and unsubstituted **10**.

If both bimacrocycles are looked at from the side (i.e., with the imidazolinium ring in the paper plane), the angle defined by the two aryl heterocycle bonds between the imidazolinium nitrogen atoms and the bridgehead carbon atoms seems to be considerably larger for dimethylated compound **19** than for unmethylated wider bimacrocycle **10**. In such a projection, this angle is 133° for unmethylated **10** in contrast to 143° for dimethylated salt **19**. To understand this difference, several dihedral and bond angles have to be inspected. There are the following differences: Of course, the steric requirements of the methyl groups in **19** lead to a larger dihedral angle along the C4–C5 bond of the imidazolinium unit by minimizing ecliptic interactions (18 vs. 10° for **10**). With this twist, the heterocycle in **19** is less planar. The C4–C5 bond is rotated with respect to the N–C2–N moiety. This and the geminal dimethyl effect results in altered angles within the five-membered ring (angular sum of the inner angles in the pentagons: 539° for **10**, 536° for **19**). Consequently, the wings of the aryl–heterocycle–aryl unit are a bit more open. In addition, the twist of the C4–C5 bond versus the N–C2–N unit results in a movement of one aryl ring out of the paper plane towards the observer and the other one is pushed behind the paper plane. This movement adds to the opening of the wings and leads to the observed differences in the above discussed

angles observed in the side projection: 133° for **10** and 143° for **19**. The visible differences seem to be even larger because the bridgeheads are not perfectly planar. In wider methylated **19**, the aromatic bridgeheads themselves are distorted a bit to the *exo* side, whereas they adopt a more *endo* shape in unmethylated **10**.

It will be interesting to see the influence of this altered geometry of **19** not only in enantioselective reactions with enantiopure **19** but also with racemic material in organocatalytic reactions as carried out already.[24] Note, however, that the geometrical differences have been found in the solid state. In solution, the molecules are flexible, and **10** inverts to its enantiomer quickly.[25]

For investigation of the configurational stability of new dimethylated axially chiral concave bimacrocycle **19**, two NMR experiments were carried out: First, racemic imidazolinium chloride **19** was converted into a diastereomeric salt with enantiopure Λ-BINPHAT[27] (Figure 5). We showed that in case of the 4,5-nonsubstituted chiral imidazolinium salt **10**, the use of enantiopure Λ-BINPHAT (**20**) as a counterion led to NMR spectra with two sets of signals with different intensities.[25] The rational is that one enantiomeric imidazolium ion interacts more strongly with the chiral counterion than the other and is stabilized by this ion pair formation. Noteworthy is that the amplification of one species can only happen by rotation along the N–C_{Ar} bonds (Scheme 1) and only if the energy of the rotation barrier is low.

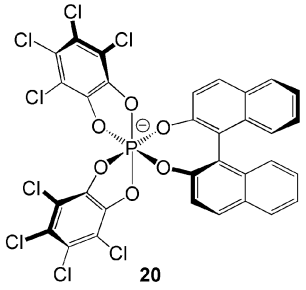


Figure 5. Structure of the chiral Λ-BINPHAT ion (**20**).

Thus, if the two methyl groups in the 4-postion of chiral imidazolinium chloride **19** are able to stop the interconversion by rotation, no amplification of one of the diastereomeric ion pairs should be observed. Indeed, the intensities of the isolated signals like H-5_{nap}, H-4_{ph}, and H-8_{nap} (Figure 6) are equal for both diastereomeric species over time.

Because of the diastereotopicity of the methyl groups in the 4-position of N-heterocycle **19**, two different singlets are detected by ^{1}H NMR spectroscopy at 298 K. If there were fast rotation along the N–C_{Ar} bonds, the methyl groups would become indistinguishable and they would appear as one singlet in the spectrum. To study the height of the rotational barrier, NMR spectra were recorded at different temperatures. Three of them are shown in Figure 7.

In the case of a low rotational barrier, coalescence of the two singlets of the methyl groups at δ = 1.65 ppm would have been observed when increasing the temperature, but,

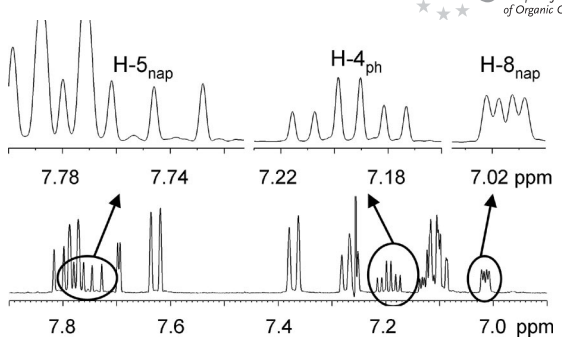


Figure 6. Expanded section of the ^{1}H NMR spectrum of the diastereomeric imidazolium Λ-BINPHAT salt. Zooms on representative signals show the equal intensities of the respective signals.

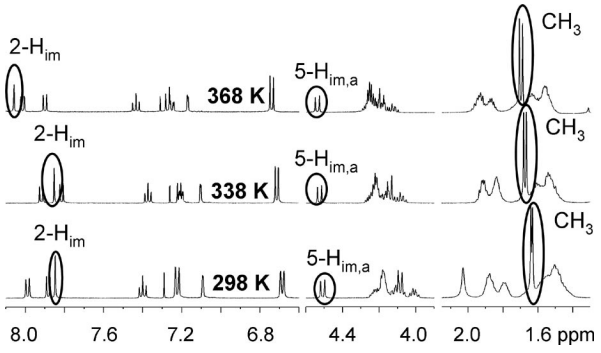


Figure 7. ^{1}H NMR spectra (500 MHz) of chiral concave imidazolium chloride **19** in $C_2D_2Cl_4$ at various temperatures.

on the contrary, a slight separation of the signals is observable. The doublet at δ = 4.5 ppm, attributable to one proton in the 5-position of the N-heterocycle, shows the same tendency. Moreover, by changing the temperature, a shift in the imidazolium proton in the 2-positon (δ = 7.85 ppm) was clearly detectable.

It is possible to estimate the energy of a rotational barrier $\Delta G^{\ddagger}_C$ with Equation (1).[28]

$$\Delta G_C^{\neq} = 0.01914 \cdot T_C \left(10.32 + \log \frac{T_C}{2.22 \Delta \upsilon}\right) \frac{kJ}{mol} \quad (1)$$

where T_C is the coalescence temperature and $\Delta\upsilon$ is the distance between the separated signals at low temperature. Moreover, for physical separation of atropisomers, the need of an energy barrier $\Delta G^{\ddagger}_{298} \geq 90$ kJ/mol is postulated.[29] In this case, with $\Delta\nu$ = 4.8 Hz, the coalescence temperature should be at least 398 K for a rotation barrier of 90 kJ/mol or more. Measurement at this temperature was not possible but until 368 K no tendency of coalescence was observable.

Conclusions

Starting from a bromoalkanoyl bromide **13** and aminoarenes **11** and **12**, chiral concave NHC precursor **19** was synthesized in 43% total yield over six synthetic steps. By dimethylation in the 4-position of the imidazolinium ring, the configurational stability of chiral bimacrocycle **19** was

enhanced. Reaction with enantiopure Λ-BINPHAT resulted in a 1:1 mixture of two diastereomers, which were stable. This now allows the deracemization of **19** to be tackled, for instance, by chromatography on chiral columns or by separation of diastereomeric salts such as **19**·Λ-BINPHAT. Because of its potential in enantioselective catalyses, the enantiopure NHC shall be tested, for instance, as an organocatalyst in the asymmetric reaction of aldehydes with enals,[19,24] or could be employed as a chiral ligand for transition metals.

Moreover, analysis of the crystal structures showed that the naphthyl unit in **19** is positioned orthogonally with respect to the N-heterocycle and that the overall structure of the bimacrocycle is different to that of **10**. This may result in altered selectivities for instance in organocatalytic reactions[24] even with racemic **19**.

Experimental Section

General Remarks: The following chemicals were obtained commercially and used without further purification: benzylidenebis(tricyclohexylphosphane)dichlororuthenium (Aldrich), (Λ,*R*)-BINPHAT tetrabutylammonium salt (Aldrich), 2-bromo-2-methylpropionyl bromide (ABCR), Celite (Fluka), ethyl vinyl ether (Acros), hydrogen chloride (4 M in 1,4-dioxane, Lancester), lithium aluminum hydride (Merck), palladium/charcoal (10% Pd, Merck), sodium hydride (Acros), and triethyl orthoformate (Merck). 2,6-Bis(pent-4-enyloxy)aniline[23] and 2,7-bis(pent-4-enyloxy)naphthylamine[25] were synthesized according to literature procedures. Tetrahydrofuran was dried by heating at reflux with lithium aluminum hydride. Dichloromethane was dried by heating at reflux with calcium hydride. All syntheses except hydrogenations were carried out under an atmosphere of dry nitrogen. Column chromatography was carried out with silica gel (Macherey–Nagel). NMR spectra were recorded with a Bruker DRX 500 instrument. Assignments are supported by COSY, HSQC, and HMBC. Even when obtained by DEPT, the type of ^{13}C signal is always listed as singlet, doublet, etc. All chemical shifts are referenced to TMS. For a definite designation, "im" for imidazolium, "nap" for naphthyl, and "ph" for phenyl were used as indices. Mass spectra were recorded with a Finnigan MAT 8200 or MAT 8230. ESI mass spectra were recorded with an Applied Biosystems Mariner Spectrometry Workstation. IR spectra were recorded with a Perkin–Elmer Spectrum 100 equipped with an MKII Golden GateTM Single Reflection ATR unit. Elemental analyses were carried out with a Euro EA 3000 Elemental Analyzer from Euro Vector.

***N*-[2,6-Bis(pent-4-enyloxy)phenyl]-2-bromo-2-methylpropanamide (14):** Aniline **11** (1.97 g, 7.54 mmol) and triethylamine (1.53 g, 15.1 mmol) were dissolved in dry dichloromethane (25 mL). At 0 °C, bromopropionyl bromide **13** (1.91 g, 8.29 mmol) was added slowly to the solution. After a few minutes, a white solid precipitated. The mixture was stirred for 1.5 h. Then, dichloromethane (25 mL) and a saturated aqueous solution of ammonium chloride (50 mL) were added. The aqueous layer was extracted with dichloromethane (3 × 50 mL), and the organic layer was dried with magnesium sulfate. After evaporation of the solvent, the product was purified by column chromatography [silica gel, cyclohexane/ethyl acetate (10:1), R_f = 0.13]. A colorless oil (2.88 g, 7.02 mmol, 93%) was obtained. ^1H NMR (500 MHz, $CDCl_3$, 300 K): δ = 7.90 (s, 1 H, N-H), 7.13 (t, ^3J = 8.4 Hz, 1 H, 4-H), 6.54 (d, ^3J = 8.4 Hz, 2 H, 3-H, 5-H), 5.83 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 2 H, CH=), 5.05 (ddt, ^3J = 17.1 Hz, ^2J = 1.8 Hz, ^4J = 1.6 Hz, 2 H, =CH_EH_Z), 4.98 (ddt, ^3J = 10.2 Hz, ^2J = 1.8 Hz, ^4J = 1.2 Hz, 2 H, =CH_EH_Z), 3.98 (t, ^3J = 6.2 Hz, 4 H, OCH_2), 2.24 (m_c, 4 H, CH_2CH=), 2.06 (s, 6 H, CH_3), 1.86 (m_c, 4 H, OCH_2CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 170.0 (s, C=O), 154.8 (s, C-2, C-6), 137.9 (d, CH=), 127.7 (d, C-4), 115.2 (t, $=CH_2$), 114.4 (s, C-1), 105.1 (d, C-3, C-5), 67.8 (t, OCH_2), 63.1 (s, C-Br), 32.7 (q, CH_3), 30.1 (t, CH_2CH=), 28.6 (t, OCH_2CH_2) ppm. IR (ATR): $\tilde{\nu}$ = 3398 (N–H), 3076 (=C–H), 2976, 2934, 2872 (aliph. C–H), 1687 (C=O), 1596, 1508 (arom. C=C), 1257 (=C–O), 1100 (O–CH_2), 909 (alkenyl = C–H), 767 (1,2,3-trisubs. ph C–H) cm^{-1}. MS (ESI, $CHCl_3/CH_3OH$): *m*/*z* (%) = 432 (83) $[C_{20}H_{28}{}^{79}BrNO_3 + Na]^+$, 434 (100) $[C_{20}H_{28}{}^{81}BrNO_3 + Na]^+$. ($C_{20}H_{28}BrNO_3$) (410.35): calcd. C 58.54, H 6.88, N 3.41; found C 58.73, H 7.11, N 3.48.

***N*-[2,6-Bis(pent-4-enyloxy)phenyl]-2-[2,7-bis(pent-4-enyloxy)naphthylamino]-2-methylpropanamide (15):** A dispersion of sodium hydride (60%) in mineral oil (332 mg, 8.30 mmol) was added to a solution of naphthylamine **12** (1.33 g, 4.30 mmol) in dry tetrahydrofuran (50 mL). Over a period of 2 h, a solution of bromo propanamide **14** (1.65 g, 4.00 mmol) in dry tetrahydrofuran (100 mL) was added dropwise while stirring. Then, the mixture was stirred for 16 h at room temperature. Saturated aqueous solution of ammonium chloride (100 mL) was added, and the aqueous layer was extracted with *tert*-butyl methyl ether (3 × 100 mL). The organic layer was dried with magnesium sulfate, the solvent was evaporated, and the product was purified by column chromatography [silica gel, cyclohexane/ethyl acetate (20:1), R_f = 0.05]. A colorless oil (2.04 g, 3.18 mmol, 79%) was obtained. ^1H NMR (500 MHz, $CDCl_3$, 300 K): δ = 9.67 (s, 1 H, CONH), 7.60 (d, ^3J = 8.9 Hz, 1 H, 5_{naph}-H), 7.47 (d, ^3J = 8.9 Hz, 1 H, 4_{naph}-H), 7.44 (d, ^2J = 2.4 Hz, 1 H, 8_{naph}-H), 7.10 (t, ^3J = 8.4 Hz, 1 H, 4_{ph}-H), 7.07 (d, ^3J = 8.9 Hz, 1 H, 3_{naph}-H), 6.98 (dd, ^3J = 8.9 Hz, ^4J = 2.4 Hz, 1 H, 6_{naph}-H), 6.58 (d, ^3J = 8.4 Hz, 2 H, 3_{ph}-H, 5_{ph}-H), 5.86 [ddt, ^3J_Z = 17.0 Hz, ^3J_E = 10.3 Hz, ^3J = 6.7 Hz, 1 H, 2_{naph}-$O(CH_2)_3CH$], 5.72 [ddt, ^3J_Z = 17.0 Hz, ^3J_E = 10.3 Hz, ^3J = 6.7 Hz, 1 H, 7_{naph}-$O(CH_2)_3$-CH], 5.64 [ddt, ^3J_Z = 17.0 Hz, ^3J_E = 10.3 Hz, ^3J = 6.8 Hz, 2 H, 2_{ph}-$O(CH_2)_3CH$, 6_{ph}-$O(CH_2)_3CH$], 5.07 [ddt, ^3J = 17.1 Hz, ^4J = 1.8 Hz, ^2J = 1.6 Hz, 1 H, 2_{naph}-$O(CH_2)_3CHCH_EH_Z$], 5.02 [ddt, ^3J = 10.2 Hz, ^2J = 1.8 Hz, ^4J = 1.2 Hz, 1 H, 2_{naph}-$O(CH_2)_3$-$CHCH_EH_Z$], 4.92 [ddt, ^3J = 17.1 Hz, ^4J = 1.8 Hz, ^2J = 1.6 Hz, 1 H, 7_{naph}-$O(CH_2)_3CHCH_EH_Z$], 4.88 [ddt, ^3J = 10.2 Hz, ^2J = 1.8 Hz, ^4J = 1.2 Hz, 1 H, 7_{naph}-$O(CH_2)_3CHCH_EH_Z$], 4.87–4.82 [m, 4 H, 2_{ph}-$O(CH_2)_3CHCH_2$, 6_{Ph}-$O(CH_2)_3CHCH_2$], 4.36 [s, 1 H, $C(CH_3)_2$-N*H*], 4.13 (t, ^3J = 6.5 Hz, 2 H, 2_{naph}-OCH_2), 3.89 (t, ^3J = 6.4 Hz, 4 H, 2_{ph}-OCH_2, 6_{ph}-OCH_2), 3.85 (t, ^3J = 6.5 Hz, 2 H, 7_{naph}-OCH_2), 2.28 [m_c, 2 H, 2_{naph}-$O(CH_2)_2CH_2$], 2.09 [m_c, 4 H, 2_{ph}-$O(CH_2)_2CH_2$, 7_{ph}-$O(CH_2)_2CH_2$], 1.99–1.91 [m, 4 H, 2_{naph}-OCH_2CH_2, 7_{naph}-$O(CH_2)_2CH_2$], 1.75–1.63 (m, 6 H, 2_{ph}-OCH_2CH_2, 6_{ph}-OCH_2CH_2, 7_{naph}-OCH_2CH_2), 1.47 (s, 6 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 175.3 (s, C=O), 157.2 (s, C-7_{naph}), 154.1 (s, C-2_{naph}), 149.5 (s, C-2_{ph}, C-6_{ph}), 138.2 [d, =*C*H$(CH_2)_3$OC-7_{naph}], 137.9 [d, =*C*H$(CH_2)_3$OC-2_{ph}, =*C*H$(CH_2)_3$OC-6_{ph}], 137.6 [d, =*C*H$(CH_2)_3$OC-2_{naph}], 132.5 (s, C-$8a_{naph}$), 129.4 (d, C-5_{naph}), 127.8 (s, C-1_{naph}), 126.3 (d, C-4_{ph}), 124.9 (s, C-$4a_{naph}$), 123.9 (d, C-4_{naph}), 117.1 (d, C-6_{naph}), 115.5 (s, C-1_{ph}), 115.4 [t, *C*H_2CH$(CH_2)_3$OC-2_{naph}], 114.8 [t, *C*H_2CH$(CH_2)_3$OC-2_{ph}, *C*H_2CH$(CH_2)_3$OC-6_{ph}], 114.6 [t, *C*H_2CH$(CH_2)_3$OC-7_{naph}], 110.8 (d, C-3_{naph}), 105.1 (d, C-3_{ph}, C-5_{ph}), 103.6 (d, C-8_{naph}), 68.4 (t, *C*H_2OC-2_{naph}), 67.8 (t, *C*H_2OC-2_{ph}, *C*H_2OC-6_{ph}), 67.2 (t, *C*H_2OC-7_{naph}), 61.7 [s, *C*$(CH_3)_2$], 30.3 [t, *C*$H_2(CH_2)_2$OC-2_{naph}], 30.1 [t, *C*$H_2(CH_2)_2$OC-2_{ph}, *C*$H_2(CH_2)_2$OC-6_{ph}], 30.0 [t, *C*$H_2(CH_2)_2$OC-7_{naph}], 28.8 (t, *C*H_2CH_2OC-7_{naph}), 28.6 (t, *C*H_2CH_2OC-2_{naph}), 28.5 (t, *C*H_2CH_2OC-2_{ph}, *C*H_2CH_2OC-6_{ph}), 26.9 (q, CH_3) ppm. IR (ATR):

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$\tilde{\nu}$ = 3344 (N–H), 3076 (=C–H), 2933, 2872 (aliph. C–H), 1696 (C=O), 1628, 1598, 1505 (arom. C=C), 1257, 1213 (=C–O), 1097, 1056 (O–CH_2), 992, 909 (alkenyl = C–H), 825 (1,2,7-trisubst. naph C–H) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 640 (13) $[M]^+$, 352 (100) $[C_{23}H_{30}NO_2]^+$. MS (CI, isobutane): *m*/*z* (%) = 641 (83) $[M]^+$, 352 (35) $[C_{23}H_{30}NO_2]^+$, 332 (100) $[C_{20}H_{30}NO_3]^+$, 312 (76) $[C_{20}H_{26}NO_2]^+$, 352 (35) $[C_{23}H_{30}NO_2]^+$, 352 (35) $[C_{23}H_{30}NO_2]^+$. $C_{40}H_{54}N_2O_4$ (640.85): calcd. C 74.48, H 8.18, N 4.44; found C 74.66, H 8.61, N 4.14.

2-[2,7-Bis(pent-4-enyloxy)naphthylamino]-3-[2,6-bis(pent-4-enyloxy)-phenylamino]-2-methylpropane (16): Lithium aluminum hydride (604 mg, 15.9 mmol) was suspended in dry tetrahydrofuran (40 mL). At 0 °C, a solution of amino propanamide **15** (2.04 g, 3.18 mmol) in dry tetrahydrofuran (60 mL) was added slowly. Then, the mixture was heated at reflux for 16 h. After cooling to room temperature, the suspension was poured into ice water (100 mL), and the aqueous layer was extracted with *tert*-butyl methyl ether (3 × 80 mL). After evaporation of the solvent, the product was purified by column chromatography [silica gel, cyclohexane/ethyl acetate (14:1), R_f = 0.37]. A reddish oil (1.59 g, 2.54 mmol, 80%) was obtained. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 7.76 (d, ^4J = 2.2 Hz, 1 H, 8_{naph}-H), 7.60 (d, ^3J = 8.9 Hz, 1 H, 5_{naph}-H), 7.48 (d, ^3J = 8.9 Hz, 1 H, 4_{naph}-H), 7.06 (d, ^3J = 8.9 Hz, 1 H, 3_{naph}-H), 6.93 (dd, ^3J = 8.9 Hz, ^4J = 2.2 Hz, 1 H, 6_{naph}-H), 6.71 (t, ^3J = 8.2 Hz, 1 H, 4_{ph}-H), 6.53 (d, ^3J = 8.2 Hz, 2 H, 3_{ph}-H, 5_{ph}-H), 5.89–5.76 [m, 2 H, 2_{naph}-O$(CH_2)_3$C*H*, 7_{naph}-O$(CH_2)_3$C*H*], 5.73 [ddt, ^3J_Z = 17.0 Hz, ^3J_E = 10.3 Hz, ^3J = 6.8 Hz, 2 H, 2_{ph}-O$(CH_2)_3$C*H*, 6_{ph}-O$(CH_2)_3$C*H*], 5.08–4.93 [m, 4 H, 2_{naph}-O$(CH_2)_3$CHCH_2, 7_{naph}-O$(CH_2)_3$CHCH_2], 4.90 [m_c, 4 H, 2_{ph}-O$(CH_2)_3$CHCH_2, 6_{ph}-O$(CH_2)_3$CHCH_2], 4.08 (t, ^3J = 6.5 Hz, 2 H, 2_{naph}-OCH_2), 3.98 (t, ^3J = 6.4 Hz, 4 H, 2_{ph}-OCH_2, 6_{ph}-OCH_2), 3.92 (t, ^3J = 6.4 Hz, 2 H, 7_{naph}-OCH_2), 3.45 (s, 2 H, NCH_2), 2.27 [q, ^3J = 7.1 Hz, 2 H, 2_{naph}-O$(CH_2)_2$CH_2], 2.19 [q, ^3J = 7.2 Hz, 4 H, 2_{ph}-O$(CH_2)_2$CH_2, 6_{ph}-O$(CH_2)_2$CH_2], 2.08 [q, ^3J = 7.2 Hz, 2 H, 7_{naph}-O$(CH_2)_2$CH_2], 1.84 (quint., ^3J = 6.9 Hz, 4 H, 2_{ph}-OCH_2CH_2, 6_{ph}-OCH_2CH_2), 1.94 (quint., ^3J = 6.9 Hz, 2 H, 2_{naph}-OCH_2CH_2), 1.73 (quint., ^3J = 6.9 Hz, 2 H, 7_{naph}-OCH_2CH_2), 1.16 (s, 6 H, CH_3) ppm; no NH signals observed. ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 157.3 (s, C-7_{naph}), 152.0 (s, C-2_{naph}), 150.1 (s, C-2_{ph}), 138.5 [d, =*C*H$(CH_2)_3$OC-7_{naph}], 138.2 [d, =*C*H$(CH_2)_3$OC-2_{ph}, =*C*H$(CH_2)_3$OC-6_{ph}], 138.1 [d, =*C*H$(CH_2)_3$OC-2_{naph}], 135.2 (s, C-$8a_{naph}$), 129.6 (s, C-1_{ph}), 129.3 (d, C-4_{naph}), 128.9 (s, C-1_{naph}), 125.3 (s, C-$4a_{naph}$), 124.6 (d, C-5_{naph}), 118.8 (d, C-4_{ph}), 117.2 (d, C-6_{naph}), 115.6 [t, *C*H_2CH$(CH_2)_3$OC-2_{naph}], 115.4 [t, *C*H_2CH$(CH_2)_3$OC-2_{ph}, *C*H_2CH$(CH_2)_3$OC-6_{ph}], 115.1 [t, *C*H_2CH$(CH_2)_3$OC-7_{naph}], 111.2 (d, C-3_{naph}), 106.4 (d, C-3_{ph}, C-5_{ph}), 104.2 (d, C-8_{naph}), 68.4 (t, *C*H_2OC-2_{naph}, *C*H_2OC-2_{ph}, *C*H_2OC-6_{ph})*, 67.4 (t, *C*H_2OC-7_{naph}), 58.6 [s, *C*$(CH_3)_2$], 58.3 (t, NCH_2), 30.7 [t, *C*$H_2(CH_2)_2$OC-2_{naph}], 30.6 [t, *C*$H_2(CH_2)_2$OC-2_{ph}, *C*$H_2(CH_2)_2$OC-6_{ph}], 30.5 [t, *C*$H_2(CH_2)_2$-OC-7_{naph}], 29.2 (t, *C*H_2CH$_2$OC-2_{naph}), 29.1 (t, *C*H_2CH$_2$OC-2_{ph}, *C*H_2CH$_2$OC-6_{ph}), 28.9 (t, *C*H_2CH$_2$OC-7_{naph}), 27.1 (q, CH_3) ppm; *signals overlaid. IR (ATR): $\tilde{\nu}$ = 3356 (N–H), 3076 (=C–H), 2937, 2870 (aliph. C–H), 1627, 1597 (arom. C=C), 1255, 1214 (=C–O), 1095, 1055 (O–CH_2), 991, 909 (alkenyl = C–H), 824 (1,2,7-trisubst. naph C–H) cm^{-1}. MS (ESI, $CHCl_3$/MeOH): *m*/*z* (%) = 627 (100) $[M + H]^+$, 316 (35) $[C_{20}H_{30}NO_2]^+$. $C_{40}H_{54}N_2O_4$ (626.41): calcd. C 76.64, H 8.68, N 4.47. $C_{40}H_{54}N_2O_4$·0.25H_2O: calcd. C 76.09, H 8.70, N 4.44; found C 76.05, H 8.56, N 4.63.

3-[2,7-Bis(pent-4-enyloxy)naphthyl]-1-[2,6-bis(pent-4-enyloxy)-phenyl]-4,4-dimethyl-4,5-imidazolinium Chloride (17): To a solution of diamine **16** (618 mg, 986 μmol) in dry dichloromethane (5 mL) was added HCl (4 M in 1,4-dioxane, 1 mL). After stirring for 10 min, the solvent was evaporated. The residue was dissolved in triethyl orthoformate (5 mL) and stirred for 1 h at 140 °C. After evaporation of the solvent, the product was purified by column chromatography [silica gel, dichloromethane/methanol (10:1), R_f = 0.36]. A white solid (614 mg, 952 μmol, 96%) was obtained. M.p. 153–154 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.21 (s, 1 H, 2-H_{im}), 7.96 (d, ^3J = 9.0 Hz, 1 H, 5-H_{naph}), 7.80 (d, ^3J = 9.0 Hz, 1 H, 4-H_{naph}), 7.37 (t, ^3J = 8.5 Hz, 1 H, 4-H_{ph}), 7.23 (d, ^3J = 9.0 Hz, 1 H, 3-H_{naph}), 7.14 (dd, ^3J = 9.0 Hz, ^4J = 2.3 Hz, 1 H, 6-H_{naph}), 7.09 (d, ^4J = 2.3 Hz, 1 H, 8-H_{naph}), 6.68 (d, ^3J = 8.5 Hz, 2 H, 3-H_{ph}, 5-H_{ph}), 5.86 [ddt, ^3J_Z = 17.0 Hz, ^3J_E = 10.3 Hz, ^3J = 6.7 Hz, 1 H, 7_{naph}-O$(CH_2)_3$C*H*], 5.79 [ddt, ^3J_Z = 17.0 Hz, ^3J_E = 10.3 Hz, ^3J = 6.7 Hz, 1 H, 2_{naph}-O$(CH_2)_3$C*H*], 5.76 [ddt, ^3J_Z = 17.6 Hz, ^3J_E = 9.7 Hz, ^3J = 6.6 Hz, 2 H, 2_{ph}-O$(CH_2)_3$C*H*, 6_{ph}-O$(CH_2)_3$C*H*], 5.07 [ddt, ^3J_Z = 17.0 Hz, ^2J = 1.8 Hz, ^4J = 1.6 Hz, 1 H, 7_{naph}-O$(CH_2)_3$-CHCH_EH$_Z$], 5.03–4.94 [m, 7 H, 2_{naph}-O$(CH_2)_3$CHCH_2, 7_{naph}-O$(CH_2)_3$CHCH$_E$H$_Z$, 2_{ph}-O$(CH_2)_3$CHCH_2, 6_{ph}-O$(CH_2)_3$CHCH_2], 4.64 (d, ^3J = 11.4 Hz, 1 H, 5-$H_{im,a}$), 4.35 (d, ^3J = 11.4 Hz, 1 H, 5-$H_{im,b}$), 4.22 (m_c, 2 H, 2_{naph}-OCH_2), 4.16–4.05 (m, 6 H, 7_{naph}-OCH_2, 2_{ph}-OCH_2, 6_{ph}-OCH_2), 2.29 [dt, ^3J = 7.9 Hz, ^3J = 6.7 Hz, 2 H, 2_{naph}-O$(CH_2)_2$CH_2], 2.23–2.17 [m, 6 H, 7_{naph}-O$(CH_2)_2$CH_2, 2_{ph}-O$(CH_2)_2$CH_2, 6_{ph}-O$(CH_2)_2$CH_2], 2.00–1.90 (m, 8 H, 2_{naph}-OCH_2CH_2, 7_{naph}-OCH_2CH_2, 2_{ph}-OCH_2CH_2, 6_{ph}-OCH_2CH_2), 1.74 (s, 3 H, CH_3), 1.67 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 161.3 (d, C-2_{im}), 159.3 (s, C-7_{naph}), 154.5 (s, C-2_{ph}, C-6_{ph}, C-2_{naph}),* 137.6 [d, =*C*H$(CH_2)_3$OC-7_{naph}], 137.0 [d, =*C*H$(CH_2)_3$OC-2_{naph}], 136.9 [d, =*C*H$(CH_2)_3$OC-2_{ph}, =*C*H$(CH_2)_3$-OC-6_{ph}], 133.7 (s, C-$8a_{naph}$), 132.8 (d, C-5_{naph}), 131.6 (d, C-4_{ph}), 130.6 (d, C-4_{naph}), 124.5 (s, C-$4a_{naph}$), 116.7 (d, C-6_{naph}), 115.8 [t, *C*H_2CH$(CH_2)_3$OC-2_{ph}, *C*H_2CH$(CH_2)_3$OC-6_{ph}], 115.8 [t, *C*H_2CH$(CH_2)_3$OC-2_{naph}], 115.4 [t, *C*H_2CH$(CH_2)_3$OC-7_{naph}], 112.6 (s, C-1_{naph}), 112.2 (s, C-1_{ph}), 110.6 (d, C-3_{naph}), 105.3 (d, C-3_{ph}, C-5_{ph}), 102.0 (d, C-8_{naph}), 72.1 (s, C-4_{im}), 68.9 (t, *C*H_2OC-2_{naph}), 68.5 (t, *C*H_2OC-2_{ph}, *C*H_2OC-6_{ph}), 67.5 (t, *C*H_2OC-7_{naph}), 63.6 (t, C-5_{im}), 30.1 [t, *C*$H_2(CH_2)_2$OC-7_{naph}], 30.0 [t, *C*$H_2(CH_2)_2$OC-2_{ph}, *C*$H_2(CH_2)_2$OC-6_{ph}], 30.0 [t, *C*$H_2(CH_2)_2$OC-2_{naph}], 28.4 (t, *C*H_2CH$_2$OC-7_{naph}), 28.3 (t, *C*H_2CH$_2$OC-2_{naph}, *C*H_2CH$_2$OC-2_{ph}, *C*H_2CH$_2$OC-6_{ph}),* 27.3 (q, CH_3), 25.9 (q, CH_3) ppm; *signals overlaid respectively. IR (ATR): $\tilde{\nu}$ = 3077 (=C–H), 2977, 2938, 2873, 2841 (aliph. C–H), 1625, 1599 (arom. C=C), 1259, 1217 (=C–O), 1096, 1060 (O–CH_2), 990, 906 (alkenyl = C–H), 830 (1,2,7-trisubst. naph C–H), 779 (1,2,3-trisubst. ph C–H) cm^{-1}. MS (ESI, $CHCl_3$/MeOH): *m*/*z* (%) = 637 (100) $[M - Cl]^+$. $C_{41}H_{53}ClN_2O_4$ (673.32): calcd. C 73.14, H 7.93, N 4.16; $C_{41}H_{53}ClN_2O_4$·0.5CH_3OH: calcd. C 72.31, H 8.04, N 4.06; found C 72.07, H 8.31, N 4.40.

2,11,13,22-Tetraoxa-1(1,3,2)-benzena-12(2,7,1)-naphthalena-23(1,3)-4,4-dimethylimidazoliuminabicyclo[10.10.1]tricosaphane-6,17-diene Chloride (18): Tetraene **17** (433 mg, 643 μmol) and benzylidenebis(tricyclohexylphosphane)dichlororuthenium (52.9 mg, 64.3 μmol) were dissolved in dry dichloromethane (500 mL), and the mixture was stirred for 24 h at room temperature. Then, ethyl vinyl ether (1 mL) was added, and the mixture was stirred for 1 h. After evaporation of the solvent, the product was purified twice by column chromatography [silica gel, dichloromethane/methanol (10:1), R_f = 0.42]. A white solid (350 mg, 567 μmol, 88%) was obtained. M.p. 147–150 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.22 (s, 0.2 H, 2-H_{im}), 8.11 (s, 0.7 H, 2-H_{im}), 8.02 (s, 0.1 H, 2-H_{im}), 7.94 (d, ^3J = 9.1 Hz, 1 H, 4-H_{naph}), 7.79 (d, ^3J = 9.7 Hz, 1 H, 5-H_{naph}), 7.36 (t, ^3J = 8.5 Hz, 0.2 H, 4-H_{ph}), 7.35 (t, ^3J = 8.5 Hz, 0.1 H, 4-H_{ph}), 7.34 (t, ^3J = 8.5 Hz, 0.7 H, 4-H_{ph}), 7.25 (d, ^3J = 9.1 Hz, 0.2 H, 3-H_{naph}), 7.24 (d, ^3J = 9.1 Hz, 0.7 H, 3-H_{naph}), 7.21 (d, ^3J = 9.1 Hz, 0.1 H, 3-H_{naph}), 7.14–7.09 (m, 1.8 H, 6-H_{naph}, 8-H_{naph}), 7.05 (d, ^4J = 2.4 Hz, 0.2 H, 8-

H_{naph}), 6.71–6.63 (m, 2 H, 3-H_{ph}, 5-H_{ph}), 5.7–5.4 (m, 4 H, C*H*=CH_2), 4.76 (d, ^2J = 11.6 Hz, 0.7 H, 5-$H_{im,a}$), 4.4–3.9 (m, 9.3 H, 5-$H_{im,b}$, OCH_2), 2.6–1.7 (m, 22 H, CH_3, OCH_2CH_2, CH_2CH=) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 161.6 (s), 160.4 (s), 159.4 (s), 159.3 (s), 155.1 (s), 155.0 (s), 154.9 (s), 154.7 (s), 154.2 (s), 133.9 (s), 133.8 (s), 132.8 (d), 131.7 (s), 131.6 (d), 130.6 (d), 130.54 (d), 130.50 (d), 130.0 (d), 129.89 (d), 129.88 (d), 129.5 (d), 129.4 (d), 129.1 (d), 124.6 (s), 124.5 (s), 117.5 (d), 117.3 (d), 112.9 (s), 112.6 (s), 112.5 (s), 112.4 (s), 110.6 (d), 105.5 (d), 105.3 (d), 105.2 (d), 105.0 (d), 101.8 (d), 101.6 (d), 77.3 (d), 72.2 (s), 72.0 (s), 69.7 (t), 69.5 (t), 68.7 (t), 67.3 (s), 67.2 (t), 66.61 (t), 66.57 (t), 63.9 (t), 29.9 (t), 29.8 (t), 29.7 (t), 29.3 (t), 28.7 (d), 28.4 (t), 28.1 (t), 27.8 (t), 27.6 (t), 26.2 (d), 25.8 (d), 24.6 (t), 24.3 (s), 23.7 (s), 23.3 (t), 23.1 (t), 23.0 (t) ppm. IR (ATR): $\tilde{\nu}$ = 2936, 2879 (aliph. C–H), 1615 (arom. C=C), 1256, 1221 (=C–O), 1096, 1065 (O–CH_2), 832, 777, 741 (=C–H) cm^{-1}. MS (ESI, $CHCl_3$/MeOH): *m*/*z* (%) = 581 (100) [M – Cl]$^+$. $C_{37}H_{45}ClN_2O_4$ (617.22): calcd. C 73.14, H 7.93, N 4.16; $C_{37}H_{49}ClN_2O_4 \cdot 0.75CHCl_3$: calcd. C 64.15, H 6.52, N 3.96; found C 64.48, H 6.77, N 4.22.

2,11,13,22-Tetraoxa-1(1,3,2)-benzena-12(2,7,1)-naphthalena-23(1,3)-4,4-dimethylimidazoliuminabicyclo[10.10.1]tricosaphane Chloride (19): Diene **18** (370 mg, 600 μmol) and palladium (10% on charcoal, 31.9 mg, 30 μmol) were dissolved in methanol (30.0 mL), and the mixture was stirred under an atmosphere of hydrogen at room temperature for 24 h. The mixture was filtered through Celite, and after evaporation of the solvent, the product was purified by column chromatography [silica gel, dichloromethane/methanol (10:1), R_f = 0.38]. A white solid (323 mg, 520 μmol, 87%) was obtained. M.p. 156–158 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.09 (s, 1 H, 2-H_{im}), 7.97 (d, ^3J = 9.1 Hz, 1 H, H-4$_{naph}$), 7.86 (d, ^3J = 9.0 Hz, 1 H, H-5$_{naph}$), 7.37 (t, ^3J = 8.5 Hz, 1 H, 4-H_{ph}), 7.27 (d, ^3J = 9.1 Hz, 1 H, 3-H_{naph}), 7.20 (dd, ^3J = 9.1 Hz, ^4J = 2.3 Hz, 1 H, 6-H_{naph}), 7.16 (d, ^4J = 2.3 Hz, 1 H, 8-H_{naph}), 6.68 (d, ^3J = 8.5 Hz, 2 H, 3-H_{ph}, 5-H_{ph}), 4.63 (d, ^2J = 11.4 Hz, 1 H, 5-$H_{im,a}$), 4.28–4.00 (m, 9 H, 5-$H_{im,b}$, OCH_2), 2.0–1.4 [m, 30 H, CH_3, $OCH_2(CH_2)_6CH_2O$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 160.6 (s, C-2$_{im}$), 159.2 (s, C-7$_{naph}$), 155.18 (s, C-2$_{naph}$)*, 155.15 (s, C-2$_{ph}$)*, 154.6 (s, C-6$_{ph}$)*, 133.9 (s, C-8a$_{naph}$), 133.1 (d, C-4$_{naph}$), 131.7 (d, C-4$_{ph}$), 130.9 (d, C-5$_{naph}$), 124.4 (s, C-4a$_{naph}$), 114.2 (d, C-6$_{naph}$), 112.3 (s, C-1$_{ph}$), 111.9 (s, C-1$_{naph}$), 111.0 (d, C-3$_{naph}$), 105.09 (d, C-3$_{ph}$)*, 105.07 (d, C-5$_{ph}$)*, 104.6 (d, C-8$_{naph}$), 71.8 (s, C-4$_{im}$), 70.2 (t, OCH_2), 70.0 (t, OCH_2), 69.0 (t, OCH_2), 68.7 (t, OCH_2), 63.8 (t, C-5$_{im}$), 28.7 (t, CH_2), 28.4 (t, CH_2), 27.8 (q, CH_3), 27.1 (t, CH_2), 26.9 (t, CH_2), 26.8 (t, CH_2), 26.24 (t, CH_2), 26.17 (t, CH_2), 26.14 (t, CH_2), 25.9 (q, CH_3), 24.7 (t, CH_2), 24.4 (t, CH_2), 24.3 (t, CH_2) ppm; *assignments may be interchanged, respectively. IR (ATR): $\tilde{\nu}$ = 2930, 2856 (aliph. C–H), 1616 (arom. C=C), 1257, 1221 (=C–O), 1093 (O–CH_2), 832 (1,2,7-trisubst. naph. C–H), 773 (1,2,3-trisubst. phen. C–H) cm^{-1}. MS (ESI, $CHCl_3$/MeOH): *m*/*z* (%) = 585 (100) [M – Cl]$^+$. ($C_{37}H_{49}ClN_2O_4$) (621.25): calcd. C 71.53, H 7.95, N 4.51. $C_{37}H_{49}ClN_2O_4 \cdot 0.5CH_3OH$: calcd. C 70.68, H 8.07, N 4.40; found C 70.70, H 8.14, N 4.40.

X-ray Structural Data: $C_{37}H_{49}ClN_2O_4 \cdot CHCl_3$, formula weight 740.60 g mol^{-1}, crystal size 0.4 × 0.3 × 0.3 mm, crystal system triclinic, space group $P\bar{1}$, unit cell dimensions: a = 9.7324(7) Å, b = 11.903(1) Å, c = 19.592(2) Å, α = 81.29(1)°, β = 80.67(1)°, γ = 84.77(1)°, V = 2208.6(3) Å^3, Z = 2, $D_{calcd.}$ = 1.114 Mg m^{-3}, absorption coefficient 0.303 mm^{-1}, radiation: Mo-K_α (0.71073 Å), T = 200(2) K, $2\theta_{max}$ = 26.02°, 19062 reflections collected, 8320 independent reflections and 5943 reflections with $I > 2\sigma(I)$. R_{int} = 0.0341, structure solution was performed with SHELXS-97 and structure refinement was done using SHELXL-97. 488 parameters, R_1 for all reflections with $I > 2\sigma(I)$ = 0.0592, wR_2 for all independent reflections = 0.1867, largest diff. peak and hole 0.430 and –0.295 e Å^{-3}. The chloroform molecule is disordered and was refined using a split model.

CCDC-794911 (for **19**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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