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Chiral Concave Imidazolinium Salts as Precursors to Chiral Concave *N*-Heterocyclic Carbenes[‡]

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Imidazolinium moieties have been incorporated into bimacrocycles to generate precursors for concave *N*-heterocyclic carbenes (NHCs). By using one symmetrically substituted benzene bridgehead and one naphthalene bridgehead devoid of local C_2-symmetry, axially chiral concave imidazolinium ions have been obtained. Starting from 2,7-dihydroxy-1-nitronaphthalene (**7**), the phenol groups have been transformed to 4-pentenyl ethers **8**, and the nitro group was then reduced to the corresponding amine **9**. Next, **9** and a 2,6-bis(alkenyloxy)aniline **10** were connected by an oxalic acid linker. After reduction of the diamide **13** to diamine **14**, a bridge was installed with triethyl orthoformate to give a tetraalkenyl-substituted imidazolinium salt **15**. Ring-closing metathesis of **15** followed by hydrogenation of the products **16** yielded the bimacrocyclic salts **17** in 9–18 % overall yield (based on **7**), giving amounts up to >300 mg. The configurational stability of **17** was investigated by NMR using chiral enantiopure anions TRISPHAT **18** and BINPHAT **19** as stereodynamic probes.

Introduction

Thiamine-dependent biochemical transformations use the ability of a thiazolium ion to act as a nucleophile after deprotonation.[1,2] By reaction with a base, the proton in the 2-position of the thiazolium ring is abstracted resulting in the formation of a betaine. Due to the electronegativity of the nitrogen, the drawing of a mesomeric carbene structure is also reasonable. Starting from imidazolinium,[3,4] imidazolium,[5] and other azolium ions, related carbenes have been made accessible, and they have been named *N*-heterocyclic carbenes (NHCs) (Figure 1). Many of them are thermodynamically stable.[6]

These and other NHCs are active are active as nucleophilic catalysts.[7–9] In addition, they are interesting stabilizing ligands for transition metals,[10–14] the 2nd generation Grubbs' catalyst being a prominent example.

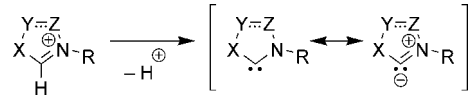
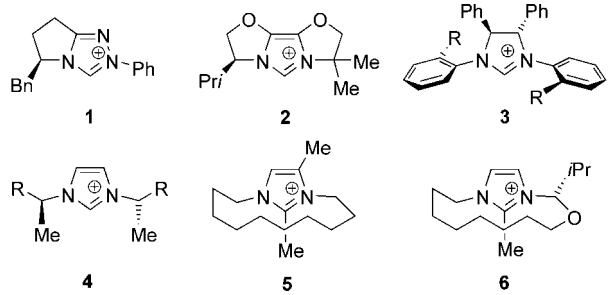


Figure 1. Heterocyclic azolium ions are the precursors for *N*-heterocyclic carbenes (NHCs), which are also drawn in their mesomeric betain form.[6] Examples: thiazolium (X = S, Y = Z = CR′), imidazolium (X = NR′′, Y = Z = CR′), imidazolinium (X = NR′′, Y = Z = CR'_2), and triazolium (X = NR′′, Y = N, Z = CR′).

Quite a few examples of chiral NHC precursors exist in the literature.[15] The carbene derived from **1** was successfully applied in asymmetric intramolecular Stetter reactions,[8,16] the carbene from **2** was successfully applied in the formation of γ-butyrolactones,[17] and deprotonated **3** is a ligand for ruthenium in enantioselective ring-closing metathesis.[18] The NHC from **4** was used for the kinetic resolution of racemic secondary alcohols by enantioselective acylation.[19]



1 **2** **3** **4** **5** **6**

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Planar-chiral imidazolium derivatives, such as moieties **5**[20] and **6**,[21] also exist and are used in the context of chiral ionic-liquid chemistry. Notably, the presence of methyl groups at C-2 is essential for high configurational stability.

In enzymes, the thiamine unit is located in the cavity of the protein. Its geometry and chirality is responsible for the selectivity of the enzymatic reaction. By incorporation of an imidazolinium ion into a bimacrocyclic framework, we have already realized structures containing concave shielding.[22] The purpose of this work is to go further and incorporate chiral information into the concave structure. Reactions with the NHC part take place inside the cavity. Therefore, any introduction of stereogenic elements on the convex outside will probably not lead to a reasonable asymmetric induction. But if one dissymmetric aryl bridgehead moiety (devoid of local C_2-symmetry) is used, then an axially chiral bimacrocycle with a non-symmetric cavity will result.

Results and Discussion

The general strategy for the synthesis of an axially chiral concave imidazolinium ion was adopted from the route leading to non-chiral analogues: preparation of bis-alkenyl-substituted anilines, construction of the imidazolinium ion, ring-closing metathesis and hydrogenation of the double bonds.[22] But instead of using two phenyl bridgeheads which carry identical substituents in positions 2 and 6, a 2,7-disubstituted aminonaphthalene was chosen as one of the bridgeheads. In principle, the incorporation of two naphthalene moieties should give rise to a chiral C_2-symmetric bimacrocycle. However, since the resulting derivative could also adopt an achiral C_s-symmetric (*meso*) conformation with a mirror plane bisecting the molecule, the strategy to incorporate only one naphthalene bridgehead was chosen (see Figure 2).

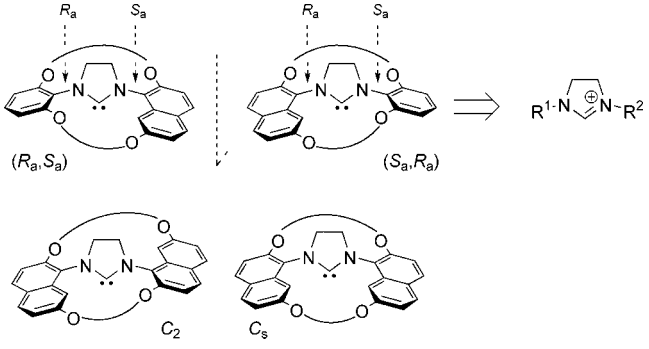
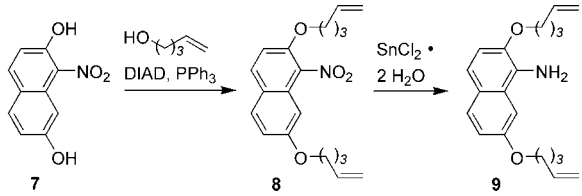


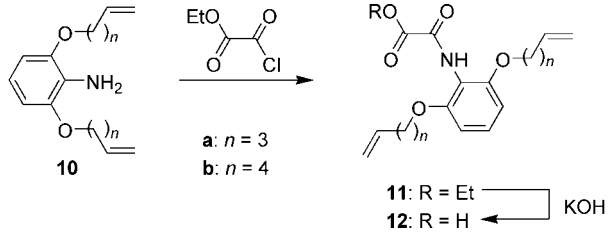
Figure 2. Schematic representation of axially chiral bimacrocyclic concave *N*-heterocyclic carbenes, which may be obtained from their respective imidazolinium ions [(R_a,S_a) and (S_a,R_a) enantiomers]. The use of two naphthalene bridgeheads may lead to the formation of a chiral C_2-symmetric (bottom left) or achiral C_s-symmetric (bottom right) NHC.

Synthesis of Axially Chiral Imidazolinium Chlorides

2,7-Dihydroxy-1-nitronaphthalene (**7**) was used as starting material for the synthesis of the aminonaphthalene bridgehead precursor **9**. By a Mitsunobu reaction, the two phenolic OH groups of **7** were coupled with pent-4-enol giving the diether **8** in 90% yield. Reaction with stannous chloride afforded the reduction of **8** to the aminonaphthalene **9** in 74% yield.



Next, an oxalic acid derivative had to be connected with the aminoaryl bridgeheads. In analogy to literature experiments,[23,24] two homologous mono-esters **11** were generated by reacting ethyl chloroglyoxalate with 2,6-bis(alkenyloxy)anilines **10**[22] in 83% yield (**11a**) and 91% (**11b**) yield, respectively. Subsequent saponification with potassium hydroxide yielded the acids **12a** (98%) and **12b** (97%).

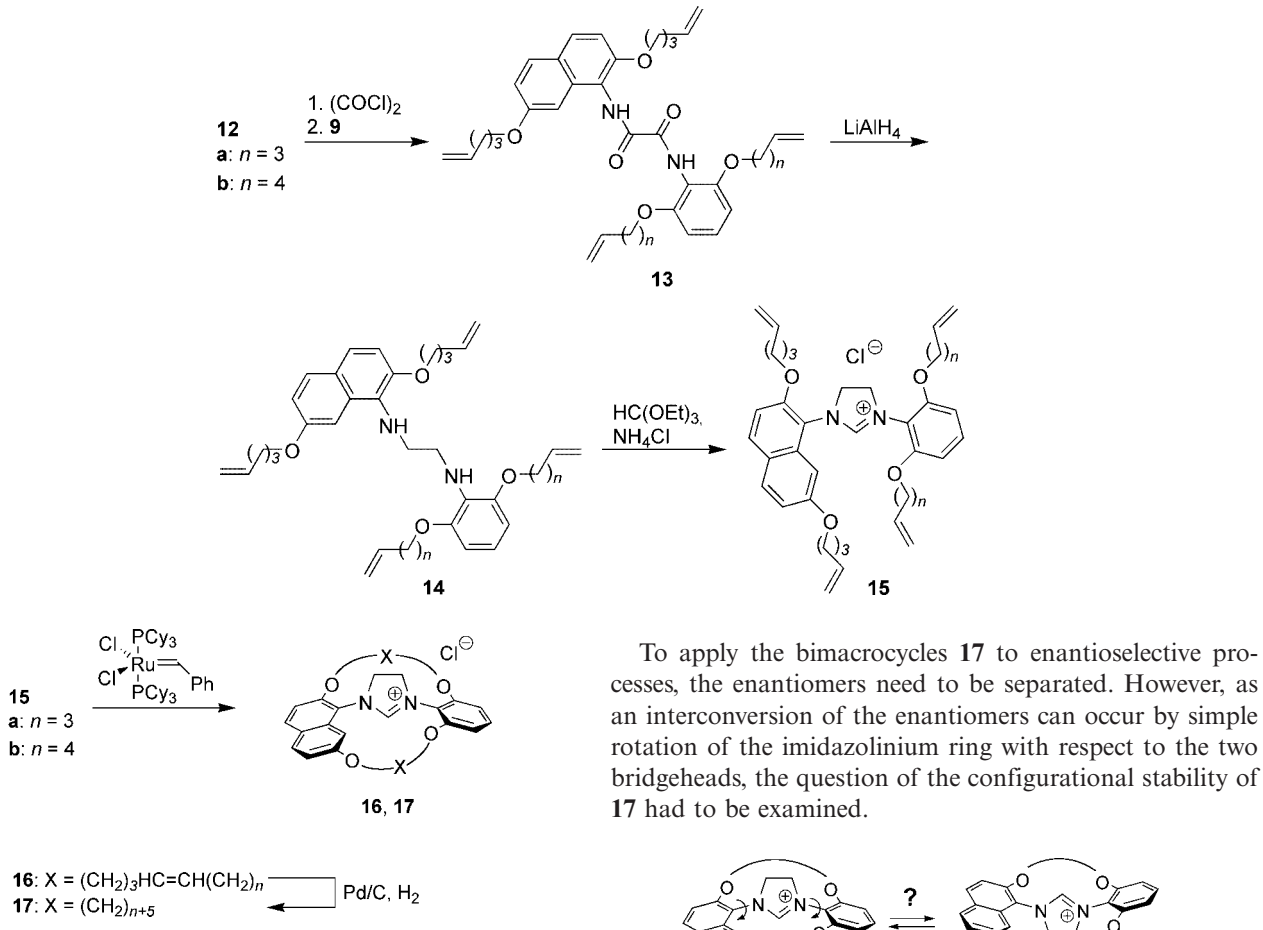


The acids **12** were transformed into their chlorides by reaction with oxalyl chloride and were then reacted with the naphthaleneamine **9**. The mixed diamides **13a** and **13b** could be isolated in 69% yield and 65% yield, respectively. Using lithium aluminum hydride, the diamides could be reduced to the respective diamines **14a** (50%) and **14b** (74%).

In these diamines **14**, already four of the five atoms of the imidazolinium moiety exist. The remaining carbon atom (position 2 of the imidazolinium ion) was incorporated by reaction with triethyl orthoformate in the presence of ammonium chloride. The imidazolinium salts were isolated as chlorides in 65% yield (**15a**) and 77% yield (**15b**), respectively.

Next, the bimacrocycles **16** were built up by ring-closing metathesis using Grubbs' catalyst. Both bimacrocycles **16a** and **16b** were obtained in 92% yield. The NMR spectra are complex for two reasons: each atom in the chiral molecules leads to one signal, and due to the formation of (*E*) and (*Z*) isomers at the double bonds, four isomers are formed {(*E*,*E*), (*E*,*Z*), (*Z*,*E*) [not identical to (*E*,*Z*)!], and (*Z*,*Z*)}. By catalytic hydrogenation using palladium on charcoal as the catalyst, the (*E*/*Z*) isomers of **16** could be transformed into one (*E*/*Z*) conformer-free racemic bimacrocycle (**17a**: 83% yield, **17b**: 90% yield).

The structures of the bimacrocycles **17a** and **17b** were elucidated by spectroscopic methods. For **17b**, suitable crystals were grown by diffusion of diethyl ether into a solution of **17b** in 1,2-dichloroethane, and an X-ray structural analysis was carried out. The crystal contained both enantiomers, and the (S_a,R_a) enantiomer is shown in Figure 3. Po-



sition 2 of the imidazolinium unit points into the bimacrocyclic structure. The twist angles between the aryl rings and the imidazolinium ring are 41.5° (phenyl) and 69.6° (naphthyl), respectively. The asymmetry of the cavity is obvious; even the chloride counterion occupies a slightly dislocated position. In contrast to achiral analogous bimacrocyclic NHC precursors in which the counter chloride ion is perfectly centered in the cavity,[22] the angle defined by the carbon atom in position 2 of the imidazolinium ring, its hydrogen atom and the chloride ion accounts for 168.2° in **17b**.

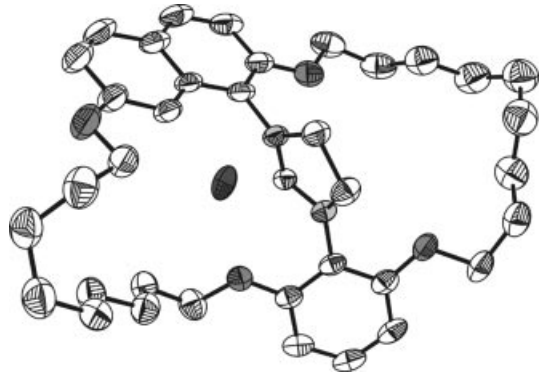
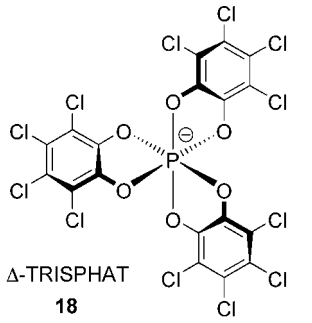


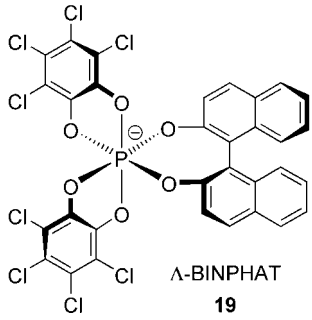
Figure 3. Crystal structure of **17b** with displacement ellipsoids drawn at the 50% probability level [both enantiomers are present in the cell, but only the (S_a,R_a) enantiomer is represented here]. Hydrogens were omitted for clarity.

To apply the bimacrocycles **17** to enantioselective processes, the enantiomers need to be separated. However, as an interconversion of the enantiomers can occur by simple rotation of the imidazolinium ring with respect to the two bridgeheads, the question of the configurational stability of **17** had to be examined.

At 20 °C, ^{1}H NMR experiments for **17a** and **17b** showed the signals of diastereotopic hydrogen atoms, indicating slow stereodynamics on the NMR time scale (ms) and thus a barrier of interconversion of the enantiomers higher than 56 kJ/mol. However, as this value is much lower than that required for the physical separation of the atropisomers at room temperature ($\Delta G^{\ddagger}_{298} \geq 90$ kJ/mol),[25] the question of the configurational stability of moieties **17** remained.

Previously, hexacoordinate phosphorus anions TRISPHAT **18**[26,27] and BINPHAT **19**[28] have been shown to be general NMR chiral solvating, resolving and asymmetry-inducing reagents for chiral cationic species.[29–31] When associated with configurationally stable cations, they behave as general NMR chiral solvating and resolving agents.[32–38] When associated with configurationally labile cations, supramolecular diastereoselective interactions can occur, and one diastereomeric ion pair can become predominant in solution; the occurrence of such a behavior (Pfeiffer effect[39–46]) is a good indication of the lack of configurational stability of the cation.[47–52] For this reason, cations **17a** and **17b** were studied in the presence of hexacoordinate phosphorus anions TRISPHAT and BINPHAT. Salts [**17a**][Δ-**18**], [**17a**][Λ-**19**], [**17b**][Δ-**18**], and [**17b**][Λ-**19**] were prepared according to a literature procedure,[53] and studied by ^{1}H NMR spectroscopy.





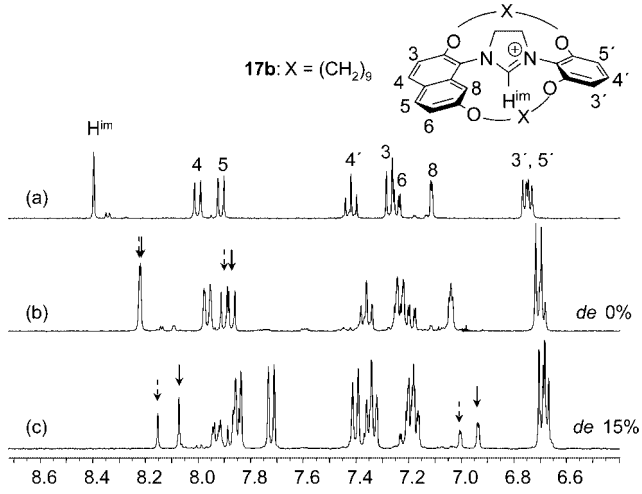


Figure 4. ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 293 K, parts) of salts of **17b**. Counterions: (a) chloride; (b) Δ-**18**; (c) Λ-**19** and the resulting diastereoselectivity. Plain and dashed arrows indicate signals of diastereomeric protons.

As expected, both anions **18** and **19** behaved as NMR chiral solvating agents in CD_2Cl_2. For [**17b**][Δ-**18**], the largest induced separation of the NMR signals ($\Delta\delta$) was observed for the proton in 5-position of the naphthyl ring (δ =0.03 ppm). The signals of the acidic proton at the imidazolinium ring was only slightly split ($\Delta\delta$ = 0.006 ppm). The ratio between the two diastereomeric ion pairs was 1: 1, as it could be expected for a racemic mixture of cations **17b**. For [**17b**][Λ-**19**], the acidic imidazolinium proton was nicely separated into two singlet signals ($\Delta\delta$ = 0.08 ppm). Due to overlap with the signals of BINPHAT, most of the aromatic protons of **17b** could not be monitored with the exception of the naphthyl signal 8-H ($\Delta\delta$ = 0.07 ppm). Overall, as it is most often the case with organic cations, BINPHAT was more effective as a chiral NMR solvating agent than TRISPHAT. Furthermore and in sharp contrast to the situation in the TRISPHAT salt, integration of the separated signals indicated an imbalance in the diastereomeric population and the predominance of one atropisomeric cation over the other (*dr* = 1.35:1, *de* = 15%). The corresponding spectra are shown in Figure 4.

Virtually identical results were obtained for the diastereomeric salts of the smaller bimacrocycle **17a**. With Δ-**18**, only a very marginal split could be observed for a few signals, and a 1:1 diastereomeric ratio was observed. In the case of salt Λ-**19**, effective enantiodifferentiation by the BINPHAT anion and an imbalance between the diastereomers was again noticed (*dr* = 1.47:1 and *de* = 19% in CD_2Cl_2).

Two hypotheses may be considered to explain the above-described results: (i) a configurational stability for ions **17** and a partial resolution of their enantiomers during the ion pair metathesis of the chloride to the BINPHAT salts or (ii) a configurational lability for **17a** and **17b** and the occurrence of a supramolecular stereocontrol from anion Λ-BINPHAT over the geometry of cations **17**;[47] one of the diastereomeric ion pairs, [(S_a,R_a)-**17**][Λ-**19**] or [(R_a,S_a)-**17**][Λ-**19**], is thermodynamically more stable and thus preferred in solution.

To discriminate between these two hypotheses, a series of studies was performed in solvents or solvent combinations of various polarity. It is well known that stereoselective recognition among chiral ions regularly is only achieved in low-polarity solvents.[54,55] In high-polarity media, poor chiral discriminations occur as a result of weaker electrostatic interactions and solvent competition.[56] Thus, with salts made of configurationally labile cations, the maximum diastereoselectivity is achieved in low-polarity solvents and varies with modifications of the solvent polarity. If the cation is configurationally stable, ratios between diastereomers are, on the contrary, solvent independent.

In a first series of experiments, solutions of salt [**17b**][Λ-**19**] were prepared in halogenated solvents of different polarity, namely $CDCl_3$, $C_2D_2Cl_4$, CD_2Cl_2, and $C_2D_4Cl_2$. The spectra are reported in Figure 5. Clearly, the BINPHAT anion behaves as an NMR chiral solvating agent in all cases, and different values are obtained for the diastereomeric ratios in the different solvents (as shown by the various integration values). The diastereoselectivity is best in $CDCl_3$ (*de* = 40%, ε = 4.89) and decreases gradually from $C_2D_2Cl_4$ (*de* = 17%, ε = 8.42) to CD_2Cl_2 (*de* = 15%, ε = 9.02) and $C_2D_4Cl_2$ (*de* = 10%, ε = 10.74), which represents increasing solvent polarity.[57] With [**17a**][Λ-**19**], to a lesser extent, an analogous behavior can be observed for solutions in $CDCl_3$ (*de* = 21%) and CD_2Cl_2 (*de* = 19%).

In a second series of experiments, CD_2Cl_2 solutions of [**17b**][Λ-**19**] were prepared with some content of polar [D_6]-DMSO (10% and 20%). In accordance with the above results, the diastereoselectivity decreased gradually to 7% and 0%, respectively.

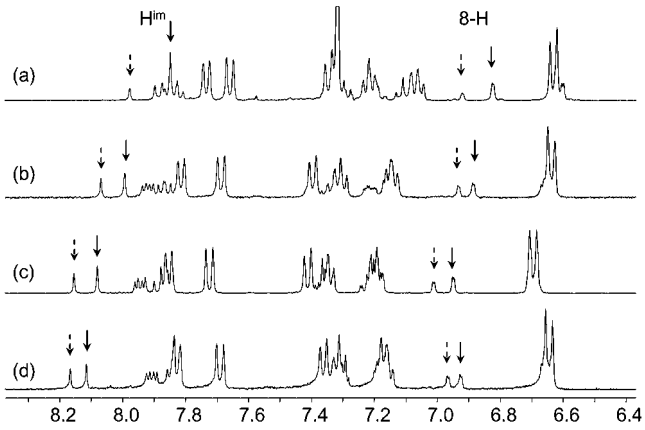


Figure 5. ^{1}H NMR spectra (400 MHz, parts, 293 K) of [**17b**][Λ-**19**] in different halogenated solvents and the subsequent diastereoselectivity: (a) $CDCl_3$ (*de* = 40%, ε = 4.89); (b) $C_2D_2Cl_4$ (*de* = 17%, ε = 8.42); (c) CD_2Cl_2 (*de* = 15%, ε = 9.02); (d) $C_2D_4Cl_2$ (*de* = 10%, ε = 10.74). Plain and dashed arrows indicate signals of the major and minor diastereomers, respectively.

With these results in hands, only the second hypothesis that considers a configurational lability for anions **17a** and **17b** was plausible. From the latter experiment, a maximum value for the energy barrier of enantiomerization of the bimacrocyclic cation **17b** could be estimated. ^{1}H NMR spectra were recorded immediately after the addition of [D_6]-DMSO, and the changes in diastereomeric populations were already complete within a minute. Assuming that it takes ten half-lives to reach equilibrium, the maximum half-life for the enantiomerization of **17b** can be estimated to be 6 s. This in turn corresponds to an upper limit for the energy for enantiomerization of 77 kJ/mol, which is far below that required for a physical separation of the atropisomers at room temperature.[25]

Finally, in an additional experiment to confirm the configurational lability of cations **17**, a variable-temperature (VT) NMR experiment was carried out on a solution of [**17b**][Λ-**19**] in CD_2Cl_2 (213–298 K); the purpose of the experiment was to observe a change in the diastereomeric population as a function of temperature, and thus, an indication of the presence of an equilibrium between [(S_a,R_a)-**17**][Λ-**19**] and [(R_a,S_a)-**17**][Λ-**19**]. Of all the signals, that of proton H^{im} of the imidazolinium cation is particularly easy to monitor. The resulting spectra are shown in Figure 6 (a). As the temperature is decreased, a better enantiodifferentiation is observed (larger $\Delta\delta$) along with a moderate but definite increase in chiral recognition (*de* going from 12% to 27%). Figure 6 (b) shows clearly the variation in $\Delta\delta$ and diastereoselectivity.

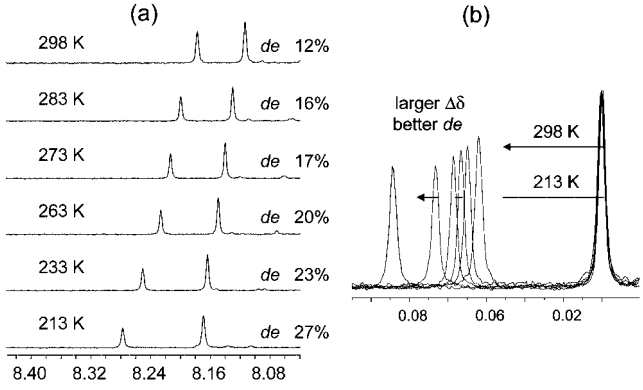


Figure 6. Temperature-dependent ^{1}H NMR spectra (500 MHz, CD_2Cl_2, H^{im} signals, 213–298 K) spectra of [**17b**][Λ-**19**]. (a) separated spectra; (b) superimposed spectra.

Conclusions

Chiral concave imidazolinium salts **17** can readily be synthesized when one naphthalene bridgehead devoid of local C_2-symmetry is incorporated into a bimacrocycle. With chiral counterions such as BINPHAT **19**, diastereomeric ion pairs are generated of which the chiral anion behaves as a stereodynamic probe. Compounds **17** are configurationally labile and the barrier of rotation along the chiral axes in **17a** and **17b** is too small to allow their physical resolution at room temperature. To obtain configurationally stable derivatives, the steric interactions along the chiral axis must be increased in order to enlarge the rotational barrier. Substitution is possible in the 8-position of the naphthalene ring or at the imidazolinium ring. For planar chiral systems **5**[20] and **6**[21] (see above), such an increase of the rotational barrier was achieved by substitution of the 2-position with a methyl group. However, for NHC applications, the 2-position needs to be unsubstituted. Therefore substituents have to be incorporated into positions 4 and 5. Experiments in this vein are underway.

Experimental Section

General Remarks: The following chemicals were obtained commercially and used without further purification: benzylidene-bis(tricyclohexylphosphane)dichlororuthenium (Aldrich), diisopropylazodicarboxylate (Fluka), 2,7-dihydroxynaphthalene (Fluka), dimethyl sulfate (Acros), 5-hexen-1-ol (Merck), lithium aluminum hydride (Merck), 2-nitroresorcinol (Alfa Aesar), oxalyl chloride (Fluka), palladium/charcoal (10% Pd, Merck), 4-penten-1-ol (Alfa Aesar), stannous chloride dihydrate (Fluka), triethyl orthoformate (Merck), and triphenylphosphane (Fluka). 2,6-Bis(pent-4-enyloxy)-aniline[22] (**10a**), 2,6-bis(hex-5-enyloxy)aniline[22] (**10b**), 2,7-dihydroxy-1-nitronaphthalene[58] (**7**), and ethyl chloroglyoxalate[59] 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) or neutral alumina (Macherey–Nagel, activity I). ^{1}H and ^{13}C NMR spectra were recorded with Bruker AMX-400, DRX 500 or AV 600 instruments. Assignments are supported by COSY, HSQC and HMBC. IR spectra were recorded with a Perkin–Elmer Paragon 1000 spectrometer. Mass spectra were recorded with a Finnigan MAT 8200 or MAT 8230 spectrometer. ESI mass spectra were recorded with an Applied Biosystems Mariner Spectrometry Workstation. Elemental analyses were carried out with a EuroEA 3000 Elemental Analyzer

from Euro Vector. As an alternative proof of composition, high-resolution mass spectra were recorded from samples which were pure according to NMR spectra.

General Procedure A. Ethyl Oxalamates 11: The respective aniline **10** was dissolved in tetrahydrofuran. At 0 °C, ethyl chloroglyoxalate (2 equiv.) was slowly added, and the mixture was stirred at room temperature for 1 h. After evaporation of the solvent, the product was purified by column chromatography with silica gel.

General Procedure B. Oxalamic Acids 12: Ethyl oxalamate **11** was heated to 50 °C with potassium hydroxide (1.5 equiv.) in ethanol for 0.5 h. After evaporation of the solvent, the residue was dissolved in water and acidified with hydrochloric acid. The aqueous layer was extracted with dichloromethane, the organic layer was dried with magnesium sulfate, and the solvent was evaporated to dryness.

General Procedure C. Synthesis of Oxalamides 13: Oxalamic acid **12** was stirred with oxalyl chloride (1 equiv.) and two drops of dimethylformamide in tetrahydrofuran at room temperature for 1 h. After the addition of 2,7-bis(pent-4-enyloxy)naphthyl-1-amine (**9**) in tetrahydrofuran, the mixture was stirred at room temperature for 2 h. After evaporation of the solvent, the product was purified by column chromatography with silica gel and recrystallization from cyclohexane.

General Procedure D. Synthesis of Ethane-1,2-diamines 14: The oxalamide **13** was dissolved in tetrahydrofuran and added slowly to a suspension of lithium aluminum hydride (10 equiv.) in tetrahydrofuran at 0 °C. The mixture was then refluxed for 9 h. After cooling to 0 °C, water was added, the layers were separated, and the aqueous layer was extracted with diethyl ether. The organic layer was dried with magnesium sulfate, and the solvents were evaporated to dryness. The product was purified by column chromatography with alumina.

General Procedure E. Synthesis of Imidazolinium Chlorides 15: The ethane-1,2-diamine **14** was heated to 110 °C with ammonium chloride (1.2 equiv.) in triethyl orthoformate for 3 h under a nitrogen flow to remove ethanol. After cooling to room temperature, the product was filtered off and purified by column chromatography with silica gel.

General Procedure F. Synthesis of Unsaturated Imidazoliniuma-bicyclophane Chlorides 16: The imidazolinium chloride **15** was stirred with benzylidene-bis(tricyclohexylphosphane)dichlororuthenium (10 mol-%) in dichloromethane at room temperature for 24 h. After evaporation of the solvent to dryness, the product was purified by column chromatography with silica gel.

General Procedure G. Synthesis of Imidazoliniuma-bicyclophane Chlorides 17: The imidazolinium chloride **16** was stirred with palladium/charcoal (10% Pd) in methanol under an atmosphere of hydrogen at room temperature for 24 h. After filtration of the mixture and evaporation of the solvent to dryness, the product was purified by column chromatography with silica gel.

1-Nitro-2,7-bis(pent-4-enyloxy)naphthalene (8): 2,7-Dihydroxy-1-nitronaphthalene (**7**, 2.73 g, 13.3 mmol), 4-penten-1-ol (4.59 g, 53.3 mmol), and triphenylphosphane (10.5 g, 40.0 mmol) were dissolved in tetrahydrofuran (220 mL). At 0 °C, diisopropyl azodicarboxylate (10.3 mL, 52.4 mmol) in tetrahydrofuran (20 mL) was slowly added and the mixture was stirred at room temperature for 20 h. Sodium hydroxide (0.5 N, 120 mL) was added, the layers were separated, and the aqueous layer was extracted with diethyl ether (2 × 50 mL). The organic layer was dried with magnesium sulfate and concentrated, keeping the triphenylphosphane oxide in solution. Column chromatography [silica gel, cyclohexane/ethyl acetate (10:1), R_f = 0.44] yielded **8** as an orange oil (4.10 g, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C):[60] δ = 7.80 (d, ^3J = 9.0 Hz, 1 H, 4-H), 7.68 (d, ^3J = 9.0 Hz, 1 H, 5-H), 7.10 (d, ^3J = 9.0 Hz, 1 H, 3-H), 7.07 (dd, ^3J = 9.0 Hz, ^4J = 2.4 Hz, 1 H, 6-H), 6.90 (d, ^4J = 2.4 Hz, 1 H, 8-H), 5.86 (ddt, ^3J = 17.0 Hz, ^3J = 10.3 Hz, ^3J = 6.7 Hz, 1 H$^{\#}$, =C*H*), 5.85 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^4J = 6.6 Hz, 1 H$^{\#}$, =C*H*), 5.07 [m_c (br. d), ^3J = 17.1 Hz, 2 H, H_ZHC=], 5.01 [m_c (br. d), ^3J = 10.2 Hz, 2 H, H_EHC=], 4.19 (t, ^3J = 6.3 Hz, 2 H, OCH_2), 4.04 (t, ^3J = 6.4 Hz, 2 H, OCH_2), 2.25 (m_c, 4 H, =CHCH_2), 1.92 (m_c, 4 H, OCH$_2$CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 159.7 (C-7), 149.0 (C-2), 137.6 (=*C*H), 137.3 (=*C*H), 131.6 (C-4), 129.7 (C-5), 127.3 (C-8a), 123.8 (C-4a), 118.5 (C-6), 115.6 (H_2C=), 115.4 (H_2C=), 111.1 (C-3), 99.2 (C-8), 69.1 (O*C*H$_2$), 67.4 (O*C*H$_2$), 30.1 (=CH*C*H$_2$), 29.8 (=CH*C*H$_2$), 28.3 (OCH$_2$*C*H$_2$), 28.2 (OCH$_2$*C*H$_2$) ppm; no signal for C-1 observed. IR (KBr): $\tilde{\nu}$ = 3077, 2941, 1634, 1526, 1460, 1440, 1387, 1359, 1274, 1252, 1230, 1215, 1136, 1078, 1017, 992, 914, 828, 794, 660 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 341 (17) [M]$^+$, 295 (78), 69 (100). MS (CI): *m*/*z* (%) = 342 (25) [M + H]$^+$. HRMS: calcd. for $C_{20}H_{23}NO_4$ 341.16272; found 341.16243 (δ = 0.8 ppm); calcd. for $C_{19}{}^{13}CH_{23}NO_4$ 342.16608; found 342.16596 (δ = 0.3 ppm). $C_{20}H_{23}NO_4$ (341.40): calcd. C 70.36, H 6.79, N 4.10. $C_{20}H_{23}NO_4 \cdot 0.1H_2O$: calcd. C 69.99, H 6.81, N 4.08; found C 69.84, H 6.92, N 4.40.

2,7-Bis(pent-4-enyloxy)naphthyl-1-amine (9): 1-Nitro-2,7-bis(pent-4-enyloxy)naphthalene (**8**, 1.52 g, 4.45 mmol) was refluxed in ethanol (50 mL) with stannous chloride dihydrate (9.9 g, 44 mmol) for 6 h. After cooling to room temperature, the mixture was poured into ice water, and potassium hydroxide (30 g) was added. The mixture was extracted with dichloromethane (3 × 75 mL), the organic layer was dried with magnesium sulfate, and the solvents were evaporated to dryness. Column chromatography [silica gel, cyclohexane/ethyl acetate (10:1), R_f = 0.32] yielded **9** as a red oil (1.03 g, 74% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C):[60] δ = 7.63 (d, ^3J = 8.9 Hz, 1 H, 5-H), 7.23 (d, ^3J = 8.8 Hz, 1 H, 4-H), 7.05 (d, ^3J = 8.8 Hz, 1 H, 3-H), 7.00 (dd, ^3J = 8.8 Hz, ^4J = 2.3 Hz, 1 H, 6-H), 6.98 (d, ^4J = 2.2 Hz, 1 H, 8-H), 5.89, (ddt, ^3J = 17.0 Hz, ^3J = 10.3 Hz, ^4J = 6.6 Hz, 1 H$^{\#}$, =C*H*), 5.88 (ddt, ^3J = 17.0 Hz, ^3J = 10.3 Hz, ^3J = 6.6 Hz, 1 H$^{\#}$, =C*H*), 5.08 (ddt, ^3J = 17.1 Hz, ^2J = 1.8 Hz, ^4J = 1.6 Hz, 2 H, H_ZHC=), 5.01 (ddt, ^3J = 10.4 Hz, ^2J = 1.8 Hz, ^4J = 1.2 Hz, 2 H, H_EHC=), 4.11 (t, ^3J = 6.5 Hz, 2 H, OCH_2), 4.09 (t, ^3J = 6.5 Hz, 2 H, OCH_2), 2.28 (m_c, 4 H, =CHCH_2), 1.94 (m_c, 4 H, OCH$_2$CH_2) ppm; no signal for NH_2 observed. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 156.9 (C-7), 142.7 (C-2), 137.9 (=*C*H), 137.9 (=*C*H), 130.0 (C-5), 128.7 (C-1), 125.3 (C-8a), 125.0 (C-4a), 118.7 (C-4), 116.6 (C-6), 115.2 (H_2C=), 115.2 (H_2C=), 112.3 (C-3), 100.0 (C-8), 68.9 (O*C*H$_2$), 67.2 (O*C*H$_2$), 30.3 (=CH*C*H$_2$), 30.2 (=CH*C*H$_2$), 28.9 (OCH$_2$*C*H$_2$), 28.5 (OCH$_2$*C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3448, 3367, 3075, 2939, 1630, 1515, 1459, 1376, 1342, 1266, 1219, 1148, 1051, 1017, 992, 913, 824 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 311 (100) [M]$^+$, 242 (85). MS (CI): *m*/*z* (%) = 312 (77) [M + H]$^+$. HRMS: calcd. for $C_{20}H_{25}NO_2$ 311.18854; found 311.18851 (δ = 0.1 ppm); calcd. for $C_{19}{}^{13}CH_{25}NO_2$ 312.19189; found 312.19218 (δ = 0.9 ppm).

Ethyl *N*-[2,6-Bis(pent-4-enyloxy)phenyl]oxalamate (11a). General Procedure A: 2,6-Bis(pent-4-enyloxy)aniline (**10a**, 1.96 g, 7.51 mmol) in tetrahydrofuran (15 mL), ethyl chloroglyoxalate (1.5 mL, 13 mmol). Column chromatography [silica gel, cyclohexane/ethyl acetate (4:1), R_f = 0.34] yielded **11a** as a colorless oil (2.24 g, 83% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 8.28 (s, 1 H, N*H*), 7.15 (t, ^3J = 8.4 Hz, 1 H, 4-H), 6.56 (d, ^3J = 8.4 Hz, 2 H, 3,5-H), 5.83 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 2

H, =C*H*), 5.04 (ddt, ^3J = 17.1 Hz, ^2J = 1.9 Hz, ^4J = 1.6 Hz, 2 H, H_ZHC=), 4.98 (ddt, ^3J = 10.2 Hz, ^2J = 2.0 Hz, ^4J = 1.2 Hz, 2 H, H_EHC=), 4.42 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH$_3$), 4.01 (t, ^3J = 6.5 Hz, 4 H, OCH_2CH$_2$), 2.20 (m_c, 4 H, =CHCH_2), 1.87 (m_c, 4 H, OCH$_2$CH_2), 1.42 (t, ^3J = 7.1 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (150 MHz, CDCl$_3$, 25 °C): δ = 160.9 (O*C*=O), 154.5 (C-2,6), 154.2 (N*C*=O), 137.8 (=*C*H), 128.1 (C-4), 115.1 (H$_2$*C*=), 113.2 (C-1), 105.2 (C-3,5), 68.1 (O*C*H$_2$CH$_2$), 63.2 (O*C*H$_2$CH$_3$), 30.1 (=CH*C*H$_2$), 28.4 (OCH$_2$*C*H$_2$), 14.0 (*C*H$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3398, 3077, 2942, 1761, 1720, 1640, 1599, 1518, 1461, 1390, 1369, 1301, 1259, 1176, 1160, 1103, 1017, 913, 764, 714 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 361 (86) [M]$^+$, 288 (43), 220 (100), 152 (86). MS (CI): *m*/*z* (%) = 362 (100) [M + H]$^+$. $C_{20}H_{27}NO_5$ (361.44): calcd. C 66.46, H 7.53, N 3.88; found C 66.33, H 7.63, N 4.06.

Ethyl *N*-[2,6-bis(hex-5-enyloxy)phenyl]oxalamate (11b). General Procedure A: 2,6-Bis(hex-5-enyloxy)aniline (**10b**, 2.52 g, 8.71 mmol) in tetrahydrofuran (12 mL), ethyl chloroglyoxalate (2.0 mL, 18 mmol). Column chromatography [silica gel, cyclohexane/ethyl acetate (4:1), R_f = 0.46] yielded **11b** as a colorless oil (3.10 g, 91% yield). ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): δ = 8.28 (s, 1 H, N*H*), 7.16 (t, ^3J = 8.4 Hz, 1 H, 4-H), 6.56 (d, ^3J = 8.4 Hz, 2 H, 3,5-H), 5.81 (ddt, ^3J = 17.1 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 2 H, =C*H*), 5.02 (ddt, ^3J = 17.1 Hz, ^2J = 2.0 Hz, ^4J = 1.6 Hz, 2 H, H_ZHC=), 4.96 (ddt, ^3J = 10.2 Hz, ^2J = 2.0 Hz, ^4J = 1.2 Hz, 2 H, H_EHC=), 4.41 (q, ^3J = 7.2 Hz, 2 H, OCH_2CH$_3$), 4.00 (t, ^3J = 6.5 Hz, 4 H, OCH_2CH$_2$), 2.10 (m_c, 4 H, =CHCH_2), 1.78 (m_c, 4 H, OCH$_2$CH_2), 1.53 (m_c, 4 H, OCH$_2$CH$_2$CH_2), 1.42 (t, ^3J = 7.2 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (150 MHz, CDCl$_3$, 25 °C): δ = 160.8 (O*C*=O), 154.5 (C-2,6), 154.1 (N*C*=O), 138.5 (=*C*H), 128.2 (C-4), 114.7 (H$_2$*C*=), 113.0 (C-1), 105.1 (C-3,5), 68.6 (O*C*H$_2$CH$_2$), 63.2 (O*C*H$_2$CH$_3$), 33.3 (=CH*C*H$_2$), 28.6 (OCH$_2$*C*H$_2$), 25.2 (OCH$_2$CH$_2$*C*H$_2$), 14.0 (*C*H$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3400, 3076, 2941, 1763, 1721, 1640, 1599, 1517, 1461, 1390, 1299, 1258, 1177, 1101, 1017, 910, 765, 714 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 389 (31) [M]$^+$, 316 (24), 307 (25), 234 (63), 152 (100). MS (CI): *m*/*z* (%) = 390 [M + H]$^+$. $C_{22}H_{31}NO_5$ (389.49): calcd. C 67.84, H 8.02, N 3.60; found C 67.57, H 8.17, N 3.60.

***N*-[2,6-Bis(pent-4-enyloxy)phenyl]oxalamic Acid (12a). General Procedure B:** Ethyl *N*-[2,6-bis(pent-4-enyloxy)phenyl]oxalamate (**11a**, 1.27 g, 3.52 mmol), potassium hydroxide (297 mg, 5.30 mmol) in ethanol (15 mL). Work up yielded **12a** as a colorless solid (1.15 g, 98% yield). M.p. 101 °C. ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): δ = 8.44 (s, 1 H, N*H*), 7.20 (t, ^3J = 8.5 Hz, 1 H, 4-H), 6.60 (d, ^3J = 8.5 Hz, 2 H, 3,5-H), 5.82 (ddt, ^3J = 17.0 Hz, ^3J = 10.3 Hz, ^3J = 6.7 Hz, 2 H, =C*H*), 5.04 (ddt, ^3J = 17.1 Hz, ^2J = 1.8 Hz, ^4J = 1.6 Hz, 2 H, H_ZHC=), 4.99 (ddt, ^3J = 10.2 Hz, ^2J = 1.9 Hz, ^4J = 1.2 Hz, 2 H, H_EHC=), 4.01 (t, ^3J = 6.4 Hz, 4 H, OCH_2), 2.19 (m_c, 4 H, =CHCH_2), 1.86 (m_c, 4 H, OCH$_2$CH_2) ppm; no signal for O*H* observed. ^{13}C NMR (150 MHz, CDCl$_3$, 25 °C): δ = 159.8 (O*C*=O), 155.3 (N*C*=O), 154.4 (C-2,6), 137.6 (=*C*H), 128.9 (C-4), 115.3 (H$_2$*C*=), 112.0 (C-1), 105.0 (C-3,5), 68.1 (O*C*H$_2$), 30.1 (=CH*C*H$_2$), 28.3 (OCH$_2$*C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3252, 3081, 3057, 2954, 2863, 1765, 1694, 1643, 1603, 1533, 1458, 1389, 1343, 1311, 1263, 1208, 1107, 996, 935, 920, 772, 716, 646 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 333 (46) [M]$^+$, 288 (15), 265 (28), 220 (31), 197 (40), 152 (100). MS (CI): *m*/*z* (%) = 334 (100) [M + H]$^+$. $C_{18}H_{23}N_2O_5$ (333.38): calcd. C 64.85, H 6.95, N 4.20; found C 64.75, H 7.17, N 4.58.

***N*-[2,6-Bis(hex-5-enyloxy)phenyl]oxalamic Acid (12b). General Procedure B:** Ethyl *N*-[2,6-bis(hex-5-enyloxy)phenyl]oxalamate (**11b**, 1.65 g, 4.24 mmol), potassium hydroxide (346 mg, 6.17 mmol) in ethanol (15 mL). Work up yielded **12b** as a colorless solid (1.48 g, 97% yield). M.p. 114 °C. ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): δ = 8.30 (s, 1 H, N*H*), 7.20 (t, ^3J = 8.4 Hz, 1 H, 4-H), 6.57 (d, ^3J = 8.5 Hz, 2 H, 3,5-H), 5.80 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 2 H, =C*H*), 5.02 [m_c (br. d), ^3J = 17.1 Hz, 2 H, H_ZHC=], 4.97 [m_c (br. d), ^3J = 10.2 Hz, 2 H, H_EHC=], 4.00 (t, ^3J = 6.4 Hz, 4 H, OCH_2), 2.10 (m_c, 4 H, =CHCH_2), 1.77 (m_c, 4 H, OCH$_2$CH_2), 1.52 (m_c, 4 H, OCH$_2$CH$_2$CH_2) ppm; no signal for O*H* observed. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 162.2 (O*C*=O), 157.0 (N*C*=O), 155.3 (C-2,6), 138.6 (=*C*H), 128.2 (C-4), 114.9 (H$_2$*C*=), 114.1 (C-1), 105.5 (C-3,5), 68.1 (O*C*H$_2$), 32.8 (=CH*C*H$_2$), 28.2 (OCH$_2$*C*H$_2$), 24.6 (OCH$_2$CH$_2$*C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3246, 3080, 2947, 1764, 1694, 1641, 1610, 1591, 1535, 1479, 1462, 1388, 1345, 1261, 1210, 1106, 993, 940, 912, 794, 765, 705, 628 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 361 (21) [M]$^+$, 289 (40), 197 (38), 152 (71), 125 (100). MS (CI): *m*/*z* (%) = 362 (100) [M + H]$^+$. $C_{20}H_{27}NO_5$ (361.43): calcd. C 66.46, H 7.53, N 3.88; found C 66.35, H 7.72, N 4.19.

***N*-[2,6-Bis(pent-4-enyloxy)phenyl]-*N*′-[2,7-bis(pent-4-enyloxy)-1-naphthyl]oxalamide (13a). General Procedure C:** *N*-[2,6-Bis(pent-4-enyloxy)phenyl]oxalamic acid (**12a**, 1.27 g, 3.81 mmol), oxalyl chloride (483 mg, 3.80 mmol) in tetrahydrofuran (20 mL). 2,7-Bis(pent-4-enyloxy)naphthyl-1-amine (**9**, 737 mg, 2.55 mmol) in tetrahydrofuran (15 mL). Column chromatography [dichloromethane, R_f = 0.62] and recrystallization from cyclohexane yielded **13a** as a colorless solid (1.10 g, 69% yield). M.p. 129 °C. ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C):[60] δ = 9.15 (s, 1 H, N*H*), 8.81 (s, 1 H, N*H*), 7.72 (d, ^3J = 8.9 Hz, 1 H, 4-H$_{naph}$), 7.68 (m_c, 1 H, 5-H$_{naph}$), 7.18 (t, ^3J = 8.4 Hz, 1 H, 4-H$_{ph}$), 7.12 (d, ^3J = 9.0 Hz, 1 H, 3-H$_{naph}$), 7.04–7.02 (m, 2 H, 6,8-H$_{naph}$), 6.60 (d, ^3J = 8.4 Hz, 2 H, 3,5-H$_{ph}$), 5.87 (ddt, ^3J = 17.0 Hz, ^3J = 10.3 Hz, ^3J = 6.6 Hz, 1 H$^{\#}$, =CH_{naph}), 5.83 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 1 H$^{\#}$, =CH_{naph}), 5.82 (ddt, ^3J = 17.0 Hz, ^3J = 10.3 Hz, ^3J = 6.7 Hz, 2 H$^{\#}$, =CH_{ph}), 5.06 (ddt, ^3J = 17.1 Hz, ^2J = 1.8 Hz, ^4J = 1.6 Hz, 1 H, H_ZHC=$_{naph}$), 5.05 [m_c (br. d), ^3J = 17.1 Hz, 3 H, H_ZHC=$_{naph}$, H_ZHC=$_{ph}$], 5.01–4.06 (m, 4 H, H_EHC=), 4.14 (t, ^3J = 6.5 Hz, 2 H, OC$H_{2\,naph}$), 4.07 (t, ^3J = 6.3 Hz, 2 H, OC$H_{2\,naph}$), 4.05 (t, ^3J = 6.5 Hz, 4 H, OC$H_{2\,ph}$), 2.25 (m_c, 8 H, =CHCH_2), 1.90 (m_c, 8 H, OCH$_2$CH_2) ppm. ^{13}C NMR (150 MHz, CDCl$_3$, 25 °C):[60] δ = 158.8 (*C*=O*), 158.2 (C-7$_{naph}$*), 157.8 (*C*=O*), 154.6 (C-2,6$_{ph}$), 151.8 (C-2$_{naph}$), 137.9 (=*C*H), 137.7 (=*C*H), 131.8 (C-8a$_{naph}$), 129.7 (C-4$_{naph}$*), 128.7 (C-4$_{ph}$*), 128.0 (C-5$_{naph}$*), 124.6 (C-4a$_{naph}$), 117.2 (C-6$_{naph}$), 116.7 (C-1$_{naph}$), 115.4 (H$_2$*C*=), 115.1 (H$_2$*C*=), 113.3 (C-1$_{ph}$), 111.3 (C-3$_{naph}$), 105.2 (C-3,5$_{ph}$), 101.8 (C-8$_{naph}$), 68.5 (O*C*H$_{2\,naph}$), 68.0 (O*C*H$_{2\,ph}$), 67.1 (O*C*H$_{2\,naph}$), 30.2 (=CH*C*H$_{2\,naph}$), 30.1 (=CH*C*H$_{2\,ph}$), 30.0 (=CH*C*H$_{2\,naph}$), 28.6 (OCH$_2$*C*H$_{2\,naph}$), 28.5 (OCH$_2$*C*H$_{2\,naph}$), 28.4 (OCH$_2$*C*H$_{2\,ph}$) ppm. IR (KBr): $\tilde{\nu}$ = 3257, 3077, 2941, 2869, 1628, 1632, 1600, 1503, 1458, 1391, 1326, 1262, 1230, 1143, 1107, 992, 910, 842, 766, 712 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 626 (76) [M]$^+$, 261 (100). MS (CI): *m*/*z* (%) = 627 (100) [M + H]$^+$. $C_{38}H_{46}N_2O_6$ (626.79): calcd. C 72.82, H 7.40, N 4.47; found C 72.92, H 7.59, N 4.83.

***N*-[2,6-Bis(hex-5-enyloxy)phenyl]-*N*′-[2,7-bis(pent-4-enyloxy)-1-naphthyl]oxalamide (13b). General Procedure C:** *N*-[2,6-Bis(hex-5-enyloxy)phenyl]oxalamic acid (**12b**, 1.48 g, 4.09 mmol), oxalyl chloride (527 mg, 4.15 mmol) in tetrahydrofuran (20 mL). 2,7-Bis(pent-4-enyloxy)naphthyl-1-amine (**9**, 1.25 g, 4.01 mmol) in tetrahydrofuran (5 mL). Column chromatography [silica gel, cyclohexane/ethyl acetate (9:1), R_f = 0.27] and recrystallization from cyclohexane yielded **13b** as a colorless solid (1.71 g, 65% yield). M.p. 119 °C. ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C):[60] δ = 9.14 (s, 1 H, N*H*), 8.80 (s, 1 H, N*H*), 7.72 (d, ^3J = 8.9 Hz, 1 H, 4-H$_{naph}$), 7.67 (m_c, 1 H, 5-H$_{naph}$), 7.19 (t, ^3J = 8.4 Hz, 1 H, 4-H$_{ph}$), 7.13 (d, ^3J = 9.0 Hz, 1 H, 3-H$_{naph}$), 7.05–7.02 (m, 2 H, 6,8-H$_{naph}$), 6.61 (d, ^3J = 8.5 Hz, 2 H, 3,5-H$_{ph}$), 5.87 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J =

6.6 Hz, 1 H#, =CH_{naph}), 5.83 (m_c, 1 H#, =CH_{naph}), 5.78 (ddt, ^3J = 17.1 Hz, ^3J = 10.3 Hz, ^3J = 6.7 Hz, 2 H#, =CH_{ph}), 5.07 (ddt, ^3J = 17.1 Hz, ^2J = 1.8 Hz, ^4J = 1.6 Hz, 1 H, H_ZHC=$_{naph}$), 5.05 (ddt, ^3J = 17.1 Hz, ^2J = 1.8 Hz, ^4J = 1.6 Hz, 1 H, H_ZHC=$_{naph}$), 5.02–4.96 (m, 4 H, H_ZHC=$_{ph}$, H_EHC=$_{naph}$), 4.92 (ddt, ^3J = 10.2 Hz, ^2J = 2.0 Hz, ^4J = 1.2 Hz, 2 H, H_EHC=$_{ph}$), 4.15 (t, ^3J = 6.5 Hz, 2 H, OC$H_{2\,naph}$), 4.07 (t, ^3J = 6.3 Hz, 2 H, OC$H_{2\,naph}$), 4.04 (t, ^3J = 6.6 Hz, 4 H, OC$H_{2\,ph}$), 2.26 (m_c, 4 H, =CHC$H_{2\,naph}$), 2.10 (m_c, 4 H, =CHC$H_{2\,ph}$), 1.92 (m_c, 4 H, OCH$_2$C$H_{2\,naph}$), 1.81 (m_c, 4 H, OCH$_2$C$H_{2\,ph}$), 1.56 (m_c, 4 H, OCH$_2$CH$_2$C$H_{2\,ph}$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C):[60] δ = 158.8 (*C*=O*), 158.1 (C-7$_{naph}$*), 157.8 (*C*=O*), 154.6 (C-2,6$_{ph}$), 151.8 (C-2$_{naph}$), 138.5 (=*C*H$_{ph}$), 137.9 (=*C*H$_{naph}$), 137.7 (=*C*H$_{naph}$), 131.8 (C-8a$_{naph}$), 129.7 (C-4$_{naph}$*), 128.8 (C-4$_{ph}$*), 128.0 (C-5$_{naph}$*), 124.6 (C-4a$_{naph}$), 117.1 (C-6$_{naph}$), 116.7 (C-1$_{naph}$), 115.4 (H$_2$*C*=$_{naph}$), 115.2 (H$_2$*C*=$_{naph}$), 114.8 (H$_2$*C*=$_{ph}$), 113.3 (C-1$_{ph}$), 111.3 (C-3$_{naph}$), 105.2 (C-3,5$_{ph}$), 101.9 (C-8$_{naph}$), 68.6 (O*C*H$_{2\,ph}$), 68.5 (O*C*H$_{2\,naph}$), 67.2 (O*C*H$_{2\,naph}$), 33.3 (=CH*C*H$_{2\,ph}$), 30.2 (=CH*C*H$_{2\,naph}$), 30.1 (=CH*C*H$_{2\,naph}$), 28.6 (OCH$_2$*C*H$_{2\,ph}$), 28.6 (OCH$_2$*C*H$_{2\,naph}$), 28.5 (OCH$_2$*C*H$_{2\,naph}$), 25.1 (OCH$_2$CH$_2$*C*H$_{2\,ph}$) ppm. IR (KBr): $\tilde{\nu}$ = 3261, 3076, 2941, 2869, 1672, 1631, 1604, 1502, 1458, 1391, 1326, 1264, 1230, 1108, 992,911, 824, 766, 711 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 654 (100) [M]$^+$, 289 (70). MS (CI): *m*/*z* (%) = 655 (100) [M + H]$^+$. $C_{40}H_{50}N_2O_6$ (654.84): calcd. C 73.37, H 7.70, N 4.28; found C 73.47, H 7.80, N 4.44.

***N*-[2,6-Bis(pent-4-enyloxy)-phenyl]-*N*′-[2,7-bis(pent-4-enyloxy)-1-naphthyl]ethane-1,2-diamine (14a). General Procedure D:** *N*-[2,6-Bis(pent-4-enyloxy)-phenyl]-*N*′-[2,7-bis(pent-4-enyloxy)-1-naphthyl]oxalamide (**13a**, 627 mg, 1.00 mmol), lithium aluminum hydride (380 mg, 10.0 mmol) in tetrahydrofuran (30 mL). Workup: Water (15 mL), extraction with diethyl ether (3 × 25 mL). Column chromatography [alumina, cyclohexane/ethyl acetate (9:1), R_f = 0.75] yielded **14a** as a colorless oil (302 mg, 50% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C):[60] δ = 7.63 (d, ^3J = 8.9 Hz, 1 H, 5-H$_{naph}$), 7.43 (br. s, 1 H, 8-H$_{naph}$), 7.40 (d, ^3J = 8.8 Hz, 1 H, 4-H$_{naph}$), 7.06 (d, ^3J = 8.8 Hz, 3-H$_{naph}$), 6.98 (dd, ^3J = 8.9 Hz, ^4J = 2.4 Hz, 6-H$_{naph}$), 6.75 (t, ^3J = 8.3 Hz, 1 H, 4-H$_{ph}$), 6.52 (d, ^3J = 8.3 Hz, 2 H, 3,5-H$_{ph}$), 5.88–5.80 (m, 2 H#, =CH_{naph}), 5.78 (ddt, ^3J = 17.0 Hz, ^3J = 10.3 Hz, ^3J = 6.6 Hz, 2 H#, =CH_{ph}), 5.06–4.92 (m, 8 H, H_2C=), 4.35 (br. s, 2 H, N*H*), 4.09 (t, ^3J = 6.7 Hz, 2 H, OC$H_{2\,naph}$), 4.03 (t, ^3J = 6.4 Hz, 2 H, OC$H_{2\,naph}$), 3.97 (t, ^3J = 6.6 Hz, 4 H, OC$H_{2\,ph}$), 3.45 (t, ^3J = 5.6 Hz, 2 H, NCH_2), 3.28 (t, ^3J = 5.6 Hz, 2 H, NCH_2), 2.25–2.15 (m, 8 H, =CHCH_2), 1.94–1.82 (m, 8 H, OCH$_2$C$H_{2\,ph}$) ppm.^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 157.1 (C-7$_{naph}$), 150.4 (C-2,6$_{ph}$), 148.3 (C-2$_{naph}$), 138.0 (=*C*H$_{naph}$), 137.8 (=*C*H$_{ph}$), 137.8 (=*C*H$_{naph}$), 131.4 (C-1$_{naph}$), 130.2 (C-8a$_{naph}$), 129.7 (C-5$_{naph}$), 127.6 (C-1$_{ph}$), 125.4 (C-4a$_{naph}$), 122.6 (C-4$_{naph}$), 119.5 (C-4$_{ph}$), 116.8 (C-6$_{naph}$), 115.3 (H$_2$*C*=$_{naph}$), 115.1 (H$_2$*C*=$_{ph}$), 115.0 (H$_2$*C*=$_{naph}$), 111.8 (C-3$_{naph}$), 105.8 (C-3,5$_{ph}$), 102.3 (C-8$_{naph}$), 68.9 (O*C*H$_{2\,naph}$), 68.1 (O*C*H$_{2\,ph}$), 67.2 (O*C*H$_{2\,naph}$), 49.8 (*C*H$_2$N$_{naph}$), 47.4 (*C*H$_2$N$_{ph}$), 30.2 (=CH*C*H$_{2\,ph}$), 30.2 (=CH*C*H$_{2\,naph}$), 28.8 (OCH$_2$*C*H$_{2\,naph}$), 28.6 (OCH$_2$*C*H$_{2\,ph}$), 28.5 (OCH$_2$*C*H$_{2\,naph}$) ppm. IR (KBr): $\tilde{\nu}$ = 3349, 3075, 2940, 2870, 1628, 1600, 1514, 1492, 1450, 1389, 1260, 1229, 1215, 1118, 1094, 992, 912, 825, 763, 723 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 598 (78) [M]$^+$, 325 (57), 275 (100). MS (CI): *m*/*z* (%) = 599 (100) [M + H]$^+$. HRMS: calcd. For $C_{38}H_{50}N_2O_4$ 598.37708; found 598.37695 (δ = 0.2 ppm); calcd. for $C_{37}{}^{13}CH_{50}N_2O_4$ 599.38043; found 599.38024 (δ = 0.3 ppm).

***N*-[2,6-Bis(hex-5-enyloxy)phenyl]-*N*′-[2,7-bis(pent-4-enyloxy)-1-naphthyl]ethane-1,2-diamine (14b). General Procedure D:** *N*-[2,6-Bis(hex-5-enyloxy)phenyl]-*N*′-[2,7-bis(pent-4-enyloxy)-1-naphthyl]oxalamide (**13b**, 1.71 g, 2.61 mmol), lithium aluminum hydride (992 mg, 26.1 mmol) in tetrahydrofuran (80 mL). Workup: water (30 mL) extraction with diethyl ether (2 × 50 mL). Column chromatography [alumina, cyclohexane/ethyl acetate (20:1), R_f = 0.28] yielded **14b** as a colorless oil (1.21 g, 74% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C):[60] δ = 7.63 (d, ^3J = 8.9 Hz, 1 H, 5-H$_{naph}$), 7.43 (d, ^4J = 2.3 Hz, 1 H, 8-H$_{naph}$), 7.40 (d, ^3J = 8.9 Hz, 1 H, 4-H$_{naph}$), 7.06 (d, ^3J = 8.9 Hz, 3-H$_{naph}$), 6.98 (dd, ^3J = 8.9 Hz, ^4J = 2.4 Hz, 6-H$_{naph}$), 6.75 (t, ^3J = 8.3 Hz, 1 H, 4-H$_{ph}$), 6.52 (d, ^3J = 8.3 Hz, 2 H, 3,5-H$_{ph}$), 5.87–5.79 (m, 2 H#, =CH_{naph}), 5.72 (ddt, ^3J = 17.0 Hz, ^3J = 10.3 Hz, ^3J = 6.7 Hz, 2 H#, =CH_{ph}), 5.06–4.86 (m, 8 H, H_2C=), 4.52 (br. s, 1 H, N*H*), 4.25 (br. s, 1 H, N*H*), 4.09 (t, ^3J = 6.7 Hz, 2 H, OC$H_{2\,naph}$), 4.03 (t, ^3J = 6.4 Hz, 2 H, OC$H_{2\,naph}$), 3.96 (t, ^3J = 6.6 Hz, 4 H, OC$H_{2\,ph}$), 3.44 (m_c, 2 H, NCH_2), 3.26 (m_c, 2 H, NCH_2), 2.22 (m_c, 4 H, =CHC$H_{2\,naph}$), 2.03 (m_c, 4 H, =CHC$H_{2\,ph}$), 1.90 (m_c, 4 H, OCH$_2$C$H_{2\,naph}$), 1.76 (m_c, 4 H, OCH$_2$C$H_{2\,ph}$), 1.51 (m_c, 4 H, OCH$_2$CH$_2$C$H_{2\,ph}$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 157.0 (C-7$_{naph}$), 150.1 (C-2,6$_{ph}$), 148.3 (C-2$_{naph}$), 138.4 (=*C*H$_{ph}$), 138.0 (=*C*H$_{naph}$), 137.7 (=*C*H$_{naph}$), 131.3 (C-1$_{naph}$), 130.2 (C-8a$_{naph}$), 129.7 (C-5$_{naph}$), 127.4 (C-1$_{ph}$), 125.4 (C-4a$_{naph}$), 122.6 (C-4$_{naph}$), 119.5 (C-4$_{ph}$), 116.8 (C-6$_{naph}$), 115.3 (H$_2$*C*=$_{naph}$), 115.0 (H$_2$*C*=$_{naph}$), 114.7 (H$_2$*C*=$_{ph}$), 111.7 (C-3$_{naph}$), 105.7 (C-3,5$_{ph}$), 102.2 (C-8$_{naph}$), 68.8 (O*C*H$_{2\,naph}$), 68.6 (O*C*H$_{2\,ph}$), 67.2 (O*C*H$_{2\,naph}$), 49.7 (N*C*H$_2$), 47.3 (N*C*H$_2$), 33.4 (=CH*C*H$_{2\,ph}$), 30.2 (=CH*C*H$_{2\,naph}$), 30.2 (=CH*C*H$_{2\,naph}$), 28.8 (OCH$_2$*C*H$_{2\,ph}$), 28.7 (OCH$_2$*C*H$_{2\,naph}$), 28.5 (OCH$_2$*C*H$_{2\,naph}$), 25.4 (OCH$_2$CH$_2$*C*H$_{2\,ph}$) ppm. IR (KBr): $\tilde{\nu}$ = 3349, 3075, 2938, 2868, 1640, 1628, 1600, 1514, 1492, 1450, 1389, 1324, 1260, 1228, 1215, 1119, 1098, 993, 911, 825, 764, 722 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 626 (100) [M]$^+$, 325 (49), 303 (85). MS (CI): *m*/*z* (%) = 627 (67) [M + H]$^+$. HRMS: calcd. for $C_{40}H_{54}N_2O_4$ 626.40839; found 626.40828 (δ = 0.2 ppm); calcd. for $C_{39}{}^{13}CH_{54}N_2O_4$ 627.41174; found 627.41147 (δ = 0.4 ppm).

1-[2,6-Bis(pent-4-enyloxy)phenyl]-3-[2,7-bis(pent-4-enyloxy)-1-naphthyl]-4,5-imidazolinium Chloride (15a). General Procedure E: *N*-[2,6-Bis(pent-4-enyloxy)-phenyl]-*N*′-[2,7-bis(pent-4-enyloxy)-1-naphthyl]ethane-1,2-diamine (**14a**, 274 mg, 458 μmol), ammonium chloride (27 mg, 0.51 mmol) in triethyl orthoformate (3.0 mL, 18 mmol). Column chromatography [silica gel, dichloromethane/ethanol (10:1), R_f = 0.23] yielded **15a** as a colorless solid (194 mg, 65% yield). M.p. 196 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C):[60] δ = 8.13 (s, 1 H, 2-H$_{im}$), 7.84 (d, ^3J = 9.0 Hz, 1 H, 4-H$_{naph}$), 7.73 (d, ^3J = 9.0 Hz, 1 H, 5-H$_{naph}$), 7.29 (t, ^3J = 8.5 Hz, 1 H, 4-H$_{ph}$), 7.12 (d, ^3J = 9.1 Hz, 1 H, 3-H$_{naph}$), 7.09 (dd, ^3J = 8.9 Hz, ^4J = 2.3 Hz, 1 H, 6-H$_{naph}$), 7.06 (d, ^4J = 2.3 Hz, 1 H, 8-H$_{naph}$), 6.62 (d, ^3J = 8.6 Hz, 2 H, 3,5-H$_{ph}$), 5.85 (ddt, ^3J = 16.9 Hz, ^3J = 10.3 Hz, ^3J = 6.6 Hz, 1 H, =CH_{naph}), 5.76 (ddt, ^3J = 16.9 Hz, ^3J = 10.2 Hz, ^3J = 6.6 Hz, 1 H#, =CH_{naph}), 5.72 (ddt, ^3J = 17.0 Hz, ^3J = 10.3 Hz, ^3J = 6.6 Hz, 2 H#, =CH_{ph}), 5.04 (ddt, ^3J = 17.1 Hz, ^2J = 1.7 Hz, ^4J = 1.6 Hz, 1 H, H_ZHC=$_{naph}$), 4.99–4.89 (m, 7 H, H_2C=$_{naph}$, H_EHC=$_{naph}$, H_2C=$_{ph}$), 4.19 (br. s, 2 H, OC$H_{2\,naph}$), 4.17 (t, ^3J = 6.7 Hz, 2 H, OC$H_{2\,naph}$), 4.07 (t, ^3J = 6.8 Hz, 4 H, OC$H_{2\,ph}$), 2.27 (m_c, 2 H, =CHC$H_{2\,naph}$), 2.17 (m_c, 2 H, =CHC$H_{2\,naph}$), 2.14 (m_c, 4 H, =CHC$H_{2\,ph}$), 1.95–1.88 (m, 8 H, OCH$_2$CH_2) ppm; no signal observed for 4,5-H$_{im}$. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C):[60] δ = 161.5 (C-2$_{im}$), 159.9 (C-7$_{naph}$), 154.3 (C-2,6$_{ph}$), 152.7 (C-2$_{naph}$), 137.9 (=*C*H$_{naph}$), 137.0 (=*C*H$_{naph}$), 136.9 (=*C*H$_{ph}$), 132.0 (C-8a$_{naph}$), 131.9 (C-4$_{ph}$), 131.1 (C-4$_{naph}$*), 130.4 (C-5$_{naph}$*), 124.2 (C-4a$_{naph}$), 117.2 (C-6$_{naph}$), 115.7 (H$_2$*C*=$_{naph}$), 115.7 (H$_2$*C*=$_{ph}$), 115.6 (C-1$_{naph}$), 115.0 (H$_2$*C*=$_{naph}$), 112.8 (C-1$_{ph}$), 110.3 (C-3$_{naph}$), 105.3 (C-3,5$_{ph}$), 100.3 (C-8$_{naph}$), 68.8 (O*C*H$_{2\,naph}$), 68.7 (O*C*H$_{2\,ph}$), 68.0 (O*C*H$_{2\,naph}$), 52.5, 52.3 (C-4,5$_{im}$), 30.1 (=CH*C*H$_{2\,naph}$), 30.0 (=CH*C*H$_{2\,ph}$), 29.9 (=CH*C*H$_{2\,naph}$), 28.5 (OCH$_2$*C*H$_{2\,naph}$), 28.3 (OCH$_2$*C*H$_{2\,naph}$), 28.1 (OCH$_2$*C*H$_{2\,ph}$) ppm. IR (KBr): $\tilde{\nu}$ = 3074, 2941, 2871, 1618, 1512, 1480, 1459, 1438, 1390, 1262, 1225, 1103,

990, 909, 829, 775, 728 cm^{-1}. HRMS (ESI, MeOH): calcd. for $C_{39}H_{49}N_2O_4$ 609.3687 [M]; found 609.3679.

1-[2,6-Bis(hex-5-enyloxy)phenyl]-3-[2,7-bis(pent-4-enyloxy)-1-naphthyl]-4,5-imidazolinium Chloride (15b). General Procedure E: *N*-[2,6-Bis(hex-5-enyloxy)phenyl])-*N*′-[2,7-bis(pent-4-enyloxy)-1-naphthyl)ethane-1,2-diamine (**14b**, 740 mg, 1.18 mmol), ammonium chloride (69 mg, 1.3 mmol) in triethyl orthoformate (5 mL, 30 mmol). Column chromatography [silica gel, dichloromethane/methanol (10:1), R_f = 0.19] yielded **15b** as a colorless solid (608 mg, 77% yield). M.p. 194 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 8.13 (s, 1 H, 2-H_{im}), 7.88 (d, ^3J = 9.0 Hz, 1 H, 4-H_{naph}), 7.77 (d, ^3J = 9.7 Hz, 1 H, 5-H_{naph}), 7.33 (t, ^3J = 8.5 Hz, 1 H, 4-H_{ph}), 7.16–7.12 (m, 3 H, 3,6,8-H_{naph}), 6.65 (d, ^3J = 8.6 Hz, 2 H, 3,5-H_{ph}), 5.89 (ddt, ^3J = 17.0 Hz, ^3J = 10.3 Hz, ^3J = 6.6 Hz, 1 H, =CH_{naph}), 5.80 (ddt, ^3J = 17.0 Hz, ^3J = 10.3 Hz, ^3J = 6.7 Hz, 1 H, =CH_{naph}), 5.66 (ddt, ^3J = 17.0 Hz, ^3J = 10.3 Hz, ^3J = 6.7 Hz, 2 H, =CH_{ph}), 5.08 (ddt, ^3J = 17.1 Hz, ^2J = 1.8 Hz, ^4J = 1.6 Hz, 1 H, H_ZHC=$_{naph}$), 5.03–4.97 (m, 3 H, H_2C=$_{naph}$, H_EHC=$_{naph}$), 4.91 (ddt, ^3J = 17.1 Hz, ^2J = 1.9 Hz, ^4J = 1.6 Hz, 2 H, H_ZHC=$_{ph}$), 4.88 (ddt, ^3J = 10.2 Hz, ^2J = 1.9 Hz, ^4J = 1.2 Hz, 2 H, H_EHC=$_{ph}$), 4.27 (br. s, 2 H, OC$H_{2\ naph}$), 4.20 (t, ^3J = 6.6 Hz, 2 H, OC$H_{2\ naph}$), 4.10 (t, ^3J = 6.8 Hz, 4 H, OC$H_{2\ ph}$), 2.32 (m_c, 2 H, =CHC$H_{2\ naph}$), 2.22 (m_c, 2 H, =CHC$H_{2\ naph}$), 2.04 (m_c, 4 H, =CHC$H_{2\ ph}$), 1.96 (m_c, 4 H, OCH$_2$C$H_{2\ naph}$), 1.85 (m_c, 4 H, OCH$_2$C$H_{2\ ph}$), 1.49 (m_c, 4 H, OCH$_2$CH$_2$C$H_{2\ ph}$) ppm; no signal for 4,5-H_{im} observed. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C):[60] δ = 161.5 (C-2$_{im}$), 159.9 (C-7$_{naph}$), 154.3 (C-2,6$_{ph}$), 152.7 (C-2$_{naph}$), 137.9 (=*C*H$_{naph}$), 137.9 (=*C*H$_{ph}$), 137.0 (=*C*H$_{naph}$), 132.0 (C-8a$_{naph}$), 131.9 (C-4$_{ph}$), 131.0 (C-4$_{naph}$*), 130.4 (C-5$_{naph}$*), 124.3 (C-4a$_{naph}$), 117.4 (C-6$_{naph}$), 115.8 (C-1$_{naph}$), 115.8 (H_2C=$_{naph}$), 115.0 (H_2C=$_{naph}$), 115.0 (H_2C=$_{ph}$), 112.9 (C-1$_{ph}$), 110.3 (C-3$_{naph}$), 105.2 (C-3,5$_{ph}$), 100.4 (C-8$_{naph}$), 69.2 (O*C*H$_{2\ ph}$), 68.7 (O*C*H$_{2\ naph}$), 68.1 (O*C*H$_{2\ naph}$), 52.6, 52.4 (C-4,5$_{im}$), 33.1 (=CH*C*H$_{2\ ph}$), 30.2 (=CH*C*H$_{2\ naph}$), 30.0 (=CH*C*H$_{2\ naph}$), 28.5 (OCH$_2$*C*H$_{2\ naph}$), 28.4 (OCH$_2$*C*H$_{2\ ph}$), 28.4 (OCH$_2$*C*H$_{2\ naph}$), 25.2 (OCH$_2$CH$_2$*C*H$_{2\ ph}$) ppm. IR (KBr): $\tilde{\nu}$ = 3074, 2945, 2865, 1619, 1514, 1480, 1464, 1390, 1265, 1226, 1145, 1106, 992, 908, 839, 775, 731 cm^{-1}. ESI-MS (MeOH): *m*/*z* (%) = 637.40 (100) $[C_{41}H_{53}N_2O_4]^+$. HRMS: calcd. for $C_{41}H_{53}N_2O_4$ 637.40051; found 637.40020 (δ = 0.5 ppm); calcd. for $C_{40}{}^{13}CH_{53}N_2O_4$ 638.40387; found 638.40340 (δ = 0.7 ppm). $C_{41}H_{53}ClN_2O_4$ (673.35): calcd. C 73.14, H 7.93, N 4.16. $C_{41}H_{53}ClN_2O_4{\cdot}CH_3OH$: calcd. C 71.52, H 8.15, N 3.97; found C 71.22, H 8.08, N 4.40.

2,11,13,22-Tetraoxa-1(1,3,2)-benzena-12(2,7,1)-naphthalena-23(1,3)-imidazoliniuma-bicyclo[10.10.1]tricosaphane-6,17-diene Chloride (16a). General Procedure F: 1-[2,6-Bis(pent-4-enyloxy)-phenyl]-3-[2,7-bis(pent-4-enyloxy)-1-naphthyl)-4,5-imidazolinium chloride (**15a**, 75 mg, 0.12 mmol), benzylidene-bis(tricyclohexylphosphane)dichlororuthenium (10 mg, 12 μmol) in dichloromethane (80 mL). Column chromatography [silica gel, dichloromethane/methanol (10:1), R_f = 0.21] yielded **16a** as a colorless solid (67 mg, 92% yield). M.p. 187–204 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C):[61] δ = 8.18 (s, 0.2 H, 2-H_{im}), 8.04 (s, 0.8 H, 2-H_{im}), 7.89 (m_c, 1 H, 4-H_{naph}), 7.75 (m_c, 1 H, 5-H_{naph}), 7.33 (m_c, 1 H, 4-H_{ph}), 7.18 (m_c, 1 H, 3-H_{naph}), 7.10 (m_c, 1 H, 6-H_{naph}), 7.06 (m_c, 1 H, 8-H_{naph}), 6.65 (m_c, 2 H, 3,5-H_{ph}), 5.51 (m_c, 4 H, *H*C=C*H*), 5.05–4.82 (m, 2 H, 4,5-$H_{a\ im}$), 4.73–4.45 (m, 2 H, 4,5-$H_{b\ im}$), 4.31 (m_c, 1 H, OC*H*H), 4.22 (m_c, 2 H, OC*H*H), 4.15 (m_c, 4 H, OC*H*H), 4.05 (m_c, 1 H, OC*H*H), 2.50–2.20 (m, 6 H, CH_2), 2.10–1.80 (m, 10 H, CH_2) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C):[61] δ = 162.2 (d), 161.5 (d), 160.5 (d), 159.7 (s), 159.5 (s), 154.7 (s), 154.4 (s), 154.3 (s), 153.8 (s), 153.1 (s), 153.0 (s), 132.8 (d), 132.1 (d), 132.0 (d), 132.0 (s), 131.8 (s), 131.2 (d), 131.2 (d), 130.5 (d), 130.3 (d), 130.3 (d), 130.3 (d), 130.2 (d), 129.6 (d), 129.4 (d), 129.4 (d), 129.2 (d), 129.2 (d), 129.1 (d), 123.9 (s), 117.3 (d), 117.3 (d), 117.2 (d), 114.9 (s), 112.5 (s), 110.1 (d), 110.0 (d), 110.0 (d), 105.7 (d), 105.2 (d), 105.1 (d), 105.1 (d), 104.7 (d), 99.7 (d), 99.3 (d), 69.6 (t), 69.2 (t), 68.7 (t), 68.5 (t), 67.2 (t), 66.9 (t), 66.7 (t), 52.1 (t), 52.0 (t), 51.8 (t), 29.7 (t), 29.6 (t), 29.2 (t), 29.2 (t), 29.1 (t), 28.5 (t), 28.1 (t), 27.7 (t), 27.6 (t), 27.4 (t), 24.2 (t), 23.8 (t), 23.4 (t), 23.2 (t), 22.9 (t) ppm. IR (KBr): $\tilde{\nu}$ = 2938, 2874, 1624, 1512, 1479, 1466, 1458, 1438, 1388, 1329, 1266, 1225, 1103, 979, 924, 830, 774, 730 cm^{-1}. HRMS (ESI, MeOH): calcd. for $C_{35}H_{41}N_2O_4$ 553.3061 [M]; found 553.3051.

2,12,14,24-Tetraoxa-1(1,3,2)-benzena-13(2,7,1)-naphthalena-25(1,3)-imidazoliniuma-bicyclo[11.11.1]pentacosaphane-7,18-diene Chloride (16b). General Procedure F: 1-[2,6-Bis(hex-5-enyloxy)-phenyl]-3-[2,7-bis(pent-4-enyloxy)-1-naphthyl)-4,5-imidazolinium chloride (**15b**, 550 mg, 817 μmol), benzylidene-bis(tricyclohexylphosphane)dichlororuthenium (80 mg, 0.10 mmol) in dichloromethane (500 mL). Column chromatography [silica gel, dichloromethane/methanol (10:1), R_f = 0.17], yielded **16b** as a colorless solid (463 mg, 92% yield). M.p. 173–181 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C):[61] δ = 8.20 (s, 0.32 H, 2-H_{im}), 8.14 (s, 0.08 H, 2-H_{im}), 8.06 (s, 0.14 H, 2-H_{im}), 8.04 (s, 0.44 H, 2-H_{im}), 7.86 (m_c, 1 H, 4-H_{naph}), 7.74 (m_c, 1 H, 5-H_{naph}), 7.31 (m_c, 1 H, 4-H_{ph}), 7.13 (m_c, 2 H, 3,6-H_{naph}), 7.05 (m_c, 1 H, 8-H_{naph}), 6.64 (m_c, 2 H, 3,5-H_{ph}), 5.46 (m_c, 4 H, *H*C=C*H*), 5.18 (m_c, 1 H, 5-$H_{a\ im}$), 5.00 (m_c, 1 H, 4-$H_{a\ im}$), 4.83 (m_c, 1 H, 5-$H_{b\ im}$), 4.40–3.90 (m, 9 H, 4-$H_{b\ im}$, OCH_2), 2.40–1.40 (m, 20 H, CH_2) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C):[61] δ = 161.9 (d), 161.5 (d), 161.2 (d), 160.9 (d), 160.3 (s), 160.2 (s), 160.2 (s), 160.2 (s), 160.0 (s), 155.4 (s), 155.2 (s), 154.8 (s), 154.7 (s), 154.6 (s), 154.1 (s), 154.1 (s), 153.4 (s), 154.1 (s), 152.8 (s), 152.8 (s), 152.5 (s), 132.4 (s), 132.3 (s), 132.1 (d), 132.1 (s), 132.1 (d), 132.0 (d), 132.0 (d), 132.0 (d), 131.9 (d), 131.6 (d), 131.5 (d), 131.3 (d), 131.3 (d), 131.2 (d), 130.9 (d), 130.8 (d), 130.7 (d), 130.6 (d), 130.5 (d), 130.4 (d), 130.2 (d), 130.2 (d), 130.1 (d), 130.1 (d), 130.1 (d), 130.1 (d), 129.9 (d), 129.9 (d), 129.7 (d), 129.1 (d), 129.0 (d), 124.2 (s), 124.1 (s), 124.0 (s), 118.8 (d), 117.8 (d), 117.5 (d), 115.6 (s), 115.6 (s), 115.4 (s), 115.4 (s), 115.4 (s), 115.4 (s), 112.8 (s), 112.7 (s), 112.4 (s), 112.4 (s), 112.0 (s), 112.0 (s), 110.6 (d), 110.4 (d), 110.1 (d), 110.1 (d), 105.3 (d), 105.1 (d), 105.1 (d), 105.0 (d), 104.9 (d), 104.9 (d), 104.7 (d), 99.8 (d), 99.6 (d), 98.0 (d), 69.6 (t), 69.5 (t), 69.4 (t), 69.1 (t), 69.0 (t), 69.0 (t), 69.0 (t), 67.5 (t), 67.3 (t), 67.3 (t), 67.2 (t), 66.2 (t), 66.0 (t), 52.6 (t), 52.5 (t), 52.3 (t), 52.2 (t), 52.1 (t), 52.1 (t), 52.0 (t), 31.4 (t), 31.2 (t), 31.1 (t), 31.0 (t), 29.6 (t), 29.5 (t), 28.7 (t), 28.7 (t), 28.6 (t), 28.6 (t), 28.5 (t), 28.5 (t), 28.5 (t), 28.4 (t), 28.4 (t), 28.3 (t), 27.9 (t), 27.8 (t), 27.7 (t), 27.6 (t), 27.5 (t), 27.5 (t), 27.4 (t), 27.2 (t), 27.0 (t), 27.0 (t), 26.6 (t), 26.5 (t), 26.4 (t), 25.6 (t), 25.2 (t), 25.2 (t), 25.1 (t), 24.4 (t), 24.1 (t), 24.1 (t), 24.0 (t), 23.2 (t), 23.2 (t) ppm. IR (KBr): $\tilde{\nu}$ = 3069, 2934, 2851, 1627, 1513, 1465, 1438, 1387, 1332, 1262, 1225, 1213, 1147, 1099, 969, 832, 776, 727, 647 cm^{-1}. HRMS (ESI, MeOH): calcd. for $C_{37}H_{45}N_2O_4$ 581.3374 [M]; found 581.3359.

2,11,13,22-Tetraoxa-1(1,3,2)-benzena-12(2,7,1)-naphthalena-23(1,3)-imidazoliniuma-bicyclo[10.10.1]tricosaphane Chloride (17a). General Procedure G: 2,11,13,22-Tetraoxa-1(1,3,2)-benzena-12(2,7,1)-naphthalena-23(1,3)-imidazoliniuma-bicyclo[10.10.1]-tricosaphane-6,17-diene chloride (**16a**, 60 mg, 0.10 mmol), palladium/charcoal (5 mg) in methanol (5 mL). Column chromatography [silica gel, dichloromethane/methanol (10:1), R_f = 0.19] yielded **17a** as a colorless solid (49 mg, 83% yield). M.p. 215 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C):[60] δ = 8.13 (s, 1 H, 2-H_{im}), 7.90 (d, ^3J = 9.0 Hz, 1 H, 4-H_{naph}), 7.83 (d, ^3J = 9.0 Hz, 1 H, 5-H_{naph}), 7.33 (dd, ^3J = 8.5 Hz, ^3J = 8.5 Hz, 1 H, 4-H_{ph}), 7.19 (d, ^3J = 9.1 Hz, 1 H, 3-H_{naph}), 7.18 (dd, ^3J = 9.0 Hz, ^4J = 2.4 Hz, 1 H, 6-H_{naph}), 7.14 (d, ^4J = 2.3 Hz, 1 H, 8-H_{naph}), 6.65 (br. d, ^3J = 8.5 Hz, 1 H$^{\#}$, 3-H_{ph}*), 6.64 (br. d, ^3J = 8.6 Hz, 1 H$^{\#}$, 5-H_{ph}*), 4.99

(m_c, 1 H, 5-$H_{a\ im}$), 4.88 (m_c, 1 H, 4-$H_{a\ im}$), 4.64 (m_c, 1 H, 5-$H_{b\ im}$), 4.50 (m_c, 1 H, 4-$H_{b\ im}$), 4.31 (m_c, 2 H, OC*H*H), 4.22 (m_c, 1 H, OC*H*H), 4.17 (m_c, 1 H, OC*H*H), 4.12 (m_c, 3 H, OC*H*H), 3.99 (m_c, 1 H, OC*H*H), 1.95–1.75 (m, 8 H, CH_2), 1.70–1.37 (m, 16 H, CH_2) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C):[60] δ = 160.9 (C-2_{im}), 159.6 (C-7_{naph}), 155.0 (C-2_{ph}*), 154.3 (C-6_{ph}*), 153.5 (C-2_{naph}), 132.3 (C-4_{naph}), 132.0 (C-$8a_{naph}$), 131.3 (C-4_{ph}), 130.7 (C-5_{naph}), 124.1 (C-$4a_{naph}$), 114.7 (C-6_{naph}), 114.6 (C-1_{naph}), 112.4 (C-1_{ph}), 110.6 (C-3_{naph}), 105.0 (C-3_{ph}*), 104.9 (C-5_{ph}*), 102.5 (C-8_{naph}), 70.1 (O*C*H$_2$), 69.9 (O*C*H$_2$), 68.8 (O*C*H$_2$), 68.6 (O*C*H$_2$), 52.2 (C-5_{im}*), 52.1 (C-4_{im}*), 28.6, 28.3, 28.1, 27.1, 26.9, 26.7, 26.2, 25.6, 24.3, 24.2, 24.0 (*C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2937, 2854, 1624, 1514, 1459, 1388, 1330, 1261, 1224, 1100, 832, 778 cm^{-1}. HRMS (ESI, MeOH): calcd. for $C_{35}H_{45}N_2O_4$ 557.3374 [M]; found 557.3380.

2,12,14,24-Tetraoxa-1(1,3,2)-benzena-13(2,7,1)-naphthalena-25(1,3)-imidazoliniuma-bicyclo[11.11.1]pentacosaphane Chloride (17b). General Procedure G: 2,12,14,24-Tetraoxa-1(1,3,2)-benzena-13(2,7,1)-naphthalena-25(1,3)-imidazoliniuma-bicyclo[11.11.1]-pentacosaphane-7,18-diene chloride (**16b**, 365 mg, 592 μmol), palladium/charcoal (15 mg) in methanol (15 mL). Column chromatography [silica gel, dichloromethane/methanol (10:1), R_f = 0.17] yielded **17b** as a colorless solid (331 mg, 90% yield). M.p. 218 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C):[60] δ = 8.27 (s, 1 H, 2-H_{im}), 7.89 (d, ^3J = 9.0 Hz, 1 H, 4-H_{naph}), 7.80 (d, ^3J = 9.0 Hz, 1 H, 5-H_{naph}), 7.32 (dd, ^3J = 8.5 Hz, ^3J = 8.5 Hz, 1 H, 4-H_{ph}), 7.18 (d, ^3J = 9.1 Hz, 1 H, 3-H_{naph}), 7.15 (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}), 6.66 (br. d, ^3J = 8.5 Hz, 1 H$^{\#}$, 3-H_{ph}*), 6.65 (br. d, ^3J = 8.5 Hz, 1 H$^{\#}$, 5-H_{ph}*), 5.09 (m_c, 1 H, 5-$H_{a\ im}$), 5.00 (m_c, 1 H, 4-$H_{a\ im}$), 4.71 (m_c, 1 H, 5-$H_{b\ im}$), 4.37 (m_c, 1 H, 4-$H_{b\ im}$), 4.30 (m_c, 2 H, OC*H*H), 4.20 (m_c, 3 H, OC*H*H), 4.12 (m_c, 1 H, OC*H*H), 4.07 (m_c, 2 H, OC*H*H), 1.98–1.77 (m, 8 H, CH_2), 1.65–1.55 (m, 4 H, CH_2), 1.55–1.35 (m, 16 H, CH_2) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C):[60] δ = 161.0 (C-2_{im}), 160.0 (C-7_{naph}), 154.6 (C-2_{ph}*), 153.5 (C-6_{ph}*), 152.9 (C-2_{naph}), 132.2 (C-4_{naph}), 132.0 (C-$8a_{naph}$), 130.9 (C-4_{ph}), 130.6 (C-5_{naph}), 124.1 (C-$4a_{naph}$), 116.3 (C-6_{naph}), 114.9 (C-1_{naph}), 113.1 (C-1_{ph}), 110.2 (C-3_{naph}), 105.3 (C-3_{ph}*), 104.9 (C-5_{ph}*), 100.8 (C-8_{naph}), 69.6 (O*C*H$_2$), 69.4 (O*C*H$_2$), 69.3 (O*C*H$_2$), 67.6 (O*C*H$_2$), 52.5 (C-5_{im}), 52.1 (C-4_{im}), 29.2, 28.7, 28.1, 27.3, 27.3, 27.2, 27.1, 27.0, 26.6, 25.9, 25.7, 25.0, 24.3, 23.7 (*C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2930, 2853, 1627, 1512, 1461, 1390, 1263, 1225, 1148, 1097, 982, 925, 832, 776, 725, 636 cm^{-1}. ESI-MS (MeOH): *m*/*z* (%) = 585.37 (100) $[C_{37}H_{49}N_2O_4]^+$. HRMS: calcd. for $C_{37}H_{49}N_2O_4$ 585.36926; found 585.36922 (δ = 0.1 ppm); calcd. for $C_{36}{}^{13}CH_{49}N_2O_4$ 586.37256; found 586.37260 (δ = 0.1 ppm).

X-ray Crystal Structure Determination of 17b: Suitable crystals were grown by diffusion of diethyl ether into a solution of **17b** in 1,2-dichloroethane. Empirical formula $C_{37}H_{49}ClN_2O_4$, *MW* = 621.23 g/mol, *a* = 20.5926(16) Å, *b* = 7.487(4) Å, *c* = 22.0092(16) Å, β = 93.348(9)°, *V* = 3387.7(4) Å^3, *T* = 220(2) K, $\rho_{calcd.}$ = 1.218 g/cm^3, μ = 0.154 mm^{-1}, monoclinic, space group $P2_1/n$, *Z* = 4, STOE Imaging Plate Diffraction System (IPDS-1), Mo-K_α (λ = 0.71073 Å), 20540 measured reflections in the range of 5° ≤ 2θ ≤ 50°, 5841 independent reflections used for refinement, R_{int} = 0.0489. Structure solution was done with SHELXS-97. Structure refinement was performed against F^2 using SHELXL-97; 397 parameters, R_1 for all 3958 reflections with $F_o > 4\sigma(F_o)$ = 0.0481, wR_2 for all 5841 reflections = 0.1310, GoF = 1.022, residual electron density 0.33/–0.27 e/Å^3. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and refined isotropic using a riding model. The crystal structure data have been deposited at the Cambridge Crystallographic Data Centre. CCDC-642189 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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[60] #: The signals coincide, so only the total integration of the coinciding protons could be determined. *: Assignments may be interchanged; subscripts are used to differentiate between atoms/groups which are part of/bound to naphthyl ($_{naph}$), phenyl ($_{ph}$) or imidazolinium ($_{im}$) where needed.
[61] Because of the formation of (*Z*) and (*E*) double bonds in the metathesis, four diastereomers may be formed: (*Z,Z*), (*Z,E*), (*E,Z*) and (*E,E*).

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