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

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Concave bimacrocyclic imidazolinium ions **8** have been synthesized as precursors for N-heterocyclic carbenes **9** (NHC) in 13 to 29% overall yields based on 2-nitroresorcinol (**1**). As bridgeheads, 2,6-bis(ω-alkenyloxy)anilines **3** have been synthesized from **1**. Reaction of **3** with oxalyl chloride, reduction to respective diamines **5**, and ring closure with triethyl orthoformate gave *N*,*N*-diaryl-substituted imidazolinium ions **6**. The terminal vinyl groups were connected by ring-closing metathesis to give bimacrocyclic imidazolinium ions **7**, whose alkene functions were hydrogenated to give saturated bimacrocyles **8**. The structure of **8a** was elucidated by X-ray analysis. The respective NHC **9** was generated by deprotonation with potassium *tert*-butoxide, and **9** was scavenged with CS_2 to give adduct **10**.

Introduction

In 1958, Breslow[1] elucidated the nature of the "active aldehyde" in thiamine-dependent biochemical transformations[2] and suggested nucleophilic catalysis. He postulated that by deprotonation of thiamine's thiazolium unit in the 2-position, a betaine was formed which acted as the nucleophile. Later, Wanzlick[3,4] and Arduengo[5] synthesized nucleophilic stable carbenes derived from imidazolinium or imidazolium ions. Their activity in nucleophilic catalysis was also shown and has been reviewed recently.[6,7] All reactive species have in common that their nature can be described by two mesomeric forms, a betaine, as published by Breslow, or a carbene, as described by Wanzlick and Arduengo. Triazols can also be used as precursors to nucleophilic catalysts.[7]

Besides their catalytic power as nucleophilic organocatalysts,[6,9–18] the carbenes of Figure 1 may also be employed as ligands for transition metal catalysis,[8,19,20] the 2nd generation of Grubbs' catalyst being a prominent example.[21]

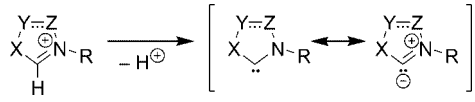

Figure 1. N-Heterocycles are the precursors for N-heterocyclic carbenes (NHC) which are also drawn in their mesomeric betaine form.[8] Examples: thiazolium: X = S, Y = Z = CR′, imidazolium: X = NR′′, Y = Z = CR′, imidazolinium: X = NR′′, Y = Z = CR'_2, triazolium: X = NR′′, Y = N, Z = CR′.

In enzymes, the thiamine unit is embedded into the cavity of an enzyme. This geometry is responsible for the selectivity of the enzymatic reaction. In principle, an N-heterocyclic carbene (NHC), or its precursor, respectively, can also be embedded in a suitable shielding which in return shall be responsible for enhanced selectivities in the reactions catalyzed by the NHC. By applying the concept of concave reagents, we envisaged a bimacrocyclic NHC as depicted in Figure 2 and developed a synthetic route to respective substituted imidazolinium[22] ions.

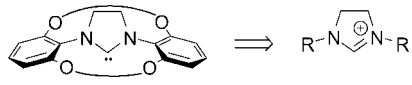

Figure 2. Schematic representation of a bimacrocyclic concave N-heterocyclic carbene which may be obtained from respective imidazolinium ions.

Several strategies are conceivable to construct a concave bimacrocycle which contains an imidazolium or an imidazolinium moiety as a precursor for an N-heterocyclic carbene as shown in Figure 2. All strategies must provide (1) access to the trisubstituted aryl bridgeheads, (2) a bimacro-

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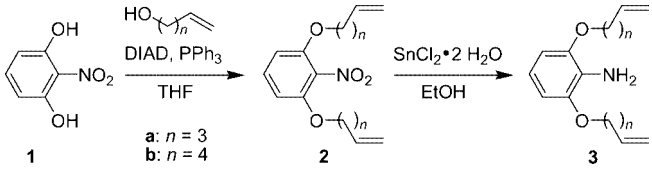
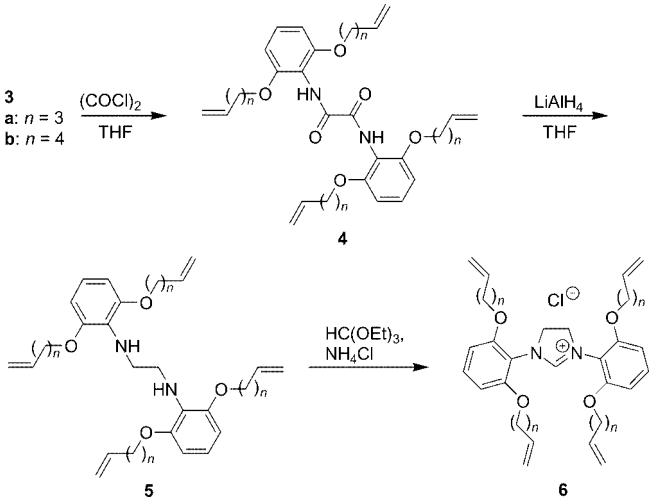
cyclization strategy, and (3) a suitable synthesis of the heterocycle. We have selected ruthenium catalyzed metathesis for the ring closure to provide the bimacrocycle because such bimacrocyclizations have proven to be very successful for the synthesis of a number of concave reagents.[23–25] Thus a precursor is demanded which contains the aryl bridgeheads and the heterocycle. Prominent strategies[26–29] for the synthesis of imidazolium and imidazolinium ions start from anilines which are condensed with a C_2 and a C_1 unit ending up in the heterocycle as carbon atoms 4 and 5, and carbon atom 2, respectively.

Thus, the first task was to synthesize respective bis-*ortho*-substituted anilines **3**. In a two-step reaction, **3a** and **3b** can be obtained from commercially available 2-nitroresorcinol (**1**) in 67% and 47% overall yield, respectively. The reaction sequence first uses the Mitsunobu coupling of the phenol OH groups of **1** with the respective ω-alkenols. Resulting nitroarenes **2** can then be reduced to anilines **3** by tin(II) chloride.



Next, 2 equiv. of anilines **3** were connected by oxalyl chloride to give diamides **4a** and **4b** in 87% and 52% yield, respectively. Reduction with lithium aluminium hydride afforded diamines **5a** and **5b** in 80% and 90% yield, respectively. In the final step towards imidazolinium ions **6**, the nitrogen atoms of **5** were connected with triethyl orthoformate. Resulting salts **6a** and **6b** were isolated in 83% and 73% yield, respectively.



In imidazolinium ions **6**, two functionalized aryl bridgeheads are now bound to the central heterocycle. With the use of the well-established reaction conditions for macrocyclizations of concave reagents by ring-closing metathesis,[23–25] the ω-alkene units were now connected by adding Grubbs' catalyst. In 81% and 92% yield, respectively, bimacrocycles **7a** and **7b** could be isolated. As with other related macrocycles,[23–25] the new double bonds are formed with (*E*) and (*Z*) configurations. To simplify the products, the double bonds were subsequently hydrogenated in 91% and 88% yield, respectively. Bimacrocyclic concave imidazolinium salts **8** were characterized, and the structure of **8a** was proven by X-ray analysis.

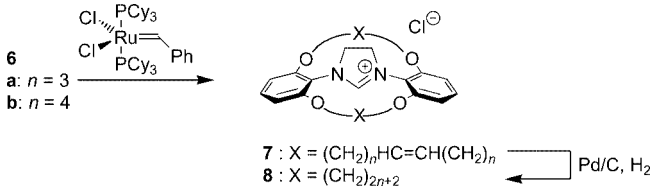
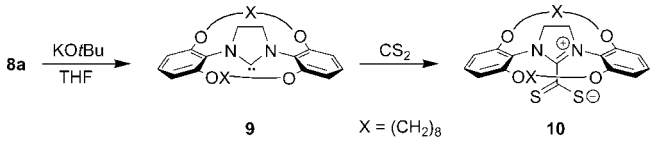


Figure 3 shows that the imidazolinium ion of **8a** adopts a C_2 symmetrical structure in the solid state. This contrasts the data in solution. As apparent in the time-averaged NMR spectra, the cation of **8a** possesses two mirror planes: one mirror plane is identical with the averaged plane of the imidazolinium heterocycle, the other mirror plane is orthogonal to it cutting the first plane through C1 and in the middle of the bond between C2 and C2A (for numbering see Figure 3). In the crystal structure, however, the ion is distorted: (1) the imidazolinium ring is not planar, (2) the twist angles between the aryl bridgeheads and the plane through N1–C1–N1A are not 90° as expected from NMR but 54°. Similar twists between aromatic rings and the heterocycles of imidazolium or imidazolinium ions or even NHCs derived therefrom have been observed frequently.[30–32] In **8a**, the torque is rather large. A view of the whole structure, including counterion and solvent molecules, shows that the chloroform molecules fit nicely into the octamethylene chains only with the existing twist. This complementarity is probably responsible for the unusual torque between the heterocycle and the aryl rings.

Finally, imidazolinium salt **8a** was treated with potassium *tert*-butoxide in THF to generate N-heterocyclic carbene **9**. As proof of its existence, the reaction mixture was treated with carbon disulfide and adduct **10** was isolated. The ^{13}C-NMR signals for C-2 and CS_2 appear at δ = 166.0 and 221.3 ppm, respectively. The composition ($C_{32}H_{42}N_2O_4S_2$) was determined from an ESI mass spectrum (deviation from calculated values 0.2 to 1.5 ppm, see Experimental Section). According to ^{1}H NMR spectroscopic analysis, the product contained approximately 0.5 equiv. of THF.



Conclusions

Two concave imidazolinium salts, **8a** and **8b**, have been synthesized in seven steps starting from 2-nitroresorcinol in 29% and 13% (nonoptimized) overall yield. By deprotonation, the respective N-heterocyclic carbenes can be generated, which was proven for **9** by scavenging it with CS_2.

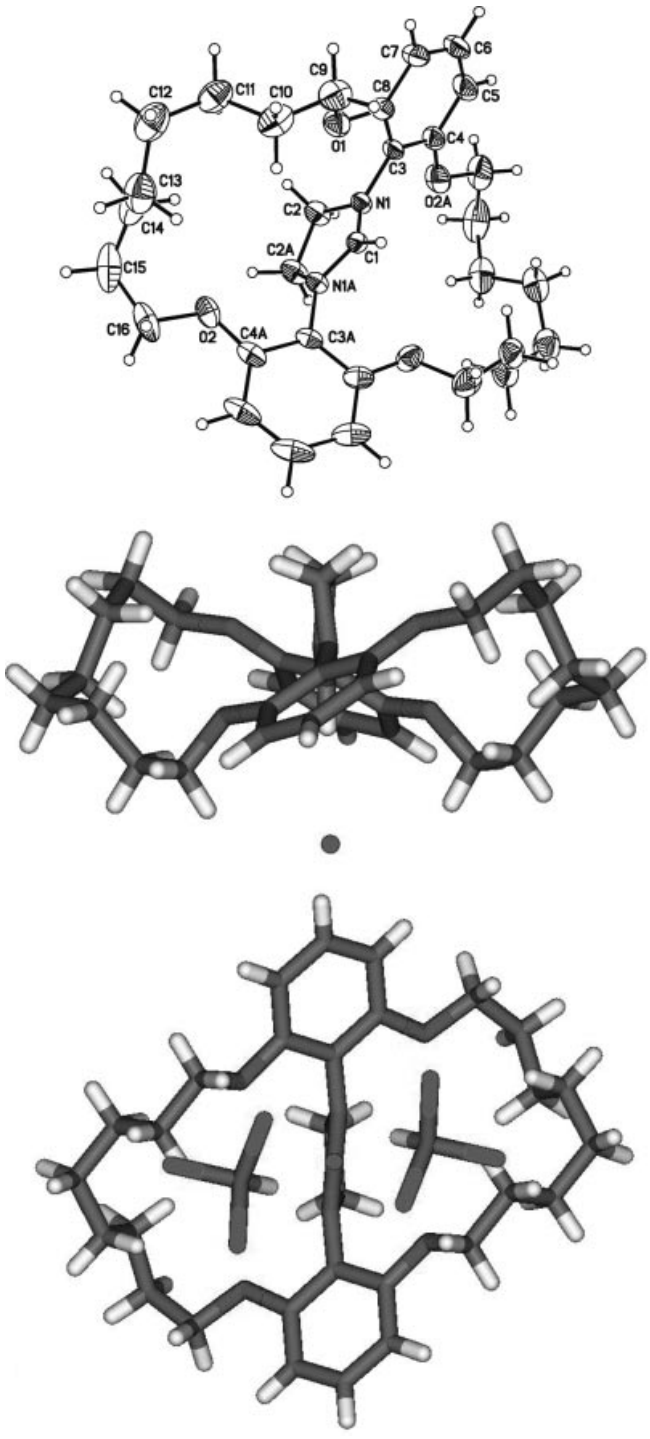


Figure 3. Crystal structure of **8a**. Top: View into the cavity from below showing the bimacrocyclic structure of the cation. The chloride counterion is omitted. Middle: View of the cation along an axis bridgehead 1–imidazolinium unit–bridgehead 2. The C_2 symmetry and the 54° twist of the aryl rings with respect to the N1–C1–N1A plane are clearly visible. The position of the chloride counterion next to C1 becomes visible. Bottom: view of the imidazolinium ion along an axis through the middle of the C2–C2A bond and atom C1. This structure also shows the positions of two additional chloroform molecules. They are in contact with the chloride counterion which obscures C1. Again the C_2 symmetry and the twist within the molecule can clearly be detected.

Because of concave shielding, these modified NHCs should be able to enhance selectivities in reactions that are catalyzed by NHCs as organocatalysts, but also in metal-catalyzed reactions in which NHCs can be used as ligands. With **8a** and **8b**, chemo-, regio-, and diastereoselectivity can be expected. In order to tackle enantioselectivity, the synthesis of chiral concave NHCs is underway.

Experimental Section

General Remarks: The following chemicals were obtained commercially and used without further purification: benzylidenebis(tricyclohexylphosphane)dichlororuthenium (Aldrich), carbon disulfide (Fluka), diisopropylazodicarboxylate (Fluka), 5-hexen-1-ol (Merck), lithium aluminium hydride (Merck), 2-nitroresorcinol (Alfa Aesar), oxalyl chloride (Fluka), palladium/charcoal (10% Pd) (Merck), 4-penten-1-ol (Alfa Aesar), potassium *tert*-butoxide (Acros), stannous chloride dihydrate (Fluka), triethyl orthoformate (Merck), triphenylphosphane (Fluka). Tetrahydrofuran was dried by heating at reflux with lithium aluminium 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 a Bruker ARX 300, DRX 500, or AV 600 instrument. IR spectra were recorded with a Perkin–Elmer Paragon 1000. Mass spectra were recorded with a Finnigan MAT 8200 or MAT 8230. ESI mass spectra were recorded with an Applied Biosystems Mariner Spectrometry Workstation. Elemental analyses were carried out with an EuroEA 3000 Elemental Analyzer from Euro Vector or VarioEL from Elementaranalysensysteme. As alternative proof of composition, high resolution mass spectra were recorded for samples which were pure according to NMR spectra.

General Procedure A – Synthesis of Nitrobenzenes 2: 2-Nitroresorcinol (**1**, 1 equiv.), the respective alkenol (3 equiv.), and triphenylphosphane (2 equiv.) were dissolved in tetrahydrofuran. At 0 °C, diisopropylazodicarboxylate (3 equiv.) was slowly added, and the mixture was stirred at room temp. for 20 h. Sodium hydroxide solution (0.5 N) was added, the layers were separated, and the aqueous layer was extracted with diethyl ether. The organic layer was dried with magnesium sulfate and concentrated, keeping the triphenylphosphane oxide in solution. The product was purified by column chromatography on silica gel.

General Procedure B – Synthesis of Anilines 3: Nitrobenzene **2** was heated at reflux in ethanol with stannous chloride dihydrate (7 equiv.) for 3 h. After cooling to room temp., the mixture was poured into ice water and potassium hydroxide was added. After extraction with dichloromethane, the organic layer was dried with magnesium sulfate and the solvents evaporated to dryness. The product was purified by column chromatography on silica gel.

General Procedure C – Synthesis of Oxalamides 4: Aniline **3** was dissolved in tetrahydrofuran and cooled to 0 °C. Oxalyl chloride (0.5 equiv.) was slowly added, the mixture was warmed to room temp., and stirred for 1 h. After addition of water, the layers were separated, and the aqueous layer was extracted with dichloromethane. The organic layer was dried with magnesium sulfate, and the solvents evaporated to dryness. The product was purified by column chromatography on silica gel.

General Procedure D – Synthesis of Ethane-1,2-diamines 5: Oxalamide **4** was dissolved in tetrahydrofuran and added slowly to a

suspension of lithium aluminium hydride (10 equiv.) in tetrahydrofuran at 0 °C. The mixture was then heated at reflux for 5 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 evaporated to dryness. The product was purified by column chromatography on alumina.

General Procedure E – Synthesis of Imidazolinium Chlorides 6: Ethane-1,2-diamine **5** was heated to 110 °C with ammonium chloride (1.2 equiv.) in triethyl orthoformate (10 equiv.) for 3 h under a nitrogen flow to remove ethanol. After cooling to room temp., the product was filtered off and purified by column chromatography on silica gel.

General Procedure F – Synthesis of Imidazoliniumabicyclophan Chlorides 7: Imidazolinium chloride **6** was stirred with benzylidenbis(tricyclohexylphosphane)dichlororuthenium (10 mol-%) in dichloromethane at room temp. for 24 h. After evaporation to dryness, the product was purified by column chromatography on silica gel.

General Procedure G – Synthesis of Imidazoliniumabicyclophan Chlorides 8: Imidazolinium chloride **7** was stirred with palladium/charcoal (10% Pd) in methanol under an atmosphere of hydrogen at room temp. for 24 h. After filtration and evaporation to dryness, the product was purified by column chromatography on silica gel.

2-Nitro-1,3-bis(pent-4-enyloxy)benzene (2a): General procedure **A**: 2-Nitroresorcinol (**1**, 3.00 g, 19.4 mmol), 4-penten-1-ol (5.00 g, 58.0 mmol), triphenylphosphane (10.2 g, 38.8 mmol), DIAD (11 mL, 58 mmol) in tetrahydrofuran (100 mL). Work up: Sodium hydroxide solution (0.5 N, 75 mL), extraction with diethyl ether (2 × 100 mL). Column chromatography [silica gel, cyclohexane/ethyl acetate (7:1), R_f = 0.36] yielded oily colorless product **2a** (4.70 g, 82%). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.27 (t, ^3J = 8.5 Hz, 1 H, 5-H), 6.58 (d, ^3J = 8.6 Hz, 2 H, 4-H, 6-H), 5.80 (ddt, ^3J = 17.0 Hz, ^3J = 10.3 Hz, ^3J = 6.7 Hz, 2 H, =C*H*), 5.05 (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=), 4.04 (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. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 151.2 (*C*-1,3), 137.4 (=*C*H), 132.5 (*C*-2), 130.9 (*C*-5), 115.5 (H_2C=), 105.2 (*C*-4,6), 68.5 (O*C*H$_2$), 29.8 (=CH*C*H$_2$), 27.9 (OCH$_2$*C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3078, 2945, 1641, 1611, 1586, 1536, 1483, 1466, 1375, 1263, 1105, 995, 916, 851, 778, 733 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 245 (70), 203 (8), 189 (7), 177 (15), 155 (15), 137 (36), 109 (44), 69 (100). MS (CI): *m*/*z* (%) = 292 (9) [M + H]$^+$.

1,3-Bis(hex-5-enyloxy)-2-nitrobenzene (2b): General procedure **A**: 2-Nitroresorcinol (**1**, 4.00 g, 25.8 mmol), 5-hexen-1-ol (7.7 g, 77 mmol), triphenylphosphane (13.5 g, 51.6 mmol), DIAD (15 mL, 77 mmol) in tetrahydrofuran (100 mL). Work up: Sodium hydroxide solution (0.5 N, 100 mL), extraction with diethyl ether (2 × 100 mL). Column chromatography [silica gel, cyclohexane/ethyl acetate (7:1), R_f = 0.44] yielded oily colorless product **2b** (6.37 g, 78%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.26 (t, ^3J = 8.5 Hz, 1 H, 5-H), 6.58 (d, ^3J = 8.5 Hz, 2 H, 4-H, 6-H), 5.80 (ddt, ^3J = 17.0 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 = 10.1 Hz, ^2J = 2.1 Hz, ^4J = 1.2 Hz, 2 H, H_EHC=), 4.04 (t, ^3J = 6.4 Hz, 4 H, OCH_2), 2.09 (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. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 151.3 (*C*-1,3), 138.3 (=*C*H), 130.8 (*C*-5), 114.9 (H_2C=), 105.2 (*C*-4,6), 69.3 (O*C*H$_2$), 33.2 (=CH*C*H$_2$), 28.3 (OCH$_2$*C*H$_2$), 25.0 (OCH$_2$CH$_2$*C*H$_2$) ppm. *C*-2 was not observed. IR (KBr): $\tilde{\nu}$ = 3077, 2942, 1640, 1612, 1586, 1537, 1483, 1466, 1375, 1262, 1105, 994, 912, 852, 778, 733 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 319 (1) [M]$^+$, 273 (67), 155 (39), 137 (52), 109 (53), 81 (100), 67 (81). MS (CI): *m*/*z* (%) = 320 (4) [M + H]$^+$.

2,6-Bis(pent-4-enyloxy)aniline (3a): General procedure **B**: 2-Nitro-1,3-bis(pent-4-enyloxy)benzene (**2a**, 4.42 g, 15.2 mmol), stannous chloride dihydrate (23.9 g, 106 mmol) in ethanol (60 mL). Work up: Potassium hydroxide (100 g), extraction with dichloromethane (2 × 200 mL). Column chromatography [silica gel, cyclohexane/ethyl acetate (10:1), R_f = 0.43] yielded crystalline colorless product **3a** (3.25 g, 82%). M.p. 34 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.64 (t, ^3J = 8.2 Hz, 1 H, 4-H), 6.51 (d, ^3J = 8.2 Hz, 2 H, 3-H, 5-H), 5.87 (ddt, ^3J = 17.1 Hz, ^3J = 10.2 Hz, ^3J = 6.6 Hz, 2 H, =C*H*), 5.08 (ddt, ^3J = 17.1 Hz, ^2J = 1.9 Hz, ^4J = 1.6 Hz, 2 H, H_ZHC=), 5.01 (ddt, ^3J = 10.2 Hz, ^2J = 1.9 Hz, ^4J = 1.2 Hz, 2 H, H_EHC=), 4.02 (t, ^3J = 6.4 Hz, 4 H, OCH_2), 3.84 (br. s, 2 H, NH_2), 2.26 (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 = 146.9 (*C*-2,6), 137.9 (=*C*H), 125.9 (*C*-1), 116.8 (*C*-4), 115.1 (H_2C=), 105.1 (*C*-3,5), 67.8 (O*C*H$_2$), 30.3 (=CH*C*H$_2$), 28.6 (OCH$_2$*C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3461, 3371, 3073, 2951, 2872, 1640, 1609, 1507, 1469, 1397, 1294, 1269, 1181, 1140, 1060, 999, 913, 757, 714 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 261 (100) [M]$^+$, 193 (25), 125 (84), 69 (31). MS (CI): *m*/*z* (%) = 262 (14) [M + H]$^+$. $C_{16}H_{23}NO_2$ (261.36): calcd. C 73.53, H 8.87, N 5.36; found C 73.48, H 9.00, N 5.46.

2,6-Bis(hex-5-enyloxy)aniline (3b): General procedure **B**: 1,3-Bis-(hex-5-enyloxy)-2-nitrobenzene (**2b**, 2.50 g, 7.84 mmol), stannous chloride dihydrate (14 g, 63 mmol) in ethanol (30 mL). Work up: Potassium hydroxide (50 g), extraction with dichloromethane (3 × 100 mL). Column chromatography [silica gel, cyclohexane/ethyl acetate (20:1), R_f = 0.18] yielded oily colorless product **3b** (1.37 g, 60%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.63 (t, ^3J = 8.2 Hz, 1 H, 4-H), 6.49 (d, ^3J = 8.2 Hz, 2 H, 3-H, 5-H), 5.82 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 2 H, =C*H*), 5.03 (ddt, ^3J = 17.1 Hz, ^2J = 2.0 Hz, ^4J = 1.6 Hz, 2 H, H_ZHC=), 4.97 (ddt, ^3J = 10.2 Hz, ^2J = 2.0 Hz, ^4J = 1.2 Hz, 2 H, H_EHC=), 3.99 (t, ^3J = 6.5 Hz, 4 H, OCH_2), 3.81 (br. s, 2 H, NH_2) 2.13 (m_c, 4 H, =CHCH_2), 1.82 (m_c, 4 H, OCH$_2$CH_2), 1.58 (m_c, 4 H, OCH$_2$CH$_2$CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 146.9 (*C*-2,6), 138.5 (=*C*H), 125.8 (*C*-1), 116.8 (*C*-4), 114.7 (H_2C=), 105.0 (*C*-3,5), 69.3 (O*C*H$_2$), 33.4 (=CH*C*H$_2$), 28.9 (OCH$_2$*C*H$_2$), 25.4 (OCH$_2$CH$_2$*C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3482, 3386, 3076, 2938, 2869, 1640, 1607, 1566, 1504, 1469, 1390, 1293, 1180, 1145, 1073, 995, 910, 759, 713 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 289 (80) [M]$^+$, 207 (17), 125 (100). MS (CI): *m*/*z* (%) = 290 (100) [M + H]$^+$. HRMS: calcd. for $C_{18}H_{27}NO_2$ 289.20419; found 289.20416 (0.1 ppm); calcd. for $C_{17}{}^{13}CH_{27}NO_2$ 290.20752; found 290.20752 (0 ppm).

***N*,*N*′-Bis[2,6-bis(pent-4-enyloxy)phenyl]oxaldiamide (4a):** General procedure **C**: 2,6-Bis(pent-4-enyloxy)aniline (**3a**, 2.33 g, 8.90 mmol), oxalyl chloride (0.36 mL, 4.3 mmol) in tetrahydrofuran (10 mL). Work up: Water (8 mL), extraction with dichloromethane (3 × 30 mL). Column chromatography [silica gel, cyclohexane/ethyl acetate (3:1), R_f = 0.49] yielded colorless crystalline product **4a** (2.15 g, 87%). M.p. 111 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 8.75 (s, 2 H, N*H*), 7.17 (t, ^3J = 8.4 Hz, 2 H, 4-H), 6.58 (d, ^3J = 8.5 Hz, 4 H, 3-H, 5-H), 5.82 (ddt, ^3J = 17.0 Hz, ^3J = 10.3 Hz, ^3J = 6.7 Hz, 4 H, =C*H*), 5.04 (ddt, ^3J = 17.1 Hz, ^2J = 1.9 Hz, ^4J = 1.6 Hz, 4 H, H_ZHC=), 5.01 (ddt, ^3J = 10.3 Hz, ^2J = 1.9 Hz, ^4J = 1.1 Hz, 4 H, H_EHC=), 4.01 (t, ^3J = 6.5 Hz, 8 H, OCH_2), 2.21 (m_c, 8 H, =CHCH_2), 1.87 (m_c, 8 H, OCH$_2$CH_2) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 157.8 (*C*=O), 154.5 (*C*-2,6), 137.8 (=*C*H), 127.9 (*C*-4), 115.2 (H_2C=), 113.2 (*C*-1), 105.1 (*C*-3,5), 67.9

(OCH_2), 30.0 (=CHCH_2), 28.3 (OCH_2CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 3273, 3073, 2944, 2864, 1680, 1639, 1600, 1513, 1450, 1393, 1261, 1106, 910, 802, 758, 715 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 576 (42) $[M]^+$, 491 (8), 261 (100). MS (CI): *m*/*z* (%) = 577 (100) $[M + H]^+$. HRMS: calcd. for $C_{34}H_{44}N_2O_6$ 576.31995; found 576.32021 (0.5 ppm); calcd for $C_{33}{}^{13}CH_{44}N_2O_6$ 577.32330; found 577.32317 (0.2 ppm). $C_{34}H_{44}N_2O_6$ (576.73): calcd. C 70.81, H 7.69, N 4.86; found C 70.81, H 7.84, N 4.98.

***N*,*N*′-Bis[2,6-bis(hex-5-enyloxy)phenyl]oxaldiamide (4b):** General procedure **C**: 2,6-Bis(hex-5-enyloxy)aniline (**3b**, 1.59 g, 5.51 mmol), oxalyl chloride (0.23 mL, 2.7 mmol) in tetrahydrofuran (5 mL). Work up: Water (6 mL), extraction with dichloromethane (3 × 20 mL). Column chromatography [silica gel, cyclohexane/ethyl acetate (2:1), R_f = 0.69] yielded colorless crystalline product **4b** (891 mg, 52%). M.p. 97 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.72 (s, 2 H, N*H*), 7.16 (t, ^3J = 8.4 Hz, 2 H, 4-H), 6.58 (d, ^3J = 8.4 Hz, 4 H, 3-H, 5-H), 5.79 (ddt, ^3J = 17.0 Hz, ^3J = 10.2, ^3J = 6.6 Hz, 4 H, =C*H*), 5.00 (ddt, ^3J = 17.1 Hz, ^2J = 2.0 Hz, ^4J = 1.6 Hz, 4 H, H_ZHC=), 4.93 (ddt, ^3J = 10.2 Hz, ^2J = 2.0 Hz, ^4J = 1.2 Hz, 4 H, H_EHC=), 4.01 (t, ^3J = 6.6 Hz, 8 H, OCH_2), 2.09 (m_c, 8 H, =CHCH_2), 1.79 (m_c, 8 H, OCH_2CH_2), 1.54 (m_c, 8 H, $OCH_2CH_2CH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 157.8 (*C*=O), 154.6 (*C*-2,6), 138.5 (=*C*H), 127.8 (*C*-4), 114.7 (H_2C=), 113.5 (*C*-1), 105.2 (*C*-3,5), 68.5 (OCH_2), 33.3 (=CHCH_2), 28.6 (OCH_2CH_2), 25.1 ($OCH_2CH_2CH_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3266, 3076, 2944, 2866, 1679, 1641, 1607, 1590, 1513, 1454, 1394, 1262, 1107, 908, 798, 762, 709 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 632 (38) $[M]^+$, 289 (100). HRMS: calcd. for $C_{38}H_{52}N_2O_6$ 632.38251; found 632.38281 (0.5 ppm); calcd. for $C_{37}{}^{13}CH_{52}N_2O_6$ 633.38586; found 633.38604 (0.3 ppm). $C_{38}H_{52}N_2O_6$ (632.84): calcd. H 72.12, H 8.28, N 4.43; found C 72.09, H 8.45, N 4.43.

***N*,*N*′-Bis[2,6-bis(pent-4-enyloxy)phenyl]ethane-1,2-diamine (5a):** General procedure **D**: *N*,*N*′-Bis[2,6-bis(pent-4-enyloxy)phenyl]oxaldiamide (**4a**, 2.06 g, 3.56 mmol), lithium aluminium hydride (1.33 g, 35.0 mmol) in tetrahydrofuran (100 mL). Work up: Water (60 mL), extraction with diethyl ether (2 × 100 mL). Column chromatography [alumina, cyclohexane/ethyl acetate (3:1), R_f = 0.83] yielded crystalline colorless product **5a** (1.57 g, 80%). M.p. 62 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.73 (t, ^3J = 8.2 Hz, 2 H, 4-H), 6.50 (d, ^3J = 8.3 Hz, 4 H, 3-H, 5-H), 5.81 (ddt, ^3J = 17.0 Hz, ^3J = 10.3 Hz, ^3J = 6.6 Hz, 4 H, =C*H*), 5.02 (ddt, ^3J = 17.1 Hz, ^2J = 1.9 Hz, ^4J = 1.6 Hz, 4 H, H_ZHC=), 4.96 (ddt, ^3J = 10.2 Hz, ^2J = 2.0 Hz, ^4J = 1.2 Hz, 4 H, H_EHC=), 4.21 (br. s, 2 H, N*H*), 3.96 (t, ^3J = 6.6 Hz, 8 H, OCH_2), 3.37 (s, 4 H, NCH_2), 2.19 (m_c, 8 H, =CHCH_2), 1.86 (m_c, 8 H, OCH_2CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 150.4 (*C*-2,6), 137.9 (=*C*H), 127.7 (*C*-1), 119.4 (*C*-4), 115.1 (H_2C=), 105.7 (*C*-3,5), 68.0 (OCH_2), 47.5 (NCH_2), 30.2 (=CHCH_2), 28.6 (OCH_2CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 3435, 3409, 3074, 2941, 2861, 1640, 1595, 1502, 1446, 1392, 1292, 1233, 1212, 1101, 996, 910, 755, 731, 718 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 548 (20), 275 (100). HRMS: calcd. for $C_{34}H_{48}N_2O_4$ 548.36139; found 548.36294 (2.8 ppm); calcd. for $C_{33}{}^{13}CH_{48}N_2O_4$ 549.36475; found 549.36797 (5.9 ppm). $C_{34}H_{48}N_2O_4$ (548.76): calcd. C 74.42, H 8.82, N 5.10; found C 74.53, H 9.04, N 5.14.

***N*,*N*′-Bis[2,6-bis(hex-5-enyloxy)phenyl]ethane-1,2-diamine (5b):** General procedure **D**: *N*,*N*′-Bis[2,6-bis(hex-5-enyloxy)phenyl]oxaldiamide (**4b**, 500 mg, 0.790 mmol), lithium aluminium hydride (316 mg, 8.32 mmol) in tetrahydrofuran (30 mL). Work up: Water (15 mL), extraction with diethyl ether (2 × 30 mL). Column chromatography [alumina, cyclohexane/ethyl acetate (4:1), R_f = 0.87] yielded crystalline colorless product **5b** (430 mg, 90%). M.p. 35 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 6.74 (t, ^3J = 8.3 Hz, 2 H, 4-H), 6.50 (d, ^3J = 8.3 Hz, 4 H, 3-H, 5-H), 5.78 (ddt, ^3J = 16.9 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 4 H, =C*H*), 5.00 (ddt, ^3J = 17.1 Hz, ^2J = 2.0 Hz, ^4J = 1.6 Hz, 4 H, H_ZHC=), 4.94 (ddt, ^3J = 10.2 Hz, ^2J = 2.1 Hz, ^4J = 1.2 Hz, 4 H, H_EHC=), 4.23 (br. s, 2 H, N*H*), 3.95 (t, ^3J = 6.7 Hz, 8 H, OCH_2), 3.34 (s, 4 H, NCH_2), 2.08 (m_c, 8 H, =CHCH_2), 1.78 (m_c, 8 H, OCH_2CH_2), 1.52 (m_c, 8 H, $OCH_2CH_2CH_2$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 150.5 (*C*-2,6), 138.5 (=*C*H), 127.5 (*C*-1), 119.5 (*C*-4), 114.7 (H_2C=), 105.5 (*C*-3,5), 68.5 (OCH_2), 47.4 (NCH_2), 33.4 (=CHCH_2), 28.8 (OCH_2CH_2), 25.3 ($OCH_2CH_2CH_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3436, 3410, 3074, 2924, 2855, 1641, 1602, 1502, 1446, 1393, 1292, 1234, 1213, 1174, 1104, 993, 908, 757, 738, 711 cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 604 (30) $[M]^+$, 303 (100).

1,3-Bis[2′,6′-bis(pent-4-enyloxy)phenyl]imidazolinium Chloride (6a): General procedure **E**: *N*,*N*′-Bis[2,6-bis(pent-4-enyloxy)phenyl]ethane-1,2-diamine (**5a**, 1.05 g, 1.91 mmol), ammonium chloride (123 mg, 2.30 mmol) in triethyl orthoformate (30.0 mL, 180 mmol). Column chromatography [silica gel, dichloromethane/methanol (10:1), R_f = 0.17] yielded crystalline colorless product **6a** (940 mg, 83%). M.p. 203 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.14 (s, 1 H, 2-H), 7.37 (t, ^3J = 8.6 Hz, 2 H, 4′-H), 6.68 (d, ^3J = 8.6 Hz, 4 H, 3′-H, 5′-H), 5.80 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.6 Hz, 4 H, =C*H*), 5.03–4.97 (m, 8 H, H_2C=), 4.59 (s, 4 H, 4-H, 5-H), 4.10 (t, ^3J = 6.7 Hz, 8 H, OCH_2), 2.19 (m_c, 8 H, =CHCH_2), 1.93 (m_c, 8 H, OCH_2CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 160.4 (*C*-2), 154.3 (*C*-2′,6′), 136.9 (=*C*H), 131.3 (*C*-4′), 115.5 (H_2C=), 112.2 (*C*-1′), 105.0 (*C*-3′,5′), 68.3 (OCH_2), 51.3 (*C*-4,5), 29.7 (=CHCH_2), 27.9 (OCH_2CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 3075, 2946, 1618, 1481, 1462, 1392, 1256, 1107, 991, 907, 775, 731, 643 cm^{-1}. ESI-MS (MeOH): *m*/*z* (%) = 559.36 (100) $[C_{35}H_{47}N_2O_4]^+$. HRMS: calcd. for $C_{35}H_{47}N_2O_4$ 559.35358; found 559.34896 (8.3 ppm); calcd. for $C_{34}{}^{13}CH_{47}N_2O_4$ 560.35693; found 560.35345 (6.2 ppm). $C_{35}H_{47}ClN_2O_4$ (595.22): calcd. C 70.63, H 7.96, N 4.71; found C 70.27, H 8.04, N 4.80.

1,3-Bis[2′,6′-bis(hex-5-enyloxy)phenyl]imidazolinium Chloride (6b): General procedure **E**: *N*,*N*′-Bis[2,6-bis(hex-5-enyloxy)phenyl]ethane-1,2-diamine (**5b**, 194 mg, 320 μmol), ammonium chloride (20 mg, 0.37 mmol) in triethyl orthoformate (5.0 mL, 30 mmol). Column chromatography [silica gel, dichloromethane/methanol (10:1), R_f = 0.16] yielded crystalline colorless product **6b** (152 mg, 73%). M.p. 206 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 8.02 (s, 1 H, 2-H), 7.34 (t, ^3J = 8.5 Hz, 2 H, 4′-H), 6.65 (d, ^3J = 8.6 Hz, 4 H, 3′-H, 5′-H), 5.74 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.6 Hz, 4 H, =C*H*), 4.98 (ddt, ^3J = 17.1 Hz, ^2J = 1.7 Hz, ^4J = 1.6 Hz, 4 H, H_ZHC=), 4.94 (ddt, ^3J = 10.2 Hz, ^2J = 1.7 Hz, ^4J = 1.2 Hz, 4 H, H_EHC=), 4.60 (s, 4 H, 4-H, 5-H), 4.08 (t, ^3J = 6.8 Hz, 8 H, OCH_2), 2.01 (m_c, 8 H, =CHCH_2), 1.84 (m_c, 8 H, OCH_2CH_2), 1.51 (m_c, 8 H, $OCH_2CH_2CH_2$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 160.3 (*C*-2), 154.5 (*C*-2′,6′), 138.0 (=*C*H), 131.3 (*C*-4′), 115.1 (H_2C=), 112.5 (*C*-1′), 105.1 (*C*-3′,5′), 69.0 (OCH_2), 51.6 (*C*-4,5), 33.1 (=CHCH_2), 28.8 (OCH_2CH_2), 25.0 ($OCH_2CH_2CH_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3076, 2944, 1618, 1482, 1463, 1396, 1257, 1108, 992, 907, 774, 730, 649 cm^{-1}. ESI-MS (MeOH): *m*/*z* (%) = 615.41 (100) $[C_{39}H_{55}N_2O_4]^+$. HRMS: calcd. for $C_{39}H_{55}N_2O_4$ 615.4162; found 615.41635 (0.2 ppm); calcd. for $C_{38}{}^{13}CH_{55}N_2O_4$ 616.41956; found 616.41938 (0.3 ppm). $C_{39}H_{55}ClN_2O_4$ (651.33): calcd. C 71.92, H 8.51 N 4.30, $C_{39}H_{55}ClN_2O_4{\cdot}0.25H_2O$ calcd. C 71.42, H 8.53, N 4.27; found C 71.24, H 8.67,N 4.40.

2,11,13,22-Tetraoxa-1,12(1,3,2)-dibenzena-23(1,3)-imidazoliniumabicyclo[10.10.1]tricosaphan-6,17-diene Chloride (7a): General procedure **F**: 1,3-Bis[2′,6′-bis(pent-4-enyloxy)phenyl]imidazolinium chloride (**6a**, 600 mg, 1.09 mmol), benzylidenbis(tricyclohexylphos-

phane)dichlororuthenium (90 mg, 0.11 mmol) in dichloromethane (600 mL). Column chromatography [silica gel, dichloromethane/methanol (10:1), R_f = 0.19] yielded crystalline colorless product **7a** (447 mg, 81%). M.p. 212 °C. ^{1}H NMR[33] (500 MHz, $CDCl_3$, 25 °C): δ = 8.07 (s, 1 H, 2-H), 7.36 (m_c, 2 H, 4′-H), 6.65 (m_c, 4 H, 3′-H, 5′-H), 5.59 (m_c, 0.7 H, =CH_Z*), 5.50 (m_c, 3.3 H, =CH_E*), 4.64 (m_c, 4 H, 4-H, 5-H), 4.15–4.05 (m, 8 H, OCH_2), 2.41 (m_c, 4 H, CH_2#), 2.17 (m_c, 4 H, CH_2#), 1.94 (m_c, 4 H, CH_2#), 1.76 (m_c, 4 H, CH_2#) ppm. ^{13}C NMR[33] (125 MHz, $CDCl_3$, 25 °C): δ = 161.0, 160.6 (*C*-2), 154.9, 154.3 (*C*-2′,6′), 131.7, 131.6 (*C*-4′), 130.8, 130.6 (=*C*H$_Z$*), 129.5, 129.5 (=*C*H$_E$*), 112.4, 111.9 (*C*-1′), 105.3, 104.9 (*C*-3′,5′), 68.8, 67.9 (O*C*H$_2$), 51.6, 50.4 (*C*-4,5), 30.1, 28.9, 28.8, 27.4, 23.7, 23.6 (*C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3030, 2938, 1628, 1599, 1480, 1459, 1299, 1259, 1102, 925, 777, 722 cm^{-1}. ESI-MS (MeOH): *m*/*z* (%) = 503.29 (100) $[C_{31}H_{39}N_2O_4]^+$. HRMS: calcd. for $C_{31}H_{39}N_2O_4$ 503.29016; found 503.28646 (7.4 ppm); calcd. for $C_{30}{}^{13}CH_{39}N_2O_6$ 504.29434; found 504.28966 (9.3 ppm).

2,13,15,26-Tetraoxa-1,14(1,3,2)-dibenzena-27(1,3)-imidazoliumabicyclo[12.12.1]heptacosaphan-7,20-diene Chloride (7b): General procedure **F**: 1,3-Bis[2′,6′-bis(hex-5-enyloxy)phenyl]imidazolinium chloride (**6b**, 80 mg, 0.12 mmol), benzylidenbis(tricyclohexylphosphane)dichlororuthenium (10 mg, 12 μmol) in dichloromethane (100 mL). Column chromatography [silica gel, dichloromethane/methanol (10:1), R_f = 0.17] yielded crystalline colorless product **7b** (65 mg, 92%). M.p. 217 °C. ^{1}H NMR[33] (500 MHz, $CDCl_3$, 25 °C): δ = 7.72 (s, 1 H, 2-H), 7.31 (m_c, 2 H, 4′-H), 6.61 (m_c, 4 H, 3′-H, 5′-H), 5.36 (m_c, 4 H, =C*H*), 4.58 (s, 4 H, 4-H, 5-H), 3.98 (t, ^3J = 8.0 Hz, 8 H, OCH_2), 2.16 (m_c, 8 H, =CHCH_2), 1.80 (m_c, 8 H, OCH$_2$CH_2), 1.48 (m_c, 8 H, OCH$_2$CH$_2$CH_2) ppm. ^{13}C NMR[33] (125 MHz, $CDCl_3$, 25 °C): δ = 159.2, 159.1 (*C*-2), 155.3, 155.3 (*C*-2′,6′), 131.5, 131.5 (*C*-4′), 131.1 (=*C*H$_Z$*), 130.3, 130.3 (=*C*H$_E$*), 112.0, 111.9 (*C*-1′), 104.9, 104.7 (*C*-3′,5′), 69.5, 69.4 (O*C*H$_2$), 51.9, 51.8 (*C*-4,5), 31.8, 31.7, 28.6, 27.7, 27.7, 26.8, 24.9, 24.1, 24.0 (*C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2944, 2853, 1619, 1600, 1468, 1256, 1103, 967, 779, 733, 638 cm^{-1}. ESI-MS (MeOH): *m*/*z* (%) = 559.35 (100) $[C_{35}H_{47}N_2O_4]^+$. HRMS: calcd. for $C_{35}H_{47}N_2O_4$ 559.35358; found 559.35357 (0.0 ppm); calcd. for $C_{34}{}^{13}CH_{47}N_2O_4$ 560.35693; found 560.35689 (0.1 ppm).

2,11,13,22-Tetraoxa-1,12(1,3,2)-dibenzena-23(1,3)-imidazoliumabicyclo[10.10.1]tricosaphane Chloride (8a): General procedure **G**: 2,11,13,22-Tetraoxa-1,12(1,3,2)-dibenzena-23(1,3)-imidazoliumabicyclo[10.10.1]tricosaphan-6,17-diene chloride (**7a**, 280 mg, 519 μmol), palladium/charcoal (10 mg) in methanol (40 mL). Column chromatography [silica gel, dichloromethane/methanol (10:1), R_f = 0.18] yielded crystalline colorless product **8a** (256 mg, 91%). M.p. 199 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.14 (s, 1 H, 2-H), 7.34 (t, ^3J = 8.5 Hz, 2 H, 4′-H), 6.64 (d, ^3J = 8.6 Hz, 4 H, 3′-H, 5′-H), 4.62 (s, 4 H, 4-H, 5-H), 4.16 (ddd, ^2J = 9.3 Hz, ^3J = 7.5 Hz, ^3J = 3.0 Hz, 4 H, OCH_aH$_b$), 4.10 (ddd, ^2J = 9.3 Hz, ^3J = 6.8 Hz, ^3J = 3.2 Hz, 4 H, OCH$_a$$H_b$), 1.80 ($m_c$, 8 H, C$H_2$), 1.61 ($m_c$, 4 H, C$H_2$), 1.47 ($m_c$, 12 H, C$H_2$) ppm. ^{13}C NMR (MHz, $CDCl_3$): δ = 160.4 (*C*-2), 155.0 (*C*-2′,6′), 131.4 (*C*-4′), 112.4 (*C*-1′), 104.9 (*C*-3′,5′), 69.0 (O*C*H$_2$), 51.7 (*C*-4,5), 28.1, 26.6, 24.3 (*C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3058, 2941, 2864, 1619, 1598, 1482, 1458, 1386, 1297, 1257, 1101, 925, 777, 721, 640 cm^{-1}. ESI-MS (MeOH): *m*/*z* (%) = 507.32 (100) $[C_{31}H_{43}N_2O_4]^+$. HRMS: calcd. for $C_{31}H_{43}N_2O_4$ 507.32230; found 507.32225 (0.1 ppm); calcd. for $C_{30}{}^{13}CH_{43}N_2O_4$ 508.32565; found 508.32563 (0.0 ppm). $C_{31}H_{43}ClN_2O_4$ (543.12): calcd. C 68.55, H 7.98, N 5.16, $C_{31}H_{43}ClN_2O_4$·CH_3OH calcd. C 66.82, H 8.24, N 4.87; found C 66.89, H 8.37, N 5.05.

X-ray Crystal Structure Determination of 8a: Suitable crystals were grown by diffusion of diethyl ether into a solution of **8a** in chloroform. Empirical formula $C_{31}H_{43}ClN_2O_4$·$2CHCl_3$, *Fw* = 781.86 g/mol, *a* = 24.435(2) Å, *b* = 12.4936(9) Å, *c* = 16.5068(9) Å, β = 129.063(5)°, *V* = 3912.7(4) Å^3, *T* = 220(2) K, $\rho_{calcd.}$ = 1.327 g/cm^3, μ = 0.544 mm^{-1}, monoclinic, space group *C*2/*c*, *Z* = 4, STOE Imaging Plate Diffraction System (IPDS-1), Mo-K_α (λ = 0.71073 Å), 14905 measured reflections in the range of $6° \leq 2\theta \leq 56°$, 4554 independent reflections used for refinement. R_{int} = 0.0363. The structure was solved with SHELXS-97. Structure refinement was performed against F^2 using SHELXL-97; 210 parameters, R_1 for all reflections with 3609 $F_o > 4\sigma(F_o)$ = 0.0551, wR_2 for all 4554 reflections = 0.1473, GoF = 1.057, residual electron density 0.63/–0.75 [e/Å^3]. All non-hydrogen atoms were refined by using anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and refined isotropically by using a riding model. CCDC-625523 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.

2,13,15,26-Tetraoxa-1,14(1,3,2)-dibenzena-27(1,3)-imidazoliumabicyclo[12.12.1]heptacosaphane Chloride (8b): General procedure **G**: 2,13,15,26-Tetraoxa-1,14(1,3,2)-dibenzena-27(1,3)-imidazoliniumabicyclo[12.12.1]heptacosaphan-7,20-diene chloride (**7b**, 45 mg, 0.76 mmol), palladium/charcoal (5 mg) in methanol (5 mL). Column chromatography [silica gel, dichloromethane/methanol (10:1), R_f = 0.18] yielded crystalline colorless product **8b** (40 mg, 88%). M.p. 209 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.24 (s, 1 H, 2-H), 7.33 (t, ^3J = 8.4 Hz, 2 H, 4′-H), 6.66 (d, ^3J = 8.4 Hz, 4 H, 3′-H, 5′-H), 4.63 (s, 4 H, 4-H, 5-H), 4.13 (t, ^3J = 6.2 Hz, 8 H, OCH_2), 1.82 (m_c, 8 H, OCH$_2$CH_2), 1.46 (m_c, 8 H, OCH$_2$CH$_2$CH_2), 1.39 (m_c, 16 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 160.7 (*C*-2), 154.5 (*C*-2′,6′), 131.1 (*C*-4′), 112.9 (*C*-1′), 105.3 (*C*-3′,5′), 69.4 (O*C*H$_2$), 51.9 (*C*-4,5), 28.5, 26.5, 26.3, 24.9 (*C*H$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 2932, 1617, 1480, 1459, 1390, 1301, 1257, 1101, 774, 728, 648 cm^{-1}. ESI-MS (MeOH): *m*/*z* (%) = 563.39 (100) $[C_{35}H_{51}N_2O_4]^+$. HRMS: calcd. for $C_{35}H_{51}N_2O_4$ 563.38489; found 563.38357 (2.3 ppm); calcd. for $C_{34}{}^{13}CH_{51}N_2O_4$ 564.38824; found 564.38928 (1.8 ppm).

2,11,13,22-Tetraoxa-1,12(1,3,2)-dibenzena-23(1,3)-imidazoliumabicyclo[10.10.1]tricosaphan-23^2-yldithiocarboxylate (10): 2,11,13,22-Tetraoxa-1,12(1,3,2)-dibenzena-23(1,3)-imidazoliniumabicyclo-[10.10.1]tricosaphane chloride (**8a**, 13 mg, 0.024 mmol) was stirred at room temp. with potassium *tert*-butoxide (4 mg, 0.04 mmol) in tetrahydrofuran (5 mL). After 15 min., carbon disulfide (0.05 mL, 0.8 mmol) was added, and the mixture was stirred for 16 h. The solvent and excess carbon disulfide were evaporated and crude product **10** was analyzed without purification. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.16 (t, ^3J = 8.5 Hz, 2 H, 4′-H), 6.47 (d, ^3J = 8.5 Hz, 4 H, 3′-H, 5′-H), 4.21 (s, 4 H, 4-H, 5-H), 4.00 (m_c, 8 H, OCH_2), 1.95 (m_c, 4 H, CH_2), 1.80–1.50 (m, 20 H, CH_2) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 221.3 (*C*S$_2$), 166.0 (*C*-2), 156.6 (*C*-2′,6′), 130.4 (*C*-4′), 113.5 (*C*-1′), 104.1 (*C*-3′,5′), 68.4 (O*C*H$_2$), 49.0 (*C*-4,5), 28.5, 26.0, 23.9 (*C*H$_2$) ppm. ESI-MS (MeOH): *m*/*z* (%) = 583.2650 (37) $[C_{32}H_{42}N_2O_4S_2 + H]^+$ (calcd. 583.2659, 1.5 ppm), 584.2686 (11) $[C_{31}{}^{13}CH_{42}N_2O_4S_2 + H]^+$ (calcd. 584.2690, 0.7 ppm), 621.2196 (100) $[C_{32}H_{42}N_2O_4S_2 + K]^+$ (calcd. 621.2223, 4.3 ppm), 622.2255 (24) $[C_{31}{}^{13}CH_{42}N_2O_4S_2 + K]^+$ (calcd. 622.2254, 0.2 ppm).

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[33] Because of the formation of (*Z*)- and (*E*)-double bonds in the metathesis, three diastereomers may be formed: (*Z*,*Z*), (*Z*,*E*), and (*E*,*E*). For **7a**, two distinct signals are observed for the protons at the double bond, for **7b** one multiplet is observed. *: assignments may be interchanged. #: *exo*- and *endo*-CH_2, no assignments possible.

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