

**Konkave *N*-heterocyclische Carbene (NHC)  
als nucleophile Katalysatoren in der Organokatalyse und  
als Liganden in der Übergangsmetallkomplex-Katalyse**



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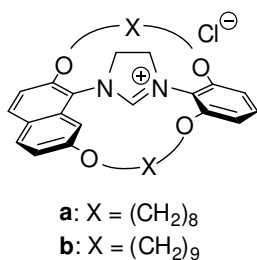
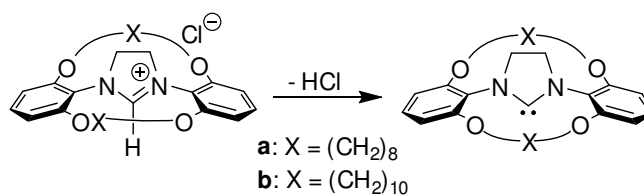
Die vorliegende Arbeit wurde unter Anleitung von  
Prof. Dr. Ulrich Lüning  
am Otto-Diels-Institut für Organische Chemie  
der Christian-Albrechts-Universität zu Kiel  
in der Zeit von September 2005 bis April 2008 angefertigt.



## Zusammenfassung

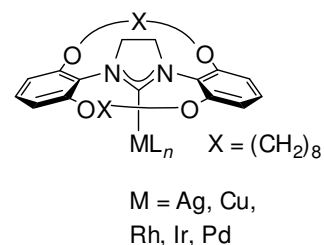
*N*-Heterocyclische Carbene (NHC) zeigen als nucleophile Katalysatoren eine hohe Aktivität in einer Vielzahl von metallfreien Reaktionen (Organokatalyse), und sie werden äußerst erfolgreich als Liganden in Übergangsmetallkatalysierten Reaktionen verwendet. In dieser Arbeit wurde ein Zugang zu konkaven NHC erarbeitet, bei denen sich das reaktive Carben-Kohlenstoffatom im Inneren eines Hohlraumes befindet. Hierdurch soll die Chemo-, Regio- oder Stereoselektivität NHC-katalysierter Reaktionen beeinflusst werden. Als NHC-Vorläufer wurden konkave Imidazoliumsalze synthetisiert, aus denen durch Deprotonierung die reaktiven NHC erhalten werden konnten.

Die Strukturen der Imidazoliumsalze konnten durch Einkristall-Röntgenstrukturanalyse bestätigt werden.



Die konkaven Bimacrocyclen wurden durch Ringschlussmetathese aufgebaut, und die Verwendung eines unsymmetrischen Naphthyl-Brückenkopfes lieferte axial-chirale Imidazoliumsalze. Diese erwiesen sich jedoch als nicht konfigurationsstabil, und die resultierenden NHC konnten nicht in der asymmetrischen Katalyse eingesetzt werden.

Insgesamt acht konkave NHC-Komplexe mit verschiedenen Metallionen wurden synthetisiert. Die Komplexe mit Silber und Kupfer sowie zwei Palladiumkomplexe konnten durch Einkristall-Röntgenstrukturanalyse charakterisiert werden. Vier der Komplexe wurden durch Transmetallierung aus dem NHC-



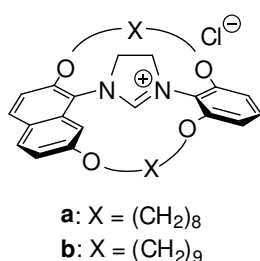
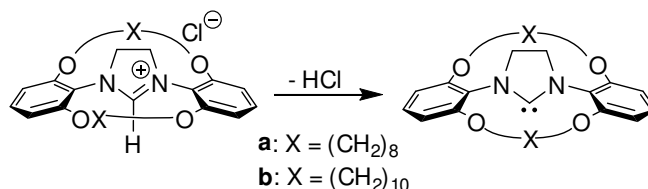
Silberkomplex erhalten. Der Kupferkomplex zeigte eine hohe katalytische Aktivität in der Cyclopropanierung von Styrol und Inden. Im Vergleich mit einem nicht-makrocyclischen NHC-Kupferkomplex wurde die Diastereoselektivität durch den konkaven NHC-Liganden jedoch nur wenig verändert. Einer der Palladiumkomplexe wurde in Suzuki- und Heck-Reaktionen getestet und erwies sich hierbei als äußerst effizienter Katalysator.

Die Reaktivität und Selektivität der konkaven NHC als nucleophile Katalysatoren wurde bei der Umsetzung von Aldehyden und Ketonen mit Enalen getestet. Hierbei ist durch NHC-Katalyse die Bildung verschiedener Produkte möglich. In den meisten Fällen wurden mit den konkaven NHC die erwarteten  $\gamma$ -Butyrolactone erhalten, in einem Fall wurde jedoch ein cyclisches Halbacetal als Hauptprodukt isoliert. Die Synthese analoger Produkte durch NHC-Katalyse wurde bislang in der Literatur nicht beschrieben.



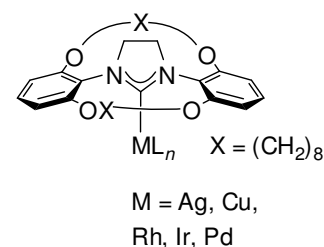
## Abstract

*N*-Heterocyclic carbenes (NHC) are frequently used in nucleophilic organocatalyses and they have also proved to be valuable ligands for organometallic catalysts. In this thesis, a synthetic pathway to concave NHC was developed. By shielding of the carbene carbon atom, which is located in the center of a cavity, the chemo-, regio- or stereoselectivity of NHC-catalyzed reactions shall be affected. Concave imidazolium salts were synthesized as NHC-pre-cursors. These yielded the reactive NHC by deprotonation. The structures of the imidazolium salts were elucidated by single crystal X-ray analysis.



The synthesis of the bimakrocycles was achieved via ring closing metathesis (RCM). By using a naphthalene bridgehead devoid of local C<sub>2</sub>-symmetry, axially chiral concave imidazolium salts were obtained. Unfortunately, these turned out to be configurationally labile and the respective NHC could not be applied to asymmetric catalysis.

Eight concave NHC complexes with different metal ions were synthesized. The complexes of silver and copper and two palladium complexes were characterized by single crystal X-ray analysis. Four of the complexes were synthesized by transmetallation from the NHC silver complex. The copper complex proved to be an active catalyst for the cyclopropanation of styrene and indene. The change in diastereoselectivity caused by the concave NHC ligand was small in comparison to a non-macrocylic NHC copper complex. One of the palladium complexes was tested in Suzuki and Heck reactions and turned out to be a very efficient catalyst for these transformations.



The reactivity and selectivity of the concave NHC in nucleophilic organocatalysis was tested in the reaction of aldehydes and ketones with enals. Several different products may be formed from these substrates by NHC-catalysis. The expected  $\gamma$ -butyrolactones were formed in most of the cases, but in one case a cyclic hemiacetal was isolated as the main product. The synthesis of respective products by NHC-catalysis is hitherto unknown in the literature.





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# 1 Einleitung

## 1.1 Katalysatoren und Enzyme

Der Begriff Katalyse (griech. Auflösung) wurde erstmals von Jöns Jacob Berzelius verwendet, der in seiner Definition von 1835 einen Katalysator als einen Körper ansah, der durch seine „katalytische Kraft“ Reaktionen auszulösen vermag.<sup>[1]</sup> Die noch heute gültige Definition eines Katalysators geht auf Wilhelm Ostwald zurück und besagt, dass ein Katalysator ein Stoff ist, der die Geschwindigkeit einer chemischen Reaktion erhöht, ohne selbst dabei verbraucht zu werden und ohne die endgültige Lage des thermodynamischen Gleichgewichts dieser Reaktion zu verändern. Ostwald schrieb 1894: „Katalyse ist die Beschleunigung eines langsam verlaufenden chemischen Vorganges durch die Gegenwart eines fremden Stoffes.“<sup>[2]</sup>

Katalysatoren spielen sowohl in der chemischen Synthese als auch in der Natur eine entscheidende Rolle. Sie ermöglichen durch eine Absenkung der Aktivierungsenergie Reaktionen, die ohne den entsprechenden Katalysator nicht ohne weiteres ablaufen. Durch die Verwendung geeigneter Katalysatoren ist zudem eine selektive Reaktionsführung zu nur einem von mehreren denkbaren Produkten möglich. Je nach Art der Selektivität unterscheidet man chemo-, regio-, diastereo- und enantioselektive Katalysatoren.

Als Katalysatoren werden in der chemischen Synthese häufig Übergangsmetalle oder Übergangsmetallionen verwendet, die organische Liganden tragen.<sup>[3-5]</sup> Die Selektivität der katalysierten Reaktion kann hierbei durch die Wahl geeigneter Liganden beeinflusst und gesteigert werden. Im Gegensatz dazu werden bei der Organokatalyse<sup>[6,7]</sup> Reaktionen ohne Verwendung von Metallen durch niedermolekulare, organische Moleküle katalysiert, und auch in diesem Fall ist eine Einflussnahme auf die Selektivität durch Modifikation des verwendeten Katalysators möglich.

In der Natur ermöglicht die Enzymkatalyse bemerkenswerte Selektivitäten bei biochemischen Prozessen, die oft mit quantitativer Ausbeute verlaufen.<sup>[8]</sup> Enzyme bestehen aus einem Proteinteil und der katalytisch aktiven Funktionalität. Neben funktionellen Gruppen des Proteinrückgrats können dies organische Moleküle oder komplexierte Metallionen sein, die nur vorübergehend an das Protein binden (Coenzyme) oder kovalent mit dem Protein verbunden sind (prosthetische Gruppen). Das aktive Zentrum, die Substratbindungsstelle des Enzyms, entsteht durch Faltung des Proteins und hat oft die Form einer Tasche, Furche oder Höhle. Durch die vom Proteinteil vorgegebene Gestalt des aktiven Zentrums wird die hohe Selektivität enzymkatalysierter Reaktionen bewirkt, da nur das „passende“ Substrat umgesetzt werden kann.

Das Zusammenwirken von Proteinteil und Coenzym soll am Beispiel des Thiamins (**1a**, Vitamin B<sub>1</sub>) verdeutlicht werden, das als Coenzym an verschiedenen Stoffwechselreaktionen beteiligt ist.<sup>[9]</sup> Die jeweils ablaufende Transformation wird dabei durch die vom Proteinteil vorgegebene Geometrie und chemische Umgebung des Coenzym beeinflusst. Die Wirkform von Thiamin ist das Thiamindiphosphat (**1b**, TDP).

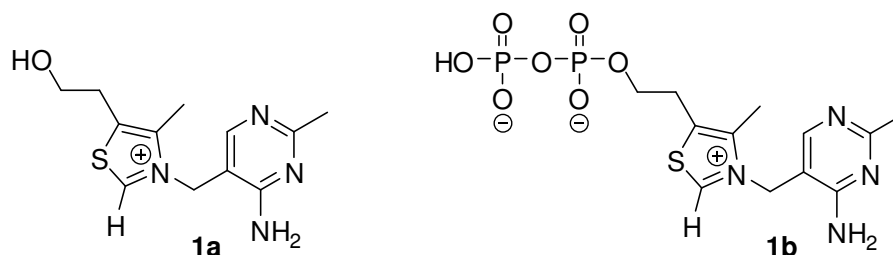


Abbildung 1.1: Thiamin (**1a**, Vitamin B<sub>1</sub>), Thiamindiphosphat (**1b**, TDP).

Das in Abbildung 1.2 exemplarisch gezeigte Enzym Transketolase<sup>[10]</sup> ist am Pentosephosphatweg beteiligt. Das Coenzym TDP (**1b**) katalysiert in diesem Fall die Übertragung einer C<sub>2</sub>-Einheit von Xylulose-5-phosphat auf Ribose-5-phosphat zum Sedoheptulose-7-phosphat.<sup>[8]</sup> Bei der alkoholischen Gärung bewirkt TDP (**1b**) die Decarboxylierung von Pyruvat (Pyruvat-Decarboxylase), und im Citratcyclus ermöglicht es als Coenzym der Pyruvat-Dehydrogenase letztendlich die Umwandlung von Pyruvat in Acetyl-Coenzym A.<sup>[8]</sup>

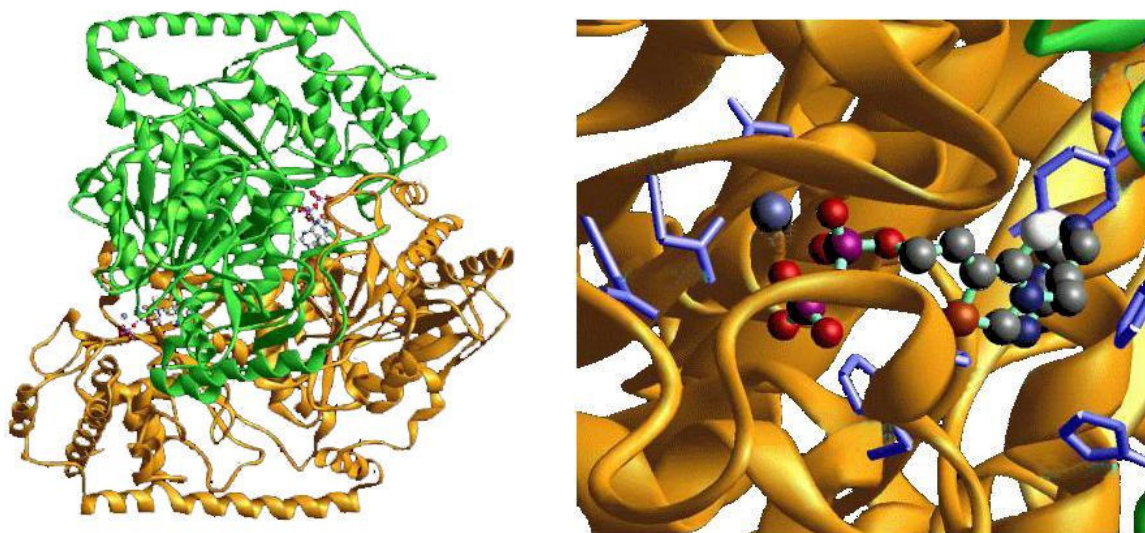


Abbildung 1.2: Transketolase (aus Hefe), rechts: Aktives Zentrum mit dem Coenzym TDP (**1b**).<sup>[11]</sup>

Aufgrund ihrer hohen Selektivität wird die Enzymkatalyse auch in der synthetischen Chemie genutzt,<sup>[9,10,12]</sup> beispielsweise bei der kommerziellen Synthese von (*R*)-Phenylacetylcarbinol, einem Vorläufer des Ephedrins, die durch Hefe katalysiert wird.<sup>[13]</sup>

## 1.2 Konkave Reagenzien

Nach dem Vorbild der Natur werden konkave Reagenzien als Katalysatoren entwickelt, bei denen sich die katalytisch aktive Funktionalität abgeschirmt in einem Hohlraum befindet. Das Prinzip der Enzymkatalyse wird dabei auf einfachere Systeme übertragen, die strukturell anspruchsloser, aber auch chemisch unempfindlicher als Proteine sind. Sie können in ihrer Struktur der zu katalysierenden Reaktion angepasst werden und sind vielseitig einsetzbar.

Das Konzept der konkaven Reagenzien wurde 1987 von Ulrich Lüning vorgestellt.<sup>[14]</sup> Hierbei handelt es sich um meist bimakrocyclische, supramolekulare Strukturen, deren reaktive Zentren sich in Hohlräumen befinden. Die ersten Beispiele für konkave Reagenzien waren konkave Pyridine,<sup>[14,15]</sup> die erfolgreich als Katalysatoren bei der Addition von Alkoholen an Ketene eingesetzt wurden.<sup>[16]</sup> Konkave 1,10-Phenanthroline konnten unter anderem als selektivitätssteigernde Liganden in kupferkatalysierten Cyclopropanierungen verwendet werden.<sup>[17-19]</sup> Als Beispiel für nicht-makrocyclische konkave Reagenzien sind *m*-Terphenyle zu nennen, die mit einer Vielzahl unterschiedlicher Funktionalitäten zugänglich sind.<sup>[20]</sup> Ein Nachteil bei der Synthese bimakrocyclischer konkaver Reagenzien war die oft geringe Ausbeute der Cyclisierungsreaktionen, beispielsweise bei der Synthese bimakrocyclischer *m*-Terphenyle.<sup>[20]</sup> Dieses Problem konnte durch Verwendung der Ringschlussmetathese (ring closing metathesis, RCM) zur Cyclisierung der Bimakrocyclen gelöst werden.<sup>[21-25]</sup>

Bei der RCM handelt es sich um die Verknüpfung zweier meist endständiger Doppelbindungen unter Abspaltung von Ethen zu 1,2-disubstituierten, cyclischen Olefinen.<sup>[26]</sup> Die Reaktion wird häufig bei der Synthese von Naturstoffen genutzt.<sup>[27,28]</sup> Als Katalysatoren werden für die Metathese neben den von Richard Schrock entwickelten Wolfram-<sup>[29]</sup> und Molybdänkomplexen<sup>[30]</sup> heutzutage hauptsächlich die auf Robert Grubbs zurückgehenden Rutheniumkomplexe<sup>[31,32]</sup> verwendet. Diese erwiesen sich als relativ unempfindlich gegenüber Luft und Feuchtigkeit und werden unter der Bezeichnung „Grubbs-Katalysator“ beständig weiterentwickelt. Durch Variation der Liganden am Ruthenium werden hierbei sowohl stabilere als auch aktivere Katalysatoren erhalten.<sup>[33,34]</sup> Besonders die Verwendung *N*-heterocyclischer Carbene (NHC) als Liganden<sup>[35-38]</sup> („Grubbs-Katalysator der zweiten Generation“) und die von Amir Hoveyda entwickelten Katalysatorsysteme<sup>[39,40]</sup> („Hoveyda-Grubbs-Katalysator“) führten zu beachtlichen Verbesserungen der katalytischen Eigenschaften. Neben der Ringschlussmetathese sind als weitere wichtige Metathesereaktionen die Kreuzmetathese<sup>[41]</sup> und die Ringöffnungsmetathese-Polymerisation<sup>[42]</sup> zu nennen. Die theoretischen Grundlagen der

Metathese wurden von Yves Chauvin erarbeitet, und 2005 erhielten Chauvin, Grubbs und Schrock den Nobelpreis für ihre Verdienste bei der Entwicklung der Metathese.<sup>[43-45]</sup>

Die Synthese bimakrocyclischer konkaver Reagenzien durch zweifache RCM wurde erstmals zur Darstellung konkaver 1,10-Phenanthroline durchgeführt.<sup>[21-23]</sup> Mittlerweile konnte die RCM erfolgreich für weitere Makrocyclisierungen verwendet werden, so zum Beispiel bei der Synthese eines konkaven Säure-Base-Katalysators<sup>[24]</sup> und bei einer templatgestützten Makrocyclen-Synthese.<sup>[25]</sup>

### 1.3 N-Heterocyclische Carbene (NHC)

Bei Carbenen handelt es sich um neutrale Verbindungen mit einem divalenten Kohlenstoffatom, das nur sechs Valenzelektronen besitzt. Aufgrund ihres Elektronenmangels sind Carbene äußerst reaktiv und wurden lange Zeit lediglich als transiente Intermediate aufgefasst, wie zum Beispiel bei der Addition von Dichlorcarben an Olefine.<sup>[46]</sup> Mittlerweile ist eine Vielzahl sowohl persistenter als auch stabiler Carbene bekannt.<sup>[47]</sup> Schon 1960 versuchte Hans-Werner Wanzlick durch Eliminierung von Chloroform aus 1,3-Diphenyl-2-trichloromethyl-imidazolidin ein Carben zu erzeugen, das durch zwei Aminosubstituenten stabilisiert ist.<sup>[48]</sup> Dieses konnte jedoch nur in Form eines Dimers isoliert werden.<sup>[49]</sup> Das von Wanzlick postulierte Gleichgewicht<sup>[49]</sup> zwischen freiem Carben und Dimer konnte 1999 experimentell bestätigt werden.<sup>[50,51]</sup> Bereits 1968 berichteten Wanzlick und Öfele unabhängig voneinander über die Synthese von Übergangsmetall-Carbenkomplexen, die ausgehend von Imidazoliumsalzen erhalten wurden.<sup>[52,53]</sup> Die Isolierung eines analogen „stabilen kristallinen Carbens“ **3a** gelang Anthony Arduengo 1991 und stellte einen wissenschaftlichen Meilenstein dar.<sup>[54]</sup>

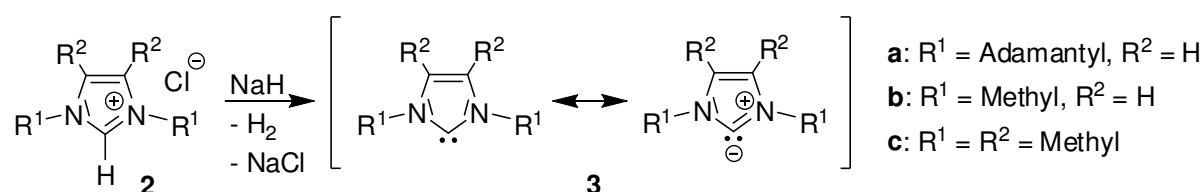


Abbildung 1.3: Synthese stabiler Imidazol-2-ylidene **3**.

Das Carben **3a** wurde durch Deprotonierung des Imidazoliumsalzes **2a** mit Natriumhydrid in nahezu quantitativer Ausbeute erhalten, erwies sich unter Ausschluss von Sauerstoff und Feuchtigkeit als unbegrenzt stabil und konnte durch Einkristall-Röntgenstrukturanalyse charakterisiert werden.<sup>[54]</sup> Die Stabilität des durch die Adamantylsubstituenten stark abgeschirmten Carbens **3a** wurde einer Kombination aus sterischen und elektronischen Faktoren



zugeschrieben. In einer darauffolgenden Publikation Arduengos konnten weitere stabile Imidazol-2-ylidene **3** aus den leicht zugänglichen Imidazoliumsalzen **2**<sup>[55]</sup> erhalten und charakterisiert werden.<sup>[56]</sup> Hierbei zeigte die Synthese der Carbene **3b** und **3c** in beeindruckender Weise, dass sterische Effekte bei der Stabilisierung der Verbindungen eine untergeordnete Rolle spielen. Während **3b** lediglich in Lösung nachgewiesen wurde, konnten **3c** und weitere Imidazol-2-ylidene **3** durch Einkristall-Röntgenstrukturanalyse charakterisiert werden.<sup>[56]</sup> Die elektronische Stabilisierung der Carbene **3** ist auf die dem Carben-Kohlenstoffatom benachbarten Stickstoffatome zurückzuführen, die die Formulierung mesomerer Grenzformeln ermöglichen (siehe Abbildung 1.3). Ronald Breslow erklärte bereits 1958 die von Thiamin (**1a**) und anderen Thiazoliumsalzen katalysierte Benzoin-Kondensation über die Bildung eines entsprechenden Zwitterions.<sup>[57]</sup> In analoger Weise können ausgehend von Imidazolinium-<sup>[58,59]</sup> und Triazoliumsalzen<sup>[60]</sup> mesomeriestabilisierte Carbene erhalten werden. All diese Verbindungen werden unter der Bezeichnung *N*-heterocyclische Carbene (NHC) zusammengefasst, und aufgrund ihrer einzigartigen Eigenschaften kommt ihnen ein stetig wachsendes Interesse zu.<sup>[61]</sup> Anwendungen finden die NHC hauptsächlich als nucleophile Katalysatoren in der Organokatalyse<sup>[62-65]</sup> und als Liganden in Übergangsmetallkomplexen.<sup>[66-70]</sup>

### 1.3.1 *N*-Heterocyclische Carbene (NHC) in der Organokatalyse

Bei der Organokatalyse werden Reaktionen ohne Verwendung von Metallen durch niedermolekulare, organische Moleküle katalysiert.<sup>[6,7]</sup> Der Begriff „organische Katalyse“ wurde erstmals in den 30er Jahren von Wolfgang Langenbeck verwendet, der unter anderem die katalytische Wirkung von Aminen bei der Decarboxylierung von  $\alpha$ -Ketosäuren untersuchte.<sup>[71]</sup> Chirale Amine werden bei der Organokatalyse äußerst erfolgreich als Katalysatoren für asymmetrische Aldol- und Mannich-Reaktionen verwendet.<sup>[72,73]</sup> Seit den 70er Jahren wird Prolin als effizienter Katalysator für asymmetrische intramolekulare Aldolkondensationen zur Synthese von Steroidvorstufen eingesetzt (Hajos-Parrish-Eder-Sauer-Wiechert-Verfahren).<sup>[74,75]</sup> Ein weiteres spektakuläres Beispiel für Organokatalyse ist die durch chirale Ammoniumsalze katalysierte asymmetrische Hydrierung  $\alpha,\beta$ -ungesättigter Aldehyde, wobei als Hydridquelle der Hantzsch-Ethylester<sup>[76]</sup> verwendet wird.<sup>[77]</sup> Im Folgenden soll jedoch nur auf die Rolle der NHC in der Organokatalyse näher eingegangen werden.

Der Mechanismus der von Thiamin (**1a**) katalysierten Benzoinkondensation wurde 1958 von Ronald Breslow über die Bildung des Zwitterions **4** erklärt, das durch Deprotonierung des Thiamins (**1a**) entsteht. Durch nucleophilen Angriff des Thiazol-2-ylidens **4** auf den Benzaldehyd **5** und anschließende Protonierung/Deprotonierung des Alkoxids **6** zum mesomeriestabilisierten Carbanion **7** wird eine Umpolung des Carbonyl-Kohlenstoffatoms des Benzaldehyds **5** ermöglicht (siehe Abbildung 1.4).<sup>[57]</sup> Nucleophiler Angriff des umgepolten Intermediats **7** auf ein weiteres Molekül Benzaldehyd **5** und Isomerisierung des Addukts **8** zu **9** liefert letztlich unter Freisetzung des Katalysators **4** das Benzoin **10**.

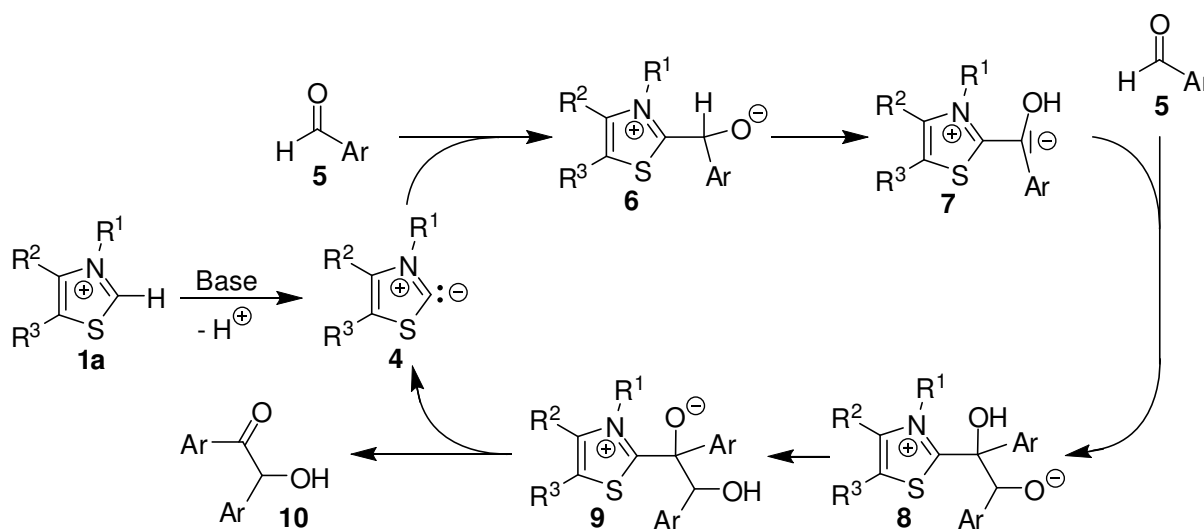


Abbildung 1.4: Mechanismus der Benzoin-Kondensation nach Breslow.

Der von Breslow vorgeschlagene Katalyse-Cyclus verläuft analog dem von Arthur Lapworth 1903 postulierten Mechanismus<sup>[78]</sup> für die durch Cyanidionen katalysierte Benzoin-Kondensation, die erstmals 1832 von Friedrich Wöhler und Justus Liebig beschrieben worden war.<sup>[79]</sup> 1976 erkannte Hermann Stetter, dass sich das Reaktionsprinzip auf die Reaktion von Aldehyden mit Michael-Akzeptoren zu 1,4-Diketonen, 4-Ketoestern und auch 4-Ketonitrilen übertragen lässt.<sup>[80]</sup> Als Katalysatoren verwendete er sowohl Cyanidionen als auch Thiazoliumsalze in Gegenwart von Basen. Die Stetter-Reaktion verläuft analog dem in Abbildung 1.4 gezeigten Mechanismus der Benzoin-Kondensation, wobei das Intermediat **7** jedoch nucleophil das  $\beta$ -Kohlenstoffatom des Michael-Systems **11** angreift (siehe Abbildung 1.5).

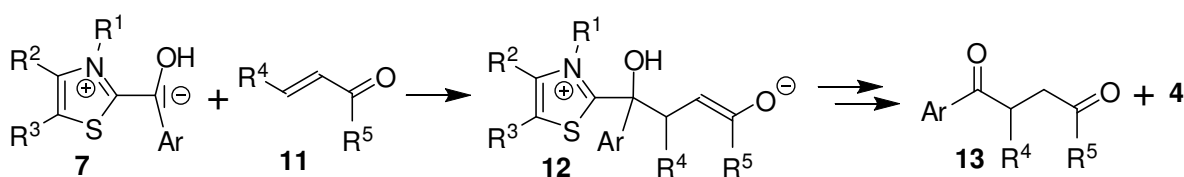


Abbildung 1.5: Stetter-Reaktion.

In beiden Reaktionen wird aus dem Carbonyl-Kohlenstoffatom des prochiralen Aldehyds ein stereogenes Zentrum, und durch die Verwendung chiraler Thiazoliumsalsen können sowohl in der Benzoin-Kondensation als auch bei der Stetter-Reaktion beachtliche Enantiomerenüberschüsse erzielt werden.<sup>[65]</sup> Neben Thiazoliumsalsen werden vor allem chirale Triazoliumsalsen äußerst erfolgreich als Prækatalysatoren für diese Reaktionen eingesetzt.<sup>[65]</sup>

Frank Glorius und Jeffrey Bode berichteten 2004 unabhängig voneinander über die Verwendung des Mesityl-substituierten Imidazoliumions **14** als Prækatalysator bei der Reaktion von Benzaldehyden **5** mit  $\alpha,\beta$ -ungesättigten Aldehyden **16**.<sup>[81,82]</sup> Hierbei wurden weder 1,4-Dicarbonyle **13** noch Benzoinne ( $\alpha$ -Hydroxyketone) **10**, sondern  $\gamma$ -Butyrolactone **21** erhalten, wobei bevorzugt das *like*-Diastereomer gebildet wurde. Aufgrund des voluminösen NHCs ist in diesem Fall eine Benzoin-Kondensation oder Stetter-Reaktion erschwert, und der postulierte Mechanismus verläuft über die Umpolung des  $\beta$ -Kohlenstoffatoms des Enals **16** durch das NHC **15** (siehe Abbildung 1.6).<sup>[81,82]</sup> Das durch Protonierung/Deprotonierung aus **17** gebildete, mesomeriestabilisierte Allylanion **18** greift den Benzaldehyd **5** nucleophil an, und nach Isomerisierung des Alkoxids **19** zum aktivierten Carbonsäurederivat **20** erfolgt unter Ringschluss zum Lacton **21** die Freisetzung des NHC-Katalysators **15**. Der vorgeschlagene Mechanismus konnte experimentell unterstützt werden<sup>[82]</sup> und einige der postulierten Intermediate wurden massenspektrometrisch nachgewiesen.<sup>[83]</sup>

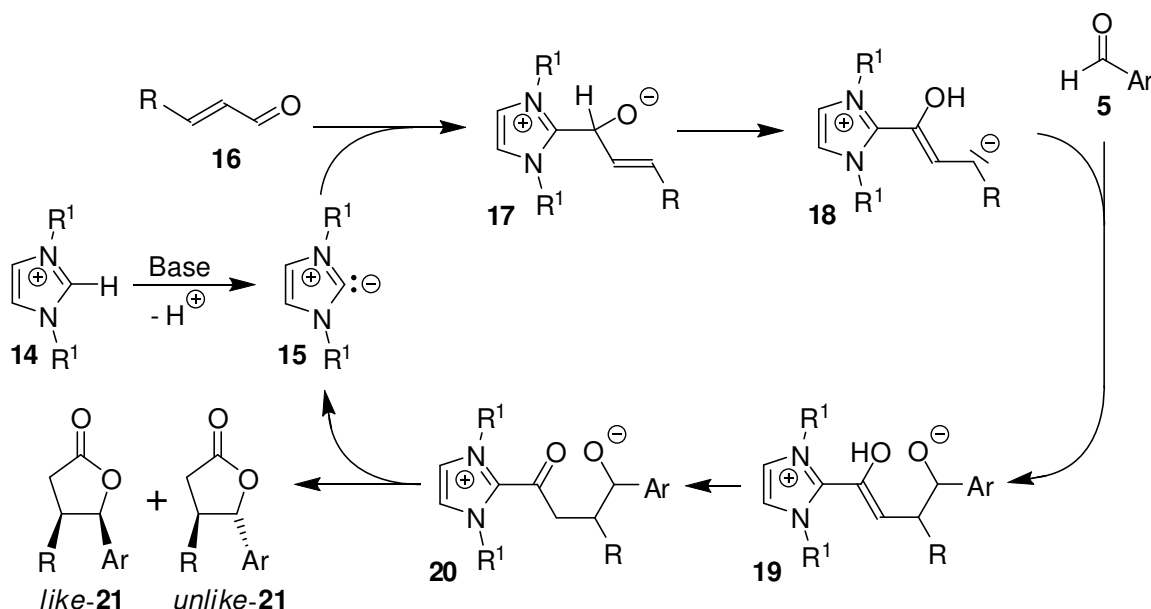


Abbildung 1.6: Mechanismus der NHC-katalysierten Lactonsynthese ( $R^1$  = Mesityl).

Das Allylanion **18** kann auch mit anderen Elektrophilen anstelle der Benzaldehyde **5** umgesetzt werden, so liefert die Reaktion beispielsweise mit elektronenarmen Ketonen 4,5,5-tri-

substituierte  $\gamma$ -Butyrolactone.<sup>[81]</sup> Die Verwendung von Iminen führt in analoger Weise zu  $\gamma$ -Lactamen,<sup>[84]</sup> mit cyclischen 1,2-Dicarbonylverbindungen werden  $\gamma$ -Spirolactone erhalten.<sup>[85]</sup> Werden Enone eingesetzt, so können unter Decarboxylierung 1,3,4-trisubstituierte Cyclopentene gebildet werden.<sup>[86,87]</sup>

Ein weiteres Anwendungsgebiet der NHC in der Organokatalyse sind Umesterungen/Acylierungen<sup>[88-90]</sup>, hierbei konnten chirale NHC erfolgreich zur kinetischen Racematspaltung sekundärer Alkohole eingesetzt werden.<sup>[91]</sup> Zudem werden NHC als Katalysatoren bei vielen weiteren Reaktionen verwendet, beispielsweise bei der Ringöffnungs-Polymerisation von Lactiden und Lactonen,<sup>[92,93]</sup> der Hydroacylierung aktivierter Ketone,<sup>[94]</sup> der Trifluormethylierung von Carbonylverbindungen<sup>[95]</sup> und der Cyclotrimerisierung von Isocyanaten.<sup>[96]</sup>

### 1.3.2 N-Heterocyclische Carbene (NHC) als Liganden

Übergangsmetalle sind aus vielen Gründen für die Katalyse besonders geeignet. Sie besitzen freie d- (oder auch f-) Orbitale, über die sie mit Reaktanden und Liganden wechselwirken können, sie können in den unterschiedlichsten Oxidationsstufen auftreten und in Übergangsmetallkomplexen können sie verschiedene Koordinationszahlen und -geometrien aufweisen.<sup>[3-5]</sup> Im Falle der Übergangsmetallkomplexe können die sterischen und elektronischen Eigenschaften des Katalysators durch die Verwendung verschiedener Liganden beeinflusst werden. So vereinfachte beispielsweise die Entwicklung voluminöser, elektronenreicher Phosphine die Verwendung von Arylchloriden in palladiumkatalysierten Kupplungsreaktionen erheblich.<sup>[97]</sup> Die häufig als Liganden verwendeten Phosphine wurden bezüglich ihrer elektronischen und sterischen Eigenschaften detailliert von Chadwick Tolman untersucht.<sup>[98]</sup>

Die NHC ähneln als starke zwei-Elektronen- $\sigma$ -Donoren in ihrer Koordinationschemie den Trialkylphosphinen<sup>[99]</sup> und sie sind elektronenreicher als die basischsten Phosphine.<sup>[100]</sup> NHC-Metallkomplexe wurden bereits 1968 von Wanzlick<sup>[52]</sup> und Öfele<sup>[53]</sup> beschrieben, doch erst in Folge von Arduengos bemerkenswerten Arbeiten<sup>[54,56]</sup> kam der Anwendung der NHC als Liganden breite Aufmerksamkeit zu.<sup>[66-70]</sup> Die NHC gehen mit nahezu jedem Übergangsmetall eine Bindung ein und wirken sowohl stabilisierend als auch aktivierend auf das Metall, so zum Beispiel beim Grubbs-Katalysator der zweiten Generation. Bei diesen Rutheniumkatalysatoren für Metathesereaktionen<sup>[101]</sup> führte der Austausch eines der beiden Phosphinliganden gegen ein NHC zu aktiveren Katalysatoren mit erhöhter thermischer Stabilität.<sup>[36-38]</sup> Die Verwendung eines Rutheniumkomplexes mit chiralem NHC-Liganden lieferte hohe Enantiomerenüberschüsse in asymmetrischen Ringschlussmetathese-Reaktionen.<sup>[102]</sup>

Besonders hervorzuheben ist die Verwendung der NHC in palladiumkatalysierten Kreuzkupplungen zur Knüpfung von Kohlenstoff-Kohlenstoff- und Kohlenstoff-Heteroatom-Bindungen.<sup>[69,97]</sup> Vor allem *N,N'*-Bisaryl-substituierte Imidazol-2-ylidene und Imidazolidin-2-ylidene (siehe Abbildung 1.8) werden erfolgreich als Alternative zu Phosphinliganden eingesetzt. Hierbei ermöglicht die Verwendung der NHC als Liganden die Umsetzung anspruchsvoller Substrate unter milden Bedingungen, und der Einsatz der reaktionsträgen Arylchloride in Kreuzkupplungen ist heutzutage etabliert. Arylchloride sind aus Kostengründen den reaktiveren Arylbromiden oder -iodiden vorzuziehen. Der vereinfachte allgemeine Katalyse-Cyclus<sup>[97]</sup> der palladiumkatalysierten Suzuki-,<sup>[103]</sup> Stille-,<sup>[104]</sup> Negishi-,<sup>[105]</sup> Kumada-<sup>[106]</sup> und Hiyama-Kupplung<sup>[107]</sup> ist in Abbildung 1.7 gezeigt. Heck-Olefinierung,<sup>[108]</sup> Buchwald-Hartwig-Aminierung<sup>[109,110]</sup> und die Sonogashira-Reaktion<sup>[111]</sup> verlaufen nach ähnlichen Mechanismen.<sup>[97]</sup>

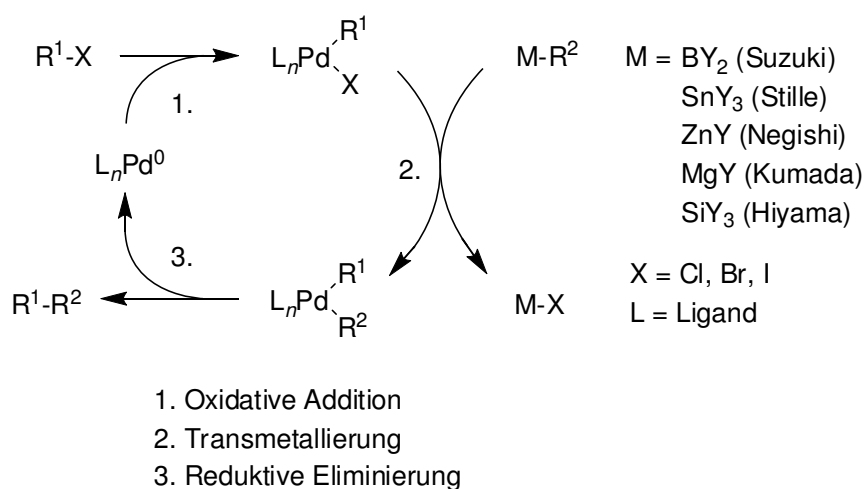


Abbildung 1.7: Allgemeiner Mechanismus palladiumkatalysierter Kreuzkupplungen.

Die oxidative Addition der Arylchloride an das Palladiumzentrum wird durch die starken  $\sigma$ -Donor-Eigenschaften der NHC begünstigt, während ihr Platzbedarf die produktbildende reductive Eliminierung erleichtert.<sup>[69]</sup> Die Generierung katalytisch aktiver NHC-Palladiumkomplexe kann in situ aus den freien NHC oder den Azoliumsalzen und einer Palladiumquelle erfolgen.<sup>[112,113]</sup> In der letzten Zeit wurden jedoch auch einige definierte NHC-Palladiumkomplexe synthetisiert, die unempfindlich gegenüber Luft und Feuchtigkeit sind und exzellente katalytische Eigenschaften besitzen.<sup>[114-116]</sup> Bei diesen Präkatalysatoren handelt es sich um Palladium<sup>II</sup>-Komplexe, aus denen unter den Reaktionsbedingungen der Kreuzkupplung die katalytisch aktiven Palladium<sup>0</sup>-Spezies gebildet werden. Die von Steven Nolan entwickelten NHC-Palladiumkomplexe **22** können bei Raumtemperatur für Suzuki-Kreuz-

kupplungen und Buchwald-Hartwig-Aminierungen mit Arylchloriden eingesetzt werden, und sie erlauben bei erhöhter Temperatur (80 °C) den Einsatz äußerst geringer Katalysatormengen (10-50 ppm Palladium).<sup>[115]</sup>

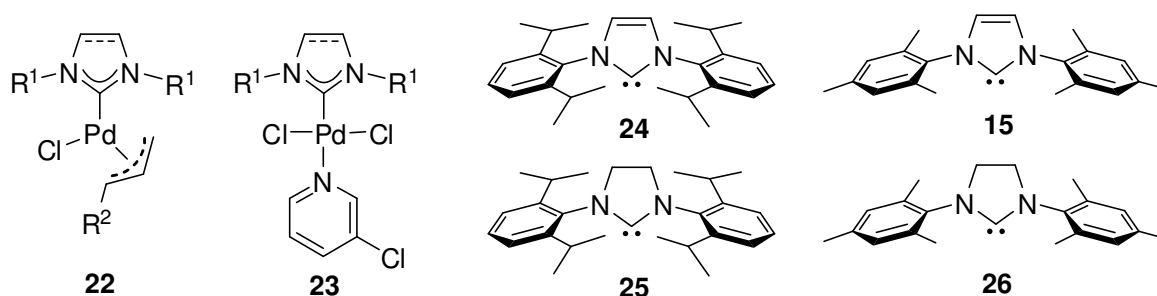


Abbildung 1.8: Häufig verwendete NHC-Palladiumkomplexe und NHC-Liganden.

Die Verwendung von 3-Chlorpyridin als stabilisierenden „Wegwerf-Liganden“ wurde von Michael Organ vorgestellt und ermöglicht eine äußerst effiziente Synthese von NHC-Palladium-Präkatalysatoren **23** in nahezu quantitativer Ausbeute aus den unempfindlichen Azoliumsalzen.<sup>[116]</sup> Eine hohe katalytische Aktivität der NHC-Palladiumkomplexe **23** wurde mit 1-2 mol% Präkatalysator bei Raumtemperatur in Suzuki-,<sup>[116]</sup> Negishi-,<sup>[117]</sup> und Kumada-Kreuzkupplungen<sup>[118]</sup> beobachtet. Die aktivsten Präkatalysatoren **22** und **23** wurden jeweils mit den sterisch anspruchsvollen NHC-Liganden **24** und **25** erhalten.<sup>[115,118]</sup> Ein entsprechender Komplex **23** wurde kürzlich erfolgreich für die Synthese von Indolen durch sequentielle Aryl-Aminierung/Heck-Kupplung verwendet.<sup>[119]</sup> Mit chiralen NHC-Liganden konnten in palladiumkatalysierten asymmetrischen  $\alpha$ -Arylierungen von Amiden beachtliche Enantiomenüberschüsse erzielt werden.<sup>[120]</sup>

Neben den Anwendungen der NHC in rutheniumkatalysierten Metathese- und palladiumvermittelten Kreuzkupplungs-Reaktionen finden die NHC vielfältige weitere Anwendungen in der metallorganischen Chemie. Eine wichtige Rolle spielen hierbei die leicht zugänglichen NHC-Silberkomplexe, aus denen durch Transmetallierung eine Vielzahl weiterer NHC-Metallkomplexe erhalten werden kann.<sup>[121]</sup> Die Verwendung dieser unempfindlichen Carben-Transfer-Reagenzien vermeidet die Freisetzung der NHC aus den Azoliumsalzen, die den Einsatz starker Basen und einen rigorosen Ausschluss von Feuchtigkeit erfordern würde. NHC-Silberkomplexe können unter milden Reaktionsbedingungen aus den Azoliumsalzen durch Reaktion mit basischen Silbersalzen erhalten werden,<sup>[121]</sup> Silberoxid wird hierfür häufig verwendet.<sup>[122-124]</sup> Die Umsetzung der so erhaltenen NHC-Silberkomplexe mit geeigneten Vorläufern ermöglicht den Liganden-Transfer auf beispielsweise Kupfer, Gold, Nickel, Palla-

dium, Platin, Rhodium, Iridium oder Ruthenium zur Synthese entsprechender NHC-Komplexe.<sup>[121]</sup>

Aus der Vielzahl der Anwendungen von NHC-Metallkomplexen seien noch einige genannt: NHC-Kupferkomplexe wurden erfolgreich als Katalysatoren in Cyclopropanierungen,<sup>[125]</sup> [3+2]-Cycloadditionen<sup>[126]</sup> und für die Hydrosilylierung von Carbonylverbindungen verwendet.<sup>[127]</sup> In Kombination mit Bis-(1,5-cyclooctadien)-nickel ermöglicht der NHC-Ligand **25** die Cycloaddition von Diinen mit Aldehyden und Ketonen<sup>[128]</sup> oder Isocyanaten.<sup>[129]</sup> In einer nickelkatalysierten Dreikomponenten-Reaktion von 1,3-Dienen, Aldehyden und Silanen zu chiralen Olefinen wurden mit Hilfe eines asymmetrischen NHC-Liganden hohe Ausbeuten und Enantiomerenüberschüsse erzielt.<sup>[130]</sup>

Die Synthese von Rhodium- und Iridium-NHC-Carbonylkomplexen ist eine populäre Methode zur Bestimmung der elektronischen Eigenschaften von NHC-Liganden anhand der Bandenlage der Carbonylschwingungen im IR-Spektrum.<sup>[100,131,132]</sup> Diese Methode zur Quantifizierung der elektronischen Eigenschaften von Liganden wurde auch von Tolman bei seinen Untersuchungen der Phosphine angewandt, wobei er Nickel-Carbonylkomplexe verwendete.<sup>[98]</sup> Das Prinzip ist jeweils gleich: Starke  $\sigma$ -Donorliganden erhöhen die Elektronendichte am Metallzentrum und ermöglichen eine starke Rückbindung zu den Carbonylliganden, so dass deren Streckschwingung zu niedrigeren Wellenzahlen verschoben wird. Auf diesem Wege konnte gezeigt werden, dass die NHC elektronenreicher als die elektronenreichsten Phosphine sind.<sup>[100]</sup> Aufgrund ihrer einzigartigen Eigenschaften ist zu vermuten, dass die NHC in den kommenden Jahren die etablierte Klasse der Phosphinliganden zum Teil ersetzen werden.

## 2 Ziele

*N*-Heterocyclische Carbene (NHC) zeigen als nucleophile Katalysatoren herausragende Aktivität in einer Vielzahl von Reaktionen,<sup>[64]</sup> und sie werden erfolgreich als Liganden in unzähligen Übergangsmetallkatalysierten Reaktionen verwendet.<sup>[66-69]</sup> Die NHC werden durch Deprotonierung aus Azoliumsalzen erhalten, und durch Modifikation der Strukturen kann ihre Reaktivität erheblich beeinflusst werden.<sup>[65,81,82]</sup> Konkave NHC könnten sich aufgrund ihrer Struktur somit als selektivitätssteigernde Katalysatoren und Liganden erweisen.

Ziel dieser Arbeit war daher die Synthese bimakrocyclischer Azoliumsalze als Vorläufer für bimakrocyclische konkave NHC. Diese sollten bezüglich ihrer Reaktivität und Selektivität in der Organokatalyse und als Liganden in metallvermittelten Reaktionen getestet werden. Aufgrund ihrer Struktur und der einfachen Zugänglichkeit<sup>[59,133]</sup> erschienen *N,N'*-Bisaryl-substituierte Imidazoliniumsalze geeignet zur Synthese entsprechender Bimakrocyclen **27** und **28**, die durch Ringschlussmetathese aufgebaut werden sollten. Mit Hilfe symmetrischer bimakrocyclischer Imidazoliniumsalze **27** könnte in geeigneten Reaktionen die Diastereoselektivität beeinflusst werden. Zudem sollte die Zugänglichkeit entsprechender axial-chiraler Bimakrocyclen **28** für asymmetrische Katalysen untersucht werden.

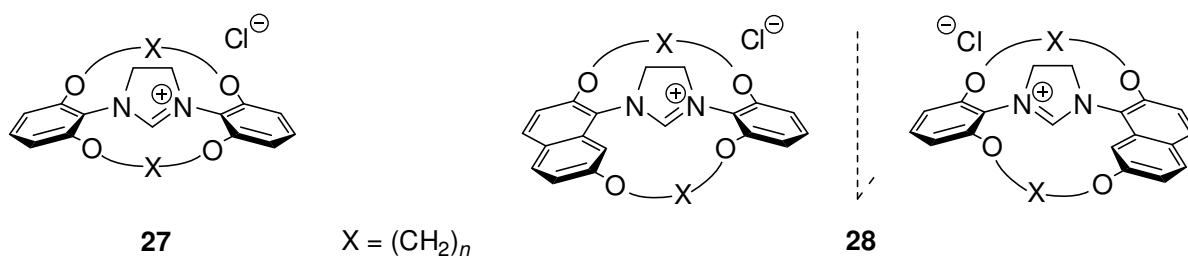


Abbildung 2.1: Zielmoleküle: Symmetrische konkave Imidazoliniumsalze **27** und axial-chirale konkave Imidazoliniumsalze **28** (beide Enantiomere sind gezeigt).

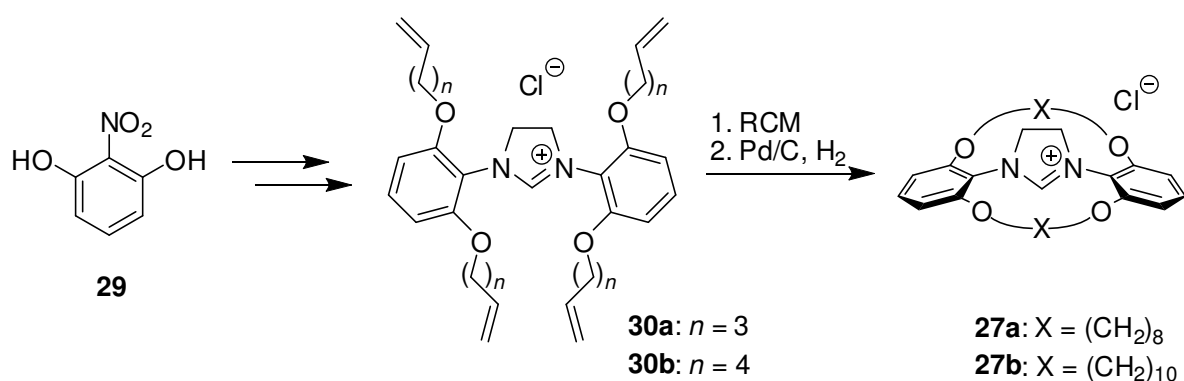


### 3 Ergebnisse

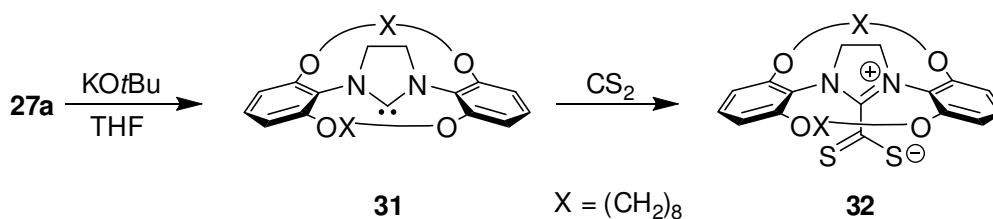
#### 3.1 Concave Reagents, 52: Concave Imidazolinium Salts as Precursors to Concave N-Heterocyclic Carbenes.

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Ausgehend von 2-Nitroresorcin (**29**) wurden in jeweils fünfstufigen Synthesen die beiden Imidazoliniumsalze **30a** und **30b** mit unterschiedlich langen Alkenyloxyketten erhalten. Diese konnten durch Ringschlussmetathese (ring closing metathesis, RCM) und anschließende Hydrierung der neu gebildeten Doppelbindungen zu den verschiedenen großen Bimakrocyclen **27a** und **27b** umgesetzt werden. Das bimakrocyclische Imidazoliniumsalz **27a** wurde durch Einkristall-Röntgenstrukturanalyse charakterisiert. Die Einkristall-Röntgenstrukturanalyse von **27b** und ein Vergleich der Strukturen von **27a** und **27b** findet sich auf Seite 58.



Das NHC **31** wurde durch Deprotonierung von **27a** mit Kalium-*tert*-butylat generiert und **31** konnte durch Reaktion mit Schwefelkohlenstoff abgefangen werden. Das Addukt **32** wurde durch <sup>1</sup>H- und <sup>13</sup>C-NMR-Spektroskopie charakterisiert und die Zusammensetzung konnte durch hochaufgelöste Massenspektrometrie zweifelsfrei bestätigt werden.



Somit wurde ein Zugang zu bimakrocyclischen Imidazoliniumsalzen erarbeitet, und es konnte gezeigt werden, dass diese sich zu entsprechenden konkaven NHC deprotonieren lassen.

# Concave Imidazolinium Salts as Precursors to Concave N-Heterocyclic Carbenes<sup>[‡]</sup>

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**Keywords:** Betaines / Carbenes / Heterocycles / Macrocycles / Supramolecular chemistry

Concave bimacrocylic 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( $\omega$ -alkenylloxy)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 bimacrocylic imidazolinium ions **7**, whose alkene functions were hydrogenated to give saturated bimacrocylics **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<sub>2</sub> to give adduct **10**.

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## Introduction

In 1958, Breslow<sup>[1]</sup> elucidated the nature of the “active aldehyde” in thiamine-dependent biochemical transformations<sup>[2]</sup> 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<sup>[3,4]</sup> and Arduengo<sup>[5]</sup> synthesized nucleophilic stable carbenes derived from imidazolinium or imidazolium ions. Their activity in nucleophilic catalysis was also shown and has been reviewed recently.<sup>[6,7]</sup> 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.<sup>[7]</sup>

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

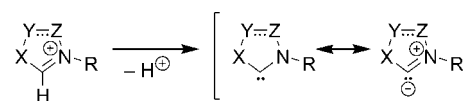


Figure 1. N-Heterocycles are the precursors for N-heterocyclic carbenes (NHC) which are also drawn in their mesomeric betaine form.<sup>[8]</sup> Examples: thiazolium: X = S, Y = Z = CR', imidazolium: X = NR'', Y = Z = CR', imidazolinium: X = NR'', Y = Z = CR', triazolium: X = NR'', Y = N, Z = CR'.

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 bimacrocylic NHC as depicted in Figure 2 and developed a synthetic route to respective substituted imidazolinium<sup>[22]</sup> ions.

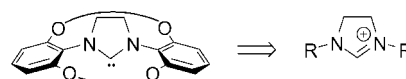


Figure 2. Schematic representation of a bimacrocylic concave N-heterocyclic carbene which may be obtained from respective imidazolinium ions.

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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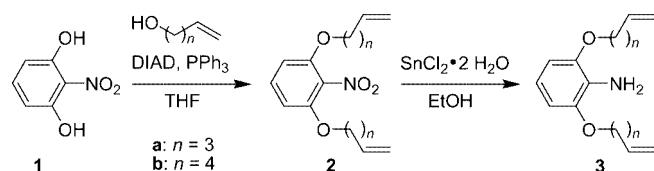
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## FULL PAPER

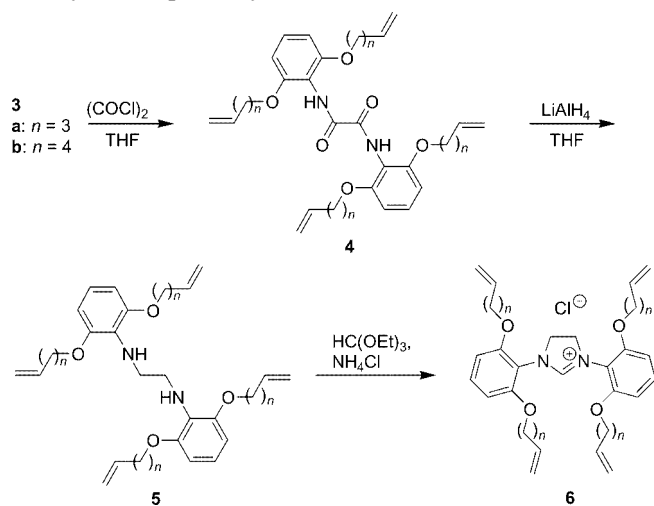
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cyclization strategy, and (3) a suitable synthesis of the heterocycle. We have selected ruthenium catalyzed metathesis for the ring closure to provide the bimacrocycle because such bimacrocyclizations have proven to be very successful for the synthesis of a number of concave reagents.<sup>[23–25]</sup> Thus a precursor is demanded which contains the aryl bridgeheads and the heterocycle. Prominent strategies<sup>[26–29]</sup> for the synthesis of imidazolium and imidazolinium ions start from anilines which are condensed with a C<sub>2</sub> and a C<sub>1</sub> 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  $\omega$ -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,<sup>[23–25]</sup> the  $\omega$ -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,<sup>[23–25]</sup> 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.

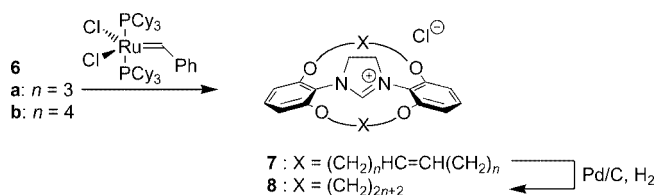
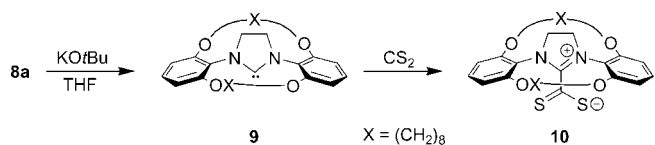


Figure 3 shows that the imidazolinium ion of **8a** adopts a C<sub>2</sub> symmetrical structure in the solid state. This contrasts the data in solution. As apparent in the time-averaged NMR spectra, the cation of **8a** possesses two mirror planes: one mirror plane is identical with the averaged plane 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.<sup>[30–32]</sup> 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 <sup>13</sup>C-NMR signals for C-2 and CS<sub>2</sub> appear at  $\delta$  = 166.0 and 221.3 ppm, respectively. The composition (C<sub>32</sub>H<sub>42</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>) was determined from an ESI mass spectrum (deviation from calculated values 0.2 to 1.5 ppm, see Experimental Section). According to <sup>1</sup>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<sub>2</sub>.

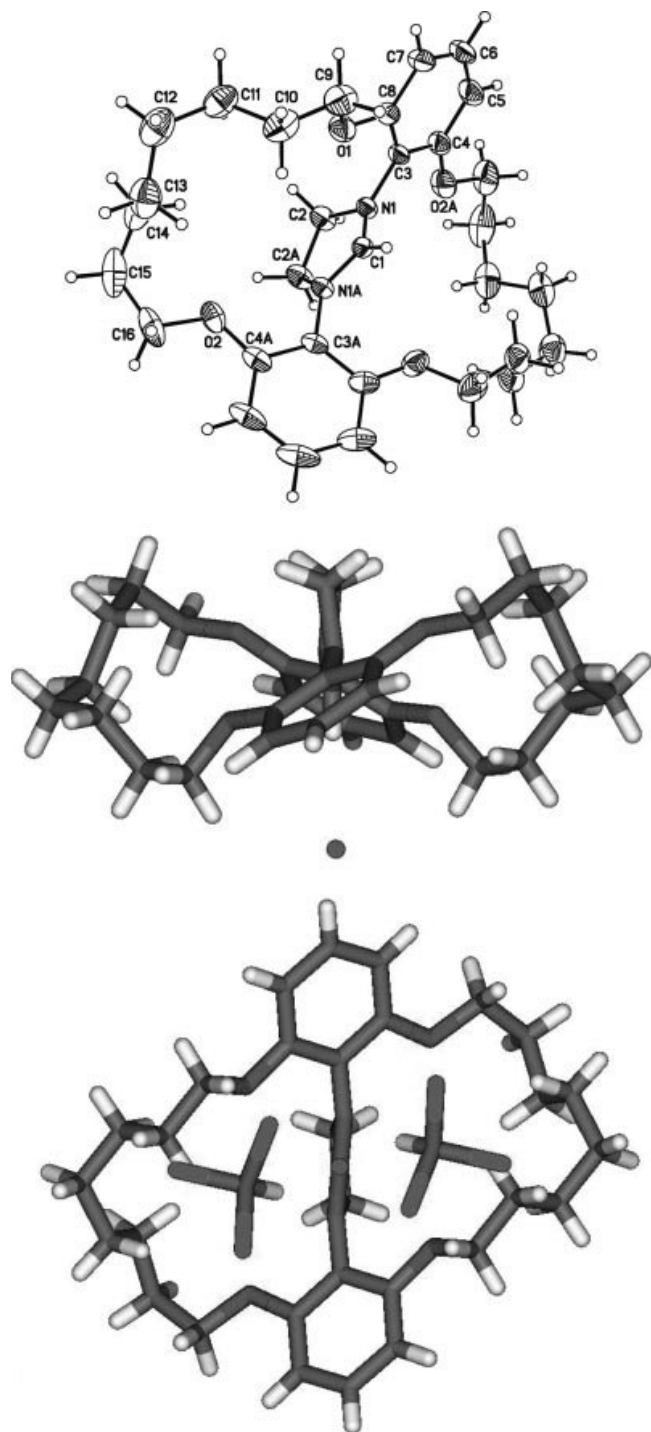


Figure 3. Crystal structure of **8a**. Top: View into the cavity from below showing the bimacroyclic structure of the cation. The chloride counterion is omitted. Middle: View of the cation along an axis bridgehead 1–imidazolium unit–bridgehead 2. The  $C_2$  symmetry and the  $54^\circ$  twist of the 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 imidazolium 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).  $^1\text{H}$ - and  $^{13}\text{C}$ -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  $0^\circ\text{C}$ , 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  $0^\circ\text{C}$ . 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

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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 Imidazoliniumbicyclophan Chlorides 7:** Imidazolinium chloride **6** was stirred with benzyldienbis(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 Imidazoliniumbicyclophan 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%).  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 7.27$  (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, =CH), 5.05 (ddt,  $^3J = 17.1$  Hz,  $^2J = 1.8$  Hz,  $^4J = 1.6$  Hz, 2 H,  $H_Z\text{HC=}$ ), 4.99 (ddt,  $^3J = 10.2$  Hz,  $^2J = 1.9$  Hz,  $^4J = 1.2$  Hz, 2 H,  $H_E\text{HC=}$ ), 4.04 (t,  $^3J = 6.4$  Hz, 4 H,  $\text{OCH}_2$ ), 2.19 (m<sub>c</sub>, 4 H, =CHCH<sub>2</sub>), 1.86 (m<sub>c</sub>, 4 H,  $\text{OCH}_2\text{CH}_2$ ) ppm.  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 151.2$  (C-1,3), 137.4 (=CH), 132.5 (C-2), 130.9 (C-5), 115.5 ( $\text{H}_2\text{C=}$ ), 105.2 (C-4,6), 68.5 ( $\text{OCH}_2$ ), 29.8 (=CHCH<sub>2</sub>), 27.9 ( $\text{OCH}_2\text{CH}_2$ ) ppm. IR (KBr):  $\tilde{\nu} = 3078, 2945, 1641, 1611, 1586, 1536, 1483, 1466, 1375, 1263, 1105, 995, 916, 851, 778, 733$  cm<sup>-1</sup>. 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]<sup>+</sup>.

**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%).  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 7.26$  (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, =CH), 5.02 (ddt,  $^3J = 17.1$  Hz,  $^2J = 2.0$  Hz,  $^4J = 1.6$  Hz, 2 H,  $H_Z\text{HC=}$ ), 4.96 (ddt,  $^3J = 10.1$  Hz,  $^2J = 2.1$  Hz,  $^4J = 1.2$  Hz, 2 H,  $H_E\text{HC=}$ ), 4.04 (t,  $^3J = 6.4$  Hz, 4 H,  $\text{OCH}_2$ ), 2.09 (m<sub>c</sub>, 4 H, =CHCH<sub>2</sub>), 1.77 (m<sub>c</sub>, 4 H,  $\text{OCH}_2\text{CH}_2$ ), 1.52 (m<sub>c</sub>, 4 H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ) ppm.  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 151.3$  (C-1,3), 138.3 (=CH), 130.8 (C-5), 114.9 ( $\text{H}_2\text{C=}$ ), 105.2 (C-4,6), 69.3 ( $\text{OCH}_2$ ), 33.2 (=CHCH<sub>2</sub>), 28.3 ( $\text{OCH}_2\text{CH}_2$ ), 25.0 ( $\text{OCH}_2\text{CH}_2\text{CH}_2$ ) 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<sup>-1</sup>. MS (EI, 70 eV):  $m/z$  (%) = 319 (1) [M]<sup>+</sup>, 273 (67), 155 (39), 137 (52), 109 (53), 81 (100), 67 (81). MS (CI):  $m/z$  (%) = 320 (4) [M + H]<sup>+</sup>.

**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.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 6.64$  (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, =CH), 5.08 (ddt,  $^3J = 17.1$  Hz,  $^2J = 1.9$  Hz,  $^4J = 1.6$  Hz, 2 H,  $H_Z\text{HC=}$ ), 5.01 (ddt,  $^3J = 10.2$  Hz,  $^2J = 1.9$  Hz,  $^4J = 1.2$  Hz, 2 H,  $H_E\text{HC=}$ ), 4.02 (t,  $^3J = 6.4$  Hz, 4 H,  $\text{OCH}_2$ ), 3.84 (br. s, 2 H,  $\text{NH}_2$ ), 2.26 (m<sub>c</sub>, 4 H, =CHCH<sub>2</sub>), 1.92 (m<sub>c</sub>, 4 H,  $\text{OCH}_2\text{CH}_2$ ) ppm.  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 146.9$  (C-2,6), 137.9 (=CH), 125.9 (C-1), 116.8 (C-4), 115.1 ( $\text{H}_2\text{C=}$ ), 105.1 (C-3,5), 67.8 ( $\text{OCH}_2$ ), 30.3 (=CHCH<sub>2</sub>), 28.6 ( $\text{OCH}_2\text{CH}_2$ ) 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<sup>-1</sup>. MS (EI, 70 eV):  $m/z$  (%) = 261 (100) [M]<sup>+</sup>, 193 (25), 125 (84), 69 (31). MS (CI):  $m/z$  (%) = 262 (14) [M + H]<sup>+</sup>. C<sub>16</sub>H<sub>23</sub>NO<sub>2</sub> (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%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 6.63$  (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, =CH), 5.03 (ddt,  $^3J = 17.1$  Hz,  $^2J = 2.0$  Hz,  $^4J = 1.6$  Hz, 2 H,  $H_Z\text{HC=}$ ), 4.97 (ddt,  $^3J = 10.2$  Hz,  $^2J = 2.0$  Hz,  $^4J = 1.2$  Hz, 2 H,  $H_E\text{HC=}$ ), 3.99 (t,  $^3J = 6.5$  Hz, 4 H,  $\text{OCH}_2$ ), 3.81 (br. s, 2 H,  $\text{NH}_2$ ), 2.13 (m<sub>c</sub>, 4 H, =CHCH<sub>2</sub>), 1.82 (m<sub>c</sub>, 4 H,  $\text{OCH}_2\text{CH}_2$ ), 1.58 (m<sub>c</sub>, 4 H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ) ppm.  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 146.9$  (C-2,6), 138.5 (=CH), 125.8 (C-1), 116.8 (C-4), 114.7 ( $\text{H}_2\text{C=}$ ), 105.0 (C-3,5), 69.3 ( $\text{OCH}_2$ ), 33.4 (=CHCH<sub>2</sub>), 28.9 ( $\text{OCH}_2\text{CH}_2$ ), 25.4 ( $\text{OCH}_2\text{CH}_2\text{CH}_2$ ) 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<sup>-1</sup>. MS (EI, 70 eV):  $m/z$  (%) = 289 (80) [M]<sup>+</sup>, 207 (17), 125 (100). MS (CI):  $m/z$  (%) = 290 (100) [M + H]<sup>+</sup>. HRMS: calcd. for C<sub>18</sub>H<sub>27</sub>NO<sub>2</sub> 289.20419; found 289.20416 (0.1 ppm); calcd. for C<sub>17</sub><sup>13</sup>C<sub>27</sub>H<sub>27</sub>NO<sub>2</sub> 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.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 8.75$  (s, 2 H, NH), 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, =CH), 5.04 (ddt,  $^3J = 17.1$  Hz,  $^2J = 1.9$  Hz,  $^4J = 1.6$  Hz, 4 H,  $H_Z\text{HC=}$ ), 5.01 (ddt,  $^3J = 10.3$  Hz,  $^2J = 1.9$  Hz,  $^4J = 1.1$  Hz, 4 H,  $H_E\text{HC=}$ ), 4.01 (t,  $^3J = 6.5$  Hz, 8 H,  $\text{OCH}_2$ ), 2.21 (m<sub>c</sub>, 8 H, =CHCH<sub>2</sub>), 1.87 (m<sub>c</sub>, 8 H,  $\text{OCH}_2\text{CH}_2$ ) ppm.  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 157.8$  (C=O), 154.5 (C-2,6), 137.8 (=CH), 127.9 (C-4), 115.2 ( $\text{H}_2\text{C=}$ ), 113.2 (C-1), 105.1 (C-3,5), 67.9

(OCH<sub>2</sub>), 30.0 (=CHCH<sub>2</sub>), 28.3 (OCH<sub>2</sub>CH<sub>2</sub>) ppm. IR (KBr):  $\tilde{\nu}$  = 3273, 3073, 2944, 2864, 1680, 1639, 1600, 1513, 1450, 1393, 1261, 1106, 910, 802, 758, 715 cm<sup>-1</sup>. MS (EI, 70 eV): *m/z* (%) = 576 (42) [M]<sup>+</sup>, 491 (8), 261 (100). MS (CI): *m/z* (%) = 577 (100) [M + H]<sup>+</sup>. HRMS: calcd. for C<sub>34</sub>H<sub>44</sub>N<sub>2</sub>O<sub>6</sub> 576.31995; found 576.32021 (0.5 ppm); calcd. for C<sub>33</sub><sup>13</sup>CH<sub>44</sub>N<sub>2</sub>O<sub>6</sub> 577.32330; found 577.32317 (0.2 ppm). C<sub>34</sub>H<sub>44</sub>N<sub>2</sub>O<sub>6</sub> (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<sub>f</sub> = 0.69] yielded colorless crystalline product **4b** (891 mg, 52%). M.p. 97 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 8.72 (s, 2 H, NH), 7.16 (t, <sup>3</sup>J = 8.4 Hz, 2 H, 4-H), 6.58 (d, <sup>3</sup>J = 8.4 Hz, 4 H, 3-H, 5-H), 5.79 (ddt, <sup>3</sup>J = 17.0 Hz, <sup>3</sup>J = 10.2, <sup>3</sup>J = 6.6 Hz, 4 H, =CH), 5.00 (ddt, <sup>3</sup>J = 17.1 Hz, <sup>2</sup>J = 2.0 Hz, <sup>4</sup>J = 1.6 Hz, 4 H, H<sub>2</sub>HC=), 4.93 (ddt, <sup>3</sup>J = 10.2 Hz, <sup>2</sup>J = 2.0 Hz, <sup>4</sup>J = 1.2 Hz, 4 H, H<sub>E</sub>HC=), 4.01 (t, <sup>3</sup>J = 6.6 Hz, 8 H, OCH<sub>2</sub>), 2.09 (m<sub>c</sub>, 8 H, =CHCH<sub>2</sub>), 1.79 (m<sub>c</sub>, 8 H, OCH<sub>2</sub>CH<sub>2</sub>), 1.54 (m<sub>c</sub>, 8 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 157.8 (C=O), 154.6 (C-2,6), 138.5 (=CH), 127.8 (C-4), 114.7 (H<sub>2</sub>C=), 113.5 (C-1), 105.2 (C-3,5), 68.5 (OCH<sub>2</sub>), 33.3 (=CHCH<sub>2</sub>), 28.6 (OCH<sub>2</sub>CH<sub>2</sub>), 25.1 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) ppm. IR (KBr):  $\tilde{\nu}$  = 3266, 3076, 2944, 2866, 1679, 1641, 1607, 1590, 1513, 1454, 1394, 1262, 1107, 908, 798, 762, 709 cm<sup>-1</sup>. MS (EI, 70 eV): *m/z* (%) = 632 (38) [M]<sup>+</sup>, 289 (100). HRMS: calcd. for C<sub>38</sub>H<sub>52</sub>N<sub>2</sub>O<sub>6</sub> 632.38251; found 632.38281 (0.5 ppm); calcd. for C<sub>37</sub><sup>13</sup>CH<sub>52</sub>N<sub>2</sub>O<sub>6</sub> 633.38586; found 633.38604 (0.3 ppm). C<sub>38</sub>H<sub>52</sub>N<sub>2</sub>O<sub>6</sub> (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<sub>f</sub> = 0.83] yielded crystalline colorless product **5a** (1.57 g, 80%). M.p. 62 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 6.73 (t, <sup>3</sup>J = 8.2 Hz, 2 H, 4-H), 6.50 (d, <sup>3</sup>J = 8.3 Hz, 4 H, 3-H, 5-H), 5.81 (ddt, <sup>3</sup>J = 17.0 Hz, <sup>3</sup>J = 10.3 Hz, <sup>3</sup>J = 6.6 Hz, 4 H, =CH), 5.02 (ddt, <sup>3</sup>J = 17.1 Hz, <sup>2</sup>J = 1.9 Hz, <sup>4</sup>J = 1.6 Hz, 4 H, H<sub>2</sub>HC=), 4.96 (ddt, <sup>3</sup>J = 10.2 Hz, <sup>2</sup>J = 2.0 Hz, <sup>4</sup>J = 1.2 Hz, 4 H, H<sub>E</sub>HC=), 4.21 (br. s, 2 H, NH), 3.96 (t, <sup>3</sup>J = 6.6 Hz, 8 H, OCH<sub>2</sub>), 3.37 (s, 4 H, NCH<sub>2</sub>), 2.19 (m<sub>c</sub>, 8 H, =CHCH<sub>2</sub>), 1.86 (m<sub>c</sub>, 8 H, OCH<sub>2</sub>CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 150.4 (C-2,6), 137.9 (=CH), 127.7 (C-1), 119.4 (C-4), 115.1 (H<sub>2</sub>C=), 105.7 (C-3,5), 68.0 (OCH<sub>2</sub>), 47.5 (NCH<sub>2</sub>), 30.2 (=CHCH<sub>2</sub>), 28.6 (OCH<sub>2</sub>CH<sub>2</sub>) 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<sup>-1</sup>. MS (EI, 70 eV): *m/z* (%) = 548 (20), 275 (100). HRMS: calcd. for C<sub>34</sub>H<sub>48</sub>N<sub>2</sub>O<sub>4</sub> 548.36139; found 548.36294 (2.8 ppm); calcd. for C<sub>33</sub><sup>13</sup>CH<sub>48</sub>N<sub>2</sub>O<sub>4</sub> 549.36475; found 549.36797 (5.9 ppm). C<sub>34</sub>H<sub>48</sub>N<sub>2</sub>O<sub>4</sub> (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<sub>f</sub> = 0.87] yielded crystalline colorless product **5b** (430 mg, 90%). M.p. 35 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 6.74 (t, <sup>3</sup>J = 8.3 Hz,

2 H, 4-H), 6.50 (d, <sup>3</sup>J = 8.3 Hz, 4 H, 3-H, 5-H), 5.78 (ddt, <sup>3</sup>J = 16.9 Hz, <sup>3</sup>J = 10.2 Hz, <sup>3</sup>J = 6.7 Hz, 4 H, =CH), 5.00 (ddt, <sup>3</sup>J = 17.1 Hz, <sup>2</sup>J = 2.0 Hz, <sup>4</sup>J = 1.6 Hz, 4 H, H<sub>2</sub>HC=), 4.94 (ddt, <sup>3</sup>J = 10.2 Hz, <sup>2</sup>J = 2.1 Hz, <sup>4</sup>J = 1.2 Hz, 4 H, H<sub>E</sub>HC=), 4.23 (br. s, 2 H, NH), 3.95 (t, <sup>3</sup>J = 6.7 Hz, 8 H, OCH<sub>2</sub>), 3.34 (s, 4 H, NCH<sub>2</sub>), 2.08 (m<sub>c</sub>, 8 H, =CHCH<sub>2</sub>), 1.78 (m<sub>c</sub>, 8 H, OCH<sub>2</sub>CH<sub>2</sub>), 1.52 (m<sub>c</sub>, 8 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 150.5 (C-2,6), 138.5 (=CH), 127.5 (C-1), 119.5 (C-4), 114.7 (H<sub>2</sub>C=), 105.5 (C-3,5), 68.5 (OCH<sub>2</sub>), 47.4 (NCH<sub>2</sub>), 33.4 (=CHCH<sub>2</sub>), 28.8 (OCH<sub>2</sub>CH<sub>2</sub>), 25.3 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) 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<sup>-1</sup>. MS (EI, 70 eV): *m/z* (%) = 604 (30) [M]<sup>+</sup>, 303 (100).

**1,3-Bis[2',6'-bis(pent-4-enyloxy)phenyl]imidazolium 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<sub>f</sub> = 0.17] yielded crystalline colorless product **6a** (940 mg, 83%). M.p. 203 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 8.14 (s, 1 H, 2-H), 7.37 (t, <sup>3</sup>J = 8.6 Hz, 2 H, 4'-H), 6.68 (d, <sup>3</sup>J = 8.6 Hz, 4 H, 3'-H, 5'-H), 5.80 (ddt, <sup>3</sup>J = 17.0 Hz, <sup>3</sup>J = 10.2 Hz, <sup>3</sup>J = 6.6 Hz, 4 H, =CH), 5.03-4.97 (m, 8 H, H<sub>2</sub>C=), 4.59 (s, 4 H, 4-H, 5-H), 4.10 (t, <sup>3</sup>J = 6.7 Hz, 8 H, OCH<sub>2</sub>), 2.19 (m<sub>c</sub>, 8 H, =CHCH<sub>2</sub>), 1.93 (m<sub>c</sub>, 8 H, OCH<sub>2</sub>CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 160.4 (C-2), 154.3 (C-2',6'), 136.9 (=CH), 131.3 (C-4'), 115.5 (H<sub>2</sub>C=), 112.2 (C-1'), 105.0 (C-3',5'), 68.3 (OCH<sub>2</sub>), 51.3 (C-4,5), 29.7 (=CHCH<sub>2</sub>), 27.9 (OCH<sub>2</sub>CH<sub>2</sub>) ppm. IR (KBr):  $\tilde{\nu}$  = 3075, 2946, 1618, 1481, 1462, 1392, 1256, 1107, 991, 907, 775, 731, 643 cm<sup>-1</sup>. ESI-MS (MeOH): *m/z* (%) = 559.36 (100) [C<sub>35</sub>H<sub>47</sub>N<sub>2</sub>O<sub>4</sub>]<sup>+</sup>. HRMS: calcd. for C<sub>35</sub>H<sub>47</sub>N<sub>2</sub>O<sub>4</sub> 559.35358; found 559.34896 (8.3 ppm); calcd. for C<sub>34</sub><sup>13</sup>CH<sub>47</sub>N<sub>2</sub>O<sub>4</sub> 560.35693; found 560.35345 (6.2 ppm). C<sub>35</sub>H<sub>47</sub>ClN<sub>2</sub>O<sub>4</sub> (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]imidazolium 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<sub>f</sub> = 0.16] yielded crystalline colorless product **6b** (152 mg, 73%). M.p. 206 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 8.02 (s, 1 H, 2-H), 7.34 (t, <sup>3</sup>J = 8.5 Hz, 2 H, 4'-H), 6.65 (d, <sup>3</sup>J = 8.6 Hz, 4 H, 3'-H, 5'-H), 5.74 (ddt, <sup>3</sup>J = 17.0 Hz, <sup>3</sup>J = 10.2 Hz, <sup>3</sup>J = 6.6 Hz, 4 H, =CH), 4.98 (ddt, <sup>3</sup>J = 17.1 Hz, <sup>2</sup>J = 1.7 Hz, <sup>4</sup>J = 1.6 Hz, 4 H, H<sub>2</sub>HC=), 4.94 (ddt, <sup>3</sup>J = 10.2 Hz, <sup>2</sup>J = 1.7 Hz, <sup>4</sup>J = 1.2 Hz, 4 H, H<sub>E</sub>HC=), 4.60 (s, 4 H, 4-H, 5-H), 4.08 (t, <sup>3</sup>J = 6.8 Hz, 8 H, OCH<sub>2</sub>), 2.01 (m<sub>c</sub>, 8 H, =CHCH<sub>2</sub>), 1.84 (m<sub>c</sub>, 8 H, OCH<sub>2</sub>CH<sub>2</sub>), 1.51 (m<sub>c</sub>, 8 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 160.3 (C-2), 154.5 (C-2',6'), 138.0 (=CH), 131.3 (C-4'), 115.1 (H<sub>2</sub>C=), 112.5 (C-1'), 105.1 (C-3',5'), 69.0 (OCH<sub>2</sub>), 51.6 (C-4,5), 33.1 (=CHCH<sub>2</sub>), 28.8 (OCH<sub>2</sub>CH<sub>2</sub>), 25.0 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) ppm. IR (KBr):  $\tilde{\nu}$  = 3076, 2944, 1618, 1482, 1463, 1396, 1257, 1108, 992, 907, 774, 730, 649 cm<sup>-1</sup>. ESI-MS (MeOH): *m/z* (%) = 615.41 (100) [C<sub>39</sub>H<sub>55</sub>N<sub>2</sub>O<sub>4</sub>]<sup>+</sup>. HRMS: calcd. for C<sub>39</sub>H<sub>55</sub>N<sub>2</sub>O<sub>4</sub> 615.4162; found 615.41635 (0.2 ppm); calcd. for C<sub>38</sub><sup>13</sup>CH<sub>55</sub>N<sub>2</sub>O<sub>4</sub> 616.41956; found 616.41938 (0.3 ppm). C<sub>39</sub>H<sub>55</sub>ClN<sub>2</sub>O<sub>4</sub> (651.33): calcd. C 71.92, H 8.51, N 4.30; found 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)-imidazolium-bicyclo[10.10.1]tricosaphan-6,17-diene Chloride (7a):** General procedure F: 1,3-Bis[2',6'-bis(pent-4-enyloxy)phenyl]imidazolium chloride (**6a**, 600 mg, 1.09 mmol), benzylidenebis(tricyclohexylphos-

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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.  $^1\text{H NMR}^{[33]}$  (500 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 8.07$  (s, 1 H, 2-H), 7.36 (m<sub>c</sub>, 2 H, 4'-H), 6.65 (m<sub>c</sub>, 4 H, 3'-H, 5'-H), 5.59 (m<sub>c</sub>, 0.7 H, = $\text{CH}_2^*$ ), 5.50 (m<sub>c</sub>, 3.3 H, = $\text{CH}_E^*$ ), 4.64 (m<sub>c</sub>, 4 H, 4-H, 5-H), 4.15–4.05 (m, 8 H,  $\text{OCH}_2$ ), 2.41 (m<sub>c</sub>, 4 H,  $\text{CH}_2^{\#}$ ), 2.17 (m<sub>c</sub>, 4 H,  $\text{CH}_2^{\#}$ ), 1.94 (m<sub>c</sub>, 4 H,  $\text{CH}_2^{\#}$ ), 1.76 (m<sub>c</sub>, 4 H,  $\text{CH}_2^{\#}$ ) ppm.  $^{13}\text{C NMR}^{[33]}$  (125 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 161.0$ , 160.6 (C-2), 154.9, 154.3 (C-2',6'), 131.7, 131.6 (C-4'), 130.8, 130.6 (=CH<sub>Z</sub>\*), 129.5, 129.5 (=CH<sub>E</sub>\*), 112.4, 111.9 (C-1'), 105.3, 104.9 (C-3',5'), 68.8, 67.9 ( $\text{OCH}_2$ ), 51.6, 50.4 (C-4,5), 30.1, 28.9, 28.8, 27.4, 23.7, 23.6 ( $\text{CH}_2$ ) ppm. IR (KBr):  $\tilde{\nu} = 3030$ , 2938, 1628, 1599, 1480, 1459, 1299, 1259, 1102, 925, 777, 722  $\text{cm}^{-1}$ . ESI-MS (MeOH):  $m/z$  (%) = 503.29 (100) [ $\text{C}_{31}\text{H}_{39}\text{N}_2\text{O}_4$ ]<sup>+</sup>. HRMS: calcd. for  $\text{C}_{31}\text{H}_{39}\text{N}_2\text{O}_4$  503.29016; found 503.28646 (7.4 ppm); calcd. for  $\text{C}_{30}^{13}\text{CH}_{39}\text{N}_2\text{O}_6$  504.29434; found 504.28966 (9.3 ppm).

**2,13,15,26-Tetraoxa-1,14(1,3,2)-dibenzena-27(1,3)-imidazoliniumabicyclo[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  $\mu\text{mol}$ ) 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.  $^1\text{H NMR}^{[33]}$  (500 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 7.72$  (s, 1 H, 2-H), 7.31 (m<sub>c</sub>, 2 H, 4'-H), 6.61 (m<sub>c</sub>, 4 H, 3'-H, 5'-H), 5.36 (m<sub>c</sub>, 4 H, =CH), 4.58 (s, 4 H, 4-H, 5-H), 3.98 (t,  $^3J = 8.0$  Hz, 8 H,  $\text{OCH}_2$ ), 2.16 (m<sub>c</sub>, 8 H, = $\text{CHCH}_2$ ), 1.80 (m<sub>c</sub>, 8 H,  $\text{OCH}_2\text{CH}_2$ ), 1.48 (m<sub>c</sub>, 8 H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ) ppm.  $^{13}\text{C NMR}^{[33]}$  (125 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 159.2$ , 159.1 (C-2), 155.3, 155.3 (C-2',6'), 131.5, 131.5 (C-4'), 131.1 (=CH<sub>Z</sub>\*), 130.3, 130.3 (=CH<sub>E</sub>\*), 112.0, 111.9 (C-1'), 104.9, 104.7 (C-3',5'), 69.5, 69.4 ( $\text{OCH}_2$ ), 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 ( $\text{CH}_2$ ) ppm. IR (KBr):  $\tilde{\nu} = 2944$ , 2853, 1619, 1600, 1468, 1256, 1103, 967, 779, 733, 638  $\text{cm}^{-1}$ . ESI-MS (MeOH):  $m/z$  (%) = 559.35 (100) [ $\text{C}_{35}\text{H}_{47}\text{N}_2\text{O}_4$ ]<sup>+</sup>. HRMS: calcd. for  $\text{C}_{35}\text{H}_{47}\text{N}_2\text{O}_4$  559.35358; found 559.35357 (0.0 ppm); calcd. for  $\text{C}_{34}^{13}\text{CH}_{47}\text{N}_2\text{O}_4$  560.35693; found 560.35689 (0.1 ppm).

**2,11,13,22-Tetraoxa-1,12(1,3,2)-dibenzena-23(1,3)-imidazoliniumabicyclo[10.10.1]tricosaphane Chloride (8a):** General procedure G: 2,11,13,22-Tetraoxa-1,12(1,3,2)-dibenzena-23(1,3)-imidazoliniumabicyclo[10.10.1]tricosaphan-6,17-diene chloride (**7a**, 280 mg, 519  $\mu\text{mol}$ ), 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.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 8.14$  (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,  $\text{OCH}_a\text{H}_b$ ), 4.10 (ddd,  $^2J = 9.3$  Hz,  $^3J = 6.8$  Hz,  $^3J = 3.2$  Hz, 4 H,  $\text{OCH}_a\text{H}_b$ ), 1.80 (m<sub>c</sub>, 8 H,  $\text{CH}_2$ ), 1.61 (m<sub>c</sub>, 4 H,  $\text{CH}_2$ ), 1.47 (m<sub>c</sub>, 12 H,  $\text{CH}_2$ ) ppm.  $^{13}\text{C NMR}$  (MHz,  $\text{CDCl}_3$ ):  $\delta = 160.4$  (C-2), 155.0 (C-2',6'), 131.4 (C-4'), 112.4 (C-1'), 104.9 (C-3',5'), 69.0 ( $\text{OCH}_2$ ), 51.7 (C-4,5), 28.1, 26.6, 24.3 ( $\text{CH}_2$ ) ppm. IR (KBr):  $\tilde{\nu} = 3058$ , 2941, 2864, 1619, 1598, 1482, 1458, 1386, 1297, 1257, 1101, 925, 777, 721, 640  $\text{cm}^{-1}$ . ESI-MS (MeOH):  $m/z$  (%) = 507.32 (100) [ $\text{C}_{31}\text{H}_{43}\text{N}_2\text{O}_4$ ]<sup>+</sup>. HRMS: calcd. for  $\text{C}_{31}\text{H}_{43}\text{N}_2\text{O}_4$  507.32230; found 507.32225 (0.1 ppm); calcd. for  $\text{C}_{30}^{13}\text{CH}_{43}\text{N}_2\text{O}_4$  508.32565; found 508.32563 (0.0 ppm).  $\text{C}_{31}\text{H}_{43}\text{ClN}_2\text{O}_4$  (543.12): calcd. C 68.55, H 7.98, N 5.16,  $\text{C}_{31}\text{H}_{43}\text{ClN}_2\text{O}_4 \cdot \text{CH}_3\text{OH}$  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 chloro-

form. Empirical formula  $\text{C}_{31}\text{H}_{43}\text{ClN}_2\text{O}_4 \cdot 2\text{CHCl}_3$ ,  $F_w = 781.86$  g/mol,  $a = 24.435(2)$  Å,  $b = 12.4936(9)$  Å,  $c = 16.5068(9)$  Å,  $\beta = 129.063(5)^\circ$ ,  $V = 3912.7(4)$  Å<sup>3</sup>,  $T = 220(2)$  K,  $\rho_{\text{calcd.}} = 1.327$  g/cm<sup>3</sup>,  $\mu = 0.544$  mm<sup>-1</sup>, monoclinic, space group  $C2/c$ ,  $Z = 4$ , STOE Imaging Plate Diffraction System (IPDS-1), Mo- $K_\alpha$  ( $\lambda = 0.71073$  Å), 14905 measured reflections in the range of  $6^\circ \leq 2\theta \leq 56^\circ$ , 4554 independent reflections used for refinement.  $R_{\text{int}} = 0.0363$ . 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,  $\text{GoF} = 1.057$ , residual electron density 0.63/−0.75 [e/Å<sup>3</sup>]. 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](http://www.ccdc.cam.ac.uk/data_request/cif).

**2,13,15,26-Tetraoxa-1,14(1,3,2)-dibenzena-27(1,3)-imidazoliniumabicyclo[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.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 8.24$  (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,  $\text{OCH}_2$ ), 1.82 (m<sub>c</sub>, 8 H,  $\text{OCH}_2\text{CH}_2$ ), 1.46 (m<sub>c</sub>, 8 H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 1.39 (m<sub>c</sub>, 16 H,  $\text{CH}_2$ ) ppm.  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 160.7$  (C-2), 154.5 (C-2',6'), 131.1 (C-4'), 112.9 (C-1'), 105.3 (C-3',5'), 69.4 ( $\text{OCH}_2$ ), 51.9 (C-4,5), 28.5, 26.5, 26.3, 24.9 ( $\text{CH}_2$ ) ppm. IR (KBr):  $\tilde{\nu} = 2932$ , 1617, 1480, 1459, 1390, 1301, 1257, 1101, 774, 728, 648  $\text{cm}^{-1}$ . ESI-MS (MeOH):  $m/z$  (%) = 563.39 (100) [ $\text{C}_{35}\text{H}_{51}\text{N}_2\text{O}_4$ ]<sup>+</sup>. HRMS: calcd. for  $\text{C}_{35}\text{H}_{51}\text{N}_2\text{O}_4$  563.38489; found 563.38357 (2.3 ppm); calcd. for  $\text{C}_{34}^{13}\text{CH}_{51}\text{N}_2\text{O}_4$  564.38824; found 564.38928 (1.8 ppm).

**2,11,13,22-Tetraoxa-1,12(1,3,2)-dibenzena-23(1,3)-imidazoliniumabicyclo[10.10.1]tricosaphan-23'-ylidithiocarboxylate (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.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 7.16$  (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<sub>c</sub>, 8 H,  $\text{OCH}_2$ ), 1.95 (m<sub>c</sub>, 4 H,  $\text{CH}_2$ ), 1.80–1.50 (m, 20 H,  $\text{CH}_2$ ) ppm.  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 221.3$  ( $\text{CS}_2$ ), 166.0 (C-2), 156.6 (C-2',6'), 130.4 (C-4'), 113.5 (C-1'), 104.1 (C-3',5'), 68.4 ( $\text{OCH}_2$ ), 49.0 (C-4,5), 28.5, 26.0, 23.9 ( $\text{CH}_2$ ) ppm. ESI-MS (MeOH):  $m/z$  (%) = 583.2650 (37) [ $\text{C}_{32}\text{H}_{42}\text{N}_2\text{O}_4\text{S}_2 + \text{H}$ ]<sup>+</sup> (calcd. 583.2659, 1.5 ppm), 584.2686 (11) [ $\text{C}_{31}^{13}\text{CH}_{42}\text{N}_2\text{O}_4\text{S}_2 + \text{H}$ ]<sup>+</sup> (calcd. 584.2690, 0.7 ppm), 621.2196 (100) [ $\text{C}_{32}\text{H}_{42}\text{N}_2\text{O}_4\text{S}_2 + \text{K}$ ]<sup>+</sup> (calcd. 621.2223, 4.3 ppm), 622.2255 (24) [ $\text{C}_{31}^{13}\text{CH}_{42}\text{N}_2\text{O}_4\text{S}_2 + \text{K}$ ]<sup>+</sup> (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<sub>2</sub>, no assignments possible.

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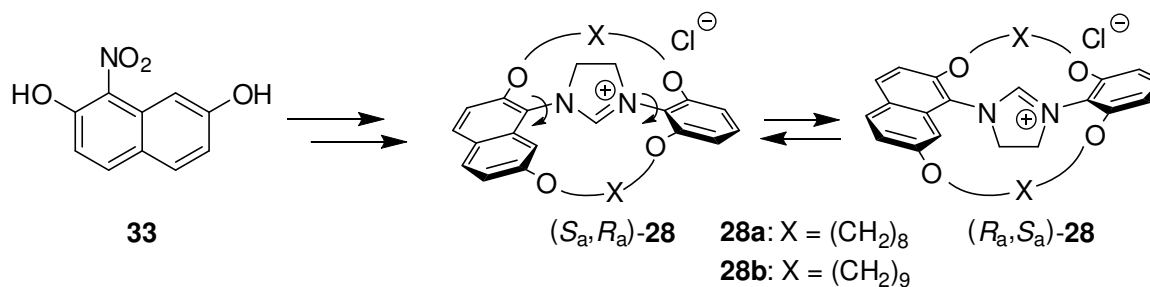
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### 3.2 Concave Reagents, 53: *Chiral Concave Imidazolium Salts as Precursors to Chiral Concave N-Heterocyclic Carbenes.*

O. Winkelmann, D. Linder, J. Lacour, C. Näther, U. Lüning, *Eur. J. Org. Chem.* **2007**, 3687-3697.

In Analogie zur Synthese symmetrischer konkaver Imidazoliumsalze **27** (siehe Seite 13) konnten durch Verwendung von 2,7-Dihydroxy-1-nitronaphthalin (**33**) als Synthesebaustein in jeweils elfstufigen Synthesen die verschieden großen axial-chiralen Bimakrocyclen **28a** und **28b** in racemischer Form erhalten werden. Aufgrund der zwei unsymmetrisch substituierten Arylbrückenköpfe enthalten die Verbindungen jeweils zwei Chiralitätsachsen. Die Struktur von **28b** konnte durch Einkristall-Röntgenstrukturanalyse bestätigt werden, wobei beide Enantiomere in der Elementarzelle enthalten waren.



Die Konfigurationsstabilität der axial-chiralen Bimakrocyclen **28** wurde mit Hilfe der von Jérôme Lacour entwickelten helical-chiralen Phosphatanionen  $\Delta$ -TRISPHAT<sup>[134]</sup> und  $\Lambda$ -BINPHAT<sup>[135]</sup> untersucht. Durch Austausch der Chloridanionen in den racemischen Salzen **28** gegen die enantiomerenreinen Phosphatanionen wurden diastereomere Ionenpaare erhalten, die per <sup>1</sup>H-NMR-Spektroskopie untersucht wurden.

Das dabei beobachtete Ungleichgewicht im Verhältnis der diastereomeren Ionenpaare ist typisch für konfigurationslabile Kationen,<sup>[136-140]</sup> und die verschieden großen Bimakrocyclen **28a** und **28b** lieferten nahezu identische Ergebnisse. Es konnte zweifelsfrei gezeigt werden, dass die enantiomeren Imidazoliumsalze (S<sub>a</sub>, R<sub>a</sub>)-**28** und (R<sub>a</sub>, S<sub>a</sub>)-**28** bei Raumtemperatur miteinander im Gleichgewicht stehen. Die Umwandlung (Racemisierung) der Enantiomere (Atropisomere) wird durch eine Rotation des Imidazoliumrings bezüglich der Arylbrückenköpfe ermöglicht. Die Aktivierungsenergie für die Racemisierung wurde experimentell abgeschätzt ( $77 \text{ kJ/mol} \geq \Delta G^\ddagger \geq 56 \text{ kJ/mol}$ ) und liegt unterhalb des für die Trennung von Atropisomeren mindestens benötigten Wertes ( $\Delta G^\ddagger \geq 90 \text{ kJ/mol}$ ).<sup>[141]</sup> Eine Anwendung der Azoliumsalze **28** in der asymmetrischen Katalyse war somit nicht möglich.

# Chiral Concave Imidazolium Salts as Precursors to Chiral Concave *N*-Heterocyclic Carbenes<sup>[‡]</sup>

Ole Winkelmann,<sup>[a]</sup> David Linder,<sup>[b]</sup> Jérôme Lacour,<sup>\*[b]</sup> Christian Näther,<sup>[c]</sup> and Ulrich Lüning<sup>\*[a]</sup>

**Keywords:** Axial chirality / Carbenes / Chiral anions / Macrocycles / NMR enantiodifferentiation / Supramolecular chemistry

Imidazolium moieties have been incorporated into bi-macrocycles 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 imidazolium 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 imidazolium 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.

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## Introduction

Thiamine-dependent biochemical transformations use the ability of a thiazolium ion to act as a nucleophile after deprotonation.<sup>[1,2]</sup> 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 imidazolium,<sup>[3,4]</sup> imidazolium,<sup>[5]</sup> 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.<sup>[6]</sup>

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

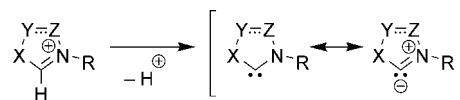
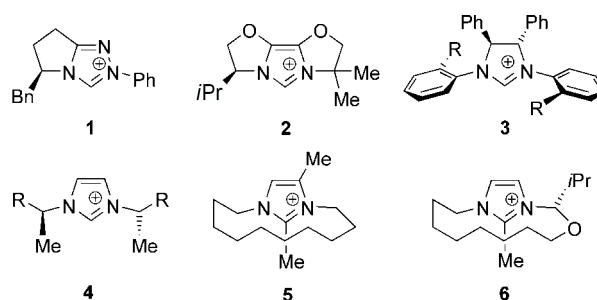


Figure 1. Heterocyclic azolium ions are the precursors for *N*-heterocyclic carbenes (NHCs), which are also drawn in their mesomeric betain form.<sup>[6]</sup> Examples: thiazolium ( $X = S$ ,  $Y = Z = CR'$ ), imidazolium ( $X = NR''$ ,  $Y = Z = CR'$ ), imidazolium ( $X = NR''$ ,  $Y = Z = CR'_2$ ),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

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



[‡] Concave Reagents, 53. Part 52: O. Winkelmann, C. Näther, U. Lüning, *Eur. J. Org. Chem.* **2007**, 981–987.

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## FULL PAPER

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Planar-chiral imidazolium derivatives, such as moieties **5**<sup>[20]</sup> and **6**,<sup>[21]</sup> 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 imidazolium ion into a bimaocyclic framework, we have already realized structures containing concave shielding.<sup>[22]</sup> 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 bimaocycle with a non-symmetric cavity will result.

## Results and Discussion

The general strategy for the synthesis of an axially chiral concave imidazolium ion was adopted from the route leading to non-chiral analogues: preparation of bis-alkenyl-substituted anilines, construction of the imidazolium ion, ring-closing metathesis and hydrogenation of the double bonds.<sup>[22]</sup> 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 bimaocycle. 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).

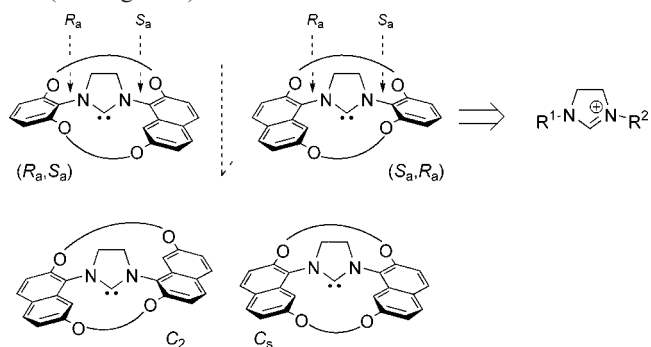
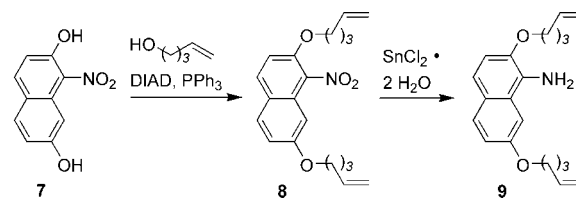


Figure 2. Schematic representation of axially chiral bimaocyclic concave *N*-heterocyclic carbenes, which may be obtained from their respective imidazolium ions [( $R_a, S_a$ ) and ( $S_a, R_a$ ) enantiomers]. The use of two naphthalene bridgeheads may lead to the formation of a chiral  $C_2$ -symmetric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

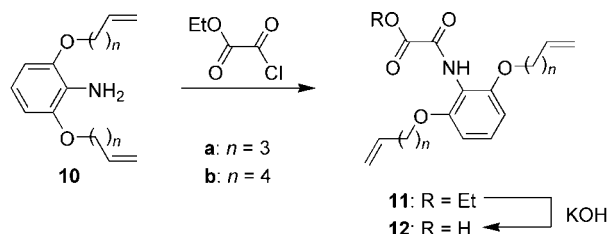
## Synthesis of Axially Chiral Imidazolium Chlorides

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,<sup>[23,24]</sup> two homologous mono-esters **11** were generated by reacting ethyl chloroglyoxalate with 2,6-bis(alkenyl-oxy)anilines **10**<sup>[22]</sup> in 83% yield (**11a**) and 91% (**11b**) yield, respectively. Subsequent saponification with potassium hydroxide yielded the acids **12a** (98%) and **12b** (97%).

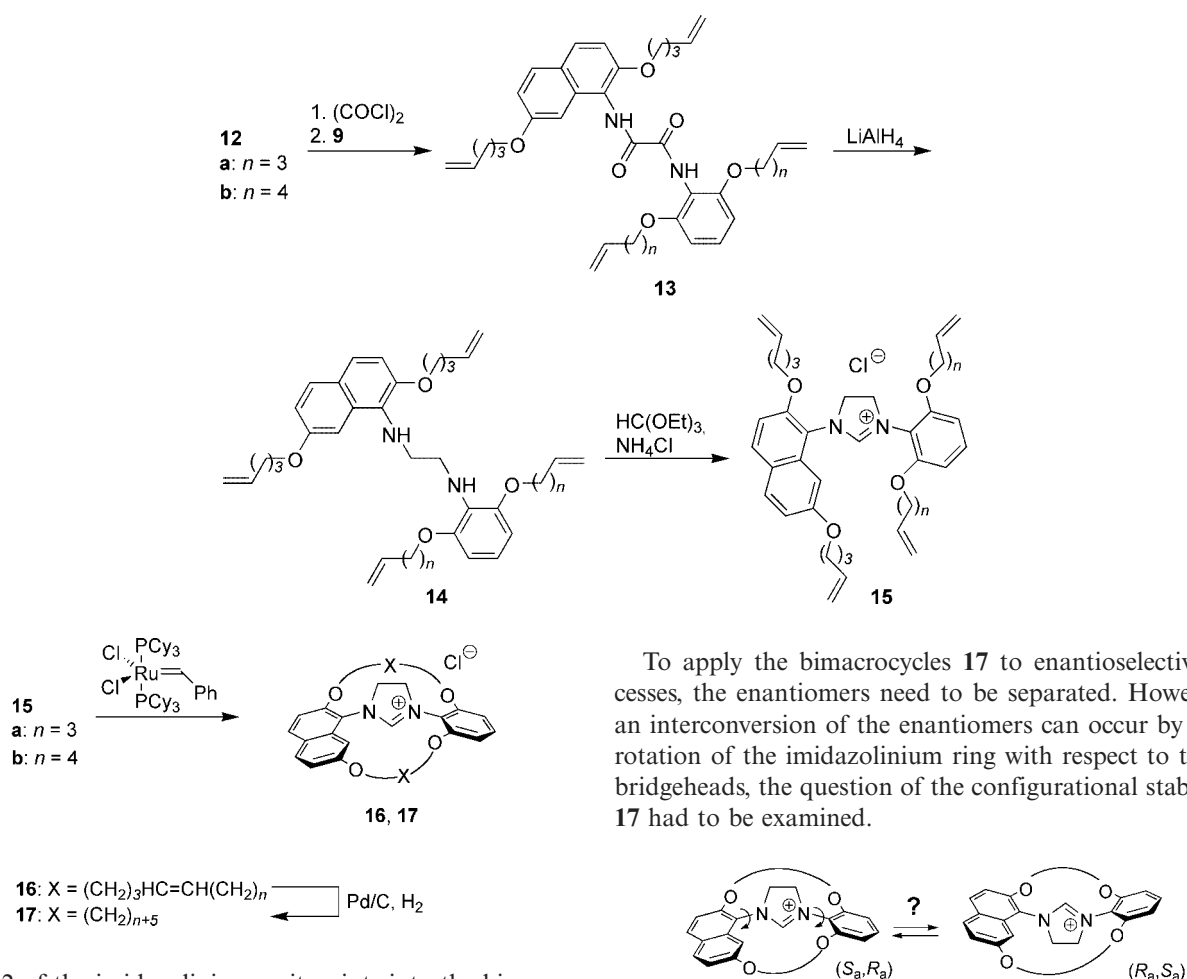


The acids **12** were transformed into their chlorides by reaction with oxalyl chloride and were then reacted with the naphthaleneamine **9**. The mixed diamides **13a** and **13b** could be isolated in 69% yield and 65% yield, respectively. Using lithium aluminum hydride, the diamides could be reduced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

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

Next, the bimaocycles **16** were built up by ring-closing metathesis using Grubbs' catalyst. Both bimaocycles **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 bimaocycle (**17a**: 83% yield, **17b**: 90% yield).

The structures of the bimaocycles **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 imidazolium unit points into the bimacrocyclic structure. The twist angles between the aryl rings and the imidazolium ring are  $41.5^\circ$  (phenyl) and  $69.6^\circ$  (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,<sup>[22]</sup> the angle defined by the carbon atom in position 2 of the imidazolium ring, its hydrogen atom and the chloride ion accounts for  $168.2^\circ$  in **17b**.

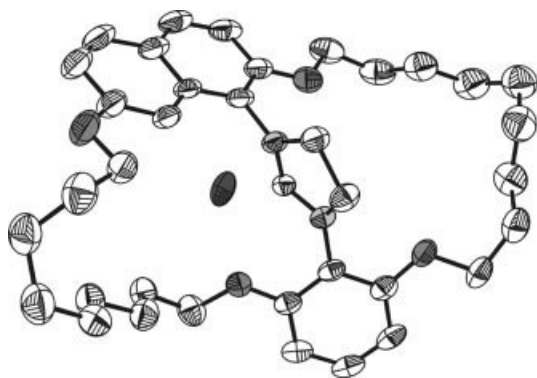
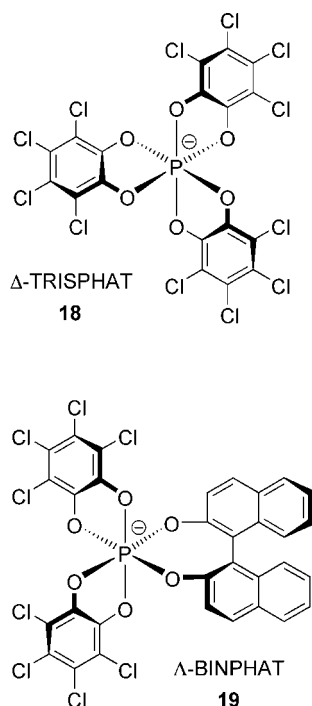


Figure 3. Crystal structure of **17b** with displacement ellipsoids drawn at the 50% probability level [both enantiomers are present in the cell, but only the ( $S_a, R_a$ ) enantiomer is represented here]. Hydrogens were omitted for clarity.

At  $20^\circ\text{C}$ ,  $^1\text{H}$  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  $56\text{ kJ/mol}$ . However, as this value is much lower than that required for the physical separation of the atropisomers at room temperature ( $\Delta G_{298}^\ddagger \geq 90\text{ kJ/mol}$ ),<sup>[25]</sup> the question of the configurational stability of moieties **17** remained.

Previously, hexacoordinate phosphorus anions TRISPHAT **18**<sup>[26,27]</sup> and BINPHAT **19**<sup>[28]</sup> have been shown to be general NMR chiral solvating, resolving and asymmetry-inducing reagents for chiral cationic species.<sup>[29–31]</sup> When associated with configurationally stable cations, they behave as general NMR chiral solvating and resolving agents.<sup>[32–38]</sup> 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<sup>[39–46]</sup>) is a good indication of the lack of configurational stability of the cation.<sup>[47–52]</sup> For this reason, cations **17a** and **17b** were studied in the presence of hexacoordinate phosphorus anions TRISPHAT and BINPHAT. Salts [**17a**][ $\Delta$ -**18**], [**17a**][ $\Lambda$ -**19**], [**17b**][ $\Delta$ -**18**], and [**17b**][ $\Lambda$ -**19**] were prepared according to a literature procedure,<sup>[53]</sup> and studied by  $^1\text{H}$  NMR spectroscopy.



As expected, both anions **18** and **19** behaved as NMR chiral solvating agents in  $\text{CD}_2\text{Cl}_2$ . For  $[\mathbf{17b}][\Delta\text{-18}]$ , the largest induced separation of the NMR signals ( $\Delta\delta$ ) was observed for the proton in 5-position of the naphthyl ring ( $\delta = 0.03$  ppm). The signals of the acidic proton at the imidazolium 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  $[\mathbf{17b}][\Lambda\text{-19}]$ , the acidic imidazolium 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 bimakrocycle **17a**. With  $\Delta\text{-18}$ , 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  $\Lambda\text{-19}$ , effective enantiodifferentiation by the BINPHAT anion and an imbalance between the diastereomers was again noticed ( $dr = 1.47:1$  and  $de = 19\%$  in  $\text{CD}_2\text{Cl}_2$ ).

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 occur-

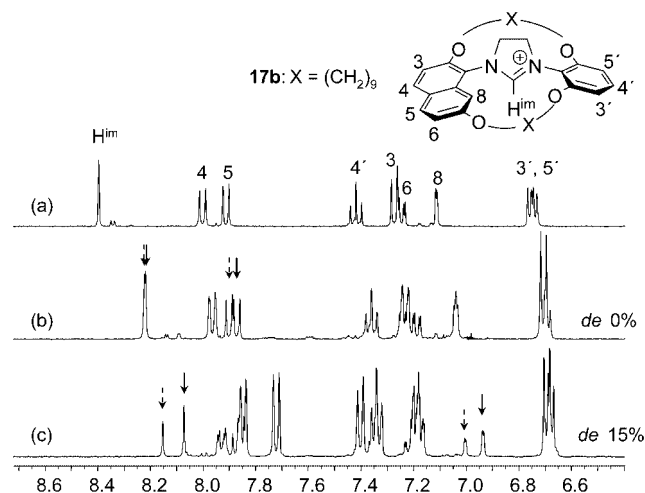


Figure 4.  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 293 K, parts) of salts of **17b**. Counterions: (a) chloride; (b)  $\Delta\text{-18}$ ; (c)  $\Lambda\text{-19}$  and the resulting diastereoselectivity. Plain and dashed arrows indicate signals of diastereomeric protons.

rence of a supramolecular stereocontrol from anion  $\Lambda\text{-BINPHAT}$  over the geometry of cations **17**,<sup>[47]</sup> one of the diastereomeric ion pairs,  $[(S_a, R_a)\text{-17}][\Lambda\text{-19}]$  or  $[(R_a, S_a)\text{-17}][\Lambda\text{-19}]$ , 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.<sup>[54,55]</sup> In high-polarity media, poor chiral discriminations occur as a result of weaker electrostatic interactions and solvent competition.<sup>[56]</sup> 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  $[\mathbf{17b}][\Lambda\text{-19}]$  were prepared in halogenated solvents of different polarity, namely  $\text{CDCl}_3$ ,  $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $\text{CD}_2\text{Cl}_2$ , and  $\text{C}_2\text{D}_4\text{Cl}_2$ . 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  $\text{CDCl}_3$  ( $de = 40\%$ ,  $\varepsilon = 4.89$ ) and decreases gradually from  $\text{C}_2\text{D}_2\text{Cl}_4$  ( $de = 17\%$ ,  $\varepsilon = 8.42$ ) to  $\text{CD}_2\text{Cl}_2$  ( $de = 15\%$ ,  $\varepsilon = 9.02$ ) and  $\text{C}_2\text{D}_4\text{Cl}_2$  ( $de = 10\%$ ,  $\varepsilon = 10.74$ ), which represents increasing solvent polarity.<sup>[57]</sup> With  $[\mathbf{17a}][\Lambda\text{-19}]$ , to a lesser extent, an analogous behavior can be observed for solutions in  $\text{CDCl}_3$  ( $de = 21\%$ ) and  $\text{CD}_2\text{Cl}_2$  ( $de = 19\%$ ).

In a second series of experiments,  $\text{CD}_2\text{Cl}_2$  solutions of  $[\mathbf{17b}][\Lambda\text{-19}]$  were prepared with some content of polar  $[\text{D}_6]\text{-DMSO}$  (10% and 20%). In accordance with the above results, the diastereoselectivity decreased gradually to 7% and 0%, respectively.

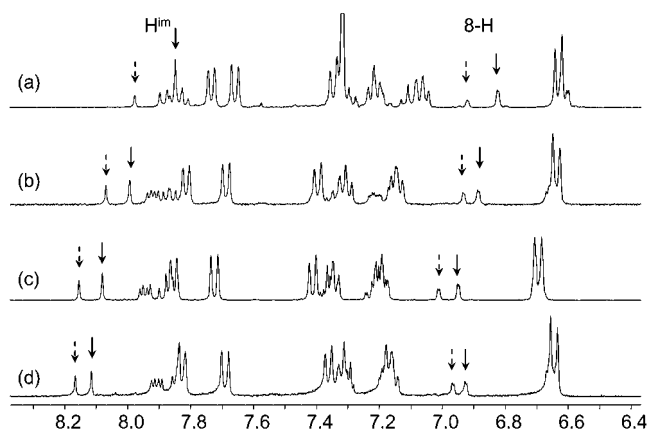


Figure 5.  $^1\text{H}$  NMR spectra (400 MHz, parts, 293 K) of  $[\mathbf{17b}][\text{A-19}]$  in different halogenated solvents and the subsequent diastereoselectivity: (a)  $\text{CDCl}_3$  ( $de = 40\%$ ,  $\epsilon = 4.89$ ); (b)  $\text{C}_2\text{D}_2\text{Cl}_4$  ( $de = 17\%$ ,  $\epsilon = 8.42$ ); (c)  $\text{CD}_2\text{Cl}_2$  ( $de = 15\%$ ,  $\epsilon = 9.02$ ); (d)  $\text{C}_2\text{D}_4\text{Cl}_2$  ( $de = 10\%$ ,  $\epsilon = 10.74$ ). 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  $\mathbf{17a}$  and  $\mathbf{17b}$  was plausible. From the latter experiment, a maximum value for the energy barrier of enantiomerization of the bimacrocyclic cation  $\mathbf{17b}$  could be estimated.  $^1\text{H}$  NMR spectra were recorded immediately after the addition of  $[\text{D}_6]$ -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  $\mathbf{17b}$  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.<sup>[25]</sup>

Finally, in an additional experiment to confirm the configurational lability of cations  $\mathbf{17}$ , a variable-temperature (VT) NMR experiment was carried out on a solution of  $[\mathbf{17b}][\text{A-19}]$  in  $\text{CD}_2\text{Cl}_2$  (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 indi-

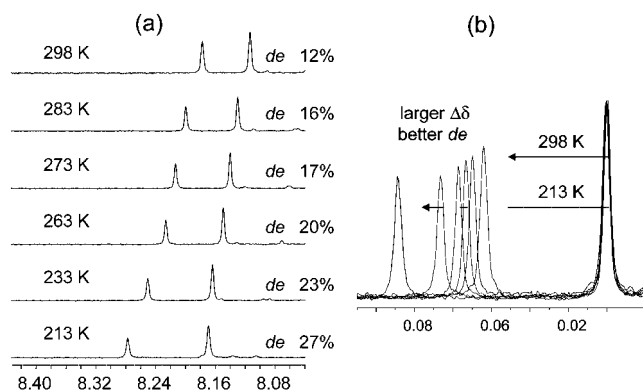


Figure 6. Temperature-dependent  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $\text{H}^{\text{im}}$  signals, 213–298 K) spectra of  $[\mathbf{17b}][\text{A-19}]$ . (a) separated spectra; (b) superimposed spectra.

cation of the presence of an equilibrium between  $[(S_a, R_a)\text{-17}][\text{A-19}]$  and  $[(R_a, S_a)\text{-17}][\text{A-19}]$ . Of all the signals, that of proton  $\text{H}^{\text{im}}$  of the imidazolium 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.

## Conclusions

Chiral concave imidazolium salts  $\mathbf{17}$  can readily be synthesized when one naphthalene bridgehead devoid of local  $C_2$ -symmetry is incorporated into a bimacrocyclic. With chiral counterions such as BINPHAT  $\mathbf{19}$ , diastereomeric ion pairs are generated of which the chiral anion behaves as a stereodynamic probe. Compounds  $\mathbf{17}$  are configurationally labile and the barrier of rotation along the chiral axes in  $\mathbf{17a}$  and  $\mathbf{17b}$  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 imidazolium ring. For planar chiral systems  $\mathbf{5}^{[20]}$  and  $\mathbf{6}^{[21]}$  (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<sup>[22]</sup> ( $\mathbf{10a}$ ), 2,6-bis(hex-5-enyloxy)aniline<sup>[22]</sup> ( $\mathbf{10b}$ ), 2,7-dihydroxy-1-nitronaphthalene<sup>[58]</sup> ( $\mathbf{7}$ ), and ethyl chloroglyoxalate<sup>[59]</sup> 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).  $^1\text{H}$  and  $^{13}\text{C}$  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

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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 Imidazolium 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 Imidazolium-bicyclopentane Chlorides 16:** The imidazolium 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 Imidazolium-bicyclopentane Chlorides 17:** The imidazolium 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 solu-

tion. Column chromatography [silica gel, cyclohexane/ethyl acetate (10:1),  $R_f = 0.44$ ] yielded **8** as an orange oil (4.10 g, 90% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 7.80$  (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<sup>#</sup>, =CH), 5.85 (ddt,  $^3J = 17.0$  Hz,  $^3J = 10.2$  Hz,  $^4J = 6.6$  Hz, 1 H<sup>#</sup>, =CH), 5.07 [m<sub>c</sub> (br. d),  $^3J = 17.1$  Hz, 2 H,  $H_{\text{ZHC}} =$ ], 5.01 [m<sub>c</sub> (br. d),  $^3J = 10.2$  Hz, 2 H,  $H_{\text{EHC}} =$ ], 4.19 (t,  $^3J = 6.3$  Hz, 2 H,  $\text{OCH}_2$ ), 4.04 (t,  $^3J = 6.4$  Hz, 2 H,  $\text{OCH}_2$ ), 2.25 (m<sub>c</sub>, 4 H, =CHCH<sub>2</sub>), 1.92 (m<sub>c</sub>, 4 H,  $\text{OCH}_2\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 159.7$  (C-7), 149.0 (C-2), 137.6 (=CH), 137.3 (=CH), 131.6 (C-4), 129.7 (C-5), 127.3 (C-8a), 123.8 (C-4a), 118.5 (C-6), 115.6 ( $\text{H}_2\text{C} =$ ), 115.4 ( $\text{H}_2\text{C} =$ ), 111.1 (C-3), 99.2 (C-8), 69.1 ( $\text{OCH}_2$ ), 67.4 ( $\text{OCH}_2$ ), 30.1 (=CHCH<sub>2</sub>), 29.8 (=CHCH<sub>2</sub>), 28.3 ( $\text{OCH}_2\text{CH}_2$ ), 28.2 ( $\text{OCH}_2\text{CH}_2$ ) 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<sup>-1</sup>. MS (EI, 70 eV):  $m/z$  (%) = 341 (17) [M]<sup>+</sup>, 295 (78), 69 (100). MS (CI):  $m/z$  (%) = 342 (25) [M + H]<sup>+</sup>. HRMS: calcd. for  $\text{C}_{20}\text{H}_{23}\text{NO}_4$  341.16272; found 341.16243 ( $\delta = 0.8$  ppm); calcd. for  $\text{C}_{19}^{13}\text{CH}_{23}\text{NO}_4$  342.16608; found 342.16596 ( $\delta = 0.3$  ppm).  $\text{C}_{20}\text{H}_{23}\text{NO}_4$  (341.40): calcd. C 70.36, H 6.79, N 4.10.  $\text{C}_{20}\text{H}_{23}\text{NO}_4 \cdot 0.1\text{H}_2\text{O}$ : 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).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 7.63$  (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<sup>#</sup>, =CH), 5.88 (ddt,  $^3J = 17.0$  Hz,  $^3J = 10.3$  Hz,  $^3J = 6.6$  Hz, 1 H<sup>#</sup>, =CH), 5.08 (ddt,  $^3J = 17.1$  Hz,  $^2J = 1.8$  Hz,  $^4J = 1.6$  Hz, 2 H,  $H_{\text{ZHC}} =$ ), 5.01 (ddt,  $^3J = 10.4$  Hz,  $^2J = 1.8$  Hz,  $^4J = 1.2$  Hz, 2 H,  $H_{\text{EHC}} =$ ), 4.11 (t,  $^3J = 6.5$  Hz, 2 H,  $\text{OCH}_2$ ), 4.09 (t,  $^3J = 6.5$  Hz, 2 H,  $\text{OCH}_2$ ), 2.28 (m<sub>c</sub>, 4 H, =CHCH<sub>2</sub>), 1.94 (m<sub>c</sub>, 4 H,  $\text{OCH}_2\text{CH}_2$ ) ppm; no signal for  $\text{NH}_2$  observed.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 156.9$  (C-7), 142.7 (C-2), 137.9 (=CH), 137.9 (=CH), 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 ( $\text{H}_2\text{C} =$ ), 115.2 ( $\text{H}_2\text{C} =$ ), 112.3 (C-3), 100.0 (C-8), 68.9 ( $\text{OCH}_2$ ), 67.2 ( $\text{OCH}_2$ ), 30.3 (=CHCH<sub>2</sub>), 30.2 (=CHCH<sub>2</sub>), 28.9 ( $\text{OCH}_2\text{CH}_2$ ), 28.5 ( $\text{OCH}_2\text{CH}_2$ ) ppm. IR (KBr):  $\tilde{\nu} = 3448, 3367, 3075, 2939, 1630, 1515, 1459, 1376, 1342, 1266, 1219, 1148, 1051, 1017, 992, 913, 824$  cm<sup>-1</sup>. MS (EI, 70 eV):  $m/z$  (%) = 311 (100) [M]<sup>+</sup>, 242 (85). MS (CI):  $m/z$  (%) = 312 (77) [M + H]<sup>+</sup>. HRMS: calcd. for  $\text{C}_{20}\text{H}_{25}\text{NO}_2$  311.18854; found 311.18851 ( $\delta = 0.1$  ppm); calcd. for  $\text{C}_{19}^{13}\text{CH}_{25}\text{NO}_2$  312.19189; found 312.19218 ( $\delta = 0.9$  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).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta = 8.28$  (s, 1 H, NH), 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, =CH), 5.04 (ddt,  $^3J = 17.1$  Hz,  $^2J = 1.9$  Hz,  $^4J = 1.6$  Hz, 2 H,  $H_Z\text{HC=}$ ), 4.98 (ddt,  $^3J = 10.2$  Hz,  $^2J = 2.0$  Hz,  $^4J = 1.2$  Hz, 2 H,  $H_E\text{HC=}$ ), 4.42 (q,  $^3J = 7.1$  Hz, 2 H,  $\text{OCH}_2\text{CH}_3$ ), 4.01 (t,  $^3J = 6.5$  Hz, 4 H,  $\text{OCH}_2\text{CH}_2$ ), 2.20 (m<sub>c</sub>, 4 H, =CHCH<sub>2</sub>), 1.87 (m<sub>c</sub>, 4 H,  $\text{OCH}_2\text{CH}_2$ ), 1.42 (t,  $^3J = 7.1$  Hz, 3 H,  $\text{OCH}_2\text{CH}_3$ ) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 160.9$  (OC=O), 154.5 (C-2,6), 154.2 (NC=O), 137.8 (=CH), 128.1 (C-4), 115.1 (H<sub>2</sub>C=), 113.2 (C-1), 105.2 (C-3,5), 68.1 (OCH<sub>2</sub>CH<sub>2</sub>), 63.2 (OCH<sub>2</sub>CH<sub>3</sub>), 30.1 (=CHCH<sub>2</sub>), 28.4 (OCH<sub>2</sub>CH<sub>2</sub>), 14.0 (CH<sub>3</sub>) 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<sup>-1</sup>. MS (EI, 70 eV): *m/z* (%) = 361 (86) [M]<sup>+</sup>, 288 (43), 220 (100), 152 (86). MS (CI): *m/z* (%) = 362 (100) [M + H]<sup>+</sup>. C<sub>20</sub>H<sub>27</sub>NO<sub>5</sub> (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<sub>f</sub>* = 0.46] yielded **11b** as a colorless oil (3.10 g, 91% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 8.28$  (s, 1 H, NH), 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, =CH), 5.02 (ddt,  $^3J = 17.1$  Hz,  $^2J = 2.0$  Hz,  $^4J = 1.6$  Hz, 2 H,  $H_Z\text{HC=}$ ), 4.96 (ddt,  $^3J = 10.2$  Hz,  $^2J = 2.0$  Hz,  $^4J = 1.2$  Hz, 2 H,  $H_E\text{HC=}$ ), 4.41 (q,  $^3J = 7.2$  Hz, 2 H,  $\text{OCH}_2\text{CH}_3$ ), 4.00 (t,  $^3J = 6.5$  Hz, 4 H,  $\text{OCH}_2\text{CH}_2$ ), 2.10 (m<sub>c</sub>, 4 H, =CHCH<sub>2</sub>), 1.78 (m<sub>c</sub>, 4 H,  $\text{OCH}_2\text{CH}_2$ ), 1.53 (m<sub>c</sub>, 4 H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 1.42 (t,  $^3J = 7.2$  Hz, 3 H,  $\text{OCH}_2\text{CH}_3$ ) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 160.8$  (OC=O), 154.5 (C-2,6), 154.1 (NC=O), 138.5 (=CH), 128.2 (C-4), 114.7 (H<sub>2</sub>C=), 113.0 (C-1), 105.1 (C-3,5), 68.6 (OCH<sub>2</sub>CH<sub>2</sub>), 63.2 (OCH<sub>2</sub>CH<sub>3</sub>), 33.3 (=CHCH<sub>2</sub>), 28.6 (OCH<sub>2</sub>CH<sub>2</sub>), 25.2 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 14.0 (CH<sub>3</sub>) ppm. IR (KBr):  $\tilde{\nu} = 3400, 3076, 2941, 1763, 1721, 1640, 1599, 1517, 1461, 1390, 1299, 1258, 1177, 1101, 1017, 910, 765, 714$  cm<sup>-1</sup>. MS (EI, 70 eV): *m/z* (%) = 389 (31) [M]<sup>+</sup>, 316 (24), 307 (25), 234 (63), 152 (100). MS (CI): *m/z* (%) = 390 [M + H]<sup>+</sup>. C<sub>22</sub>H<sub>31</sub>NO<sub>5</sub> (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. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 8.44$  (s, 1 H, NH), 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, =CH), 5.04 (ddt,  $^3J = 17.1$  Hz,  $^2J = 1.8$  Hz,  $^4J = 1.6$  Hz, 2 H,  $H_Z\text{HC=}$ ), 4.99 (ddt,  $^3J = 10.2$  Hz,  $^2J = 1.9$  Hz,  $^4J = 1.2$  Hz, 2 H,  $H_E\text{HC=}$ ), 4.01 (t,  $^3J = 6.4$  Hz, 4 H,  $\text{OCH}_2$ ), 2.19 (m<sub>c</sub>, 4 H, =CHCH<sub>2</sub>), 1.86 (m<sub>c</sub>, 4 H,  $\text{OCH}_2\text{CH}_2$ ) ppm; no signal for OH observed. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 159.8$  (OC=O), 155.3 (NC=O), 154.4 (C-2,6), 137.6 (=CH), 128.9 (C-4), 115.3 (H<sub>2</sub>C=), 112.0 (C-1), 105.0 (C-3,5), 68.1 (OCH<sub>2</sub>), 30.1 (=CHCH<sub>2</sub>), 28.3 (OCH<sub>2</sub>CH<sub>2</sub>) 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<sup>-1</sup>. MS (EI, 70 eV): *m/z* (%) = 333 (46) [M]<sup>+</sup>, 288 (15), 265 (28), 220 (31), 197 (40), 152 (100). MS (CI): *m/z* (%) = 334 (100) [M + H]<sup>+</sup>. C<sub>18</sub>H<sub>23</sub>N<sub>2</sub>O<sub>5</sub> (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. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta =$

8.30 (s, 1 H, NH), 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, =CH), 5.02 [m<sub>c</sub> (br. d),  $^3J = 17.1$  Hz, 2 H,  $H_Z\text{HC=}$ ], 4.97 [m<sub>c</sub> (br. d),  $^3J = 10.2$  Hz, 2 H,  $H_E\text{HC=}$ ], 4.00 (t,  $^3J = 6.4$  Hz, 4 H,  $\text{OCH}_2$ ), 2.10 (m<sub>c</sub>, 4 H, =CHCH<sub>2</sub>), 1.77 (m<sub>c</sub>, 4 H,  $\text{OCH}_2\text{CH}_2$ ), 1.52 (m<sub>c</sub>, 4 H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ) ppm; no signal for OH observed. <sup>13</sup>C NMR (125 MHz, [D<sub>6</sub>]DMSO, 25 °C):  $\delta = 162.2$  (OC=O), 157.0 (NC=O), 155.3 (C-2,6), 138.6 (=CH), 128.2 (C-4), 114.9 (H<sub>2</sub>C=), 114.1 (C-1), 105.5 (C-3,5), 68.1 (OCH<sub>2</sub>), 32.8 (=CHCH<sub>2</sub>), 28.2 (OCH<sub>2</sub>CH<sub>2</sub>), 24.6 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) 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<sup>-1</sup>. MS (EI, 70 eV): *m/z* (%) = 361 (21) [M]<sup>+</sup>, 289 (40), 197 (38), 152 (71), 125 (100). MS (CI): *m/z* (%) = 362 (100) [M + H]<sup>+</sup>. C<sub>20</sub>H<sub>27</sub>NO<sub>5</sub> (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<sub>f</sub>* = 0.62] and recrystallization from cyclohexane yielded **13a** as a colorless solid (1.10 g, 69% yield). M.p. 129 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):<sup>[60]</sup>  $\delta = 9.15$  (s, 1 H, NH), 8.81 (s, 1 H, NH), 7.72 (d,  $^3J = 8.9$  Hz, 1 H, 4-H<sub>naph</sub>), 7.68 (m<sub>c</sub>, 1 H, 5-H<sub>naph</sub>), 7.18 (t,  $^3J = 8.4$  Hz, 1 H, 4-H<sub>ph</sub>), 7.12 (d,  $^3J = 9.0$  Hz, 1 H, 3-H<sub>naph</sub>), 7.04–7.02 (m, 2 H, 6,8-H<sub>naph</sub>), 6.60 (d,  $^3J = 8.4$  Hz, 2 H, 3,5-H<sub>ph</sub>), 5.87 (ddt,  $^3J = 17.0$  Hz,  $^3J = 10.3$  Hz,  $^3J = 6.6$  Hz, 1 H<sup>#</sup>, =CH<sub>naph</sub>), 5.83 (ddt,  $^3J = 17.0$  Hz,  $^3J = 10.2$  Hz,  $^3J = 6.7$  Hz, 1 H<sup>#</sup>, =CH<sub>ph</sub>), 5.82 (ddt,  $^3J = 17.0$  Hz,  $^3J = 10.3$  Hz,  $^3J = 6.7$  Hz, 2 H<sup>#</sup>, =CH<sub>ph</sub>), 5.06 (ddt,  $^3J = 17.1$  Hz,  $^2J = 1.8$  Hz,  $^4J = 1.6$  Hz, 1 H,  $H_Z\text{HC=}$ <sub>naph</sub>), 5.05 [m<sub>c</sub> (br. d),  $^3J = 17.1$  Hz, 3 H,  $H_Z\text{HC=}$ <sub>naph</sub>,  $H_Z\text{HC=}$ <sub>ph</sub>], 5.01–4.06 (m, 4 H,  $H_E\text{HC=}$ ), 4.14 (t,  $^3J = 6.5$  Hz, 2 H,  $\text{OCH}_2$ <sub>naph</sub>), 4.07 (t,  $^3J = 6.3$  Hz, 2 H,  $\text{OCH}_2$ <sub>naph</sub>), 4.05 (t,  $^3J = 6.5$  Hz, 4 H,  $\text{OCH}_2$ <sub>ph</sub>), 2.25 (m<sub>c</sub>, 8 H, =CHCH<sub>2</sub>), 1.90 (m<sub>c</sub>, 8 H,  $\text{OCH}_2\text{CH}_2$ ) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25 °C):<sup>[60]</sup>  $\delta = 158.8$  (C=O\*), 158.2 (C-7<sub>naph</sub>\*), 157.8 (C=O\*), 154.6 (C-2,6<sub>ph</sub>), 151.8 (C-2<sub>naph</sub>), 137.9 (=CH), 137.7 (=CH), 131.8 (C-8<sub>naph</sub>), 129.7 (C-4<sub>naph</sub>\*), 128.7 (C-4<sub>ph</sub>\*), 128.0 (C-5<sub>naph</sub>\*), 124.6 (C-4<sub>naph</sub>), 117.2 (C-6<sub>naph</sub>), 116.7 (C-1<sub>naph</sub>), 115.4 (H<sub>2</sub>C=), 115.1 (H<sub>2</sub>C=), 113.3 (C-1<sub>ph</sub>), 111.3 (C-3<sub>naph</sub>), 105.2 (C-3,5<sub>ph</sub>), 101.8 (C-8<sub>naph</sub>), 68.5 (OCH<sub>2</sub><sub>naph</sub>), 68.0 (OCH<sub>2</sub><sub>ph</sub>), 67.1 (OCH<sub>2</sub><sub>naph</sub>), 30.2 (=CHCH<sub>2</sub><sub>naph</sub>), 30.1 (=CHCH<sub>2</sub><sub>ph</sub>), 30.0 (=CHCH<sub>2</sub><sub>naph</sub>), 28.6 (OCH<sub>2</sub>CH<sub>2</sub><sub>naph</sub>), 28.5 (OCH<sub>2</sub>CH<sub>2</sub><sub>naph</sub>), 28.4 (OCH<sub>2</sub>CH<sub>2</sub><sub>ph</sub>) 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<sup>-1</sup>. MS (EI, 70 eV): *m/z* (%) = 626 (76) [M]<sup>+</sup>, 261 (100). MS (CI): *m/z* (%) = 627 (100) [M + H]<sup>+</sup>. C<sub>38</sub>H<sub>46</sub>N<sub>2</sub>O<sub>6</sub> (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<sub>f</sub>* = 0.27] and recrystallization from cyclohexane yielded **13b** as a colorless solid (1.71 g, 65% yield). M.p. 119 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):<sup>[60]</sup>  $\delta = 9.14$  (s, 1 H, NH), 8.80 (s, 1 H, NH), 7.72 (d,  $^3J = 8.9$  Hz, 1 H, 4-H<sub>naph</sub>), 7.67 (m<sub>c</sub>, 1 H, 5-H<sub>naph</sub>), 7.19 (t,  $^3J = 8.4$  Hz, 1 H, 4-H<sub>ph</sub>), 7.13 (d,  $^3J = 9.0$  Hz, 1 H, 3-H<sub>naph</sub>), 7.05–7.02 (m, 2 H, 6,8-H<sub>naph</sub>), 6.61 (d,  $^3J = 8.5$  Hz, 2 H, 3,5-H<sub>ph</sub>), 5.87 (ddt,  $^3J = 17.0$  Hz,  $^3J = 10.2$  Hz,  $^3J =$



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6.6 Hz, 1 H<sup>#</sup>, =CH<sub>naph</sub>), 5.83 (m<sub>c</sub>, 1 H<sup>#</sup>, =CH<sub>naph</sub>), 5.78 (ddt, <sup>3</sup>J = 17.1 Hz, <sup>3</sup>J = 10.3 Hz, <sup>3</sup>J = 6.7 Hz, 2 H<sup>#</sup>, =CH<sub>ph</sub>), 5.07 (ddt, <sup>3</sup>J = 17.1 Hz, <sup>2</sup>J = 1.8 Hz, <sup>4</sup>J = 1.6 Hz, 1 H, H<sub>Z</sub>HC=<sub>naph</sub>), 5.05 (ddt, <sup>3</sup>J = 17.1 Hz, <sup>2</sup>J = 1.8 Hz, <sup>4</sup>J = 1.6 Hz, 1 H, H<sub>Z</sub>HC=<sub>naph</sub>), 5.02–4.96 (m, 4 H, H<sub>Z</sub>HC=<sub>ph</sub>, H<sub>E</sub>HC=<sub>naph</sub>), 4.92 (ddt, <sup>3</sup>J = 10.2 Hz, <sup>2</sup>J = 2.0 Hz, <sup>4</sup>J = 1.2 Hz, 2 H, H<sub>E</sub>HC=<sub>ph</sub>), 4.15 (t, <sup>3</sup>J = 6.5 Hz, 2 H, OCH<sub>2</sub><sub>naph</sub>), 4.07 (t, <sup>3</sup>J = 6.3 Hz, 2 H, OCH<sub>2</sub><sub>naph</sub>), 4.04 (t, <sup>3</sup>J = 6.6 Hz, 4 H, OCH<sub>2</sub><sub>ph</sub>), 2.26 (m<sub>c</sub>, 4 H, =CHCH<sub>2</sub><sub>naph</sub>), 2.10 (m<sub>c</sub>, 4 H, =CHCH<sub>2</sub><sub>ph</sub>), 1.92 (m<sub>c</sub>, 4 H, OCH<sub>2</sub>CH<sub>2</sub><sub>naph</sub>), 1.81 (m<sub>c</sub>, 4 H, OCH<sub>2</sub>CH<sub>2</sub><sub>ph</sub>), 1.56 (m<sub>c</sub>, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub><sub>ph</sub>) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25 °C):<sup>[60]</sup> δ = 158.8 (C=O\*), 158.1 (C-7<sub>naph</sub>\*), 157.8 (C=O\*), 154.6 (C-2,6<sub>ph</sub>), 151.8 (C-2<sub>naph</sub>), 138.5 (=CH<sub>ph</sub>), 137.9 (=CH<sub>naph</sub>), 137.7 (=CH<sub>naph</sub>), 131.8 (C-8<sub>naph</sub>), 129.7 (C-4<sub>naph</sub>\*), 128.8 (C-4<sub>ph</sub>\*), 128.0 (C-5<sub>naph</sub>\*), 124.6 (C-4<sub>naph</sub>), 117.1 (C-6<sub>naph</sub>), 116.7 (C-1<sub>naph</sub>), 115.4 (H<sub>2</sub>C=<sub>naph</sub>), 115.2 (H<sub>2</sub>C=<sub>naph</sub>), 114.8 (H<sub>2</sub>C=<sub>ph</sub>), 113.3 (C-1<sub>ph</sub>), 111.3 (C-3<sub>naph</sub>), 105.2 (C-3,5<sub>ph</sub>), 101.9 (C-8<sub>naph</sub>), 68.6 (OCH<sub>2</sub><sub>ph</sub>), 68.5 (OCH<sub>2</sub><sub>naph</sub>), 67.2 (OCH<sub>2</sub><sub>naph</sub>), 33.3 (=CHCH<sub>2</sub><sub>ph</sub>), 30.2 (=CHCH<sub>2</sub><sub>naph</sub>), 30.1 (=CHCH<sub>2</sub><sub>naph</sub>), 28.6 (OCH<sub>2</sub>CH<sub>2</sub><sub>ph</sub>), 28.6 (OCH<sub>2</sub>CH<sub>2</sub><sub>naph</sub>), 28.5 (OCH<sub>2</sub>CH<sub>2</sub><sub>naph</sub>), 25.1 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub><sub>ph</sub>) ppm. IR (KBr): ν̄ = 3261, 3076, 2941, 2869, 1672, 1631, 1604, 1502, 1458, 1391, 1326, 1264, 1230, 1108, 992, 911, 824, 766, 711 cm<sup>-1</sup>. MS (EI, 70 eV): m/z (%) = 654 (100) [M]<sup>+</sup>, 289 (70). MS (CI): m/z (%) = 655 (100) [M + H]<sup>+</sup>. C<sub>40</sub>H<sub>50</sub>N<sub>2</sub>O<sub>6</sub> (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<sub>f</sub> = 0.75] yielded 14a as a colorless oil (302 mg, 50% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):<sup>[60]</sup> δ = 7.63 (d, <sup>3</sup>J = 8.9 Hz, 1 H, 5-H<sub>naph</sub>), 7.43 (br. s, 1 H, 8-H<sub>naph</sub>), 7.40 (d, <sup>3</sup>J = 8.8 Hz, 1 H, 4-H<sub>naph</sub>), 7.06 (d, <sup>3</sup>J = 8.8 Hz, 3-H<sub>naph</sub>), 6.98 (dd, <sup>3</sup>J = 8.9 Hz, <sup>4</sup>J = 2.4 Hz, 6-H<sub>naph</sub>), 6.75 (t, <sup>3</sup>J = 8.3 Hz, 1 H, 4-H<sub>ph</sub>), 6.52 (d, <sup>3</sup>J = 8.3 Hz, 2 H, 3,5-H<sub>ph</sub>), 5.88–5.80 (m, 2 H<sup>#</sup>, =CH<sub>naph</sub>), 5.78 (ddt, <sup>3</sup>J = 17.0 Hz, <sup>3</sup>J = 10.3 Hz, <sup>3</sup>J = 6.6 Hz, 2 H<sup>#</sup>, =CH<sub>ph</sub>), 5.06–4.92 (m, 8 H, H<sub>2</sub>C=), 4.35 (br. s, 2 H, NH), 4.09 (t, <sup>3</sup>J = 6.7 Hz, 2 H, OCH<sub>2</sub><sub>naph</sub>), 4.03 (t, <sup>3</sup>J = 6.4 Hz, 2 H, OCH<sub>2</sub><sub>naph</sub>), 3.97 (t, <sup>3</sup>J = 6.6 Hz, 4 H, OCH<sub>2</sub><sub>ph</sub>), 3.45 (t, <sup>3</sup>J = 5.6 Hz, 2 H, NCH<sub>2</sub>), 3.28 (t, <sup>3</sup>J = 5.6 Hz, 2 H, NCH<sub>2</sub>), 2.25–2.15 (m, 8 H, =CHCH<sub>2</sub>), 1.94–1.82 (m, 8 H, OCH<sub>2</sub>CH<sub>2</sub><sub>ph</sub>) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25 °C): δ = 157.1 (C-7<sub>naph</sub>), 150.4 (C-2,6<sub>ph</sub>), 148.3 (C-2<sub>naph</sub>), 138.0 (=CH<sub>naph</sub>), 137.8 (=CH<sub>ph</sub>), 137.8 (=CH<sub>naph</sub>), 131.4 (C-1<sub>naph</sub>), 130.2 (C-8<sub>naph</sub>), 129.7 (C-5<sub>naph</sub>), 127.6 (C-1<sub>ph</sub>), 125.4 (C-4<sub>naph</sub>), 122.6 (C-4<sub>naph</sub>), 119.5 (C-4<sub>ph</sub>), 116.8 (C-6<sub>naph</sub>), 115.3 (H<sub>2</sub>C=<sub>naph</sub>), 115.1 (H<sub>2</sub>C=<sub>ph</sub>), 115.0 (H<sub>2</sub>C=<sub>naph</sub>), 111.8 (C-3<sub>naph</sub>), 105.8 (C-3,5<sub>ph</sub>), 102.3 (C-8<sub>naph</sub>), 68.9 (OCH<sub>2</sub><sub>naph</sub>), 68.1 (OCH<sub>2</sub><sub>ph</sub>), 67.2 (OCH<sub>2</sub><sub>naph</sub>), 49.8 (CH<sub>2</sub>N<sub>naph</sub>), 47.4 (CH<sub>2</sub>N<sub>ph</sub>), 30.2 (=CHCH<sub>2</sub><sub>ph</sub>), 30.2 (=CHCH<sub>2</sub><sub>naph</sub>), 28.8 (OCH<sub>2</sub>CH<sub>2</sub><sub>naph</sub>), 28.6 (OCH<sub>2</sub>CH<sub>2</sub><sub>ph</sub>), 28.5 (OCH<sub>2</sub>CH<sub>2</sub><sub>naph</sub>) ppm. IR (KBr): ν̄ = 3349, 3075, 2940, 2870, 1628, 1600, 1514, 1492, 1450, 1389, 1260, 1229, 1215, 1118, 1094, 992, 912, 825, 763, 723 cm<sup>-1</sup>. MS (EI, 70 eV): m/z (%) = 598 (78) [M]<sup>+</sup>, 325 (57), 275 (100). MS (CI): m/z (%) = 599 (100) [M + H]<sup>+</sup>. HRMS: calcd. For C<sub>38</sub>H<sub>50</sub>N<sub>2</sub>O<sub>4</sub> 598.37708; found 598.37695 (δ = 0.2 ppm); calcd. for C<sub>37</sub><sup>13</sup>CH<sub>50</sub>N<sub>2</sub>O<sub>4</sub> 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<sub>f</sub> = 0.28] yielded 14b as a colorless oil (1.21 g, 74% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):<sup>[60]</sup> δ = 7.63 (d, <sup>3</sup>J = 8.9 Hz, 1 H, 5-H<sub>naph</sub>), 7.43 (d, <sup>4</sup>J = 2.3 Hz, 1 H, 8-H<sub>naph</sub>), 7.40 (d, <sup>3</sup>J = 8.9 Hz, 1 H, 4-H<sub>naph</sub>), 7.06 (d, <sup>3</sup>J = 8.9 Hz, 3-H<sub>naph</sub>), 6.98 (dd, <sup>3</sup>J = 8.9 Hz, <sup>4</sup>J = 2.4 Hz, 6-H<sub>naph</sub>), 6.75 (t, <sup>3</sup>J = 8.3 Hz, 1 H, 4-H<sub>ph</sub>), 6.52 (d, <sup>3</sup>J = 8.3 Hz, 2 H, 3,5-H<sub>ph</sub>), 5.87–5.79 (m, 2 H<sup>#</sup>, =CH<sub>naph</sub>), 5.72 (ddt, <sup>3</sup>J = 17.0 Hz, <sup>3</sup>J = 10.3 Hz, <sup>3</sup>J = 6.7 Hz, 2 H<sup>#</sup>, =CH<sub>ph</sub>), 5.06–4.86 (m, 8 H, H<sub>2</sub>C=), 4.52 (br. s, 1 H, NH), 4.25 (br. s, 1 H, NH), 4.09 (t, <sup>3</sup>J = 6.7 Hz, 2 H, OCH<sub>2</sub><sub>naph</sub>), 4.03 (t, <sup>3</sup>J = 6.4 Hz, 2 H, OCH<sub>2</sub><sub>naph</sub>), 3.96 (t, <sup>3</sup>J = 6.6 Hz, 4 H, OCH<sub>2</sub><sub>ph</sub>), 3.44 (m<sub>c</sub>, 2 H, NCH<sub>2</sub>), 3.26 (m<sub>c</sub>, 2 H, NCH<sub>2</sub>), 2.22 (m<sub>c</sub>, 4 H, =CHCH<sub>2</sub><sub>naph</sub>), 2.03 (m<sub>c</sub>, 4 H, =CHCH<sub>2</sub><sub>ph</sub>), 1.90 (m<sub>c</sub>, 4 H, OCH<sub>2</sub>CH<sub>2</sub><sub>naph</sub>), 1.76 (m<sub>c</sub>, 4 H, OCH<sub>2</sub>CH<sub>2</sub><sub>ph</sub>), 1.51 (m<sub>c</sub>, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub><sub>ph</sub>) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25 °C): δ = 157.0 (C-7<sub>naph</sub>), 150.1 (C-2,6<sub>ph</sub>), 148.3 (C-2<sub>naph</sub>), 138.4 (=CH<sub>ph</sub>), 138.0 (=CH<sub>naph</sub>), 137.7 (=CH<sub>naph</sub>), 131.3 (C-1<sub>naph</sub>), 130.2 (C-8<sub>naph</sub>), 129.7 (C-5<sub>naph</sub>), 127.4 (C-1<sub>ph</sub>), 125.4 (C-4<sub>naph</sub>), 122.6 (C-4<sub>naph</sub>), 119.5 (C-4<sub>ph</sub>), 116.8 (C-6<sub>naph</sub>), 115.3 (H<sub>2</sub>C=<sub>naph</sub>), 115.0 (H<sub>2</sub>C=<sub>naph</sub>), 114.7 (H<sub>2</sub>C=<sub>ph</sub>), 111.7 (C-3<sub>naph</sub>), 105.7 (C-3,5<sub>ph</sub>), 102.2 (C-8<sub>naph</sub>), 68.8 (OCH<sub>2</sub><sub>naph</sub>), 68.6 (OCH<sub>2</sub><sub>ph</sub>), 67.2 (OCH<sub>2</sub><sub>naph</sub>), 49.7 (NCH<sub>2</sub>), 47.3 (NCH<sub>2</sub>), 33.4 (=CHCH<sub>2</sub><sub>ph</sub>), 30.2 (=CHCH<sub>2</sub><sub>naph</sub>), 30.2 (=CHCH<sub>2</sub><sub>naph</sub>), 28.8 (OCH<sub>2</sub>CH<sub>2</sub><sub>ph</sub>), 28.7 (OCH<sub>2</sub>CH<sub>2</sub><sub>naph</sub>), 28.5 (OCH<sub>2</sub>CH<sub>2</sub><sub>naph</sub>), 25.4 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub><sub>ph</sub>) ppm. IR (KBr): ν̄ = 3349, 3075, 2938, 2868, 1640, 1628, 1600, 1514, 1492, 1450, 1389, 1324, 1260, 1228, 1215, 1119, 1098, 993, 911, 825, 764, 722 cm<sup>-1</sup>. MS (EI, 70 eV): m/z (%) = 626 (100) [M]<sup>+</sup>, 325 (49), 303 (85). MS (CI): m/z (%) = 627 (67) [M + H]<sup>+</sup>. HRMS: calcd. for C<sub>40</sub>H<sub>54</sub>N<sub>2</sub>O<sub>4</sub> 626.40839; found 626.40828 (δ = 0.2 ppm); calcd. for C<sub>39</sub><sup>13</sup>CH<sub>54</sub>N<sub>2</sub>O<sub>4</sub> 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-imidazolium 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<sub>f</sub> = 0.23] yielded 15a as a colorless solid (194 mg, 65% yield). M.p. 196 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):<sup>[60]</sup> δ = 8.13 (s, 1 H, 2-H<sub>im</sub>), 7.84 (d, <sup>3</sup>J = 9.0 Hz, 1 H, 4-H<sub>naph</sub>), 7.73 (d, <sup>3</sup>J = 9.0 Hz, 1 H, 5-H<sub>naph</sub>), 7.29 (t, <sup>3</sup>J = 8.5 Hz, 1 H, 4-H<sub>ph</sub>), 7.12 (d, <sup>3</sup>J = 9.1 Hz, 1 H, 3-H<sub>naph</sub>), 7.09 (dd, <sup>3</sup>J = 8.9 Hz, <sup>4</sup>J = 2.3 Hz, 1 H, 6-H<sub>naph</sub>), 7.06 (d, <sup>4</sup>J = 2.3 Hz, 1 H, 8-H<sub>naph</sub>), 6.62 (d, <sup>3</sup>J = 8.6 Hz, 2 H, 3,5-H<sub>ph</sub>), 5.85 (ddt, <sup>3</sup>J = 16.9 Hz, <sup>3</sup>J = 10.3 Hz, <sup>3</sup>J = 6.6 Hz, 1 H, =CH<sub>naph</sub>), 5.76 (ddt, <sup>3</sup>J = 16.9 Hz, <sup>3</sup>J = 10.2 Hz, <sup>3</sup>J = 6.6 Hz, 1 H<sup>#</sup>, =CH<sub>naph</sub>), 5.72 (ddt, <sup>3</sup>J = 17.0 Hz, <sup>3</sup>J = 10.3 Hz, <sup>3</sup>J = 6.6 Hz, 2 H<sup>#</sup>, =CH<sub>ph</sub>), 5.04 (ddt, <sup>3</sup>J = 17.1 Hz, <sup>2</sup>J = 1.7 Hz, <sup>4</sup>J = 1.6 Hz, 1 H, H<sub>Z</sub>HC=<sub>naph</sub>), 4.99–4.89 (m, 7 H, H<sub>2</sub>C=<sub>naph</sub>, H<sub>E</sub>HC=<sub>naph</sub>, H<sub>2</sub>C=<sub>ph</sub>), 4.19 (br. s, 2 H, OCH<sub>2</sub><sub>naph</sub>), 4.17 (t, <sup>3</sup>J = 6.7 Hz, 2 H, OCH<sub>2</sub><sub>naph</sub>), 4.07 (t, <sup>3</sup>J = 6.8 Hz, 4 H, OCH<sub>2</sub><sub>ph</sub>), 2.27 (m<sub>c</sub>, 2 H, =CHCH<sub>2</sub><sub>naph</sub>), 2.17 (m<sub>c</sub>, 2 H, =CHCH<sub>2</sub><sub>naph</sub>), 2.14 (m<sub>c</sub>, 4 H, =CHCH<sub>2</sub><sub>ph</sub>), 1.95–1.88 (m, 8 H, OCH<sub>2</sub>CH<sub>2</sub>) ppm; no signal observed for 4,5-H<sub>im</sub>. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25 °C):<sup>[60]</sup> δ = 161.5 (C-2<sub>im</sub>), 159.9 (C-7<sub>naph</sub>), 154.3 (C-2,6<sub>ph</sub>), 152.7 (C-2<sub>naph</sub>), 137.9 (=CH<sub>naph</sub>), 137.0 (=CH<sub>naph</sub>), 136.9 (=CH<sub>ph</sub>), 132.0 (C-8<sub>naph</sub>), 131.9 (C-4<sub>ph</sub>), 131.1 (C-4<sub>naph</sub>\*), 130.4 (C-5<sub>naph</sub>\*), 124.2 (C-4<sub>naph</sub>), 117.2 (C-6<sub>naph</sub>), 115.7 (H<sub>2</sub>C=<sub>naph</sub>), 115.7 (H<sub>2</sub>C=<sub>ph</sub>), 115.6 (C-1<sub>naph</sub>), 115.0 (H<sub>2</sub>C=<sub>naph</sub>), 112.8 (C-1<sub>ph</sub>), 110.3 (C-3<sub>naph</sub>), 105.3 (C-3,5<sub>ph</sub>), 100.3 (C-8<sub>naph</sub>), 68.8 (OCH<sub>2</sub><sub>naph</sub>), 68.7 (OCH<sub>2</sub><sub>ph</sub>), 68.0 (OCH<sub>2</sub><sub>naph</sub>), 52.5, 52.3 (C-4,5<sub>im</sub>), 30.1 (=CHCH<sub>2</sub><sub>naph</sub>), 30.0 (=CHCH<sub>2</sub><sub>ph</sub>), 29.9 (=CHCH<sub>2</sub><sub>naph</sub>), 28.5 (OCH<sub>2</sub>CH<sub>2</sub><sub>naph</sub>), 28.3 (OCH<sub>2</sub>CH<sub>2</sub><sub>naph</sub>), 28.1 (OCH<sub>2</sub>CH<sub>2</sub><sub>ph</sub>) ppm. IR (KBr): ν̄ = 3074, 2941, 2871, 1618, 1512, 1480, 1459, 1438, 1390, 1262, 1225, 1103,

990, 909, 829, 775, 728 cm<sup>-1</sup>. HRMS (ESI, MeOH): calcd. for C<sub>39</sub>H<sub>49</sub>N<sub>2</sub>O<sub>4</sub> 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-imidazolium 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*<sub>f</sub> = 0.19] yielded **15b** as a colorless solid (608 mg, 77% yield). M.p. 194 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C): δ = 8.13 (s, 1 H, 2-H<sub>im</sub>), 7.88 (d, <sup>3</sup>*J* = 9.0 Hz, 1 H, 4-H<sub>naph</sub>), 7.77 (d, <sup>3</sup>*J* = 9.7 Hz, 1 H, 5-H<sub>naph</sub>), 7.33 (t, <sup>3</sup>*J* = 8.5 Hz, 1 H, 4-H<sub>ph</sub>), 7.16–7.12 (m, 3 H, 3,6,8-H<sub>naph</sub>), 6.65 (d, <sup>3</sup>*J* = 8.6 Hz, 2 H, 3,5-H<sub>ph</sub>), 5.89 (ddt, <sup>3</sup>*J* = 17.0 Hz, <sup>3</sup>*J* = 10.3 Hz, <sup>3</sup>*J* = 6.6 Hz, 1 H, =CH<sub>naph</sub>), 5.80 (ddt, <sup>3</sup>*J* = 17.0 Hz, <sup>3</sup>*J* = 10.3 Hz, <sup>3</sup>*J* = 6.7 Hz, 1 H, =CH<sub>naph</sub>), 5.66 (ddt, <sup>3</sup>*J* = 17.0 Hz, <sup>3</sup>*J* = 10.3 Hz, <sup>3</sup>*J* = 6.7 Hz, 2 H, =CH<sub>ph</sub>), 5.08 (ddt, <sup>3</sup>*J* = 17.1 Hz, <sup>2</sup>*J* = 1.8 Hz, <sup>4</sup>*J* = 1.6 Hz, 1 H, H<sub>Z</sub>HC=<sub>naph</sub>), 5.03–4.97 (m, 3 H, H<sub>2</sub>C=<sub>naph</sub>, H<sub>E</sub>HC=<sub>naph</sub>), 4.91 (ddt, <sup>3</sup>*J* = 17.1 Hz, <sup>2</sup>*J* = 1.9 Hz, <sup>4</sup>*J* = 1.6 Hz, 2 H, H<sub>Z</sub>HC=<sub>ph</sub>), 4.88 (ddt, <sup>3</sup>*J* = 10.2 Hz, <sup>2</sup>*J* = 1.9 Hz, <sup>4</sup>*J* = 1.2 Hz, 2 H, H<sub>E</sub>HC=<sub>ph</sub>), 4.27 (br. s, 2 H, OCH<sub>2</sub><sub>naph</sub>), 4.20 (t, <sup>3</sup>*J* = 6.6 Hz, 2 H, OCH<sub>2</sub><sub>naph</sub>), 4.10 (t, <sup>3</sup>*J* = 6.8 Hz, 4 H, OCH<sub>2</sub><sub>ph</sub>), 2.32 (m<sub>c</sub>, 2 H, =CHCH<sub>2</sub><sub>naph</sub>), 2.22 (m<sub>c</sub>, 2 H, =CHCH<sub>2</sub><sub>naph</sub>), 2.04 (m<sub>c</sub>, 4 H, =CHCH<sub>2</sub><sub>ph</sub>), 1.96 (m<sub>c</sub>, 4 H, OCH<sub>2</sub>CH<sub>2</sub><sub>naph</sub>), 1.85 (m<sub>c</sub>, 4 H, OCH<sub>2</sub>CH<sub>2</sub><sub>ph</sub>), 1.49 (m<sub>c</sub>, 4 H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub><sub>ph</sub>) ppm; no signal for 4,5-H<sub>im</sub> observed. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25 °C):<sup>[60]</sup> δ = 161.5 (C-2<sub>im</sub>), 159.9 (C-7<sub>naph</sub>), 154.3 (C-2,6<sub>ph</sub>), 152.7 (C-2<sub>naph</sub>), 137.9 (=CH<sub>naph</sub>), 137.9 (=CH<sub>ph</sub>), 137.0 (=CH<sub>naph</sub>), 132.0 (C-8<sub>naph</sub>), 131.9 (C-4<sub>ph</sub>), 131.0 (C-4<sub>naph</sub>\*), 130.4 (C-5<sub>naph</sub>\*), 124.3 (C-4<sub>naph</sub>), 117.4 (C-6<sub>naph</sub>), 115.8 (C-1<sub>naph</sub>), 115.8 (H<sub>2</sub>C=<sub>naph</sub>), 115.0 (H<sub>2</sub>C=<sub>naph</sub>), 115.0 (H<sub>2</sub>C=<sub>ph</sub>), 112.9 (C-1<sub>ph</sub>), 110.3 (C-3<sub>naph</sub>), 105.2 (C-3,5<sub>ph</sub>), 100.4 (C-8<sub>naph</sub>), 69.2 (OCH<sub>2</sub><sub>ph</sub>), 68.7 (OCH<sub>2</sub><sub>naph</sub>), 68.1 (OCH<sub>2</sub><sub>naph</sub>), 52.6, 52.4 (C-4,5<sub>im</sub>), 33.1 (=CHCH<sub>2</sub><sub>ph</sub>), 30.2 (=CHCH<sub>2</sub><sub>naph</sub>), 30.0 (=CHCH<sub>2</sub><sub>naph</sub>), 28.5 (OCH<sub>2</sub>CH<sub>2</sub><sub>naph</sub>), 28.4 (OCH<sub>2</sub>CH<sub>2</sub><sub>ph</sub>), 28.4 (OCH<sub>2</sub>CH<sub>2</sub><sub>naph</sub>), 25.2 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub><sub>ph</sub>) ppm. IR (KBr): ν̄ = 3074, 2945, 2865, 1619, 1514, 1480, 1464, 1390, 1265, 1226, 1145, 1106, 992, 908, 839, 775, 731 cm<sup>-1</sup>. ESI-MS (MeOH): *m/z* (%) = 637.40 (100) [C<sub>41</sub>H<sub>53</sub>N<sub>2</sub>O<sub>4</sub>]<sup>+</sup>. HRMS: calcd. for C<sub>41</sub>H<sub>53</sub>N<sub>2</sub>O<sub>4</sub> 637.40051; found 637.40020 (δ = 0.5 ppm); calcd. for C<sub>40</sub><sup>13</sup>CH<sub>53</sub>N<sub>2</sub>O<sub>4</sub> 638.40387; found 638.40340 (δ = 0.7 ppm). C<sub>41</sub>H<sub>53</sub>ClN<sub>2</sub>O<sub>4</sub> (673.35): calcd. C 73.14, H 7.93, N 4.16. C<sub>41</sub>H<sub>53</sub>ClN<sub>2</sub>O<sub>4</sub>·CH<sub>3</sub>OH: 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)-imidazolium-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-imidazolium 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*<sub>f</sub> = 0.21] yielded **16a** as a colorless solid (67 mg, 92% yield). M.p. 187–204 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):<sup>[61]</sup> δ = 8.18 (s, 0.2 H, 2-H<sub>im</sub>), 8.04 (s, 0.8 H, 2-H<sub>im</sub>), 7.89 (m<sub>c</sub>, 1 H, 4-H<sub>naph</sub>), 7.75 (m<sub>c</sub>, 1 H, 5-H<sub>naph</sub>), 7.33 (m<sub>c</sub>, 1 H, 4-H<sub>ph</sub>), 7.18 (m<sub>c</sub>, 1 H, 3-H<sub>naph</sub>), 7.10 (m<sub>c</sub>, 1 H, 6-H<sub>naph</sub>), 7.06 (m<sub>c</sub>, 1 H, 8-H<sub>naph</sub>), 6.65 (m<sub>c</sub>, 2 H, 3,5-H<sub>ph</sub>), 5.51 (m<sub>c</sub>, 4 H, HC=CH), 5.05–4.82 (m, 2 H, 4,5-H<sub>a im</sub>), 4.73–4.45 (m, 2 H, 4,5-H<sub>b im</sub>), 4.31 (m<sub>c</sub>, 1 H, OCHH), 4.22 (m<sub>c</sub>, 2 H, OCHH), 4.15 (m<sub>c</sub>, 4 H, OCHH), 4.05 (m<sub>c</sub>, 1 H, OCHH), 2.50–2.20 (m, 6 H, CH<sub>2</sub>), 2.10–1.80 (m, 10 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25 °C):<sup>[61]</sup> 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): ν̄ = 2938, 2874, 1624, 1512, 1479, 1466, 1458, 1438, 1388, 1329, 1266, 1225, 1103, 979, 924, 830, 774, 730 cm<sup>-1</sup>. HRMS (ESI, MeOH): calcd. for C<sub>35</sub>H<sub>41</sub>N<sub>2</sub>O<sub>4</sub> 553.3061 [M]; found 553.3051.

**2,12,14,24-Tetraoxa-1(1,3,2)-benzena-13(2,7,1)-naphthalena-25(1,3)-imidazolium-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-imidazolium 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*<sub>f</sub> = 0.17], yielded **16b** as a colorless solid (463 mg, 92% yield). M.p. 173–181 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):<sup>[61]</sup> δ = 8.20 (s, 0.32 H, 2-H<sub>im</sub>), 8.14 (s, 0.08 H, 2-H<sub>im</sub>), 8.06 (s, 0.14 H, 2-H<sub>im</sub>), 8.04 (s, 0.44 H, 2-H<sub>im</sub>), 7.86 (m<sub>c</sub>, 1 H, 4-H<sub>naph</sub>), 7.74 (m<sub>c</sub>, 1 H, 5-H<sub>naph</sub>), 7.31 (m<sub>c</sub>, 1 H, 4-H<sub>ph</sub>), 7.13 (m<sub>c</sub>, 2 H, 3,6-H<sub>naph</sub>), 7.05 (m<sub>c</sub>, 1 H, 8-H<sub>naph</sub>), 6.64 (m<sub>c</sub>, 2 H, 3,5-H<sub>ph</sub>), 5.46 (m<sub>c</sub>, 4 H, HC=CH), 5.18 (m<sub>c</sub>, 1 H, 5-H<sub>a im</sub>), 5.00 (m<sub>c</sub>, 1 H, 4-H<sub>a im</sub>), 4.83 (m<sub>c</sub>, 1 H, 5-H<sub>b im</sub>), 4.40–3.90 (m, 9 H, 4-H<sub>b im</sub>, OCH<sub>2</sub>), 2.40–1.40 (m, 20 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25 °C):<sup>[61]</sup> 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), 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), 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), 99.6 (t), 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), 67.3 (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): ν̄ = 3069, 2934, 2851, 1627, 1513, 1465, 1438, 1387, 1332, 1262, 1225, 1213, 1147, 1099, 969, 832, 776, 727, 647 cm<sup>-1</sup>. HRMS (ESI, MeOH): calcd. for C<sub>37</sub>H<sub>45</sub>N<sub>2</sub>O<sub>4</sub> 581.3374 [M]; found 581.3359.

**2,11,13,22-Tetraoxa-1(1,3,2)-benzena-12(2,7,1)-naphthalena-23(1,3)-imidazolium-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)-imidazolium-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*<sub>f</sub> = 0.19] yielded **17a** as a colorless solid (49 mg, 83% yield). M.p. 215 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):<sup>[60]</sup> δ = 8.13 (s, 1 H, 2-H<sub>im</sub>), 7.90 (d, <sup>3</sup>*J* = 9.0 Hz, 1 H, 4-H<sub>naph</sub>), 7.83 (d, <sup>3</sup>*J* = 9.0 Hz, 1 H, 5-H<sub>naph</sub>), 7.33 (dd, <sup>3</sup>*J* = 8.5 Hz, <sup>3</sup>*J* = 8.5 Hz, 1 H, 4-H<sub>ph</sub>), 7.19 (d, <sup>3</sup>*J* = 9.1 Hz, 1 H, 3-H<sub>naph</sub>), 7.18 (dd, <sup>3</sup>*J* = 9.0 Hz, <sup>4</sup>*J* = 2.4 Hz, 1 H, 6-H<sub>naph</sub>), 7.14 (d, <sup>4</sup>*J* = 2.3 Hz, 1 H, 8-H<sub>naph</sub>), 6.65 (br. d, <sup>3</sup>*J* = 8.5 Hz, 1 H<sup>#</sup>, 3-H<sub>ph</sub>\*), 6.64 (br. d, <sup>3</sup>*J* = 8.6 Hz, 1 H<sup>#</sup>, 5-H<sub>ph</sub>\*), 4.99

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(m<sub>c</sub>, 1 H, 5-H<sub>a im</sub>), 4.88 (m<sub>c</sub>, 1 H, 4-H<sub>a im</sub>), 4.64 (m<sub>c</sub>, 1 H, 5-H<sub>b im</sub>), 4.50 (m<sub>c</sub>, 1 H, 4-H<sub>b im</sub>), 4.31 (m<sub>c</sub>, 2 H, OCHH), 4.22 (m<sub>c</sub>, 1 H, OCHH), 4.17 (m<sub>c</sub>, 1 H, OCHH), 4.12 (m<sub>c</sub>, 3 H, OCHH), 3.99 (m<sub>c</sub>, 1 H, OCHH), 1.95–1.75 (m, 8 H, CH<sub>2</sub>), 1.70–1.37 (m, 16 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25 °C):<sup>[60]</sup> δ = 160.9 (C-2<sub>im</sub>), 159.6 (C-7<sub>naph</sub>), 155.0 (C-2<sub>ph</sub>\*), 154.3 (C-6<sub>ph</sub>\*), 153.5 (C-2<sub>naph</sub>), 132.3 (C-4<sub>naph</sub>), 132.0 (C-8<sub>naph</sub>), 131.3 (C-4<sub>ph</sub>), 130.7 (C-5<sub>naph</sub>), 124.1 (C-4<sub>naph</sub>), 114.7 (C-6<sub>naph</sub>), 114.6 (C-1<sub>naph</sub>), 112.4 (C-1<sub>ph</sub>), 110.6 (C-3<sub>naph</sub>), 105.0 (C-3<sub>ph</sub>\*), 104.9 (C-5<sub>ph</sub>\*), 102.5 (C-8<sub>naph</sub>), 70.1 (OCH<sub>2</sub>), 69.9 (OCH<sub>2</sub>), 68.8 (OCH<sub>2</sub>), 68.6 (OCH<sub>2</sub>), 52.2 (C-5<sub>im</sub>\*), 52.1 (C-4<sub>im</sub>\*), 28.6, 28.3, 28.1, 27.1, 26.9, 26.7, 26.2, 25.6, 24.3, 24.2, 24.0 (CH<sub>2</sub>) ppm. IR (KBr): ν̄ = 2937, 2854, 1624, 1514, 1459, 1388, 1330, 1261, 1224, 1100, 832, 778 cm<sup>-1</sup>. HRMS (ESI, MeOH): calcd. for C<sub>35</sub>H<sub>45</sub>N<sub>2</sub>O<sub>4</sub> 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<sub>f</sub> = 0.17] yielded **17b** as a colorless solid (331 mg, 90% yield). M.p. 218 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):<sup>[60]</sup> δ = 8.27 (s, 1 H, 2-H<sub>im</sub>), 7.89 (d, <sup>3</sup>J = 9.0 Hz, 1 H, 4-H<sub>naph</sub>), 7.80 (d, <sup>3</sup>J = 9.0 Hz, 1 H, 5-H<sub>naph</sub>), 7.32 (dd, <sup>3</sup>J = 8.5 Hz, <sup>3</sup>J = 8.5 Hz, 1 H, 4-H<sub>ph</sub>), 7.18 (d, <sup>3</sup>J = 9.1 Hz, 1 H, 3-H<sub>naph</sub>), 7.15 (dd, <sup>3</sup>J = 9.0 Hz, <sup>4</sup>J = 2.3 Hz, 1 H, 6-H<sub>naph</sub>), 7.09 (d, <sup>4</sup>J = 2.3 Hz, 1 H, 8-H<sub>naph</sub>), 6.66 (br. d, <sup>3</sup>J = 8.5 Hz, 1 H<sup>#</sup>, 3-H<sub>ph</sub>\*), 6.65 (br. d, <sup>3</sup>J = 8.5 Hz, 1 H<sup>#</sup>, 5-H<sub>ph</sub>\*), 5.09 (m<sub>c</sub>, 1 H, 5-H<sub>a im</sub>), 5.00 (m<sub>c</sub>, 1 H, 4-H<sub>a im</sub>), 4.71 (m<sub>c</sub>, 1 H, 5-H<sub>b im</sub>), 4.37 (m<sub>c</sub>, 1 H, 4-H<sub>b im</sub>), 4.30 (m<sub>c</sub>, 2 H, OCHH), 4.20 (m<sub>c</sub>, 3 H, OCHH), 4.12 (m<sub>c</sub>, 1 H, OCHH), 4.07 (m<sub>c</sub>, 2 H, OCHH), 1.98–1.77 (m, 8 H, CH<sub>2</sub>), 1.65–1.55 (m, 4 H, CH<sub>2</sub>), 1.55–1.35 (m, 16 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25 °C):<sup>[60]</sup> δ = 161.0 (C-2<sub>im</sub>), 160.0 (C-7<sub>naph</sub>), 154.6 (C-2<sub>ph</sub>\*), 153.5 (C-6<sub>ph</sub>\*), 152.9 (C-2<sub>naph</sub>), 132.2 (C-4<sub>naph</sub>), 132.0 (C-8<sub>naph</sub>), 130.9 (C-4<sub>ph</sub>), 130.6 (C-5<sub>naph</sub>), 124.1 (C-4<sub>naph</sub>), 116.3 (C-6<sub>naph</sub>), 114.9 (C-1<sub>naph</sub>), 113.1 (C-1<sub>ph</sub>), 110.2 (C-3<sub>naph</sub>), 105.3 (C-3<sub>ph</sub>\*), 104.9 (C-5<sub>ph</sub>\*), 100.8 (C-8<sub>naph</sub>), 69.6 (OCH<sub>2</sub>), 69.4 (OCH<sub>2</sub>), 69.3 (OCH<sub>2</sub>), 67.6 (OCH<sub>2</sub>), 52.5 (C-5<sub>im</sub>), 52.1 (C-4<sub>im</sub>), 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 (CH<sub>2</sub>) ppm. IR (KBr): ν̄ = 2930, 2853, 1627, 1512, 1461, 1390, 1263, 1225, 1148, 1097, 982, 925, 832, 776, 725, 636 cm<sup>-1</sup>. ESI-MS (MeOH): m/z (%) = 585.37 (100) [C<sub>37</sub>H<sub>49</sub>N<sub>2</sub>O<sub>4</sub>]<sup>+</sup>. HRMS: calcd. for C<sub>37</sub>H<sub>49</sub>N<sub>2</sub>O<sub>4</sub> 585.36926; found 585.36922 (δ = 0.1 ppm); calcd. for C<sub>36</sub><sup>13</sup>CH<sub>49</sub>N<sub>2</sub>O<sub>4</sub> 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<sub>37</sub>H<sub>49</sub>ClN<sub>2</sub>O<sub>4</sub>, 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<sup>3</sup>, T = 220(2) K, ρ<sub>calcd.</sub> = 1.218 g/cm<sup>3</sup>, μ = 0.154 mm<sup>-1</sup>, monoclinic, space group P2<sub>1</sub>/n, Z = 4, STOE Imaging Plate Diffraction System (IPDS-1), Mo-K<sub>α</sub> (λ = 0.71073 Å), 20540 measured reflections in the range of 5° ≤ 2θ ≤ 50°, 5841 independent reflections used for refinement, R<sub>int</sub> = 0.0489. Structure solution was done with SHELXS-97. Structure refinement was performed against F<sup>2</sup> using SHELXL-97; 397 parameters, R<sub>1</sub> for all 3958 reflections with F<sub>o</sub> > 4σ(F<sub>o</sub>) = 0.0481, wR<sub>2</sub> for all 5841 reflections = 0.1310, GoF = 1.022, residual electron density 0.33/–0.27 e/Å<sup>3</sup>. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and refined isotropically using a riding model. The crystal structure data have been deposited at the Cambridge Crystallographic Data Centre. CCDC-642189 con-

tains 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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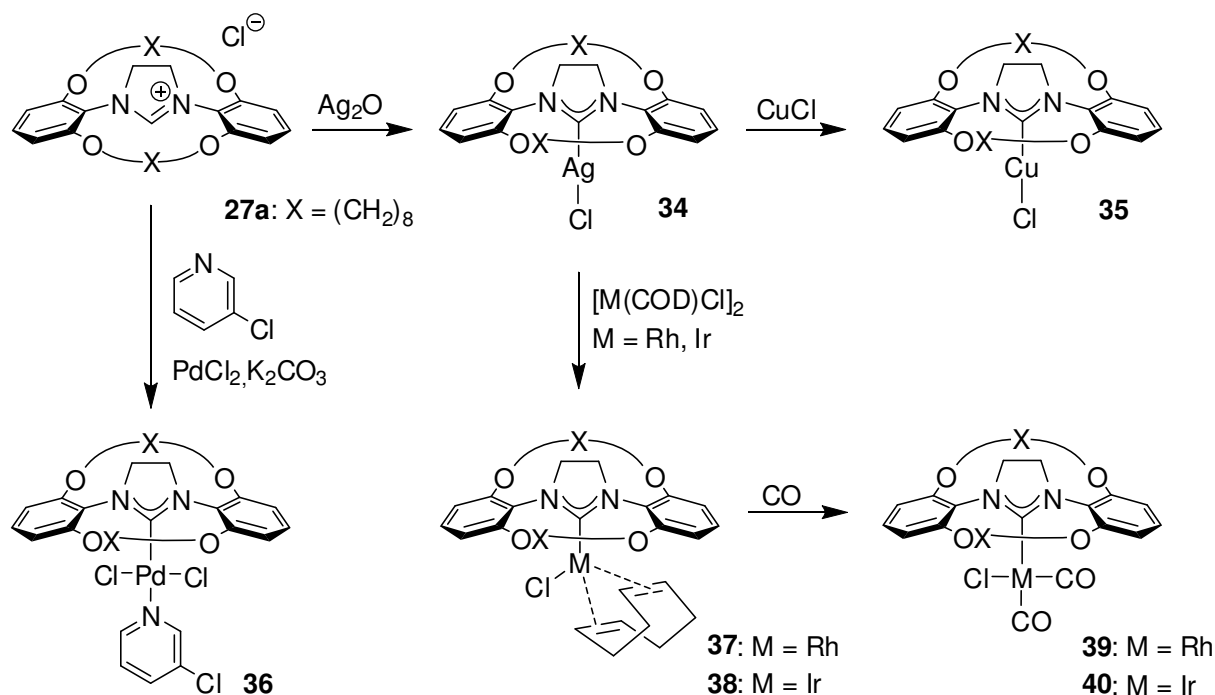
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- [60] #: The signals coincide, so only the total integration of the coinciding protons could be determined. \*: Assignments may be interchanged; subscripts are used to differentiate between atoms/groups which are part of/bound to naphthyl (<sub>naph</sub>), phenyl (<sub>ph</sub>) or imidazolium (<sub>im</sub>) 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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### 3.3 Concave Reagents, 55: *Bimacroyclic NHC Transition Metal Complexes.*

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Ausgehend vom bimakrocyclischen Imidazoliumsalz **27a** (siehe Seite 13) wurden die NHC-Metallkomplexe **34-40** synthetisiert.



Der NHC-Silberkomplex **34** ermöglichte die Synthese von Kupferkomplex **35**, Rhodiumkomplex **37** und Iridiumkomplex **38** durch Transmetallierung in guten Ausbeuten. Der NHC-Palladiumkomplex **36** konnte in nur geringer Ausbeute aus dem freien NHC erhalten werden und war nicht durch Transmetallierung aus dem Silberkomplex **34** zugänglich. Die Rhodium- und Iridium-Dicarbonylkomplexe **39** und **40** wurden durch Ligandenaustausch aus den COD-Komplexen **37** und **38** erhalten (COD = 1,5-Cyclooctadien). Silberkomplex **34**, Kupferkomplex **35** und Palladiumkomplex **36** wurden durch Einkristall-Röntgenstrukturanalyse charakterisiert.

Silberkomplex **34** und Kupferkomplex **35** wurden als Katalysatoren für die Cyclopropanierung von Styrol und Inden mit EDA (Ethyl diazoacetat) getestet. Der Kupferkomplex **35** zeigte eine ähnliche Reaktivität und Selektivität wie ein literaturbekannter NHC-Kupferkomplex,<sup>[142]</sup> während der Silberkomplex **34** sich unter den Reaktionsbedingungen zersetzte. Anhand der Bandenlage der Carbonylschwingungen der Komplexe **39** und **40** wurden die elektronischen Eigenschaften des NHC-Liganden untersucht. Dieser erwies sich als deutlich elektronenreicher als das häufig verwendete Imidazolidin-2-yliden **26**.



# Bimacrocylic NHC transition metal complexes <sup>☆</sup>

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## Abstract

The preparation of seven concave NHC metal complexes derived from bimacrocylic imidazolium salt **1** is reported. The silver complex **2**, obtained in 86% yield by reacting **1** with silver(I) oxide, was used to give copper complex **3**, rhodium complex **5** and iridium complex **6** by transmetalation in good yields. Palladium complex **4** was obtained by reaction of the azolium salt **1** with palladium dichloride in 3-chloropyridine. The rhodium and iridium dicarbonyl complexes **7** and **8** were prepared via ligand exchange from the COD complexes **5** and **6**. Silver complex **2**, copper complex **3** and palladium complex **4** were characterized by single-crystal X-ray analysis. Silver complex **2** and copper complex **3** were tested in the cyclopropanation of styrene and indene with EDA (ethyl diazoacetate), where good results were obtained with **3**, while low conversion and catalyst decomposition was observed with **2**.

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**Keywords:** Carbenes; Bimacrocylics; Transmetalation; *N*-heterocyclic carbenes; Homogeneous catalysis; Cyclopropanation

## 1. Introduction

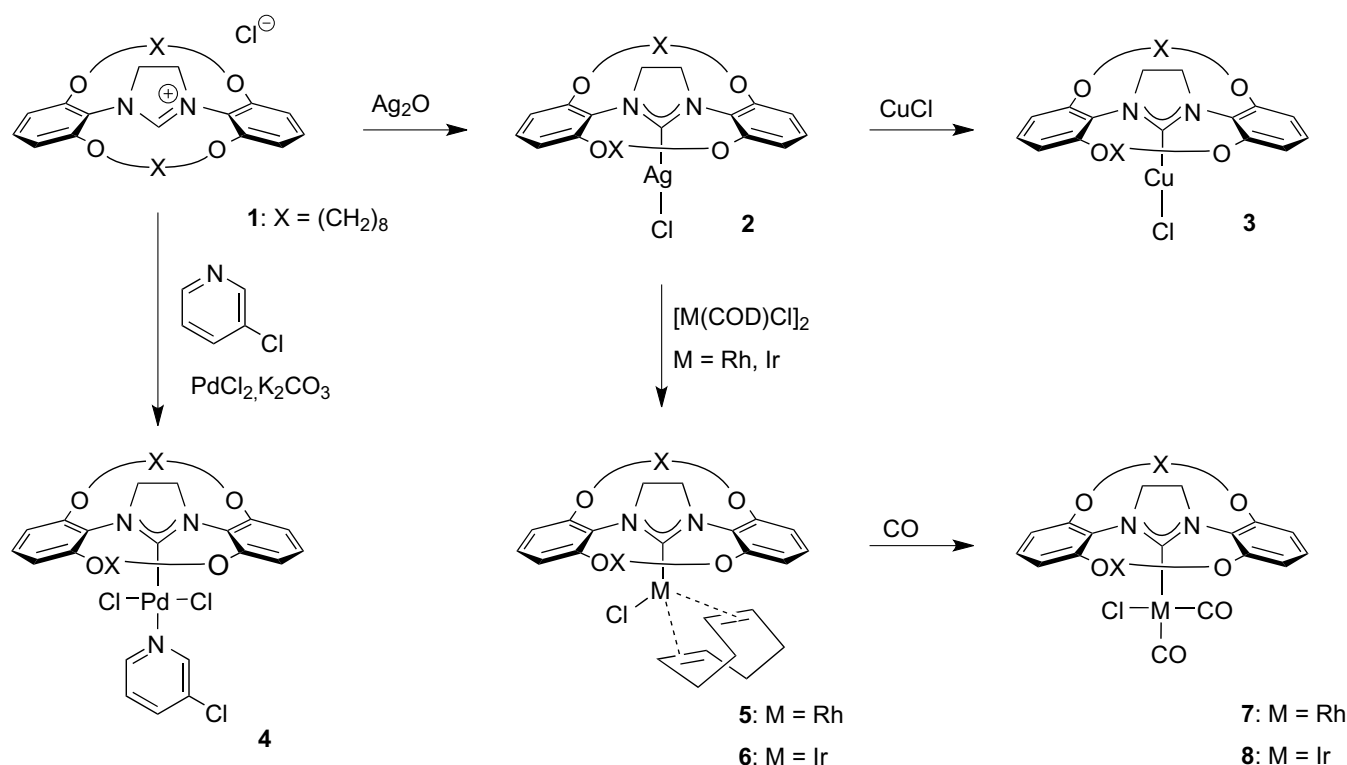
Since the first reports of *N*-heterocyclic carbene (NHC) metal complexes by Wanzlick and Schönherr [1] and Öfele [2] in 1968 and the isolation of a stable crystalline carbene by Arduengo et al. [3] in 1991, NHC and their coordination chemistry are an emerging field of research [4]. Notably, NHC also exhibit excellent catalytic activity in metal-free organocatalysis [5], including umpolung and condensation of carbonyl compounds [6] and transesterification reactions [7]. As ligands, the nucleophilic NHC are strong two-electron  $\sigma$ -donors, displaying similar ligand properties as trialkylphosphines [8]. The extent of their  $\pi$ -accepting ability is under investigation [9]. In comparison to related phosphine complexes, NHC metal complexes have

been shown to possess increased stability and catalytic activity in numerous reactions, the second generation of Grubbs' catalyst for olefin metathesis being a prominent example [10]. Besides their unique electronic properties, the steric demand of the NHC ligands is an important factor in cross-coupling reactions, and bulky NHC have been synthesized for challenging Suzuki-Miyaura [11] or Sonogashira [12] couplings. We have recently reported the synthesis of bimacrocylic imidazolium ions as precursors to respective NHC [13], expecting to effect reactivity and selectivity due to the tailored concave structure of the ligands. In this contribution, we report the synthesis of seven NHC metal complexes derived from the imidazolium salt **1** [13a] and preliminary results on their catalytic activity.

<sup>☆</sup> Concave reagents, Part ##. For part ###, see (current numbers will be inserted in the proofs).

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## 2. Results and discussion

### 2.1. Synthesis and reactivity of silver complex 2 and copper complex 3

The reaction of azolium salt **1** with silver(I) oxide in dichloromethane resulted in the formation of complex **2** in 86% yield, with no requirement to exclude oxygen or moisture from the reaction mixture. Ag(I)–NHC complexes are frequently used as carbene transfer reagents to produce NHC metal complexes by transmetalation, avoiding the handling of the sensitive free carbenes [14]. Besides this important application, Ag(I)–NHC have been reported to catalyze the diboration of alkenes [15], carbene transfer from EDA (ethyl diazoacetate) [16] and the hydrosilylation of aldehydes [17]. The thermal decomposition of Ag(I)–NHC was used to generate free carbenes as catalysts for the ring-opening polymerization of lactide and transesterification reactions [18]. The NHC migration in transmetalation reactions is explained by the lability of the Ag–C bond, with the lack of <sup>107,109</sup>Ag–<sup>13</sup>C coupling in the <sup>13</sup>C NMR being a proof of this fluxionality (on the NMR timescale) in solution [19]. The <sup>13</sup>C resonance for the carbene carbon atom C-2 in **2**, however, was observed with low intensity as a pair of well resolved doublets at 209.7 ppm (<sup>1</sup>J<sub>107AgC</sub> = 234 Hz, <sup>1</sup>J<sub>109AgC</sub> = 270 Hz), and also the resonance for C-4,5 of the NHC at 50.6 ppm was split into a doublet (<sup>3</sup>J<sub>AgC</sub> = 8.6 Hz). To the best of our knowledge, there are eight examples of Ag(I)–NHC with resolved Ag–<sup>13</sup>C couplings reported in the literature [19a,20], and some of these complexes were used in transmetalations. For IMesAgCl (IMes = 1,3-

bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), the <sup>13</sup>C resonance for C-2 could not be observed at natural abundance of the <sup>13</sup>C isotope, but for the <sup>13</sup>C labeled complex it was observed with resolved Ag–<sup>13</sup>C coupling (185 ppm, <sup>1</sup>J<sub>107AgC</sub> = 234 Hz, <sup>1</sup>J<sub>109AgC</sub> = 270 Hz) [20d]. In all cases, the ratio of the magnetogyric constants of the silver nuclei is reflected by the observed coupling constants.

Ag(I)–NHC complexes possess a great structural diversity with various ionic and neutral structures in the solid state [14,20e]. The crystal structure analysis of **2** revealed a monomeric structure with an almost linear coordinated silver atom, the angle C1–Ag1–Cl1 being 178.24(7)° (see Figs. 1 and 2). In both ESI and LD-ToF mass spectra, however, a dimeric (NHC)<sub>2</sub>Ag<sup>+</sup> cation was observed with high intensity, while (NHC)Ag<sup>+</sup> was not observed. The bond lengths C1–Ag1 and Cl1–Ag1 are 2.084(3) Å and 2.3282(7) Å, respectively, the internal ring angle N1–C1–N2 is 108.3(2)°, and these data are comparable to those reported for other Ag(I)–NHC [20a,20d,20e]. In contrast to IMesAgCl and azolium salt **1**, the complex **2** does not possess a crystallographic twofold axis bisecting the heterocycle, with the torsion angles C1–N1–C4–C9 and C1–N2–C23–C18 being 78.66(1)° and 63.16(1)°, respectively, and four different Ag–O distances, which are 3.606(5) Å for Ag1–O1, 3.174(4) Å for Ag1–O2, 4.937(4) Å for Ag1–O3 and 4.621(12) Å for Ag1–O4. This desymmetrization is probably due to packing effects, and the structure is flexible in solution as indicated by both <sup>1</sup>H and <sup>13</sup>C NMR spectra. The chlorine atom is in vague contact with two of the protons in 4,5-position of the neighbouring heterocycle, with distances of 2.971(7) Å and 2.978(5) Å, respectively.

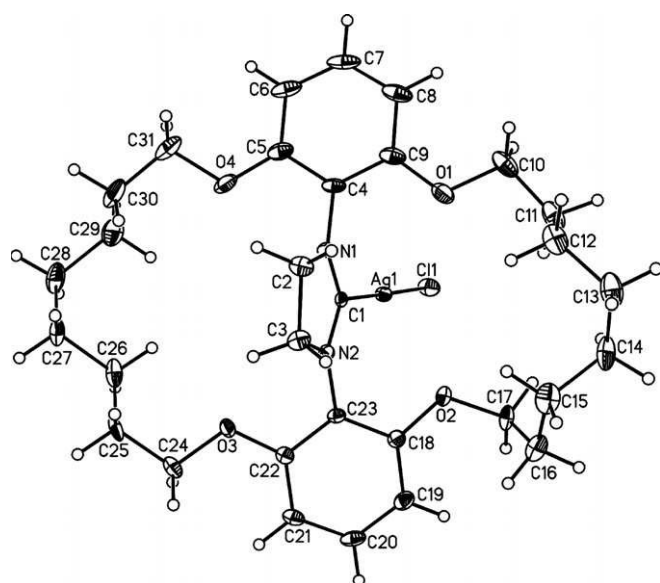


Fig. 1. Crystal structure of silver complex **2** with displacement ellipsoids drawn at the 30% probability level. Five carbon atoms in one octylene chain are disordered in two positions, and only the atoms of higher occupancy are shown for clarity.

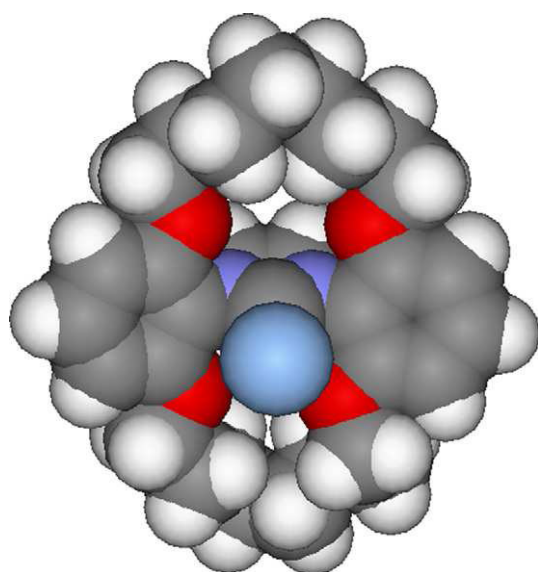


Fig. 2. Space filling representation of the X-ray structure of silver complex **2**, highlighting the concave structure. The chlorine atom is omitted for clarity.

Silver complex **2** was used for transmetalation, and copper complex **3** was obtained in 67% yield by stirring a solution of **2** in dichloromethane with copper(I) chloride. The NMR spectra of the complexes **2** and **3** are very similar (the average  $\Delta\delta$  is 0.1 ppm for  $^{13}\text{C}$  and 0.01 ppm for  $^1\text{H}$ ), but the resonance for C-2 was observed as a singlet at 205.3 ppm for **3**. Notably, the reaction of azolium salt **1** with sodium *tert*-butoxide and copper(I) chloride in THF led to a complex mixture of unidentified products, and complex **3** could not be obtained by this general method [21]. In the crystal structure of copper complex **3** (see

Fig. 3), the bond distances Cu1–C1, Cu1–Cl1 are 1.8852(19) Å and 2.1172(6) Å, respectively, in good agreement with the data reported for IPrCuCl [21b] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and SIMesCuCl [21c] (SIMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene).

The bond angles C–Cu–Cl reported for these are 178.48(13)° (SIMesCuCl) and 180.00° (IPrCuCl), while C1–Cu1–Cl1 is 173.44(6)° in **3**, respectively. As for **2**, the NHC ligand is not  $C_2$ -symmetric in the solid state, and the heterocycle is twisted out of an idealized geometry inside the bimacrocyclic, even more expressed in **3** with torsion angles of 60.51(1)° and 61.30(1)° for C1–N1–C4–C9 and C1–N2–C23–C18, respectively. The copper atom is bent out of the plane of the NHC, and the torsion angles C2–N1–C1–Cu1, C3–N2–C1–Cu1 are 169.06(0)° and 164.72(0)°, respectively. This is possibly due to a weak attraction of the copper atom to two of the neighbouring oxygen atoms (bond lengths Cu1–O1, Cu1–O2, Cu1–O3, Cu1–O4 are 2.925(4) Å, 2.868(4) Å, 4.864(10) Å, 4.929(14) Å, respectively). The internal ring angle N1–C1–N2 is 107.09(0)°.

Cu(I)–NHC have been reported to be beneficial catalysts in numerous reactions, including the reduction of  $\alpha,\beta$ -unsaturated carbonyl compounds [21a], hydrosilylation of ketones [21b,21c], [3 + 2] cycloadditions (“click chemistry”) [22] and the methylenation of aldehydes and ketones [23]. As IPrCuCl is known to catalyze the cyclopropanation of styrene [24] and both IPrCuCl and IPrAgCl were reported as catalysts for carbene transfer from EDA into unactivated C–H bonds [16], we investigated the reactivity of the complexes **2** and **3** in the cyclopropanation of styrene and indene with EDA (see Scheme 1 and Table 1).

Very low EDA consumption, along with the formation of unidentified by-products, was observed with silver com-

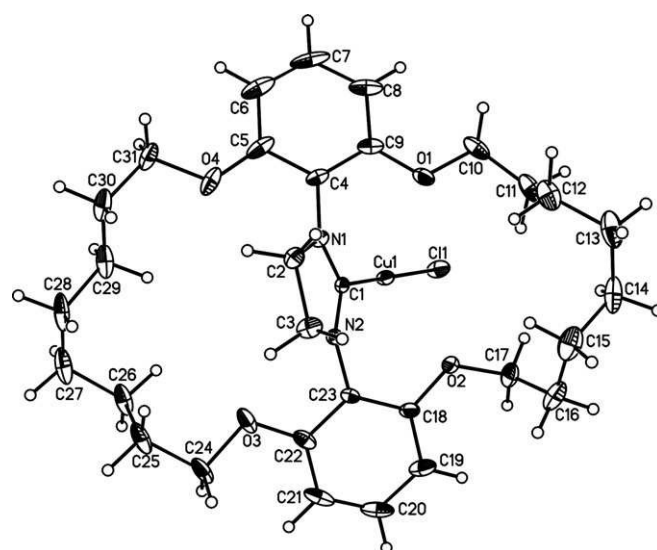
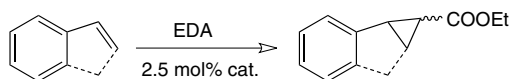


Fig. 3. Crystal structure of copper complex **3** with displacement ellipsoids drawn at the 30% probability level. The chlorine atom and all eight carbon atoms in one octylene chain are disordered in two positions, and only the atoms of higher occupancy are shown for clarity.





Scheme 1. Cyclopropanation of styrene and indene with EDA. The extra methylene group in indene is indicated by the dashed line.

Table 1  
Catalytic activity of complexes **2** and **3** in the cyclopropanation<sup>a</sup> of styrene and indene

Olefine	Catalyst	Conversion (%) <sup>b,c</sup>	d.r. <sup>c</sup>
Styrene	<b>2</b>	<5	42:58 <sup>d</sup>
Indene	<b>2</b>	<5	1:99 <sup>e</sup>
Styrene	<b>3</b>	63 (100) <sup>f</sup>	29:71 <sup>d</sup> (30:70) <sup>d,f</sup>
Indene	<b>3</b>	100	22:78 <sup>e</sup>

<sup>a</sup> Conditions: 25  $\mu$ mol catalyst, 1 mmol EDA, 10 mmol olefine, 16 h at room temperature.

<sup>b</sup> Based on EDA.

<sup>c</sup> Determined by GC, average of two experiments.

<sup>d</sup> Diastereomeric ratio *cis:trans*.

<sup>e</sup> Diastereomeric ratio *endo:exo*.

<sup>f</sup> 48 hours reaction time.

plex **2**. Product formation could not be raised with higher catalyst loadings or longer reaction time, and a precipitate of silver chloride was observed in the reaction mixtures, indicating catalyst decomposition. In contrast to these unpleasant results, copper complex **3** afforded clean conversion to cyclopropanation products, along with the formation of maleate and fumarate (approx. 20%), known by-products of the reaction. The *cis:trans* ratio (30:70) observed in the cyclopropanation of styrene is comparable to that reported for IPrCuCl (32:68). A higher reactivity and selectivity compared to styrene was observed with indene, due to the more electron-rich double bond and a greater steric hindrance of the substrate.

## 2.2. Synthesis of palladium complex **4**

In palladium catalyzed C–C and C–N cross coupling reactions, NHC have shown to be valuable ligands, allowing for the oxidative addition of challenging substrates (e.g. hindered aryl-chlorides) due to their electronic properties, while their bulkyness facilitates reductive elimination [4f]. Besides formation of the active catalyst from a palladium source and the azolium precursor in situ, stable Pd–NHC precatalysts are used, which allow to control for the optimum Pd:NHC ratio of 1:1 [25] and are activated upon dissociation of a second, labile ligand. NHC-substituted phosphapalladacycles [26], *N*-palladacycles [27] and palladium-allyl complexes [28] were found to be beneficial in this respect. The heating of azolium salts with palladium dichloride and potassium carbonate in 3-chloropyridine has recently been reported to produce Pd(II)–NHC that were found to be highly active in Suzuki–Miyaura [29], Negishi [30] and Kumada–Tamao–Corriu [31] cross coupling reactions.

Subjecting azolium salt **1** to these reaction conditions gave palladium complex **4** in very poor yield (5%), while

the reaction of silver complex **2** with palladium dichloride in 3-chloropyridine at room temperature afforded none of the desired product. The <sup>13</sup>C resonance for C-2 was observed at 183.5 ppm for **4**. In the crystal structure of **4** (see Fig. 4), the asymmetric unit contains three crystallographically independent molecules. Selected bond distances and angles are given in Table 2.

Each of the three palladium atoms adopts a slightly distorted square-planar coordination, and these data are comparable to those reported for the respective complex using the IPr NHC ligand [29]. In contrast to the crystal structures of azolium salt **1** and complexes **2** and **3**, the two phenyl substituents of the NHC are oriented almost perpendicular to the heterocycle in **4**, and the torsion angles C1–N1–C4–C5 and C1–N2–C23–C18 are 86.06(2)° and 87.81(2)°, which seems to be due to sterical interactions of the ligands alkyl chains with the two chloride anions. The internal ring angle N1–C1–N2 is 109.39(2)°. Palladium complex **4** has not yet been tested for its catalytic properties in cross coupling reactions because of the insufficient yield.

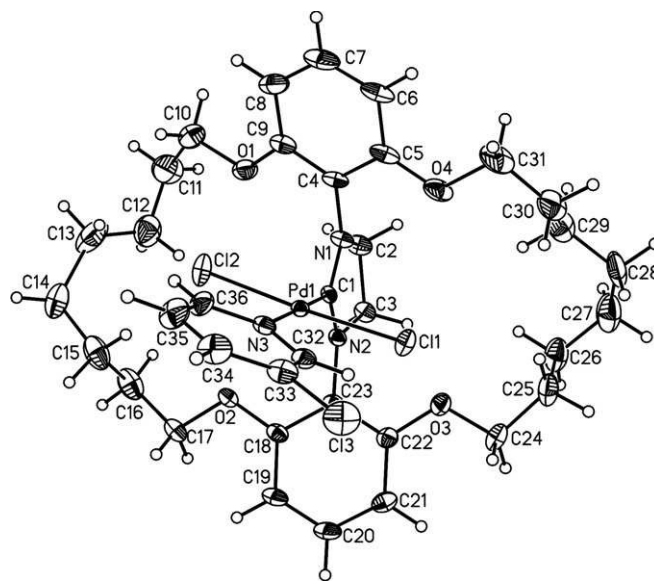


Fig. 4. Crystal structure of palladium complex **4** with displacement ellipsoids drawn at the 30% probability level. Only one of the three crystallographically independent molecules is represented.

Table 2  
Selected bond lengths (Å) and bond angles (°) for palladium complex **4**

	Pd1	Pd2	Pd3
<i>Bond lengths</i>			
Pd–C1/C41/C81	1.963(4)	1.949(19)	1.954(2)
Pd–N3/N13/N23	2.178(5)	2.148(11)	2.175(2)
Pd–Cl1/Cl11/Cl22	2.308(12)	2.316(11)	2.308(9)
Pd–Cl2/Cl12/Cl23	2.294(13)	2.294(11)	2.313(8)
<i>Bond angles</i>			
C–Pd–N	179.64(1)	178.19(1)	178.52(1)
Cl–Pd–Cl	175.22(1)	177.40(1)	176.03(1)

Pd1, Pd2, Pd3 belong to the respective crystallographically independent complexes.

The synthesis and reactivity of a related NHC–palladium–allyl complex is currently under investigation in our laboratory.

### 2.3. Synthesis of rhodium and iridium complexes **5**, **6**, **7**, **8**

We finally prepared the rhodium complex **7** and iridium complex **8** to determine their carbonyl stretching frequencies which are a popular indirect measure of the ligands' electronic properties [32,11]. A low stretching frequency (wavenumber) of CO corresponds to strong  $\sigma$ -donation of the NHC. By using a linear fit procedure [32c], the CO stretching frequencies of respective Ir(I)–NHC can be used to estimate Tolman's electronic parameter (TEP) [33], which is well documented for various phosphines. The CO stretching frequencies and TEP values of respective NHC complexes fall in a narrow range, and the NHC are more electron donating than the most donating phosphines. Compared to standard NHC, our new ligand seems

to be significantly more electron donating. The CO stretching frequencies are listed in Table 3.

The complexes were synthesized by transmetalation from silver complex **2** with the respective chloro( $\eta^4$ -1,5-cyclooctadiene = COD)metal dimers to give rhodium complex **5** and iridium complex **6** in good yields (69% and 64%, respectively). Both compounds display restricted rotation about the metal–carbene bond as can be judged from the NMR spectra. A similar behavior of Rh(I)– and Ir(I)–NHC COD complexes has been described before and explained in terms of steric interactions [32c]. The  $^{13}\text{C}$  resonance for C-2 was observed as a doublet at 215.2 ppm ( $^1J_{\text{RhC}} = 48.4$  Hz) for **5**, while the resonance for C-2 could not be observed for **6**. By bubbling CO through solutions of **5** and **6** in dichloromethane, the complexes **7** and **8** were produced in almost quantitative yields (91% and 93%, respectively). The spectra are consistent with the *cis*-conformation of both carbonyl ligands, showing two strong  $\tilde{\nu}_{\text{CO}}$  bands in the IR spectra, and three signals are observed in the  $^{13}\text{C}$  NMR spectra between 210 and 165 ppm for both **7** and **8**, corresponding to the two CO carbon atoms and C-2. By using  $^{13}\text{C}$  labeled CO in the synthesis of respective Rh(I)–NHC (derived from pyrazolium, imidazolium and benzimidazolium), Herrmann et al. could demonstrate that the two CO carbon atoms resonate at lower field than the carbene carbon atom C-2 [32e]. The C-2 resonance for rhodium complex **7**, however, was undoubtedly identified to appear at 206.6 ppm ( $^1J_{\text{RhC}} = 41.3$  Hz) by observing the correlation with 4,5-*H* in the HMBC (heteronuclear multiple bond correlation) spectrum, and so the two resonances at 186.6 ppm ( $^1J_{\text{RhC}} = 53.3$  Hz) and 183.2 ppm ( $^1J_{\text{RhC}} = 75.6$  Hz) must be assigned to the CO ligands (see Fig. 5). For iridium complex **8**, this correlation could not be observed and the assignment remains uncertain.

Table 3  
Carbonyl stretching frequencies  $\tilde{\nu}$  (measured in dichloromethane) of complexes **7**, **8** and related complexes known from the literature

Compound	$\tilde{\nu}(\text{CO})$ ( $\text{cm}^{-1}$ )	$\tilde{\nu}(\text{CO})$ ( $\text{cm}^{-1}$ )	TEP <sup>a</sup> ( $\text{cm}^{-1}$ )
<b>7</b>	2069 (2062) <sup>b</sup>	1995 (1984) <sup>b</sup>	–
SIMesRhCl(CO) <sub>2</sub> <sup>c</sup>	(2081) <sup>b</sup>	(1996) <sup>b</sup>	–
<b>8</b>	2058	1977	2050
SIMesIrCl(CO) <sub>2</sub> <sup>c</sup>	2068	1981	2055
ICyIrCl(CO) <sub>2</sub> <sup>c</sup>	2064	1982	2054

<sup>a</sup> TEP(Tolman's electronic parameter) =  $0.722[\tilde{\nu}_{\text{average}(\text{CO})}] + 593$   $\text{cm}^{-1}$ , according to Ref. [32c].

<sup>b</sup> Measured in KBr.

<sup>c</sup> Literature values [32b,32f,32g]; SIMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene, ICy = 1,3-dicyclohexylimidazol-2-ylidene.

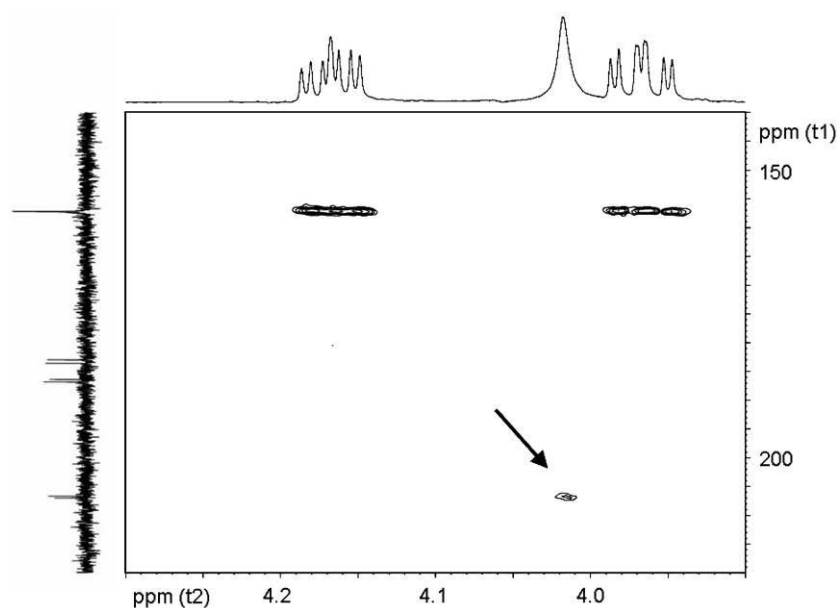


Fig. 5. HMBC spectrum (313 K, parts) of rhodium complex **7** used to assign the carbon atoms of the NHC (C-2, 206.6 ppm) and the carbonyl ligands (186.6 and 183.2 ppm, respectively). The cross-peak between C-2 and H-4,5 is indicated by an arrow.

### 3. Conclusion

Bimacrocyclic NHC metal complexes can readily be obtained from either azolium salt **1** or via transmetalation from silver complex **2**. All of the synthesized complexes are stable under ambient conditions, and copper complex **3** proved to be active as a catalyst in carbene transfer reactions. Compared to standard NHC, our new concave ligand seems to be more electron donating. The reactivity of the synthesized complexes and the accessibility of other concave NHC metal complexes are under investigation.

### 4. Experimental

#### 4.1. General

During all reactions and manipulations, no precautions were taken to exclude oxygen or moisture, except for the cyclopropanation reactions. The NHC precursor **1** was prepared according to the method reported earlier [13a]. Melting points were determined with a Büchi 530 melting point apparatus.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with Bruker DRX 500 or AV 600 instruments at room temperature and referenced to tetramethylsilane. Assignments are supported by COSY, HSQC and HMBC. The HMBC spectrum of complex **7** was recorded at 313 K, with the first  $1/2J$  delay being adjusted for a coupling constant of 5 Hz ( $\Delta = 10$  ms). The  $^{13}\text{C}$  resonances for the carbene carbon atoms C-2 were observed with low intensities for all compounds. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet,  $m_{(c)}$  = multiplet (centered), br = broad signal. The following abbreviations are used for assignments: Ar = aromatic, Im = imidazolidin, Py = 3-chloropyridine. Mass spectra were obtained using either an Applied Biosystems Mariner Spectrometry Workstation (ESI), Bruker Biflex III (LD-ToF) or Finnigan MAT 8200 (EI). IR spectra were recorded with a Perkin-Elmer Paragon 1000 spectrometer (a resolution of  $4\text{ cm}^{-1}$  was used for routine spectra, while the spectra of **7** and **8** were recorded with a resolution of  $1\text{ cm}^{-1}$ ). Elemental analyses were carried out with a EuroEA 3000 Elemental Analyzer from Euro Vector. GC analyses were performed on an Agilent 6890 N gas chromatograph.

#### 4.2. Synthesis of chloro(2,11,13,22-tetraoxa-1,12(1,3,2)-dibenzena-23-(1,3)-imidazolidina-bicyclo[10.10.1]-tricosaphane-23<sup>2</sup>-ylidene)silver(I) (**2**)

A suspension of silver(I) oxide (45 mg, 0.19 mmol) and imidazolium chloride **1** (210 mg, 387  $\mu\text{mol}$ ) in 10 mL of dichloromethane was stirred for 14 h at room temperature excluding light. The reaction mixture was passed through a short pad of silica gel, eluting with dichloromethane. After removal of the solvent *in vacuo*, **2** was obtained as a colorless solid. Yield: 215 mg (331  $\mu\text{mol}$ , 86%).

M.p. 229 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.20 (t,  $^3J = 8.5$  Hz, 2H, Ar-*H*-4), 6.57 (d,

$^3J = 8.5$  Hz, 4H, Ar-*H*-3,5), 4.12 ( $m_{(c)}$ , 4H,  $\text{OCH}_a\text{H}_b$ ), 4.01 (s, 4H, Im-4,5-*H*), 3.99 ( $m_{(c)}$ , 4H,  $\text{OCH}_a\text{H}_b$ ), 1.79 ( $m_{(c)}$ , 4H), 1.70 ( $m_{(c)}$ , 8H), 1.48 ( $m_{(c)}$ , 12H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 209.7 (dd,  $^1J_{107\text{AgC}} = 234$  Hz,  $^1J_{109\text{AgC}} = 270$  Hz, Im-C-2), 156.5 (Ar-C-2,6), 129.2 (Ar-C-4), 118.2 (Ar-C-1), 104.7 (Ar-C-3,5), 68.1 ( $\text{OCH}_2$ ), 50.6 (d,  $^3J_{\text{AgC}} = 8.6$  Hz, Im-C-4,5), 28.5, 26.4, 23.8. MS (ESI, MeOH):  $m/z$  (%) = 1119.54/1121.54 (87/100,  $[(\text{C}_{31}\text{H}_{42}\text{N}_2\text{O}_4)_2\text{Ag}]^+$ ), 507.33 (30,  $[\text{C}_{31}\text{H}_{43}\text{N}_2\text{O}_4]^+$ ). MS (LD-ToF):  $m/z$  (%) = 1119/1121 (70/100,  $[(\text{C}_{31}\text{H}_{42}\text{N}_2\text{O}_4)_2\text{Ag}]^+$ ). IR (KBr):  $\tilde{\nu}(\text{cm}^{-1}) = 2936, 2854, 1596, 1499, 1463, 1268, 1099, 775, 730$ . Anal. Calc. for  $\text{C}_{31}\text{H}_{42}\text{AgClN}_2\text{O}_4$  (649.99): C, 57.28; H, 6.51; N, 4.31. Found: C, 57.48; H, 6.61; N, 4.32%.

#### 4.3. Synthesis of chloro(2,11,13,22-tetraoxa-1,12(1,3,2)-dibenzena-23-(1,3)-imidazolidina-bicyclo[10.10.1]-tricosaphane-23<sup>2</sup>-ylidene)copper(I) (**3**)

A suspension of copper(I) chloride (32 mg, 0.32 mmol) and silver complex **2** (210 mg, 323  $\mu\text{mol}$ ) in 15 mL of dichloromethane was stirred for 20 h at room temperature. The reaction mixture was passed through a short pad of silica gel, eluting with dichloromethane. After removal of the solvent *in vacuo*, **3** was obtained as a colorless solid. Yield: 131 mg (216  $\mu\text{mol}$ , 67%).

M.p. 207 °C.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.19 (t,  $^3J = 8.4$  Hz, 2H, Ar-*H*-4), 6.57 (d,  $^3J = 8.5$  Hz, 4H, Ar-*H*-3,5), 4.12 ( $m_{(c)}$ , 4H,  $\text{OCH}_a\text{H}_b$ ), 4.00 ( $m_{(c)}$ , 4H,  $\text{OCH}_a\text{H}_b$ ), 3.99 (s, 4H, Im-4,5-*H*), 1.81 ( $m_{(c)}$ , 4H), 1.70 ( $m_{(c)}$ , 8H), 1.47 ( $m_{(c)}$ , 12H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 205.3 (Im-C-2), 156.3 (Ar-C-2,6), 128.9 (Ar-C-4), 118.2 (Ar-C-1), 104.7 (Ar-C-3,5), 68.1 ( $\text{OCH}_2$ ), 50.4 (Im-C-4,5), 28.5, 26.6, 24.0. MS (LD-ToF):  $m/z$  (%) = 569 (13,  $[\text{C}_{31}\text{H}_{42}\text{CuN}_2\text{O}_4]^+$ ), 507 (100,  $[\text{C}_{31}\text{H}_{43}\text{N}_2\text{O}_4]^+$ ). IR (KBr):  $\tilde{\nu}(\text{cm}^{-1}) = 2936, 2856, 1593, 1500, 1478, 1459, 1388, 1295, 1258, 1182, 1101, 772, 726$ . Anal. Calc. for  $\text{C}_{31}\text{H}_{42}\text{ClCuN}_2\text{O}_4$  (605.66): C, 61.47; H, 6.99; N, 4.63. Found: C, 61.72; H, 7.19; N, 4.63%.

#### 4.4. Synthesis of trans-dichloro(3-chloropyridine)-(2,11,13,22-tetraoxa-1,12(1,3,2)-dibenzena-23-(1,3)-imidazolidina-bicyclo[10.10.1]-tricosaphane-23<sup>2</sup>-ylidene)palladium(II) (**4**)

A suspension of palladium dichloride (89 mg, 0.50 mmol), imidazolium chloride **1** (299 mg, 550  $\mu\text{mol}$ ) and potassium carbonate (346 mg, 2.50 mmol) in 2 mL of 3-chloropyridine was heated for 16 h at 80 °C. After cooling, the reaction mixture was diluted with dichloromethane and passed through a short pad of silica gel covered by celite, eluting with dichloromethane. The volatiles were removed *in vacuo* and the crude product was purified by column chromatography on silica gel [dichloromethane/ethyl acetate (3:1),  $R_f = 0.12$ ] to give **4** as a yellow solid. Yield: 18 mg (23  $\mu\text{mol}$ , 5%).

M.p. 233 °C.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.54 (d,  $^4J = 2.4$  Hz, 1H, Py-*H-2*), 8.46 (dd,  $^3J = 5.5$  Hz,  $^4J = 1.3$  Hz, 1H, Py-*H-6*), 7.48 (ddd,  $^3J = 8.2$  Hz,  $^4J = 2.4$  Hz,  $^4J = 1.4$  Hz, 1H, Py-*H-4*), 7.26 (t,  $^3J = 8.4$  Hz, 2H, Ar-*H-4*), 6.99 (dd,  $^3J = 8.2$  Hz,  $^3J = 5.5$  Hz, 1H, Py-*H-5*), 6.60 (d,  $^3J = 8.4$  Hz, 4H, Ar-*H-3,5*), 4.20 (m<sub>c</sub>, 4H,  $\text{OCH}_a\text{H}_b$ ), 4.06 (s, 4H, Im-4,5-*H*), 4.01 (m<sub>c</sub>, 4H,  $\text{OCH}_a\text{H}_b$ ), 2.09 (m<sub>c</sub>, 4H), 1.75 (m<sub>c</sub>, 4H), 1.63 (m<sub>c</sub>, 4H), 1.51 (m<sub>c</sub>, 12H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 183.5 (Im-*C-2*), 157.4 (Ar-*C-2,6*), 150.4 (Py-*C-2*), 149.5 (Py-*C-6*), 137.0 (Py-*C-4*), 131.7 (Py-*C-3*), 129.3 (Ar-*C-4*), 124.0 (Py-*C-5*), 117.5 (Ar-*C-1*), 103.7 (Ar-*C-3,5*), 68.1 ( $\text{OCH}_2$ ), 50.5 (Im-*C-4,5*), 28.6, 26.8, 24.1. IR (KBr):  $\tilde{\nu}(\text{cm}^{-1}) = 3059, 2923, 2853, 1592, 1506, 1460, 1388, 1298, 1261, 1100, 1024, 802, 726$ .

#### 4.5. Synthesis of chloro( $\eta^4$ -1,5-cyclooctadiene)-(2,11,13,22-tetraoxa-1,12(1,3,2)-dibenzena-23-(1,3)-imidazolidinabicyclo[10.10.1]-tricosaphane-23<sup>2</sup>-ylidene)rhodium(I) (5)

A solution of silver complex **2** (207 mg, 318  $\mu\text{mol}$ ) in 5 mL of dichloromethane was added to chloro( $\eta^4$ -1,5-cyclooctadiene)rhodium(I) dimer (79 mg, 0.16 mmol). The reaction mixture was stirred for 16 h at room temperature and then passed through a short pad of silica gel, eluting with dichloromethane. The crude product was purified by crystallisation from dichloromethane/diethyl ether. Yellow crystals were obtained. Yield: 165 mg (219  $\mu\text{mol}$ , 69%).

M.p. 228 °C.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.27 (t,  $^3J = 8.4$  Hz, 2H, Ar-*H-4*), 6.65 (dd,  $^3J = 8.4$  Hz,  $^4J = 1.1$  Hz, 2H, Ar-*H-3*), 6.55 (dd,  $^3J = 8.4$  Hz,  $^4J = 1.1$  Hz, 2H, Ar-*H-5*), 4.39 (br s, 2H,  $=\text{CH}_{a\text{COD}}$ ), 4.30 (m<sub>c</sub>, 2H,  $\text{OCH}_{a1}\text{H}_{b1}$ ), 4.13 (m<sub>c</sub>, 2H,  $\text{OCH}_{a2}\text{H}_{b2}$ ), 3.96 (m<sub>c</sub>, 2H,  $\text{OCH}_{a1}\text{H}_{b1}$ ), 3.91 (m<sub>c</sub>, 2H,  $\text{OCH}_{a2}\text{H}_{b2}$ ), 3.89 (m<sub>c</sub>, 2H, Im-4,5-*H*<sub>a</sub>), 3.83 (m<sub>c</sub>, 2H, Im-4,5-*H*<sub>b</sub>), 3.71 (br s, 2H,  $=\text{CH}_{b\text{COD}}$ ), 2.12 (m<sub>c</sub>, 2H), 1.81–1.42 (m, 28H), 1.36 (m<sub>c</sub>, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 215.2 (d,  $^1J_{\text{RhC}} = 48.4$  Hz, Im-*C-2*), 158.2 (Ar-*C-6*), 156.9 (Ar-*C-2*), 128.9 (Ar-*C-4*), 118.7 (Ar-*C-1*), 104.7 (Ar-*C-3*), 102.7 (Ar-*C-5*), 95.9 (d,  $^1J_{\text{RhC}} = 6.7$  Hz,  $=\text{C}_a\text{H}_{\text{COD}}$ ), 68.3 ( $\text{OCH}_2$ ), 67.7 ( $\text{OCH}_2$ ), 67.5 (d,  $^1J_{\text{RhC}} = 14.2$  Hz,  $=\text{C}_b\text{H}_{\text{COD}}$ ), 50.7 (Im-*C-4,5*), 32.8, 28.8, 28.4, 28.3, 26.5, 26.1, 23.3, 23.1. MS (ESI, MeOH):  $m/z$  (%) = 717.32 (100,  $[\text{C}_{39}\text{H}_{54}\text{N}_2\text{O}_4\text{Rh}]^+$ ). IR (KBr):  $\tilde{\nu}(\text{cm}^{-1}) = 2927, 2862, 1591, 1497, 1479, 1466, 1426, 1385, 1296, 1259, 1176, 1101, 770, 722$ . Anal. Calc. for  $\text{C}_{39}\text{H}_{54}\text{ClN}_2\text{O}_4\text{Rh}$  (753.22): C, 62.19; H, 7.23; N, 3.72. Found: C, 62.24; H, 7.32; N, 3.74%.

#### 4.6. Synthesis of chloro( $\eta^4$ -1,5-cyclooctadiene)-(2,11,13,22-tetraoxa-1,12(1,3,2)-dibenzena-23-(1,3)-imidazolidinabicyclo[10.10.1]-tricosaphane-23<sup>2</sup>-ylidene)iridium(I) (6)

Dichloromethane (8 mL) was added to a flask containing silver complex **2** (100 mg, 154  $\mu\text{mol}$ ) and chloro( $\eta^4$ -1,5-cyclooctadiene)iridium(I) dimer (50 mg, 75  $\mu\text{mol}$ ). The reaction mixture was stirred for 2 h at 40 °C and then

passed through a short pad of silica gel, eluting with dichloromethane. The crude product was purified by crystallisation from dichloromethane/diethyl ether. Yellow crystals were obtained. Yield: 83 mg (99  $\mu\text{mol}$ , 64%).

M.p. 231 °C.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.23 (t,  $^3J = 8.4$  Hz, 2H, Ar-*H-4*), 6.59 (dd,  $^3J = 8.4$  Hz,  $^4J = 0.9$  Hz, 2H, Ar-*H-3*), 6.51 (dd,  $^3J = 8.4$  Hz,  $^4J = 1.0$  Hz, 2H, Ar-*H-5*), 4.26 (m<sub>c</sub>, 2H,  $\text{OCH}_{a1}\text{H}_{b1}$ ), 4.11 (m<sub>c</sub>, 2H,  $\text{OCH}_{a2}\text{H}_{b2}$ ), 4.01–3.88 (m, 12H,  $\text{OCH}_a\text{H}_b$ , Im-4,5-*H*<sub>a</sub>,  $=\text{CH}_{a\text{COD}}$ ), 3.86 (m<sub>c</sub>, 2H, Im-4,5-*H*<sub>b</sub>), 3.44 (br s, 2H,  $=\text{CH}_{b\text{COD}}$ ), 2.12 (m<sub>c</sub>, 2H), 1.80 (m<sub>c</sub>, 4H), 1.67 (m<sub>c</sub>, 4H), 1.61–1.47 (m, 16H), 1.38 (m<sub>c</sub>, 2H), 1.28 (m<sub>c</sub>, 4H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 158.0 (Ar-*C-6*), 156.8 (Ar-*C-2*), 128.8 (Ar-*C-4*), 118.5 (Ar-*C-1*), 104.5 (Ar-*C-3*), 102.8 (Ar-*C-5*), 81.6 ( $=\text{C}_a\text{H}_{\text{COD}}$ ), 68.3 ( $\text{OCH}_2$ ), 67.6 ( $\text{OCH}_2$ ), 51.4 ( $=\text{C}_b\text{H}_{\text{COD}}$ ), 51.0 (Im-*C-4,5*), 33.4, 29.0, 28.9, 28.3, 26.5, 26.2, 23.3, 23.1; no signal observed for Im-*C-2*. MS (EI):  $m/z$  (%) = 840/842 (53/100,  $[\text{C}_{39}\text{H}_{54}\text{ClIrN}_2\text{O}_4]^+$ ). IR (KBr):  $\tilde{\nu}(\text{cm}^{-1}) = 2920, 2863, 1593, 1498, 1479, 1459, 1426, 1295, 1259, 1103, 770, 722$ . Anal. Calc. for  $\text{C}_{39}\text{H}_{54}\text{ClIrN}_2\text{O}_4$  (842.53): C, 55.60; H, 6.46; N, 3.32. Found: C, 55.66; H, 6.64; N, 3.36%.

#### 4.7. Synthesis of cis-dicarbonylchloro(2,11,13,22-tetraoxa-1,12(1,3,2)-dibenzena-23-(1,3)-imidazolidinabicyclo[10.10.1]-tricosaphane-23<sup>2</sup>-ylidene)rhodium(I) (7)

CO was bubbled through a solution of **5** (25 mg, 33  $\mu\text{mol}$ ) in 2 mL of dichloromethane at 0 °C for 10 min. The solvent was removed *in vacuo*, the residue was washed with cold pentane (3  $\times$  2 mL) and dried *in vacuo*. A yellow powder was obtained. Yield: 21 mg (30  $\mu\text{mol}$ , 91%).

M.p. >250 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.24 (t,  $^3J = 8.4$  Hz, 2H, Ar-*H-4*), 6.57 (d,  $^3J = 8.5$  Hz, 4H, Ar-*H-3,5*), 4.17 (m<sub>c</sub>, 4H,  $\text{OCH}_a\text{H}_b$ ), 4.02 (s, 4H, Im-4,5-*H*), 3.96 (m<sub>c</sub>, 4H,  $\text{OCH}_a\text{H}_b$ ), 1.94 (br s, 4H), 1.76 (br s, 4H), 1.64 (m<sub>c</sub>, 4H), 1.51 (br s, 12H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 206.6 (d,  $^1J_{\text{RhC}} = 41.3$  Hz, Im-*C-2*), 186.6 (d,  $^1J_{\text{RhC}} = 53.3$  Hz, CO), 183.2 (d,  $^1J_{\text{RhC}} = 75.6$  Hz, CO), 157.1 (Ar-*C-2,6*), 129.4 (Ar-*C-4*), 117.6 (Ar-*C-1*), 104.0 (Ar-*C-3,5*), 68.0 ( $\text{OCH}_2$ ), 51.0 (Im-*C-4,5*), 28.4, 26.5, 23.4; the signal for Ar-*C-2,6* is broad and of low intensity. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu}_{\text{CO}}(\text{cm}^{-1}) = 2069, 1995$ ; IR (KBr):  $\tilde{\nu}(\text{cm}^{-1}) = 2928, 2858, 2062, 1984, 1596, 1508, 1478, 1459, 1383, 1297, 1260, 1183, 1103, 774, 726$ . Anal. Calc. for  $\text{C}_{33}\text{H}_{42}\text{ClN}_2\text{O}_6\text{Rh}$  (701.06): C, 56.54; H, 6.04; N, 4.00. Found: C, 56.48; H, 6.18; N, 4.05%.

#### 4.8. Synthesis of cis-dicarbonylchloro(2,11,13,22-tetraoxa-1,12(1,3,2)-dibenzena-23-(1,3)-imidazolidinabicyclo[10.10.1]-tricosaphane-23<sup>2</sup>-ylidene)iridium(I) (8)

CO was bubbled through a solution of **6** (34 mg, 40  $\mu\text{mol}$ ) in 2 mL of dichloromethane at 0 °C for 10 min. The solvent was removed *in vacuo*, the residue was washed

with cold pentane (3 × 2 mL) and dried *in vacuo*. A yellow powder was obtained. Yield: 29 mg (37 μmol, 93%).

M.p. 234 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.24 (t, <sup>3</sup>J = 8.4 Hz, 2H, Ar-H-4), 6.55 (d, <sup>3</sup>J = 8.4 Hz, 4H, Ar-H-3,5), 4.17 (br s, 4H, OCH<sub>a</sub>H<sub>b</sub>), 4.07–3.90 (m, 8H, 4,5-H, OCH<sub>a</sub>H<sub>b</sub>), 1.95 (br s, 4H), 1.77 (br s, 4H), 1.64 (m<sub>c</sub>, 4H), 1.52 (br s, 12H). <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>): δ (ppm) = 203.0(\*), 182.2(\*), 169.0(\*), 157.1 (Ar-C-2,6), 129.5 (Ar-C-4), 117.2 (Ar-C-1), 103.9 (Ar-C-3,5), 68.0 (OCH<sub>2</sub>), 51.2 (Im-C-4,5), 28.4, 26.4, 23.4; \*: Im-C-2 and CO, assignment uncertain; the signal for Ar-C-2,6 is broad and of low intensity. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu}_{\text{CO}}(\text{cm}^{-1}) = 2058, 1977$ ; IR (KBr):  $\tilde{\nu}(\text{cm}^{-1}) = 2928, 2857, 2050, 1968, 1595, 1508, 1478, 1459, 1383, 1296, 1183, 1101, 773, 726$ . Anal. Calc. for C<sub>33</sub>H<sub>42</sub>ClIrN<sub>2</sub>O<sub>6</sub> (790.37): C, 50.15; H, 5.36; N, 3.54. Found: C, 50.57; H, 5.52; N, 3.54%.

#### 4.9. Cyclopropanation experiments

A flask was charged with the respective catalyst (25 μmol), EDA (114 mg, 1 mmol) and 1,2-dichloroethane (2 mL). The flask was flushed with nitrogen, sealed with a rubber septum and the mixture was stirred for 5 min. The respective olefine (10 mmol) was injected via syringe and the mixture was stirred at room temperature. After 16 h, the mixture was passed through a short pad of silica gel

and the silica gel was rinsed with diethylether (20 mL). The filtrate was then filled up to 25 mL with diethylether and analyzed by GC, following an established procedure [34]; conditions: split ratio 11:1, injector temp. 250 °C, detector temp. 300 °C; column: HP-5/30 m; temperature: 80 °C for 5 min, 10 °C/min until 140 °C, 1 min 140 °C, 2 °C/min until 160 °C, 1 min 160 °C, 20 °C/min until 240 °C, 20 min 240 °C.

#### 4.10. Single-crystal X-ray structure determination of compounds 2–4

*General:* Crystal data and details of the structure determination are given in Table 4. Suitable single crystals were grown by slow diffusion of either diethyl ether (**2**, **3**) or *n*-pentane (**4**) into solutions of the respective complexes in dichloromethane. Data collection was performed using an STOE Imaging Plate Diffraction System (IPDS-1) with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Structure solutions were performed with direct methods using SHELXS-97. Structure refinements were performed against F<sup>2</sup> with SHELXL-97 [35]. Some of the carbon atoms in the alkyl chains of compounds **2**, **3** and **4** and the chlorine atom in **3** are disordered in two positions and were refined using a split model. All non-hydrogen atoms except the disordered carbon atoms of lower occupancy were refined anisotropic. The hydrogen atoms were placed in

Table 4  
Crystallographic data for 2–4

Compound	2	3	4
Formula	C <sub>31</sub> H <sub>42</sub> AgClN <sub>2</sub> O <sub>4</sub>	C <sub>31</sub> H <sub>42</sub> ClCuN <sub>2</sub> O <sub>4</sub>	C <sub>36</sub> H <sub>46</sub> Cl <sub>3</sub> N <sub>3</sub> O <sub>4</sub> Pd
Formula weight	649.99	605.66	797.51
Color/habit	Colorless/block	Colorless/block	Yellow/block
Crystal size (mm)	0.2 × 0.14 × 0.08	0.3 × 0.1 × 0.2	0.5 × 0.4 × 0.3
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P2 <sub>1</sub> /c (no. 14)	P2 <sub>1</sub> /c (no. 14)	P $\bar{1}$ (no. 2)
a (Å)	9.8314(6)	9.5044(6)	15.7630(11)
b (Å)	32.2408(15)	17.1456(10)	20.0189(14)
c (Å)	9.7324(6)	18.3443(14)	21.1372(14)
$\alpha$ (°)	90	90	108.412(8)
$\beta$ (°)	93.374(8)	92.551(8)	90.506(8)
$\gamma$ (°)	90	90	100.428(8)
V (Å <sup>3</sup> )	3079.6(3)	2986.4(3)	6208.5(7)
Z	4	4	6
T (K)	170(2)	170(2)	200(2)
$\mu$ (mm <sup>-1</sup> )	0.778	0.859	0.679
$\theta$ Range (°)	2.17–22.38	2.52–28.03	2.28–26.02
Index ranges (h, k, l)	±10, ±34, ±10	±11, ±22, ±19	±19, ±24, ±24
Measured reflections	18554	21940	48286
Independent reflections	3964	6991	23979
R <sub>int</sub>	0.0434	0.0404	0.0387
Reflections with [I > 2σ(I)]	3257	5567	17870
Parameters	370	388	1306
R <sub>1</sub> /wR <sub>2</sub> [I > 2σ(I)] <sup>a</sup>	0.0254/0.0661	0.0387/0.0972	0.0416/0.1047
R <sub>1</sub> /wR <sub>2</sub> (all data) <sup>a</sup>	0.0330/0.0685	0.0516/0.1033	0.0592/0.1113
GOF (on F <sup>2</sup> ) <sup>a</sup>	0.982	1.031	0.960
Largest difference in peak and hole (e Å <sup>-3</sup> )	+0.356 and -0.357	+0.547 and -0.591	+0.897 and -0.681

<sup>a</sup>  $R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|$ ;  $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}$ ;  $GOF = \{\sum[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$ .

ideal positions and refined using a riding model. The asymmetric unit of **4** contains three crystallographically independent molecules.

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### Appendix A. Supplementary material

CCDC 664014, 664015 and 664016 contain the supplementary crystallographic data for **2**, **3** and **4**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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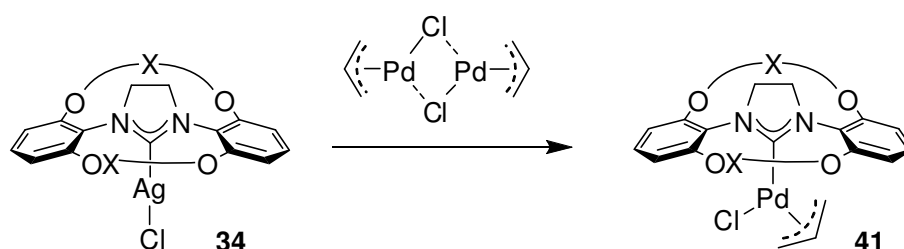
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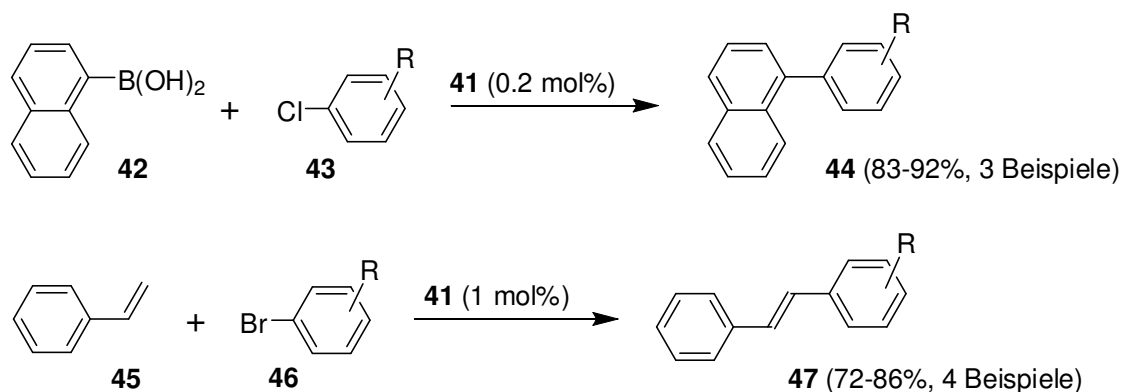
### 3.4 Concave Reagents: *Synthesis, Structure and Catalytic Activity of a Bimacroyclic NHC Palladium Allyl Complex.*

O. Winkelmann, C. Näther, U. Lüning, eingereicht bei *J. Organomet. Chem.*

Ausgehend vom bimakrocyclischen NHC-Silberkomplex **34** (siehe Seite 33) wurde der Palladiumkomplex **41** durch Transmetallierung mit Allyl-Palladiumchlorid-Dimer in 85% Ausbeute erhalten. Der Komplex **41** konnte durch Einkristall-Röntgenstrukturanalyse charakterisiert werden.



Die katalytische Aktivität des Palladiumkomplexes **41** wurde in Suzuki- und Heck-Kreuzkupplungen getestet.



In der Suzuki-Kupplung von 1-Naphthylboronsäure (**42**) mit Arylchloriden **43** ermöglichte der Palladiumkomplex **41** die Synthese der Biaryle **44** in hohen Ausbeuten. Bei der Heck-Reaktion mit Styrol (**45**) ergab die Verwendung von Arylbromiden **46** die Stilbene **47** in hohen Ausbeuten, während mit analogen Arylchloriden **43** unter den gleichen Reaktionsbedingungen unvollständiger Umsatz beobachtet wurde.

Mit Hilfe eines bimakrocyclischen chiralen NHC-Liganden könnten in einer asymmetrischen Suzuki-Kreuzkupplung axial-chirale Biaryle synthetisiert werden, entsprechende Produkte konnten in racemischer Form bereits mit dem Präkatalysator **41** erhalten werden. Die hohe Aktivität von **41** in der Suzuki-Kreuzkupplung ist vergleichbar mit analogen literaturbekannten Komplexen.<sup>[114]</sup>



## Synthesis, structure and catalytic activity of a bimacrocylic NHC palladium allyl complex ‡

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‡ Concave reagents, Part ##. For part ###, see ((current numbers will be inserted in the proofs))

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### Abstract

The preparation of a bimacrocylic NHC palladium allyl complex **4** is described. The complex was obtained by transmetalation with allyl palladium chloride dimer from the NHC silver complex **2** in 85% yield. Complex **4** was fully characterized by spectroscopic methods and by single crystal X-ray analysis. In a preliminary catalytic study, the complex **4** showed high activity in the Suzuki-Miyaura cross-coupling of unactivated aryl chlorides and bromides with 1-naphthalene-boronic acid at low catalyst loading. Good results were also obtained in the Mizoroki-Heck reaction of aryl bromides with styrene, but a decrease in yield was observed when aryl chlorides were used.

*Keywords:* Carbenes; Bimacrocylics; *N*-Heterocyclic carbenes; Palladium; Cross-coupling

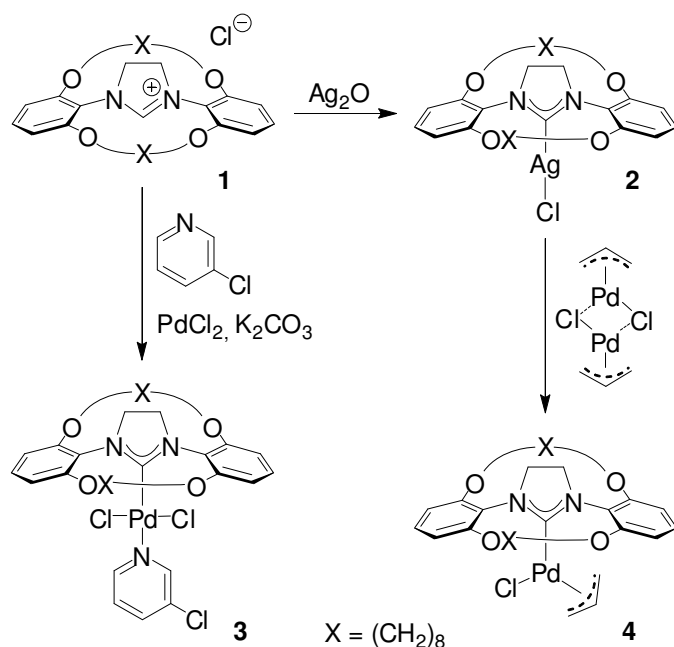
### 1. Introduction

*N*-Heterocyclic carbenes (NHCs) have received great attention since the isolation of a crystalline carbene in 1991 by Arduengo [1] and they are nowadays frequently used in either metal-free organocatalysis [2] or as beneficial ligands in organometallic chemistry [3]. As ligands, the nucleophilic NHCs are strong two-electron  $\sigma$ -donors, displaying similar properties as trialkylphosphines [4], and both species are successfully used in palladium catalyzed cross-coupling reactions [5]. In most cases of phosphine-containing catalytic systems, phosphines are used as free ligands in conjunction with a palladium source. In an

analogous fashion catalytically active NHC palladium complexes can be formed *in situ* from a palladium source and an azolium salt as the NHC precursor [6], but recently also a number of well-defined, air- and moisture-stable NHC-bearing palladium complexes with excellent catalytic activities have been reported [7]. In our continuing investigation of the catalytic properties of bimaocyclic NHCs [8], accessible from the respective azolium precursors [9], we explored the accessibility of bimaocyclic NHC palladium complexes and their catalytic activity in cross-coupling reactions.

## 2. Results and discussion

### 2.1 Synthesis and characterization of palladium complex 4



We have recently reported [8] the synthesis of a number of NHC metal complexes derived from the concave bimaocyclic imidazolium salt **1**. In contrast to other transition metal complexes, palladium complex **3** was only obtained in poor yield via the free carbene, and **3** was not accessible by transmetalation from silver complex **2** [8]. The use of NHC silver complexes as carbene transfer reagents is a popular method for the synthesis of NHC metal complexes by transmetalation, avoiding the handling of the sensitive free carbenes [10]. However, Nolan and coworkers have reported the synthesis of catalytically active NHC palladium complexes by reaction of the free carbenes with allyl palladium chloride dimer [7e]. We were delighted to find that in an analogous fashion the reaction of silver complex **2**

with allyl palladium chloride dimer led to the smooth formation of NHC palladium complex **4** in 85% yield.

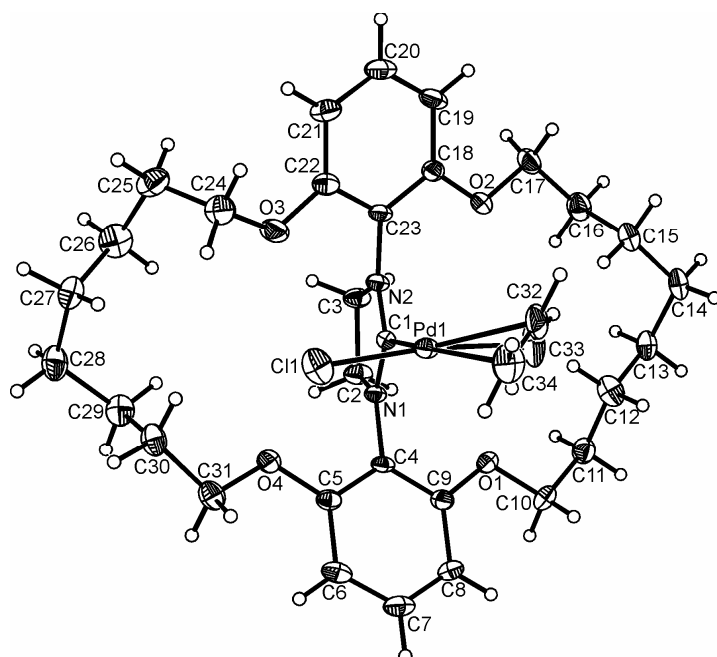


Figure 1. Crystal structure of palladium complex **4** with displacement ellipsoids drawn at the 50% probability level. Only one of the two crystallographically independent molecules is represented. The carbon atom C33 of the allyl moiety is disordered in two positions and only the atom of higher occupancy is shown for clarity.

In the crystal structure of **4** (see Figure 1), the asymmetric unit contains two crystallographically independent molecules. Selected bond lengths are given in Table 1. The structure of the NHC ligand in palladium complex **4** is similar to that in complex **3** [8], with the two phenyl substituents oriented almost perpendicular to the heterocycle, and the torsion angles C1-N1-C4-C5 and C1-N2-C23-C22 are  $81.42(1)^\circ$  and  $70.89(1)^\circ$ , respectively. The  $\eta^3$  coordination of the allyl moiety to the palladium center is comparable to that reported for the respective complex using the SIPr NHC ligand (SIPr = 1,3-bis(2,6-diisopropylphenyl)-imidazolidin-2-ylidene) [7e]. The angles C1-Pd1-C32, C1-Pd1-C34 and C34-Pd1-Cl1 are  $92.95(10)^\circ$ ,  $161.34(10)^\circ$  and  $93.67(9)^\circ$  in **4**, respectively, C1-Pd1-Cl1 is  $104.4(6)^\circ$  and C32-Pd1-C34 is  $68.72(12)^\circ$ . The internal angle of the heterocycle N1-C1-N2 is  $108.03(18)^\circ$ .

The  $^{13}\text{C}$  resonance for the carbene carbon atom of **4** was observed at 211.4 ppm which is significantly more downfield than in palladium complex **3** (183.5 ppm) [8]. A comparison of related palladium complexes with the SIPr NHC ligand shows a very similar trend: the carbene carbon atom resonates at 215.4 ppm when SIPr is incorporated into an allyl palladium

complex [7e], but in the 3-chloro-pyridine containing complex this resonance is observed at 184.9 ppm [11]. This drastic difference in chemical shifts ( $\Delta\delta$  is 30.5 ppm for SIPr and 27.9 ppm for our bimakrocyclic NHC ligand) must be due to a different electronic situation at the palladium center, caused by the varying ancillary ligands. However, both kinds of precatalysts are believed to result in the same monoligated NHC-Pd<sup>0</sup>-species as the active catalyst [3a]. A detailed reaction pathway for catalyst activation has been proposed for NHC palladium allyl complexes [7e].

Table 1  
Selected bond lengths (Å) for palladium complex **4**

	Pd1 <sup>a</sup>	Pd2 <sup>a</sup>
Pd-C1/C41	2.045(2)	2.038(2)
Pd-C32/C72	2.105(3)	2.102(3)
Pd-C33/C73	2.142(3)	2.131(3)
Pd-C34/C74	2.211(2)	2.233(2)
Pd-C11/C12	2.3875(6)	2.3674(6)

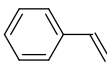
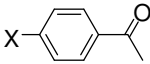
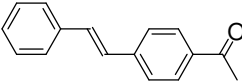
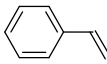

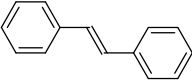
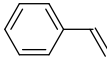

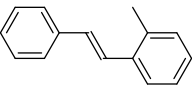
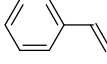
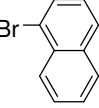
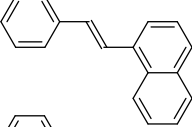
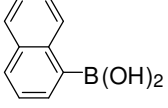

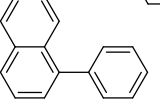
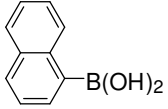
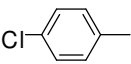
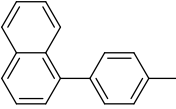
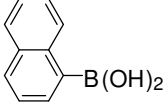

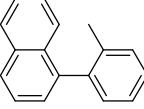
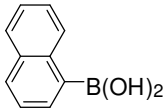
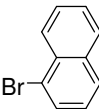
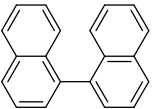
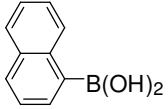
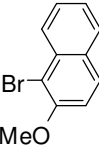
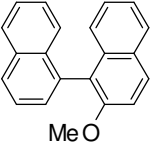
<sup>a</sup> Pd1 and Pd2 belong to the respective crystallographically independent complexes.

## 2.2 Catalytic activity of palladium complex **4**

NHC palladium complexes are known to catalyze a number of cross-coupling reactions [3,7]. We decided to investigate the reactivity of complex **4** in Mizoroki-Heck and Suzuki-Miyaura cross-coupling reactions. While the use of aryl chlorides as coupling partners is nowadays established in the latter case [7a,7b,7d,7e], the Mizoroki-Heck olefination of unactivated aryl chlorides is not trivial and mainly bromides and activated chlorides are successfully used in the reaction [7c,12]. The results obtained with catalyst **4** are summarized in table 2. The olefinations were performed in tetrabutylammonium bromide as an ionic liquid at 140 °C (16 h reaction time), following a protocol by Beller and coworkers [12c]. Using 1 mol% of catalyst **4**, good results were obtained in the reaction of activated and electronically neutral aryl bromides with styrene, and also hindered 2-bromo-toluene afforded 72% of the coupling product. Unfortunately, a decrease in yield was observed when analogous aryl chlorides were used as the coupling partners (Table 2, entries 1 and 2). While activated 4-chloro-acetophenone still afforded 37% of the desired product, only 10% yield of stilbene was

obtained with chlorobenzene. The low yields are due to incomplete conversion and could not be raised significantly with higher catalyst loadings (Table 2, entry 1).

Table 2  
Catalytic activity of complex **4** in Mizoroki-Heck<sup>a</sup> and Suzuki-Miyaura<sup>b</sup> cross-coupling reactions

Entry	Substrates	Product	Yield <sup>c</sup>
1	 		X = Br: 86% X = Cl: 37% (43%) <sup>d</sup>
2	 		X = Br: 73% X = Cl: 10%
3	 		72%
4	 		79%
5	 		83%
6	 		91%
7	 		92%
8	 		91%
9	 		21%

<sup>a</sup> Conditions: Palladium complex **4** (10  $\mu$ mol), aryl halide (1 mmol), styrene (1.5 mmol), NaOAc (1.2 mmol), KO<sup>t</sup>Bu (0.09 mmol), 16 h at 140 °C in tetrabutylammonium bromide (2 g). <sup>b</sup> Conditions: Palladium complex **4** (2  $\mu$ mol), aryl halide (1 mmol), boronic acid (1.2 mmol), KO<sup>t</sup>Bu (1.4 mmol), 2 h at 60 °C in 2-propanol (2 mL). <sup>c</sup> Isolated yield. <sup>d</sup> 20  $\mu$ mol of Palladium complex **4**.

In contrast to the low conversion of aryl chlorides observed with catalyst **4** in the olefinations, high yields were obtained in the reaction of aryl chlorides with 1-naphthaleneboronic acid at low catalyst loading in short reaction times (0.2 mol% **4**, 2 h at 60°C). As we are currently working on an axially chiral modification of the bimakroclie NHC ligand [9b], we were interested in the ability of complex **4** to produce axially chiral biaryls (however, in racemic form). 1,1'-Binaphthyl (Table 2, entry 8) could be produced in 91% yield with 1-bromo-naphthalene, but due to its low barrier of racemization [13] it might not be an appropriate candidate for asymmetric catalysis. When 1-bromo-2-methoxy-naphthalene was reacted with 1-naphthaleneboronic acid, only 21% yield of the desired product was obtained (Table 2, entry 9), along with unreacted bromide and 1,1'-binaphthyl (68%, based on boronic acid), resulting from the homocoupling of the boronic acid. A suppression of this side-reaction might be possible [14], but no efforts were taken yet to improve this yield.

### 3. Conclusion

The accessibility of the NHC palladium complex **4** by transmetallation from silver complex **2** is a great improvement compared to the synthesis of palladium complex **3** that could only be obtained in poor yield [8]. In the Suzuki-Miyaura cross-coupling reaction of aryl chlorides, the activity of the bimakroclie complex **4** is comparable to related non-macroclie NHC palladium allyl complexes [7e], but the formation of a tri-*ortho*-substituted biaryl proved to be difficult with catalyst **4** in this preliminary study. In the Mizoroki-Heck reaction, high yields of the desired coupling products were obtained with aryl bromides, while a decrease in yield was observed with the use of analogous aryl chlorides. As the catalytic activity of complex **4** in cross-coupling reactions shows promise, we are currently focusing on a chiral version of the bimakroclie NHC ligand for respective asymmetric reactions [9b].

### 4. Experimental

#### 4.1. General

The NHC silver complex **2** [8] and allyl palladium chloride dimer [7b] were prepared according to the literature. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with Bruker DRX 500 or ARX 300 instruments at room temperature and are referenced to tetramethylsilane. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m<sub>(c)</sub> = multiplet

(centered), br = broad signal. The following abbreviations are used for assignments: Ar = aromatic, Im = imidazolidin. Mass spectra were recorded with a Finnigan MAT 8200 or MAT 8230. IR spectra were recorded with a Perkin-Elmer Paragon 1000 spectrometer. Elemental analyses were carried out with an EuroEA 3000 Elemental Analyzer from Euro Vector.

#### 4.2. Synthesis of chloro( $\eta^3$ -allyl)-(2,11,13,22-tetraoxa-1,12(1,3,2)-dibenzena-23-(1,3)-imidazolidina-bicyclo[10.10.1]-tricosaphane-23<sup>2</sup>-ylidene)palladium(II) (**4**)

To a stirred solution of allyl palladium chloride dimer (24 mg, 65  $\mu$ mol) in dichloromethane (1 mL) was added silver complex **2** (90 mg, 0.14 mmol), dissolved in dichloromethane (5 mL). After stirring for 1 h at room temperature, the mixture was passed through a short pad of silica gel, and the silica gel was rinsed with dichloromethane. The filtrate was concentrated *in vacuo* and the product was precipitated by addition of *n*-pentane. The precipitate was washed with *n*-pentane and dried *in vacuo*. A yellow solid was obtained. Yield: 75 mg (0.11 mmol, 85%).

M.p. 115 °C (decomp.). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.17 (t, <sup>3</sup>*J* = 8.4 Hz, 2H, Ar-*H*-4), 6.52 (d, <sup>3</sup>*J* = 8.4 Hz, 4H, Ar-*H*-3,5), 4.68 (m<sub>c</sub>, 1H, CH<sub>allyl</sub>), 4.14 (m<sub>c</sub>, 4H, OCH<sub>2</sub>), 4.05-3.90 (m, 8H, OCH<sub>2</sub>, Im-*H*-4,5), 3.67 (d, <sup>3</sup>*J* = 7.3 Hz, 1H, HCH<sub>allyl</sub>), 3.24 (br s, 1H, HCH<sub>allyl</sub>), 2.61 (d, <sup>3</sup>*J* = 13.4 Hz, 1H, HCH<sub>allyl</sub>), 1.94 (m<sub>c</sub>, 4H, CH<sub>2</sub>), 1.80-1.60 (m, 9H, HCH<sub>allyl</sub>, CH<sub>2</sub>), 1.55-1.45 (m, 12H, CH<sub>2</sub>). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 211.4 (Im-*C*-2), 157.2 (Ar-*C*-2,6), 128.9 (Ar-*C*-4), 118.5 (Ar-*C*-1), 113.9 (CH<sub>allyl</sub>), 104.0 (Ar-*C*-3,5), 70.2 (CH<sub>2 allyl</sub>), 68.2 (OCH<sub>2</sub>), 68.0 (OCH<sub>2</sub>), 50.7 (Im-*C*-4,5), 48.7 (CH<sub>2 allyl</sub>), 28.7, 28.5, 26.4, 23.6 (CH<sub>2</sub>). IR (KBr):  $\tilde{\nu}$  (cm<sup>-1</sup>) = 3069, 2934, 2855, 1594, 1503, 1461, 1387, 1297, 1102, 776, 731. Anal. Calc. for C<sub>34</sub>H<sub>47</sub>ClN<sub>2</sub>O<sub>4</sub>Pd (689.64): C, 59.22; H, 6.87; N, 4.06. Found: C, 59.42; H, 7.01; N, 4.18%.

#### 4.3. General procedure for Mizoroki-Heck cross-coupling reactions

A flask was charged with styrene (156 mg, 1.50 mmol), tetrabutylammonium bromide (2g), sodium acetate (99 mg, 1.2 mmol), potassium *tert*-butoxide (10 mg, 89  $\mu$ mol), palladium complex **4** (7 mg, 0.01 mmol) and the aryl halide (1.0 mmol). The flask was flushed with nitrogen, sealed with a rubber septum and heated to 140 °C for 16 h. After cooling to room temperature, the mixture was triturated in water (10 mL) and extracted with diethyl ether (3  $\times$  15 mL). The organic layer was dried with magnesium sulfate, the solvent was evaporated *in*

*vacuo* and the product was purified by column chromatography on silica gel. The purity and identity of previously described *E*-stilbene [12c], *E-p*-acetyl-stilbene [12c], *E-o*-methylstilbene [12b] and 1-*E*-styryl-naphthalene [15] was confirmed by  $^1\text{H}$  NMR and mass spectrometric analysis.

#### 4.4. General procedure for Suzuki-Miyaura cross-coupling reactions

A flask was charged with potassium *tert*-butoxide (154 mg, 1.37 mmol), boronic acid (1.2 mmol) and palladium complex **4** (1.4 mg, 2.0  $\mu\text{mol}$ ). The flask was flushed with nitrogen and sealed with a rubber septum. Via syringe 2-propanol (1 mL) was added and the mixture was stirred at room temperature. After 5 min, the aryl halide (1.0 mmol), dissolved in 2-propanol (1 mL), was injected via syringe and the mixture was heated to 60 °C for 2h. After cooling to room temperature, water (10 mL) was added to the mixture and it was extracted with dichloromethane ( $3 \times 15$  mL). The organic layer was dried with magnesium sulfate, the solvent was evaporated *in vacuo* and the product was purified by column chromatography on silica gel. The purity and identity of previously described 1-phenyl-naphthalene [7b], 1-*o*-tolyl-naphthalene [7a], 1-*p*-tolyl-naphthalene [16], 1,1'-binaphthyl [7b] and 2-methoxy-1,1'-binaphthyl [17] was confirmed by  $^1\text{H}$  NMR and mass spectrometric analysis.

#### 4.5 Single-crystal X-ray structure determination of complex **4**

*General:* Crystal data and details of the structure determination are given in Table 3. Suitable single crystals were grown by slow diffusion of *n*-pentane into a solution of **4** in chloroform. Data collection was performed using an STOE Imaging Plate Diffraction System (IPDS-1) with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Structure solutions were performed with direct methods using SHELXS-97. Structure refinements were performed against  $F^2$  with SHELXL-97 [18]. One of the allylic carbon atoms is disordered in two positions and was refined using a split model. All non-hydrogen atoms except the disordered carbon atom of lower occupancy were refined anisotropically. The hydrogen atoms were placed in ideal positions and refined using a riding model. The asymmetric unit contains two crystallographically independent molecules.



Table 3  
Crystallographic data for palladium complex **4**

Formula	C <sub>34</sub> H <sub>47</sub> ClN <sub>2</sub> O <sub>4</sub> Pd
Formula weight (g/mol)	689.59
Color/habit	yellow/block
Crystal size (mm)	0.13 × 0.11 × 0.09
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c (no. 14)
<i>a</i> (Å)	28.5370(15)
<i>b</i> (Å)	9.0128(5)
<i>c</i> (Å)	26.3644(12)
$\alpha$ (°)	90
$\beta$ (°)	105.489(6)
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	6534.6(6)
<i>Z</i>	8
<i>T</i> (K)	170(2)
$\mu$ (mm <sup>-1</sup> )	0.689
$\theta$ Range (°)	1.94-26.00
Index ranges ( <i>h</i> , <i>k</i> , <i>l</i> )	±35, ±11, ±31
Measured reflections	49934
Independent reflections	12515
<i>R</i> <sub>int</sub>	0.0340
Reflections with [ <i>I</i> > 2σ( <i>I</i> )]	10898
Parameters	762
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [[ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.0318/0.0841
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data) <sup>a</sup>	0.0376/0.0872
GOF (on <i>F</i> <sup>2</sup> ) <sup>a</sup>	1.044
Largest difference in peak and hole (e Å <sup>-3</sup> )	+0.826 and -0.775

$$^a R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|; wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2};$$

$$\text{GOF} = \{\sum[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}.$$

## Appendix A. Supplementary material

CCDC 680552 contains the supplementary crystallographic data for compound **4**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

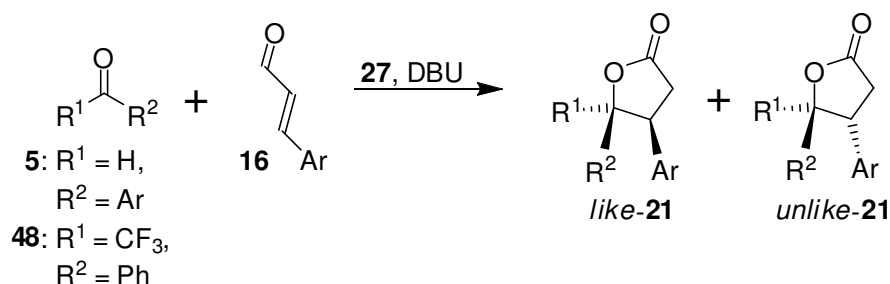
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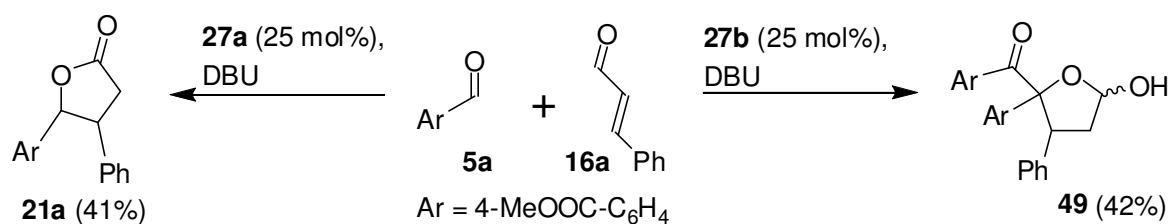
### 3.5 Concave Reagents: *Organocatalysis by Bimacrocylic NHCs: Unexpected Formation of a Cyclic Hemiacetal Instead of a $\gamma$ -Butyrolactone.*

O. Winkelmann, C. Näther, U. Lüning, eingereicht bei *Org. Biomol. Chem.*

Die bimakrocyclischen Imidazoliniumsalze **27a** und **27b** (siehe Seite 13) wurden als Präkatalysatoren in der NHC-katalysierten Synthese von  $\gamma$ -Butyrolactonen **21**<sup>[81,82]</sup> (siehe Abbildung 1.6, Seite 7) getestet. Zur Deprotonierung der Imidazoliniumsalze **27** wurde DBU (1,8-Diazabicyclo[5.4.0]undec-7-en) verwendet.



Die Reaktion  $\alpha,\beta$ -ungesättigter Aldehyde **16** mit Trifluoracetophenon **48** ergab die entsprechenden Lactone **21** in hohen Ausbeuten, erforderte jedoch die Verwendung von 25 mol% **27** und zeigte nahezu keine Diastereoselektivität (*like:unlike*  $\cong$  1:1). Mit dem Präkatalysator **14** (10 mol%) konnte das in der Literatur beschriebene Diastereomerenverhältnis (*like:unlike*  $\cong$  2:1)<sup>[81]</sup> reproduziert werden.



Die Reaktion des Benzaldehyds **5a** mit Zimtaldehyd (**16a**) lieferte bei Verwendung von **27a** als Präkatalysator das gewünschte Lacton **21a** in mäßiger Ausbeute (*like:unlike*  $\cong$  1:1), aber bei Verwendung des größeren Bimacrocyclus **27b** wurde unter den gleichen Reaktionsbedingungen ein anderes Produkt, das Hemiacetal **49**, erhalten. Ein Erklärungsversuch für diese unerwartete Reaktivität wurde anhand eines Vergleichs der Einkristall-Röntgenstrukturen von **27a** und **27b** gegeben. Der Vergleich der Strukturen lässt vermuten, dass **27b** aufgrund erleichterter Konjugation mit den elektronenreichen Brückenköpfen ein elektronenreicheres NHC liefert als **27a**. Dieses könnte die zur Bildung von **49** zunächst erforderliche Benzoinkondensation (siehe Abbildung 1.4, Seite 6) des elektronenarmen Benzaldehyds **5a** gegenüber der Lactonbildung begünstigen.

# Organocatalysis by Bimacrocylic NHCs: Unexpected Formation of a Cyclic Hemiacetal Instead of a $\gamma$ -Butyrolactone†‡

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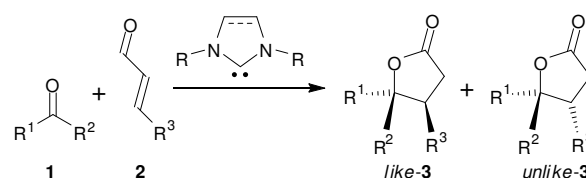
Two bimacrocylic imidazolium salts of different size, precursors to respective NHCs (*N*-heterocyclic carbenes), were tested as precatalysts in the reaction of aromatic aldehydes and ketones with enals. The expected lactones were produced in most cases, but in the reaction of methyl 4-formylbenzoate with cinnamaldehyde, the larger bimacrocycle led to the formation of a cyclic hemiacetal, while the smaller bimacrocycle gave the anticipated lactone.

The ability of thiamine to act as a nucleophilic catalyst after deprotonation was recognized in 1958 by Breslow.<sup>1</sup> He established the mechanism for the acyloin condensation catalyzed by thiamine, based on the umpolung of a carbonyl carbon atom by the deprotonated thiazolium salt, in a fashion analogous to catalysis by cyanide ions.<sup>2</sup> The scope of this reaction was expanded by Stetter in 1976, who reacted aldehydes with Michael acceptors in the presence of either cyanide or thiazolium salts and base (Stetter reaction).<sup>3</sup>

Deprotonated azolium salts have received great attention since the isolation of a stable crystalline carbene (derived from an imidazolium salt) by Arduengo in 1991,<sup>4</sup> and the term *N*-heterocyclic carbenes (NHCs) has been coined for these species which were called zwitterions by Breslow. NHCs are nowadays frequently used in organocatalysis<sup>5</sup> and they have also found numerous applications as beneficial ligands in organometallic chemistry.<sup>6</sup> A number of chiral thiazolium and triazolium salts have been synthesized and successfully applied in asymmetric acyloin condensations and Stetter reactions.<sup>7</sup>

Interestingly, neither acyloin nor Stetter products, but instead  $\gamma$ -butyrolactones **3** are formed if the imidazolium salt **4** is used as precatalyst in the reaction of aldehydes **1** ( $R^1 = H$ ) with  $\alpha,\beta$ -unsaturated aldehydes **2**. Also ketones **1** may be used in the reaction, and the favored formation of *like-3* was observed in all cases.<sup>8</sup> A reasonable mechanism was proposed for the reaction, involving the vinylogous umpolung of the  $\beta$  carbon atom of the enal **2** caused by nucleophilic attack of the NHC on its carbonyl carbon atom.<sup>8</sup> The proposed catalytic cycle was supported by the observation of postulated intermediates by ESI mass spectrometry,<sup>9</sup> but no explanation has yet been given for the high diastereoselectivity observed with **4**. It was reported that some other imidazolium salts with different *N*-substituents are less reactive and selective than **4**,<sup>8b</sup> while the use of thiazolium salts provided none of the desired lactones **3** at all.<sup>8</sup> Imidazolium salts have not been tested yet in this reaction.

We have recently reported the synthesis of bimacrocylic



this publication:

**1a:**  $R^1 = CF_3, R^2 = C_6H_5$

**1b:**  $R^1 = H, R^2 = 4\text{-Cl-C}_6\text{H}_4$

**1c:**  $R^1 = H, R^2 = 4\text{-MeOOC-C}_6\text{H}_4$

**2a:**  $R^3 = C_6H_5$

**2b:**  $R^3 = 4\text{-MeO-C}_6\text{H}_4$

**3a:**  $R^1 = CF_3, R^2 = C_6H_5,$

$R^3 = C_6H_5$

**3b:**  $R^1 = CF_3, R^2 = C_6H_5,$

$R^3 = 4\text{-MeO-C}_6\text{H}_4$

**3c:**  $R^1 = H, R^2 = 4\text{-Cl-C}_6\text{H}_4,$

$R^3 = C_6H_5$

**3d:**  $R^1 = H, R^2 = 4\text{-MeOOC-C}_6\text{H}_4,$

$R^3 = C_6H_5$

Scheme 1 NHC-catalyzed formation of lactones **3**

imidazolium salts as precursors to respective NHC catalysts, aiming to govern the selectivity in reactions catalyzed by these NHCs.<sup>10</sup> We have therefore tested the bimacrocylic salts **6a** and **6b** in the formation of  $\gamma$ -butyrolactones **3** and compared them to the precatalyst **4** which was used in the literature. In order to study the influence of the nature of the heterocycle, also the respective saturated imidazolium salt<sup>11</sup> **5** was tested in the reaction.

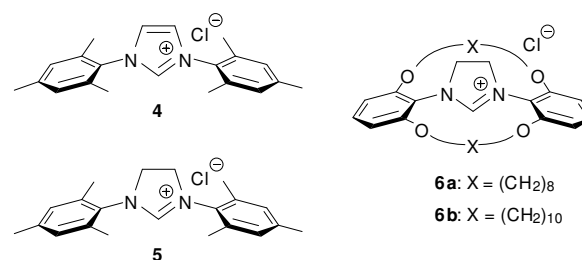


Fig. 1 NHC-precatalysts tested in the formation of lactones **3**

The results obtained with the different catalysts are summarized in table 1. Using 10 mol% of the NHC-precursors **4** or **5** and DBU as the base, high yields of the products **3a** and **3b** were obtained in the reaction of  $\alpha,\alpha,\alpha$ -trifluoroacetophenone (**1a**) with cinnamaldehyde (**2a**) or 4-methoxycinnamaldehyde (**2b**) at room temperature. Higher loadings (25 mol%) of the precatalysts **6** were needed to obtain comparable yields of the products **3a** and **3b**, while the yields could not be raised significantly at elevated temperature (40 °C). Even with 25 mol% of **6**, incomplete conversion of the enal **2b** was observed in the formation of **3b** after 16 h.

**Table 1** Catalytic activity of the NHC-precursors **4** - **6** in the formation<sup>a</sup> of  $\gamma$ -butyrolactones **3**

precatalyst	<b>3a</b> yield <sup>b</sup> ( <i>like:unlike</i> ) <sup>c</sup>	<b>3b</b> yield <sup>b</sup> ( <i>like:unlike</i> ) <sup>c</sup>	<b>3c</b> yield <sup>b</sup> ( <i>like:unlike</i> ) <sup>c</sup>	<b>3d</b> yield <sup>b</sup> ( <i>like:unlike</i> ) <sup>c</sup>
<b>4</b> (10 mol%)	92% (67:33)	94% (68:32)	39% (82:18) <sup>d</sup>	52% (82:18)
(10 mol%) <sup>e</sup>	92% (65:35) <sup>e</sup>			
<b>5</b> (10 mol%)	93% (54:46)	95% (54:46)	8% (73:27) <sup>d</sup>	2% (74:26)
(25 mol%) <sup>e</sup>				39% (73:27) <sup>e</sup>
<b>6a</b> (10 mol%)	38% (46:54)			
(25 mol%)	86% (47:53)	72% (45:55)	4% (34:66) <sup>d</sup>	41% (52:48) <sup>e</sup>
<b>6b</b> (10 mol%)	39% (48:52)			
(25 mol%)	80% (48:52)	68% (46:54)	2% (33:67) <sup>d</sup>	
(25 mol%) <sup>e</sup>	88% (48:52) <sup>e</sup>		4% (36:64) <sup>e</sup>	3% (50:50) <sup>e</sup>

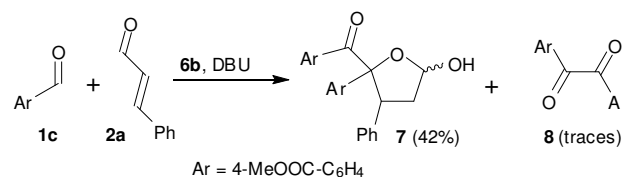
<sup>a</sup> Reaction conditions: 0.5 mmol enal **2**, 1 mmol  $\alpha,\alpha,\alpha$ -trifluoroacetophenon (**1a**) or benzaldehyde **1b/1c**, azolium salt **4** - **6** (50 or 125  $\mu$ mol), DBU (1 equiv. based on azolium salt), 16 h in 2 mL of THF at room temperature. <sup>b</sup> Determined by GC using *n*-hexadecane as the internal standard, average of two experiments. <sup>c</sup> Diastereomeric ratio determined by GC, average of two experiments. <sup>d</sup> 0.5 mmol enal **2a**, 0.5 mmol substituted benzaldehyde **1b**. <sup>e</sup> 16 h at 40 °C.

The favored formation of *like-3a* and *like-3b* was observed with precatalyst **4** as reported by Glorius and Burstein.<sup>8a</sup> Interestingly the diastereoselectivity dropped with the use of the analogous saturated NHC-precursor **5**, showing clearly that the selectivity of the reaction is affected by the nature of the NHC (imidazol-2-yliden vs. imidazolidin-2-yliden). The bimacrocycles **6** were found to be similarly little selective as **5**. While still a small excess of *like-3a* and *like-3b* was produced with **5**, a slight but definite preference for *unlike-3a* and *unlike-3b* was observed with both bimacrocycles **6a** and **6b**. The diastereoselectivities remained unchanged at 40 °C.

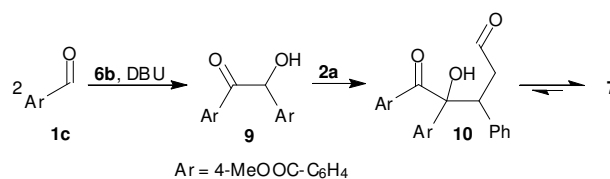
In the reaction of cinnamaldehyde (**2a**) with 4-substituted benzaldehydes **1b** and **1c** (products **3c**, **3d**), a decrease in yield compared to products **3a** and **3b** was observed with all NHC precursors, and the saturated precatalysts **5** and **6** were found to be inferior to **4**. Although the best results were obtained with the imidazolium salt **4**, the yields reported in the literature (54% for **3c**, 70% for **3d**) exceed our findings. The reported high diastereoselectivities were reproduced for both products. In the case of product **3c**, the poor yields are caused by incomplete conversion and by the formation of numerous unidentified by-products. Incomplete conversion also prevented the formation of high yields of **3d**. Interestingly, reasonable amounts of **3d** could be obtained using 25 mol% of **5** or **6a** at 40 °C, while **6b** produced only traces of the expected product under the same conditions. Regarding the *like/unlike*-selectivity, a decrease was again observed going from **4** (unsaturated) to **5** (saturated), but less expressed than for the products **3a** and **3b**. With the bimacrocyclic precatalysts **6**, the selectivity was reversed for product **3c**, while equal amounts of *like*- and *unlike-3d* were produced.

The poor yield of **3d** obtained with the NHC precursor **6b** could be attributed to the formation of an additional product: hemiacetal **7**. It results from the connection of two aldehydes **1c** with one enal **2a** and was isolated in 42% yield from the reaction mixture. Also, a small amount of benzil **8** was obtained. By GC analysis alone, the new product **7** can be overlooked. It decomposes under GC conditions and cinnamaldehyde (**2a**), benzil **8** and benzoin **9** are detected. Small amounts of these decomposition products are observed with all precatalysts in the reaction of **1c** and **2a**, but they are found as

the most prominent peaks with **6b**.

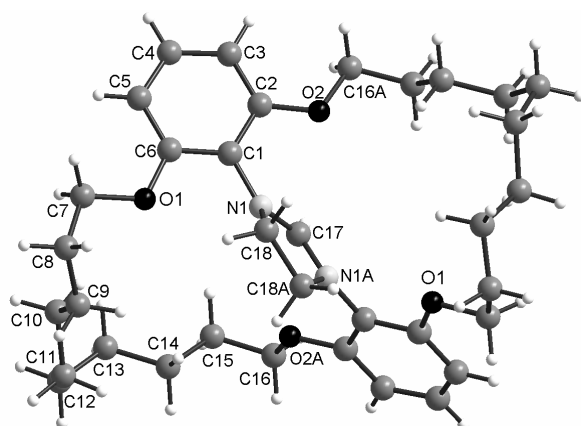


An equilibrium between both anomeric forms (ratio 10:1) of **7** is observed in CDCl<sub>3</sub> at room temperature, with the hydroxyl and phenyl group being oriented *trans* in the major anomer, as can be deduced from the NOESY spectrum. The relative stereochemistry at the quaternary carbon atom could not be assigned undoubtedly. A molecule related to **7** has been reported to be produced from cinnamaldehyde (**2a**), acetaldehyde and fermenting baker's yeast,<sup>12</sup> and the reported NMR assignments support our structure elucidation (also regarding the anomers). In analogy to the mechanistic explanation of the enzymatic reaction, the isolation of **7** implies the formation of benzoin **9**, whose anion reacts with the Michael-acceptor **2a**. The resulting hydroxyaldehyde **10** undergoes ring closure to hemiacetal **7** as the NMR spectra prove. The additionally isolated benzil **8** seems to result from the oxidation of benzoin **9** during work-up.<sup>13</sup>



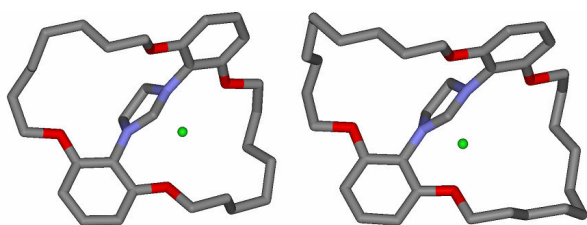
Reasonable amounts of the hemiacetal **7** were only found with precatalyst **6b**, which favors the formation of benzoin **9** over lactone **3d**, in contrast to the NHC-precursors **4**, **5** and **6a**. How does the NHC derived from **6b** differ from the other NHCs that were tested in the reaction? There are four differences to be discussed: (i) **6b** yields an NHC which contains a saturated heterocycle, (ii) the NHCs derived from **6** are more electron rich than the other NHCs,<sup>14</sup> (iii) **6b** is a bimacrocyclic compound, and (iv) the bimacrocycle in **6b** is larger than that in **6a**. Although the formation either lactone **3d** or benzoin **9** is catalyzed by the respective NHC, the

geometrical properties of the precatalysts may reflect those of the NHCs.<sup>15</sup> Both imidazolium salts **6** have been crystallized and X-ray analyses have been carried out. Figure 2 shows the structure of the larger bimacrocycle **6b**, figure 3 compares it to the structure of **6a** which has already been published.<sup>10a</sup>



**Fig. 2** Crystal structure of imidazolium chloride **6b**.<sup>16</sup> The chloride anion and two molecules of chloroform are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: N1-C17 1.315(3), N1-C18 1.483(4), N1-C1 1.429(4), C18-C18A 1.508(8); N1-C17-N1A 113.1(4), C17-N1-C18 109.4(3), N1-C18-C18A 102.6(2); C17-N1-C1-C6 132.5(3), C17-N1-C1-C2 -48.8(4).

On first glance, the structures of both bimacrocycles **6a** and **6b** seem quite similar. The phenyl substituents are substantially twisted out of a coplanarity with the heterocycle, and the conrotatory fashion of this twist leads to a  $C_2$ -symmetric structure. However, a look at the interplanar angles between the imidazolium ring and the adjacent aryl rings (derived from the torsion angles C17-N1-C1-C2, C17-N1-C1-C6) reveals that the phenyl substituents twist more out of a coplanar geometry in **6a** (the interplanar angle is 54°) than they do in the larger cycle **6b** (48°).



**Fig. 3** Comparison of the crystal structures of **6a** (left) and **6b** (right). Hydrogen atoms and solvent molecules are omitted for clarity.

In the non- $C_2$ -symmetric carbene derived from **4**, the mesityl substituents are oriented almost perpendicular to the heterocycle, with interplanar angles of 80° and 71°. In this respect, **6a** can probably behave more similar to the non-macrocyclic analogues **4** and **5**, and thus **6b** has a special combination of properties allowing to form the new product **7**. Our observations indicate that the NHC derived from **6b** is not too sterically encumbered to allow the formation of benzoin **9**, and this reaction might be favored over lactone formation and Stetter reaction due to the electron-poor benzaldehyde **1c**. However, it is still unclear why only NHC-precursor **6b** led to the formation of the new product, hemiacetal **7**, and this new

reaction pathway requires further investigation.

## Notes and references

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- † Electronic Supplementary Information (ESI) available: Experimental procedures and NMR spectra of **7-9**. See DOI: 10.1039/b000000x/
- ‡ Preceding Publication: Concave Reagents, Part ##. For Part ###, see (current numbers will be inserted in the proofs)
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  - Suitable crystals were grown by diffusion of diethyl ether into a solution of **6b** in chloroform. **Crystal data.** C<sub>35</sub>H<sub>51</sub>ClN<sub>2</sub>O<sub>4</sub> · 2 CHCl<sub>3</sub>, *M* = 837.96, monoclinic, *a* = 26.471(3), *b* = 12.5614(7), *c* = 16.7632(14) Å, β = 128.674(9)°, *U* = 4351.6(6) Å<sup>3</sup>, *T* = 220(2) K, space group C2/c (no. 15), *Z* = 4, 9095 reflections measured, 3828 unique (*R*<sub>int</sub> = 0.0469) which were used in all calculations. The final *wR*(*F*<sub>2</sub>) was 0.1870 (all data). The crystal structure data have been deposited at the Cambridge Crystallographic Data Centre. CCDC-680462 contains the supplementary crystallographic data, which can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif.
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## Supplementary Information

### Organocatalysis by Bimacroyclic NHCs: Unexpected Formation of a Cyclic Hemiacetal Instead of a $\gamma$ -Butyrolactone

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#### General

The azolium chlorides **4**,<sup>1</sup> **5**<sup>1</sup> and **6**<sup>2</sup> were synthesized according to literature procedures. Pure samples of the lactones **3** for GC-calibration were obtained with precatalyst **4** after column chromatography, matching the spectroscopic data given in the literature.<sup>3</sup> All aldehydes were purified by either distillation (**2a**) or column chromatography on silica gel (**1b**, **1c**, **2b**) before use. Dry THF was obtained by heating at reflux with lithium aluminium hydride. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with Bruker ARX 300, DRX 500 or AV 600 instruments at room temperature and are referenced to tetramethylsilane. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m<sub>(c)</sub> = multiplet (centered), br = broad signal. IR spectra were recorded with a Perkin-Elmer Paragon 1000, equipped with an ATR unit. Mass spectra were recorded with a Finnigan MAT 8200 or MAT 8230. Elemental analyses were carried out with a EuroEA 3000 Elemental Analyzer from Euro Vector. GC analyses were performed on an Agilent 6890 N gas chromatograph.

## Experimental Procedures

**General procedure for the synthesis of  $\gamma$ -butyrolactones **3**:** A flask was charged with the respective catalyst (0.05 or 0.13 mmol), the flask was flushed with nitrogen and sealed with a rubber septum. Via syringe, a solution of the enal **2** (0.50 mmol) and the electrophilic aldehyde/ketone **1** (1.0 mmol) in dry THF (2 mL) was added and the mixture was stirred for 5 min. DBU (1 equiv. based on catalyst) was added via microliter-syringe, and the mixture was stirred at room temperature. After 16 h, the mixture was passed through a short pad of silica gel and the silica gel was rinsed with ethyl acetate (20 mL). To this solution was added *n*-hexadecane as the internal standard and the mixture was analyzed by GC; conditions: split ratio 11:1, injector temp. 250 °C, detector temp. 300 °C; column: HP-5/30 m; temperature: 100 °C for 2 min, 15 °C/min until 300 °C, 10 min 300 °C.

**5-Hydroxy-2-[4-(methoxycarbonyl)-phenyl]-2-[4-(methoxycarbonyl)-phenylcarbonyl]-3-phenyl-tetrahydrofuran (**7**):** Following the general procedure, cinnamaldehyde (**2a**, 66 mg, 0.50 mmol) and methyl 4-formylbenzoate (**1c**, 164 mg, 1.00 mmol) were reacted with imidazolium chloride **6b** (75 mg, 0.13 mmol) and DBU (20  $\mu$ L, 0.13 mmol). After GC analysis, the solvent was evaporated *in vacuo* and the crude product was purified by column chromatography [silica gel, cyclohexane/ethyl acetate (3:1),  $R_f$  = 0.27]. A colorless solid was obtained (96 mg, 42%). M.p. 163 °C.  $^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )<sup>a</sup>:  $\delta$  (ppm) = 7.89 (m<sub>c</sub>, 4H, Ar-H), 7.72 (d,  $^3J$  = 8.8 Hz, 2H, Ar-H), 7.11 (m<sub>c</sub>, 2H, Ar-H), 7.05-7.00 (m, 3H, Ar-H), 6.93 (m<sub>c</sub>, 2H, Ar-H), 6.07 (dd,  $^3J$  = 5.0 Hz,  $^3J$  = 1.3 Hz, 1H, 5-H), 4.92 (dd,  $^3J$  = 8.9 Hz,  $^3J$  = 7.8 Hz, 1H, 3-H), 3.87 (s, 3H,  $\text{COOCH}_3$ ), 3.82 (s, 3H,  $\text{COOCH}_3$ ), 2.80 (br s, 1H, OH), 2.47 (ddd,  $^2J$  = 13.3 Hz,  $^3J$  = 9.0 Hz,  $^3J$  = 5.0, 1H, 4-H<sub>a</sub>), 2.41 (ddd,  $^2J$  = 13.3 Hz,  $^3J$  = 7.7 Hz,  $^3J$  = 1.5, 1H, 4-H<sub>b</sub>).  $^{13}\text{C-NMR}$  (150 MHz,  $\text{CDCl}_3$ )<sup>b</sup>:  $\delta$  (ppm) = 198.2 (CO), 166.7 ( $\text{COOCH}_3$ ), 166.2 ( $\text{COOCH}_3$ ), 142.8 (Ar-C), 138.7 (Ar-C), 138.6 (Ar-C), 133.0 (Ar-C), 130.5 (Ar-CH), 129.3 (Ar-CH), 129.2 (Ar-CH), 129.1 (Ar-CH), 127.9 (Ar-CH), 126.7 (Ar-CH), 125.5 (Ar-CH), 99.2 (C-5), 94.9 (C-2), 52.3 ( $\text{COOCH}_3$ ), 52.0 ( $\text{COOCH}_3$ ), 49.6 (C-3), 40.3 (C-4). IR:  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 3509, 2932, 1713, 1674, 1606, 1567, 1498, 1434, 1273, 1228, 1108, 1068, 1016, 990, 956, 821, 720, 696, 588. MS (EI):  $m/z$  (%) = 429 (3)  $[\text{M} - \text{OCH}_3]^+$ , 297 (100)  $[\text{M} - \text{C}_9\text{H}_7\text{O}_3]^+$ , 163 (58)  $[\text{C}_9\text{H}_7\text{O}_3]^+$ . MS (CI):  $m/z$  (%) = 461 (22)  $[\text{M} + \text{H}]^+$ . Found: C, 70.35; H, 5.57.  $\text{C}_{27}\text{H}_{24}\text{O}_7$  requires C, 70.42; H, 5.25

<sup>a</sup> Only the signals of the major anomer are listed. Most of the signals of the minor anomer are not observed due to overlap. Selected signals of the minor anomer:  $\delta$  (ppm) = 5.78 (m<sub>c</sub>, 1H, 5-



H), 4.60 (dd,  $^3J = 10.1$  Hz,  $^3J = 7.7$  Hz, 3-H), 2.61 (ddd,  $^2J = 13.4$  Hz,  $^3J = 7.7$  Hz,  $^3J = 5.5$  Hz, 1H, 4-H<sub>a</sub>), 2.32 (ddd,  $^2J = 13.5$  Hz,  $^3J = 10.0$  Hz,  $^3J = 6.0$  Hz, 1H, 4-H<sub>b</sub>). The 10:1 ratio between the anomers was deduced from integration.

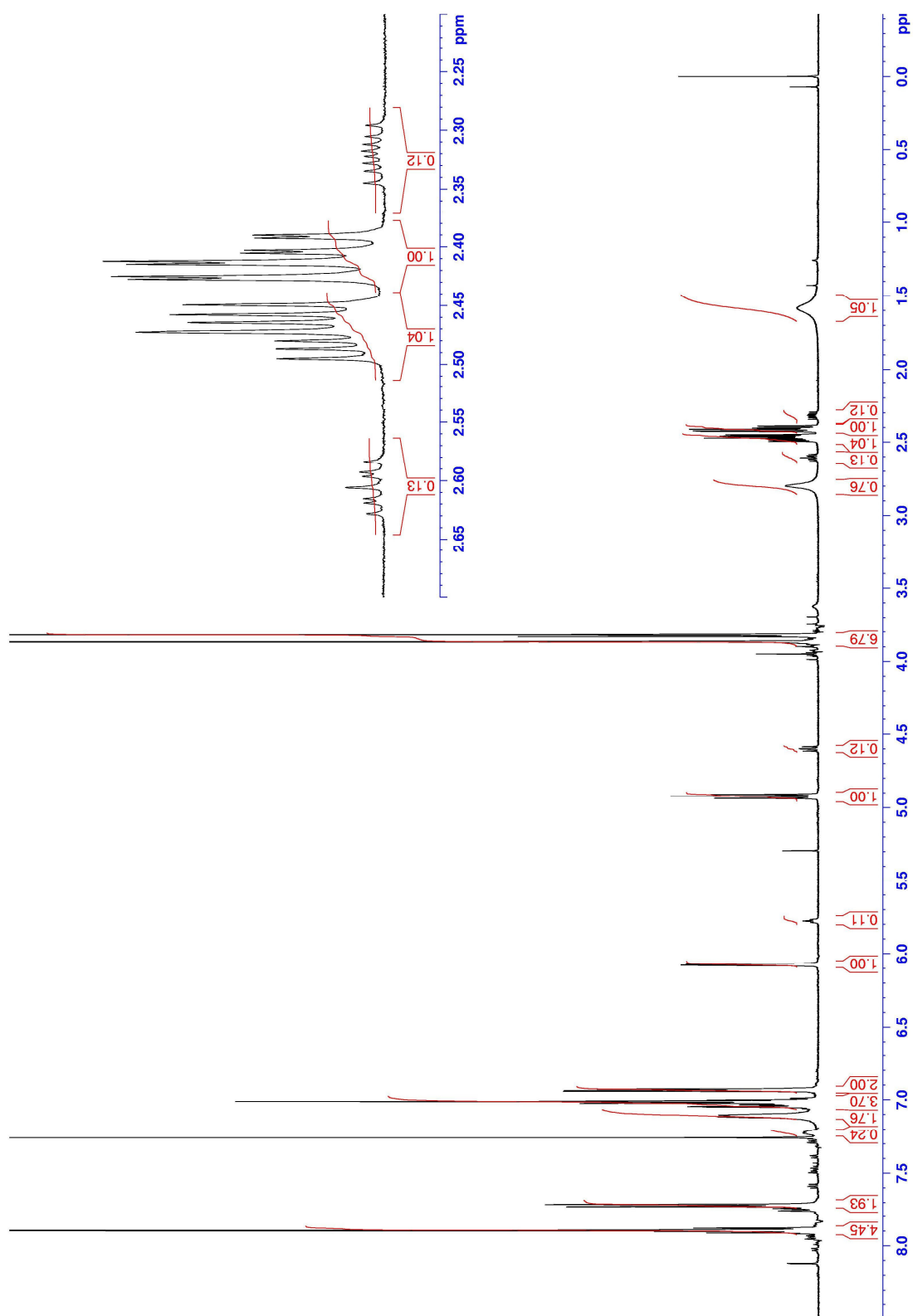
<sup>b</sup> Only the signals of the major anomer are listed. One quaternary aromatic carbon atom was not observed, possibly due to overlap or low intensity.

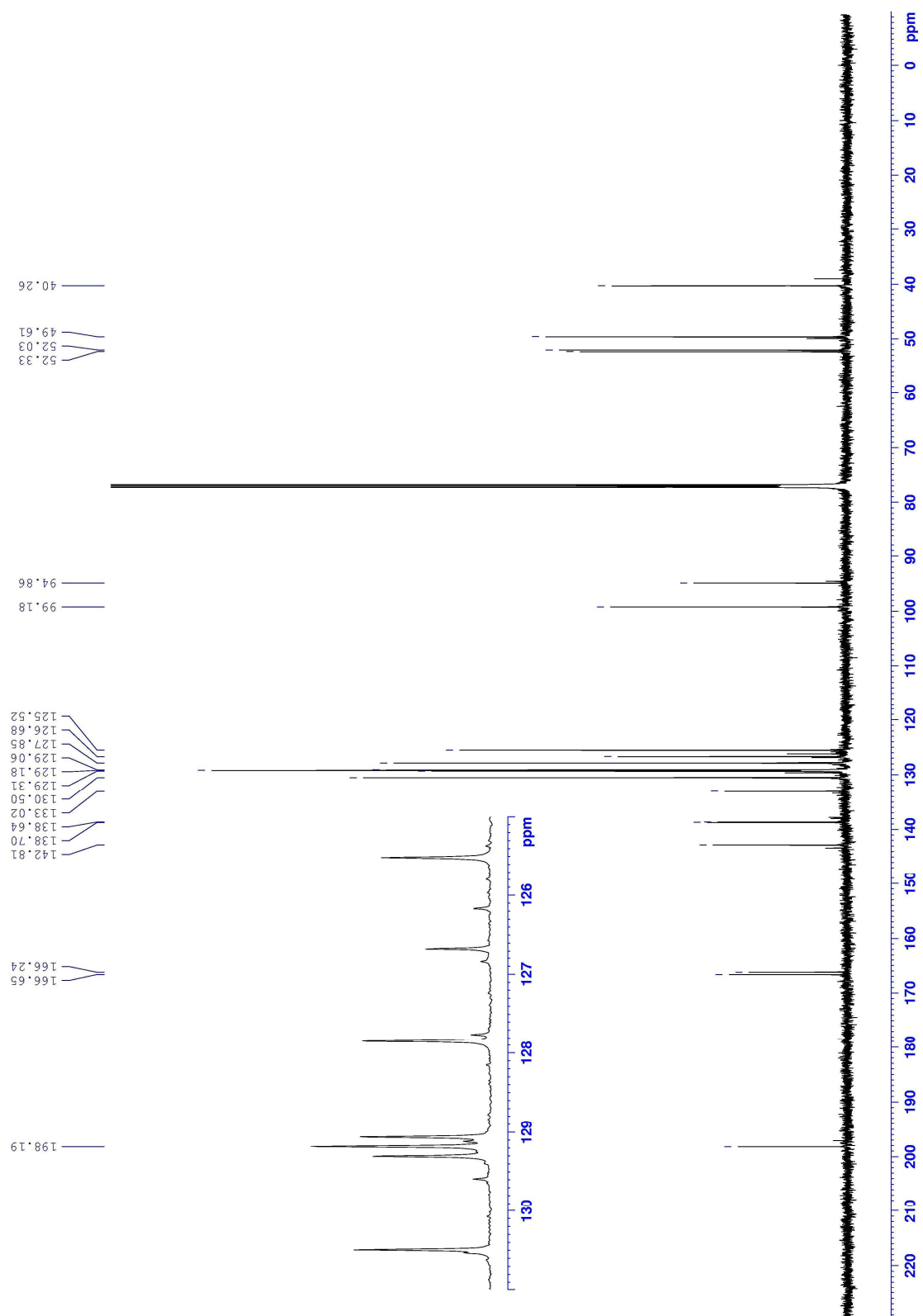
**1,2-Bis-(4-methoxycarbonylphenyl)-ethane-1,2-dione (8):** From the above described reaction was isolated **8** ( $R_f = 0.44$ ) as a yellow solid (5 mg, 4%). <sup>1</sup>H-NMR (500 MHz, [D<sub>6</sub>]-DMSO):  $\delta$  (ppm) = 8.17 (d,  $^3J = 8.6$  Hz, 4H, Ar-H), 8.11 (d,  $^3J = 8.6$  Hz, 4H, Ar-H), 3.91 (s, 6H, COOCH<sub>3</sub>). <sup>13</sup>C-NMR (125 MHz, [D<sub>6</sub>]-DMSO):  $\delta$  (ppm) = 192.9 (s, CO), 165.3 (s, COOCH<sub>3</sub>), 135.3 (Ar-C), 135.1 (Ar-C), 130.2 (Ar-CH), 129.9 (Ar-CH), 52.7 (COOCH<sub>3</sub>). IR:  $\tilde{\nu}$  (cm<sup>-1</sup>) = 2925, 1717, 1663, 1569, 1500, 1281, 1188, 1102, 1012, 949, 889, 859, 820, 781, 730, 713, 674, 629, 534. MS (EI):  $m/z$  (%) = 326 (2) [M]<sup>+</sup>, 163 (100) [C<sub>9</sub>H<sub>7</sub>O<sub>3</sub>]<sup>+</sup>. MS (CI):  $m/z$  (%) = 327 (100) [M + H]<sup>+</sup>.

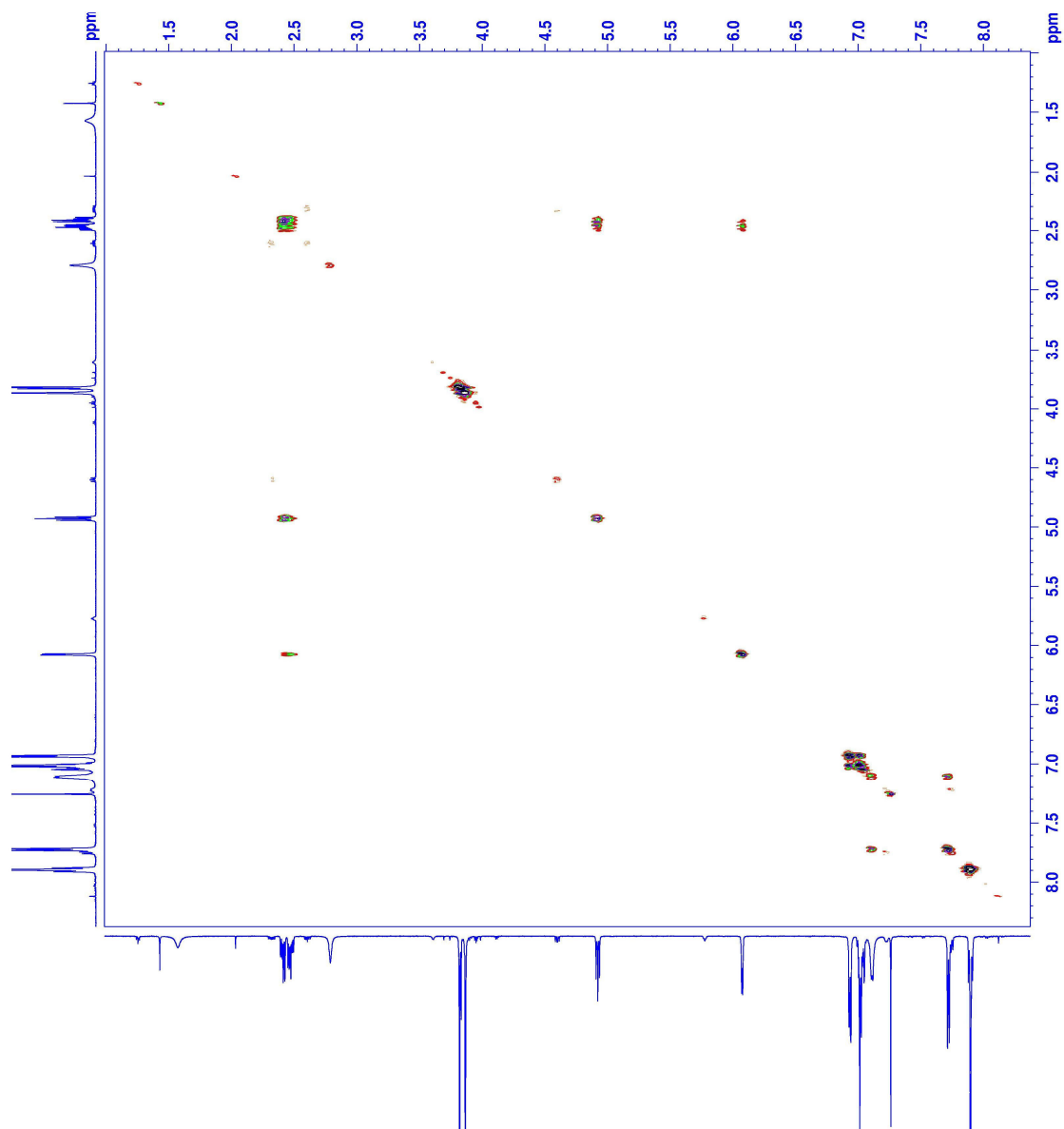
**2-Hydroxy-1,2-bis-(4-methoxycarbonylphenyl)-ethanone (9):**<sup>4</sup> Methyl 4-formylbenzoate (**1c**, 16.4 g, 100 mmol) was heated to 50 °C with sodium cyanide (1.50 g, 30.0 mmol) in a mixture of ethanol (40 mL) and water (20 mL). After 10 min, the precipitate was collected by filtration and washed with water and ethanol. The residue was dried *in vacuo*. A colorless solid was obtained (13.5 g, 82%). <sup>1</sup>H-NMR (300 MHz, [D<sub>6</sub>]-DMSO):  $\delta$  (ppm) = 8.11 (d,  $^3J = 8.6$  Hz, 2H, Ar-H), 8.00 (d,  $^3J = 8.7$  Hz, 2H, Ar-H), 7.91 (d,  $^3J = 8.4$  Hz, 2H, Ar-H), 7.57 (d,  $^3J = 8.3$  Hz, 2H, Ar-H), 6.50 (br s, 1H, HCOH), 6.19 (s, 1H, HCOH), 3.85 (s, 3H, COOCH<sub>3</sub>), 3.80 (s, 3H, COOCH<sub>3</sub>). IR:  $\tilde{\nu}$  (cm<sup>-1</sup>) = 3459, 2953, 1718, 1677, 1608, 1571, 1436, 1273, 1094, 982, 963, 814, 765, 719, 614, 535. MS (EI):  $m/z$  (%) = 163 (100) [C<sub>9</sub>H<sub>7</sub>O<sub>3</sub>]<sup>+</sup>. MS (CI):  $m/z$  (%) = 329 (100) [M + H]<sup>+</sup>.

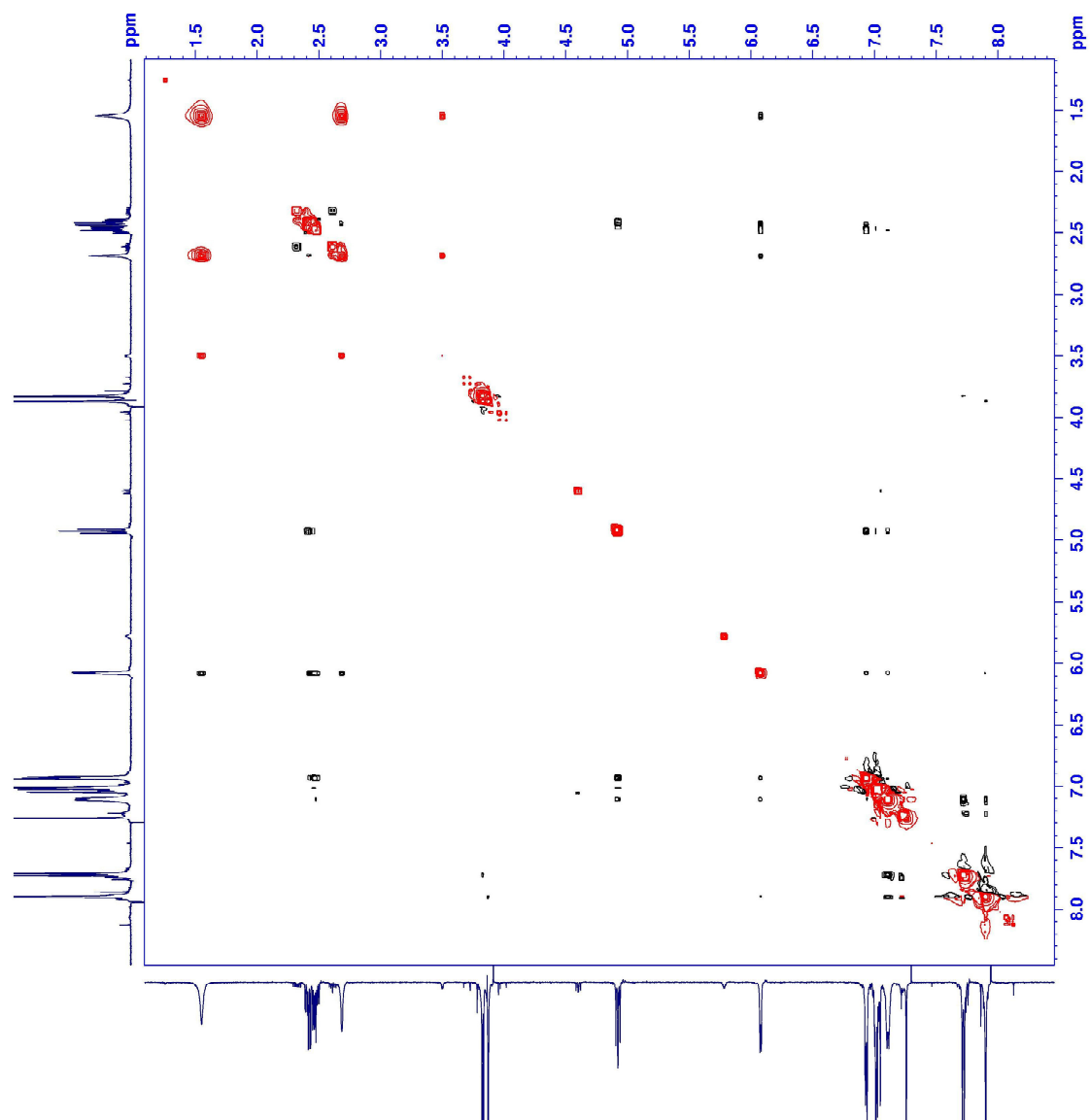
## NMR Spectral Data

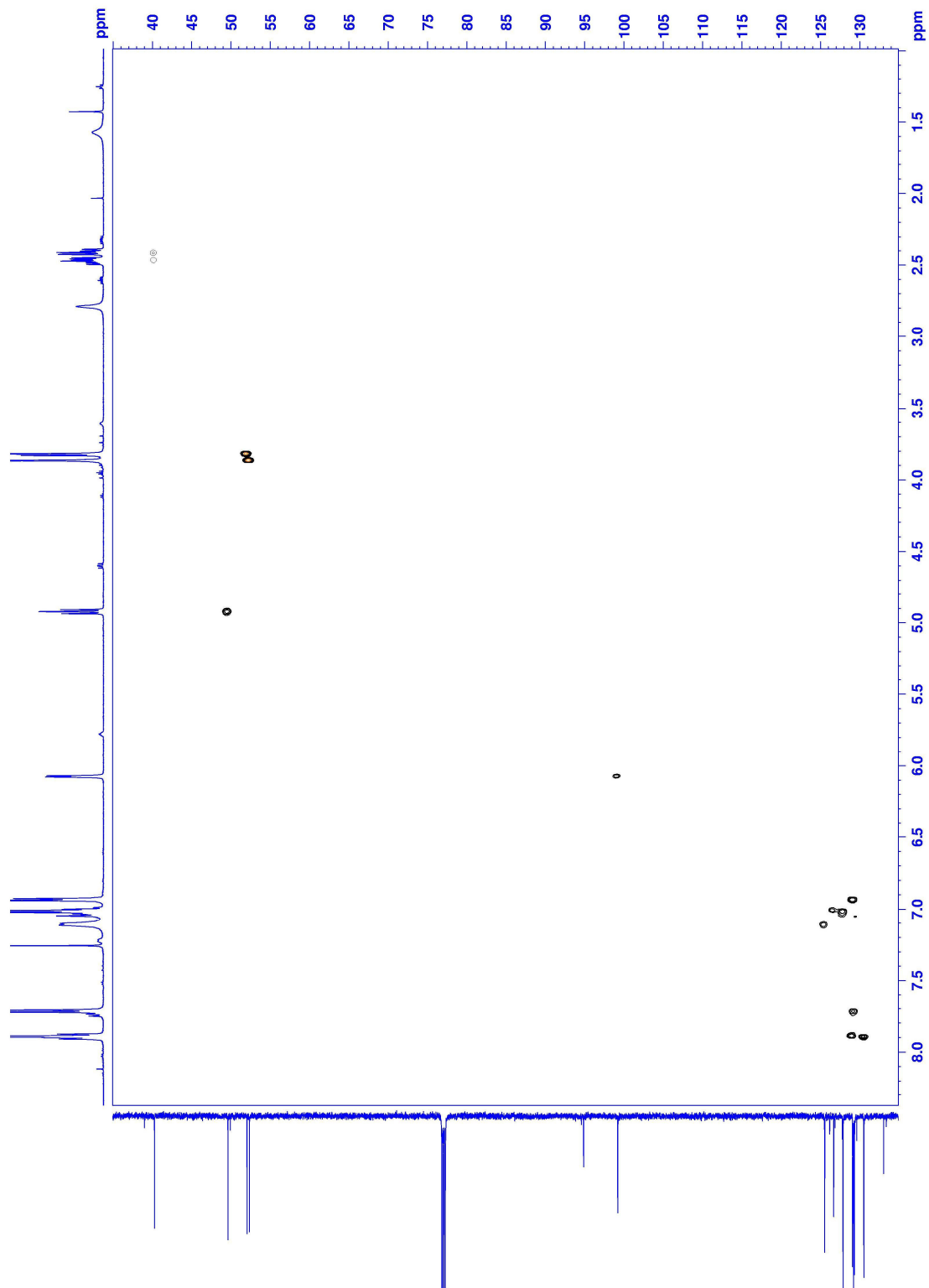
$^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ ) of hemiacetal **7**

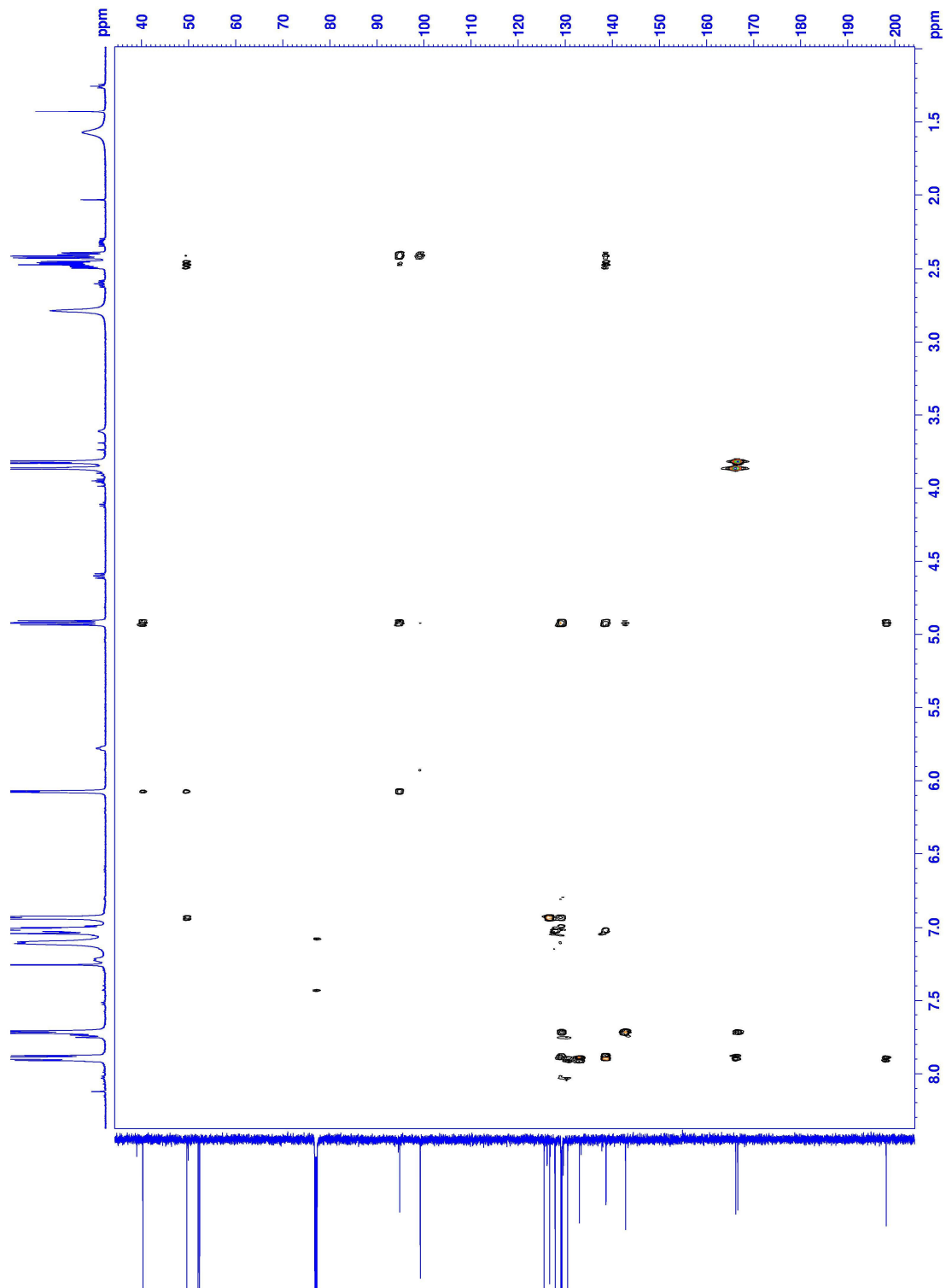


$^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of hemiacetal **7**

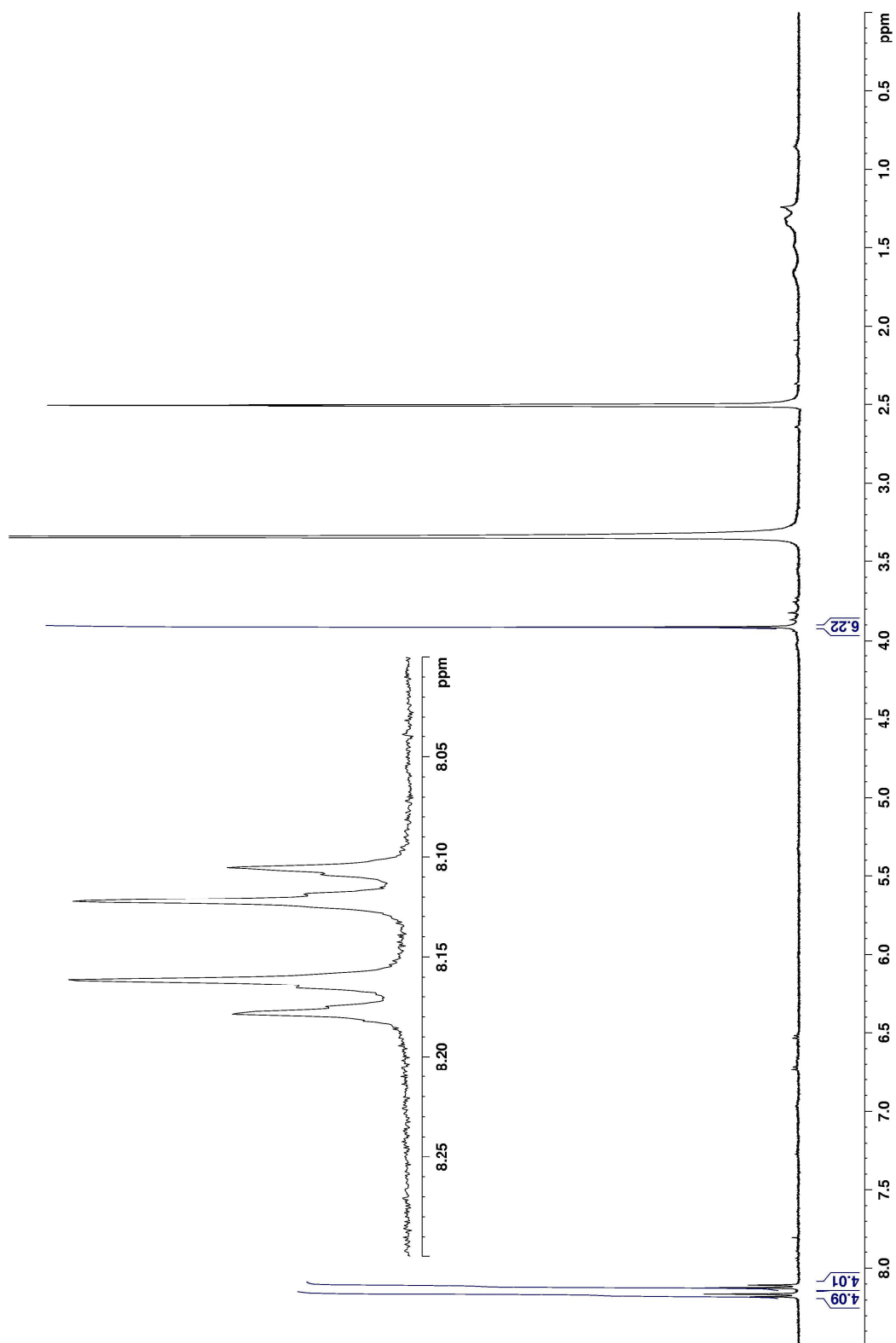
COSY spectrum (600 MHz,  $\text{CDCl}_3$ ) of hemiacetal **7**

NOESY spectrum (500 MHz, CDCl<sub>3</sub>) of hemiacetal **7**

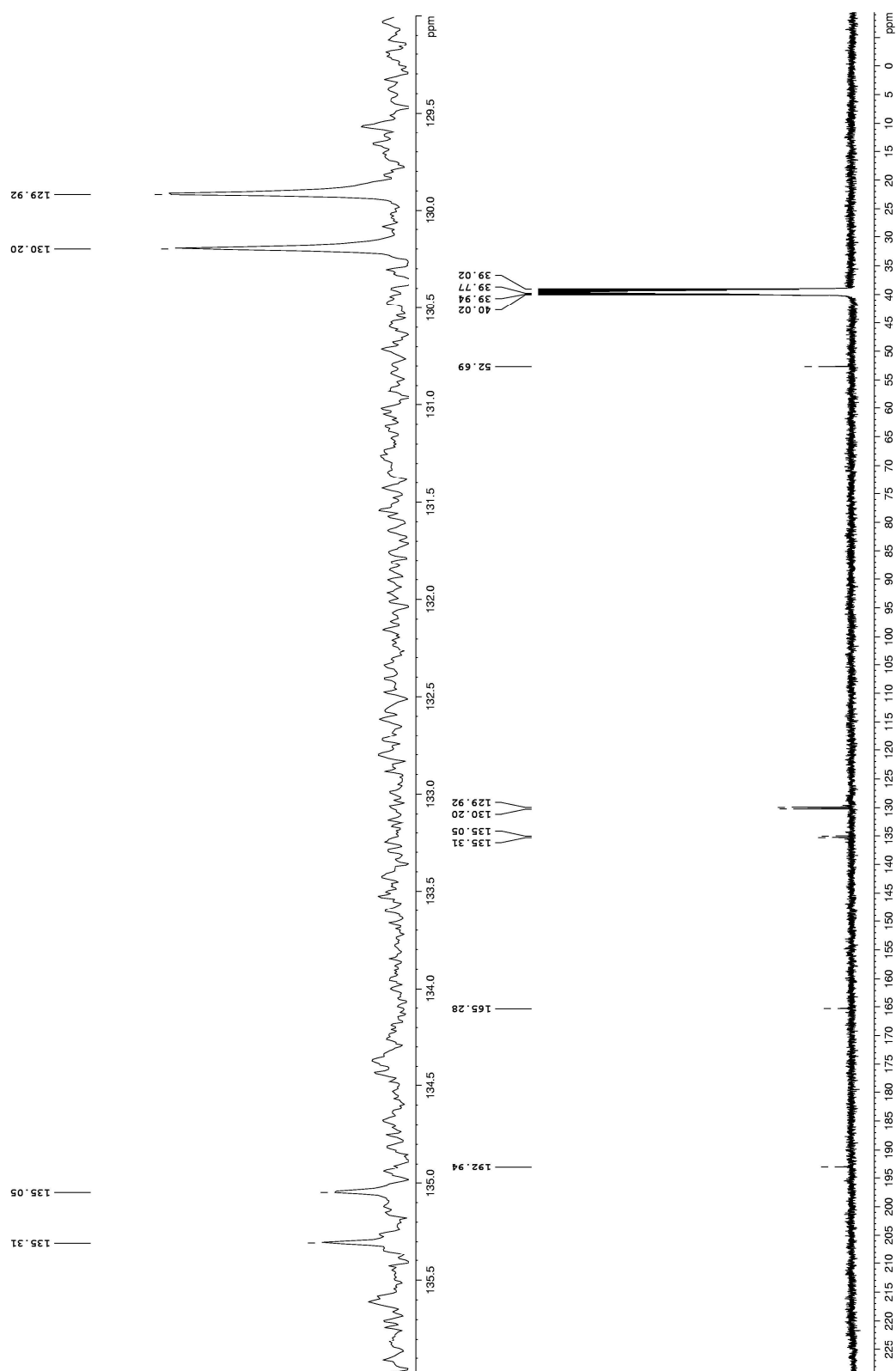
HSQC spectrum (600/150 MHz,  $\text{CDCl}_3$ ) of hemiacetal **7**

HMBC spectrum (600/150 MHz, CDCl<sub>3</sub>) of hemiacetal **7**

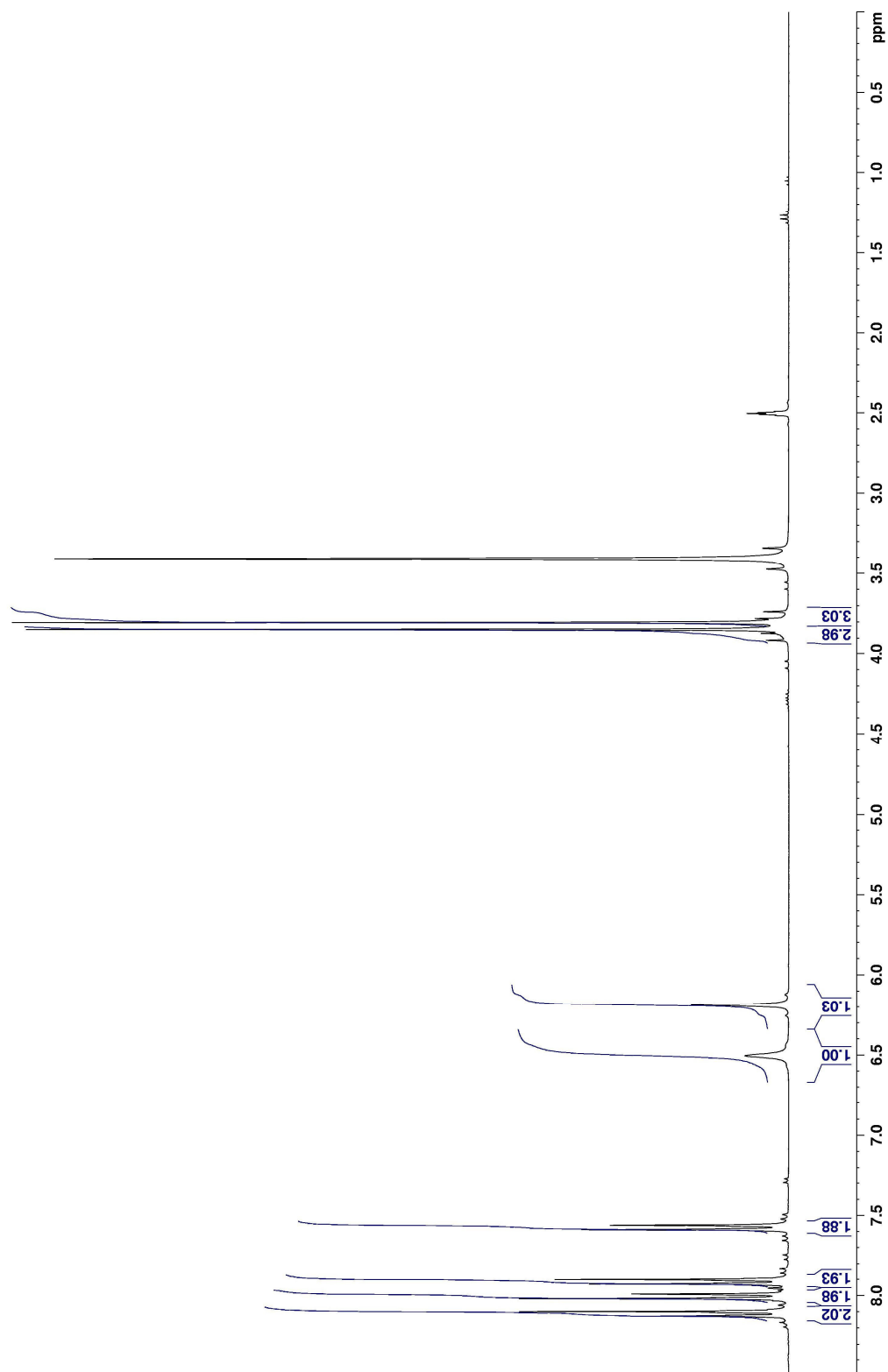
$^1\text{H}$  NMR spectrum (500 MHz,  $[\text{D}_6]$ -DMSO) of benzil **8**





$^{13}\text{C}$  NMR spectrum (125 MHz,  $[\text{D}_6]$ -DMSO) of benzil **8**

$^1\text{H}$  NMR spectrum (300 MHz,  $[\text{D}_6]$ -DMSO) of benzoin **9**



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## 4 Zusammenfassung und Ausblick

### 4.1 Zusammenfassung

Die Synthese der konkaven Imidazoliniumsalze **27** und **28** konnte erfolgreich durchgeführt werden, und aus diesen Vorläufern können durch Deprotonierung analoge konkave *N*-heterocyclische Carbene (NHC) erhalten werden. Die axial-chiralen Bimakrocyclen **28** erwiesen sich als nicht konfigurationsstabil und konnten daher nicht in der asymmetrischen Katalyse eingesetzt werden. Die Imidazoliniumsalze **27a**, **27b** und **28b** konnten durch Einkristall-Röntgenstrukturanalyse charakterisiert werden.

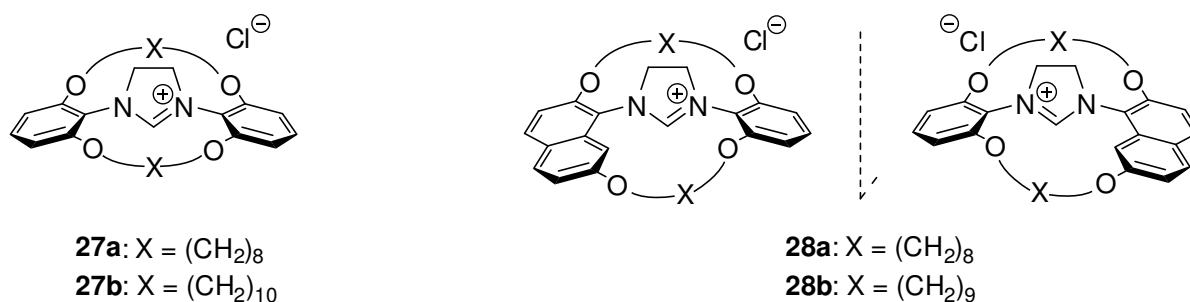


Abbildung 4.1: In dieser Arbeit synthetisierte bimakrocyclische Imidazoliniumsalze.

Ausgehend von **27a** konnten die acht NHC-Metallkomplexe **34-41** erfolgreich synthetisiert werden. Diese erwiesen sich unter Atmosphärenbedingungen als unbegrenzt stabil, lediglich der Silberkomplex **34** zeigte eine mäßige Lichtempfindlichkeit.

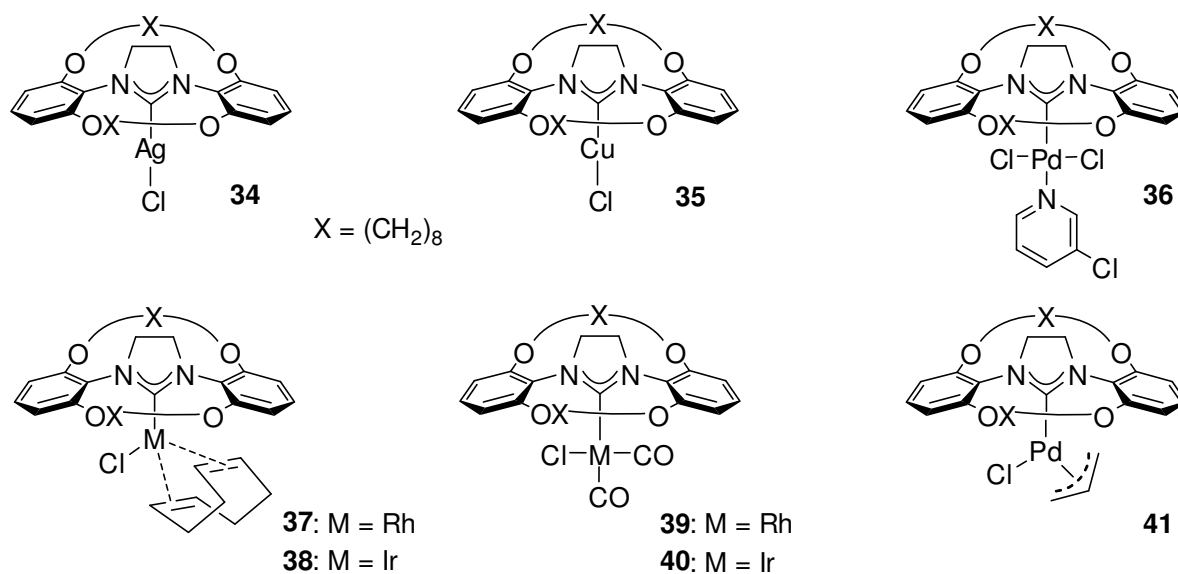
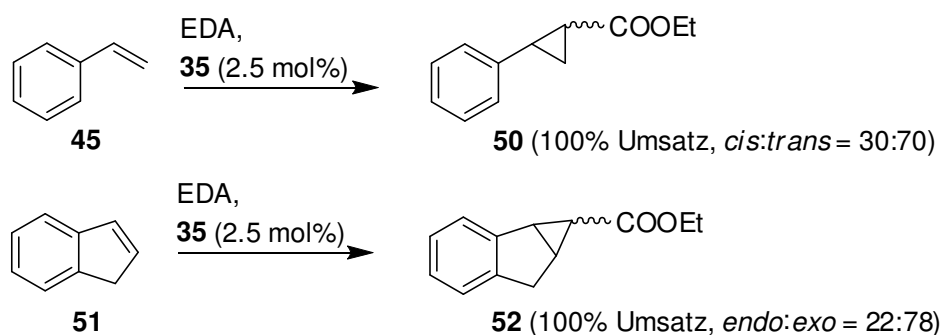


Abbildung 4.2: In dieser Arbeit synthetisierte bimakrocyclische NHC-Metallkomplexe.

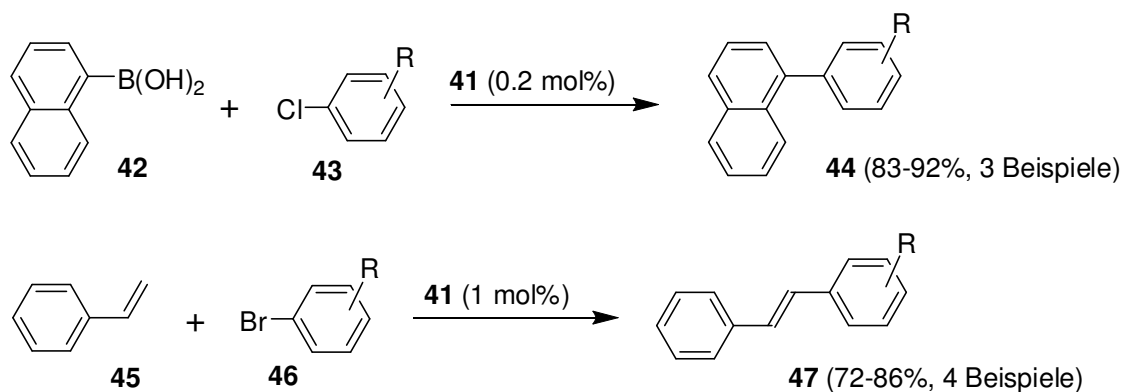
Die Synthese der Metallkomplexe **35**, **37**, **38** und **41** erfolgte in guten Ausbeuten durch Transmetallierung aus dem NHC-Silberkomplex **34**, lediglich der Palladiumkomplex **36** war auf diesem Weg nicht zugänglich und wurde in geringer Ausbeute aus dem freien NHC erhalten. Die Metallkomplexe **34**, **35**, **36** und **41** konnten durch Einkristall-Röntgenstrukturanalyse charakterisiert werden.

Anhand der Bandenlage der Carbonylschwingungen der Komplexe **39** und **40** konnte gezeigt werden, dass der aus **27a** erhältliche NHC-Ligand deutlich elektronenreicher als andere häufig verwendete NHC ist.

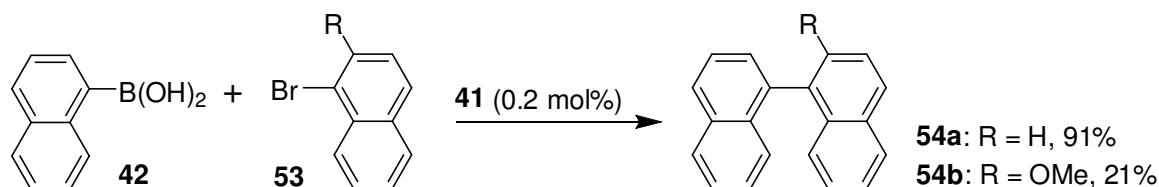
Der Kupferkomplex **35** konnte erfolgreich als Katalysator für die Cyclopropanierung von Styrol (**45**) und Inden (**51**) mit EDA (Ethyl diazoacetat) eingesetzt werden, ein selektivitätssteigernder Einfluss des konkaven NHC-Liganden konnte jedoch im Vergleich mit einem literaturbekannten, nicht-makrocyclischen NHC-Kupferkomplex nicht beobachtet werden. Der Silberkomplex **34** wurde ebenfalls als Katalysator für Cyclopropanierungen getestet, zersetzte sich jedoch unter den Reaktionsbedingungen und bewirkte nahezu keinen Umsatz.



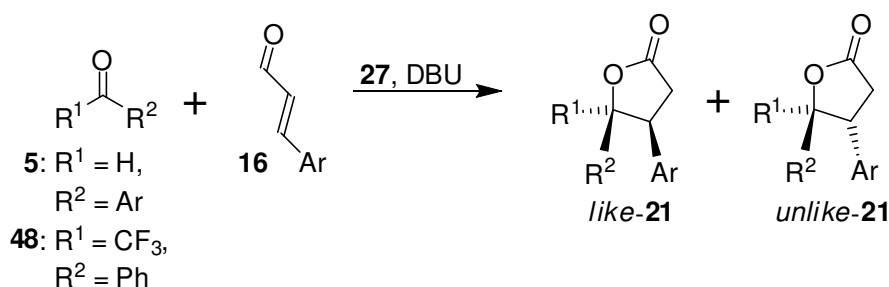
Der Palladiumkomplex **41** erwies sich als äußerst aktiver Präkatalysator für die Suzuki-Kreuzkupplung von 1-Naphthylboronsäure (**42**) mit Arylchloriden **43**. Bei der Heck-Reaktion von Styrol (**45**) mit Arylbromiden **46** lieferte die Verwendung von **41** gute Ausbeuten, mit den analogen Arylchloriden **43** wurden unter den gleichen Reaktionsbedingungen jedoch geringere Ausbeuten erzielt.



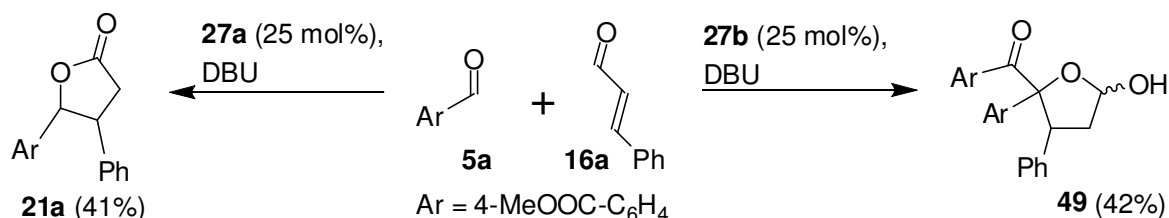
Die Synthese axial-chiraler Biaryle durch Suzuki-Kupplung stellt eine potentielle Anwendung für chirale NHC-Liganden dar, entsprechende Binaphthyle **54** konnten in racemischer Form bereits mit dem achiralen Präkatalysator **41** erhalten werden. Die Synthese des stark gehinderten **54b** gelang jedoch in nur geringer Ausbeute.



Die aus den Imidazoliniumsalzen **27a** und **27b** erhältlichen NHC wurden als Katalysatoren in der Synthese von  $\gamma$ -Butyrolactonen **21** getestet. Zur Deprotonierung der Imidazoliniumsalze **27** wurde DBU (1,8-Diazabicyclo[5.4.0]undec-7-en) verwendet.



Verschiedene Lactone **21** konnten erfolgreich synthetisiert werden, jedoch waren die bimakrocyclischen Imidazoliniumsalze **27** als Präkatalysatoren in Bezug auf Reaktivität und Selektivität dem in der Literatur verwendeten Imidazoliumsalz **14** unterlegen. Die Reaktionen erforderten den Einsatz von jeweils 25 mol% Präkatalysator **27** und lieferten nur geringe Diastereomerenüberschüsse.



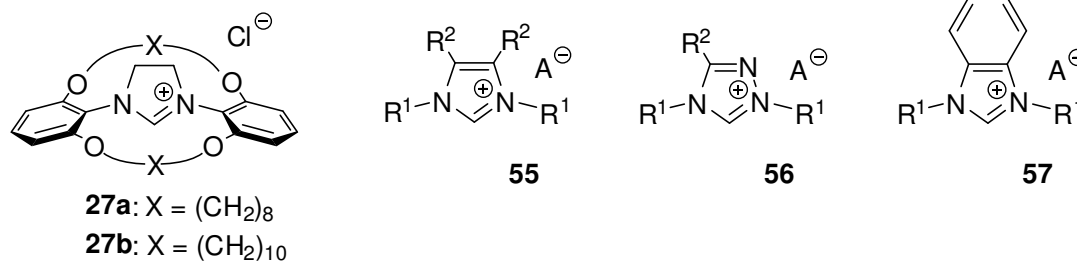
Bei der Reaktion des elektronenarmen Benzaldehyds **5a** mit Zimtaldehyd (**16a**) lieferte die Verwendung des bimakrocyclischen Imidazoliniumsalzes **27b** als Hauptprodukt das Halb-acetal **49**, während mit dem kleineren Bimakrocyclus **27a** das gewünschte Lacton **21a** erhalten werden konnte. Der Grund für die unterschiedlichen Reaktivitäten von **27a** und **27b** konnte noch nicht abschließend geklärt werden.

Aufgrund ihrer insgesamt geringeren Reaktivität scheinen gesättigte Imidazoliniumsalze wie **27** als Präkatalysatoren für die Synthese der  $\gamma$ -Butyrolactone **21** weniger geeignet als die ungesättigten Imidazoliumsalze, auch ein nicht-makrocyclisches Imidazoliniumsalz zeigte bei dieser Reaktion eine geringere Reaktivität (und Selektivität) als das Imidazoliumsalz **14**.

## 4.2 Ausblick

Anhand der in dieser Arbeit erhaltenen Ergebnisse ergeben sich drei verschiedene Anforderungen für weitere Modifikationen der konkaven NHC:

1. Für Anwendungen in der Organokatalyse ist eine Variation des NHC-Grundkörpers notwendig. Die in dieser Arbeit vorgestellten Imidazolidin-2-ylidene zeigten, im Gegensatz zu ihrem erfolgreichen Einsatz als Liganden, eine nur geringe Aktivität als nucleophile Katalysatoren. Geeigneterer NHC-Vorläufer als die Imidazoliniumsalze **27** könnten die häufig in der Organokatalyse genutzten Imidazoliumsalze **55** und Triazoliumsalze **56**, oder auch Benzimidazoliumsalze **57** sein. Die entsprechenden NHC würden neben Anwendungen in der Organokatalyse ebenfalls einen Einsatz als Liganden in metallkatalysierten Reaktionen erlauben.



2. Durch Variation der konkaven Struktur muss bei der Synthese symmetrischer NHC-Vorläufer eine stärkere Abschirmung des Carben-Kohlenstoffatoms gewährleistet werden, um im Vergleich mit den häufig verwendeten NHC **15**, **24-26** (siehe Abbildung 1.8, Seite 10) sowohl in der Organokatalyse als auch in metallkatalysierten Reaktionen eine Selektivitätssteigerung zu bewirken.

3. Die Synthese axial-chiraler konkaver Azoliumsalze bietet das größte Potential für katalytische Anwendungen und sollte durch Modifikation der in dieser Arbeit vorgestellten konfigurationslabilen Imidazoliniumsalze **28** möglich sein. Die Racemisierung der Imidazoliniumsalze **28** wurde durch die nahezu ungehinderte Rotation des Heterocyclus bezüglich der Arylbrückenköpfe des Bimakrocyclus ermöglicht. Die Einführung von sperrigen Substituenten am Heterocyclus sollte somit durch eine Anhebung der Rotationsbarriere die Konfigura-

tionsstabilität entsprechender axial-chiraler Strukturen erhöhen. In Anbetracht der geringen Reaktivität der Imidazoliniumsalze **27** in der Organokatalyse sollte auch hierbei die Synthese von Imidazoliumsalzen **55** oder Triazoliumsalzen **56** ( $R^2 \neq H$ ) angestrebt werden, ebenso könnten entsprechende Benzimidazoliumsalze **57** konfigurationsstabile axial-chirale Biomakrocyclen liefern.

Die in dieser Arbeit durchgeführte Organokatalyse, die Synthese der  $\gamma$ -Butyrolactone **21**, bedarf einer weiteren Untersuchung bezüglich des Einflusses der verschiedenen NHC-Katalysatoren auf Reaktivität und Diastereoselektivität. Zudem konnte eine abschließende Erklärung für die unerwartete Bildung des Halbacetals **49** bei Verwendung des Imidazoliniumsalzes **27b** als Präkatalysator im Rahmen dieser Arbeit nicht gegeben werden. Weitere Experimente mit geeigneten Azoliumsalzen und Substratkombinationen könnten zum besseren Verständnis dieser Reaktion beitragen. Die Lactonsynthese, sowie eine Vielzahl weiterer NHC-katalysierter Reaktionen, bietet außerdem großes Potential für axial-chirale konkave NHC.

Aufgrund des einfachen Zugangs, ihrer leichten Handhabbarkeit und der Vielzahl an Anwendungen in der Katalyse sollte auch die Synthese konkaver NHC-Metallkomplexe weiter verfolgt werden. Die hohe Aktivität des NHC-Palladiumkomplexes **41** in Suzuki- und Heck-Reaktionen lässt vermuten, dass dieser auch in weiteren palladiumkatalysierten Reaktionen erfolgreich eingesetzt werden kann. Durch Variation der konkaven Struktur sowie die Verwendung weiterer Metalle ergeben sich vielfältige Anwendungsmöglichkeiten in der Katalyse, so könnte beispielsweise ein Grubbs-Katalysator mit konkavem NHC-Liganden für diastereoselektive Metathesereaktionen oder ein Palladiumkomplex mit chiralem NHC-Liganden für asymmetrische C-C-Verknüpfungen eingesetzt werden.



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## **Eidesstattliche Erklärung**

Hiermit erkläre ich an Eides statt, dass ich die vorliegende Dissertation selbständig und nur mit den angegebenen Hilfsmitteln angefertigt habe. Es wurde bislang noch kein Promotionsversuch unternommen.

Ole Winkelmann

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