



**HAL**  
open science

# Bimacrocyclic concave N-heterocyclic carbenes (NHCs): synthesis, structure, and application in catalyses

Ulrich Lüning, Ole Winkelmann

► **To cite this version:**

Ulrich Lüning, Ole Winkelmann. Bimacrocyclic concave N-heterocyclic carbenes (NHCs): synthesis, structure, and application in catalyses. *Supramolecular Chemistry*, 2009, 21 (03-04), pp.223-229. 10.1080/10610270802468413 . hal-00513540

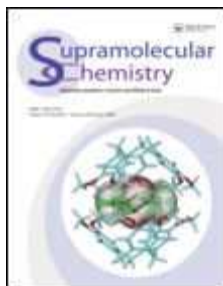
**HAL Id: hal-00513540**

**<https://hal.science/hal-00513540>**

Submitted on 1 Sep 2010

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



**Bimacrocyclic concave N-heterocyclic carbenes (NHCs):  
synthesis, structure, and application in catalyses**

Journal:	<i>Supramolecular Chemistry</i>
Manuscript ID:	GSCH-2008-0071.R1
Manuscript Type:	Special Issue Paper
Date Submitted by the Author:	26-Aug-2008
Complete List of Authors:	Lüning, Ulrich; Christian-Albrechts-Universität zu Kiel, Otto-Diels-Institut für Organische Chemie Winkelmann, Ole; Christian-Albrechts-Universität zu Kiel, Otto-Diels-Institut für Organische Chemie
Keywords:	bimacrocycles, N-heterocyclic carbenes, organocatalysis, transition metal complexes
<p>Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.</p> <p>figure 1.cdx figure 2.cdx figure 3.cdx figure 5.cdx figure 7.cdx figure 8.cdx figure 9.cdx figure 10.cdx figure 11.cdx figure 12.cdx</p>	



1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

For Peer Review Only

## MINI REVIEW

## Bimacrocylic concave N-heterocyclic carbenes (NHCs): synthesis, structure, and application in catalyses

Ole Winkelmann<sup>a</sup>, Ulrich Lüning<sup>a,\*</sup>

<sup>a</sup> *Otto-Diels-Institut für Organische Chemie, Christian-Albrechts-Universität zu Kiel,  
Olshausenstr. 40, D-24098 Kiel, Germany*

(Received xx July 2008; final version received xx yy 2008)

**Abstract:** Imidazolinium moieties have been incorporated into bimacrocycles to generate precursors for concave N-heterocyclic carbenes (NHCs). Starting from 2-nitroresorcinol and alkenols, symmetric concave imidazolinium salts **1** were obtained. Bimacrocyclization was achieved *via* ring closing metathesis (RCM). In an analogous fashion, axially chiral concave imidazolinium salts **2** were obtained by using a naphthalene bridgehead devoid of local C<sub>2</sub>-symmetry. The concave NHCs derived from the symmetric precursors **1** were used as nucleophilic catalysts for the synthesis of  $\gamma$ -butyrolactones and as ligands for transition metal catalysts. Copper complex **18** was used as catalyst for the cyclopropanation of styrene and indene with ethyl diazoacetate (EDA). Palladium complex **24** was used as catalyst for Mizoroki-Heck and Suzuki-Miyaura cross-coupling reactions.

**Keywords:** bimacrocycles; N-heterocyclic carbenes; organocatalysis; transition metal complexes

### 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 2-position, a betain was formed which acted as the nucleophile. Due to the electronegativity of the nitrogen atom, the drawing of a mesomeric carbene structure is also reasonable (Figure 1). Starting from imidazolium,<sup>3</sup> imidazolinium<sup>4</sup> and other azolium ions, related carbenes have been made accessible, and they have been named N-heterocyclic carbenes (NHCs).

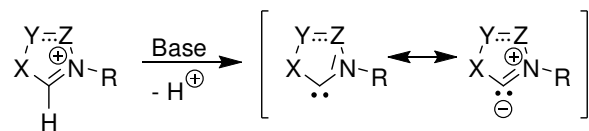


Figure 1. Heterocyclic azolium ions are the precursors for N-heterocyclic carbenes (NHCs) which are also drawn in their mesomeric betain form. Examples: thiazolium: X = S, Y = Z = CR', imidazolium: X = NR'', Y = Z = CR', imidazolinium: X = NR'', Y = Z = CR'<sub>2</sub>, triazolium: X = NR'', Y = N, Z = CR'.

These NHCs exhibit excellent catalytic activity in metal-free organocatalysis, including umpolung and condensation of carbonyl compounds<sup>5</sup> and transesterification reactions.<sup>6</sup> Metal complexes of NHCs have first been reported by Wanzlick and Schönherr<sup>7</sup> and Öfele<sup>8</sup> in 1968, but it was after the isolation of a stable crystalline carbene by Arduengo in 1991<sup>3a</sup> that the coordination chemistry of NHCs<sup>9</sup> and their use in organocatalysis<sup>10</sup> has

[\*] Corresponding author. Email: luening@oc.uni-kiel.de

become an emerging field of research. As ligands, the nucleophilic NHCs are strong two-electron  $\sigma$ -donors, displaying similar ligand properties as trialkylphosphines.<sup>11</sup> 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.<sup>12</sup> Besides their unique electronic properties, the steric demand of the NHCs is an important factor in cross-coupling reactions, and the use of NHC ligands has greatly expanded the scope of respective palladium catalyzed reactions.<sup>13</sup> Besides some frequently used NHC ligands, bulky NHCs have been synthesized for challenging Suzuki-Miyaura<sup>14</sup> or Sonogashira<sup>15</sup> cross-coupling reactions. Also quite a few examples of chiral NHCs exist in the literature.<sup>16</sup>

In enzymes, the thiamine unit is located in the cavity of an enzyme. Its geometry and chirality is responsible for the selectivity of the enzymatic reaction. In principle, a NHC or its precursor can also be embedded in a suitable shielding which in return shall be responsible for enhanced selectivities in the reactions catalyzed by the NHC. Applying the concept of concave reagents,<sup>17</sup> we envisaged imidazolium salts as precursors to concave NHCs and developed a synthetic route to bimaecyclic symmetric imidazolium salts **1**<sup>18</sup> and axially chiral derivatives **2**<sup>19</sup> (Figure 2).

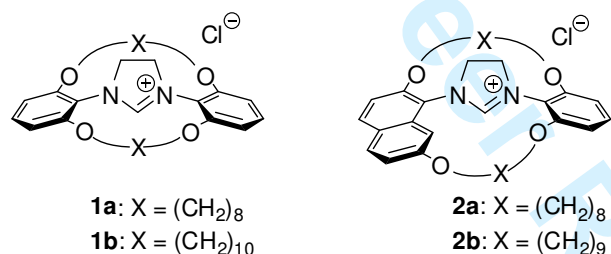


Figure 2. Symmetric NHC-precursors **1** and axially chiral NHC-precursors **2**.

## Synthesis of NHC-precursors **1** and **2**

### Symmetric NHC-precursors **1**

Several strategies are conceivable to construct a concave bimaecycle **1** which contains an imidazolium moiety as a precursor for a NHC. All strategies must provide (i) access to the tri-substituted aryl bridgeheads, (ii) a bimaecyclization strategy, and (iii) a suitable synthesis of the heterocycle. We have selected ruthenium catalyzed metathesis for the ring closure to the bimaecycle because such bimaecyclizations have proven to be very successful for the synthesis of a number of concave reagents.<sup>20</sup> Thus a precursor was demanded which contains the aryl bridgeheads and the heterocycle. Prominent strategies for the synthesis of imidazolium salts 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.<sup>4b,21</sup>

Thus, the first task was to synthesize the bis-*ortho*-substituted anilines **4**. In a two step reaction, **4a** and **4b** could be obtained from commercially available 2-nitroresorcinol (**3**). The reaction sequence first uses the Mitsunobu coupling of the phenol OH groups of **3**  $\omega$ -alkenols. The resulting nitroarenes can then be reduced to the anilines **4** by tin(II) chloride (Figure 3).

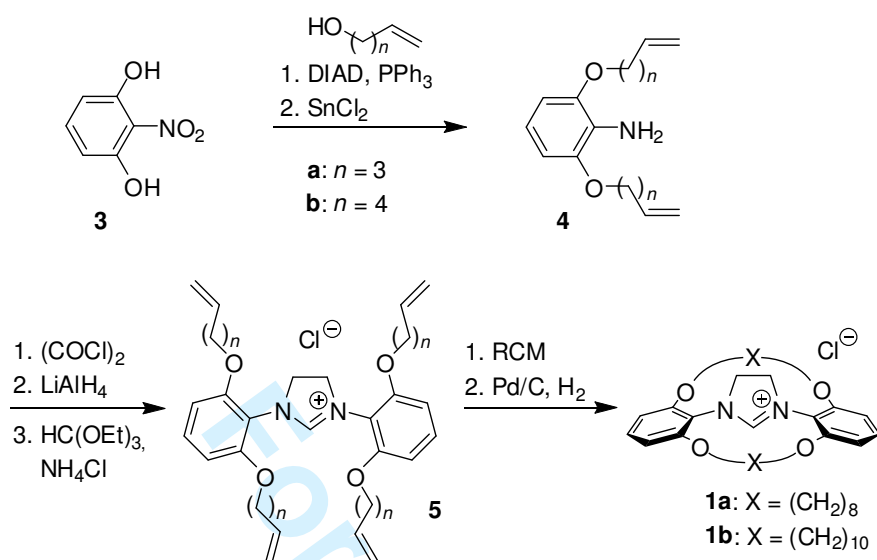


Figure 3. Synthesis of symmetric bimacrocylic imidazolium chlorides **1**.

Next, two equivalents of the anilines **4** were connected by oxalyl chloride to give respective diamides. After reduction with lithium aluminium hydride, the resulting diamines were reacted with triethyl orthoformate and ammonium chloride to give imidazolium salts **5**. After ring-closing metathesis (RCM) using Grubbs' catalyst, followed by hydrogenation of the newly formed double bonds, the bimacrocylic concave imidazolium salts **1** were obtained.<sup>18</sup> Deprotonation of **1a** led to the formation of a bimacrocylic NHC that was characterized as its thiocarboxylate (reaction of the NHC with carbon disulfide). The bimacrocylic structures of **1a**<sup>18</sup> and **1b**<sup>22</sup> were proven by single-crystal X-ray analysis (Figure 4).

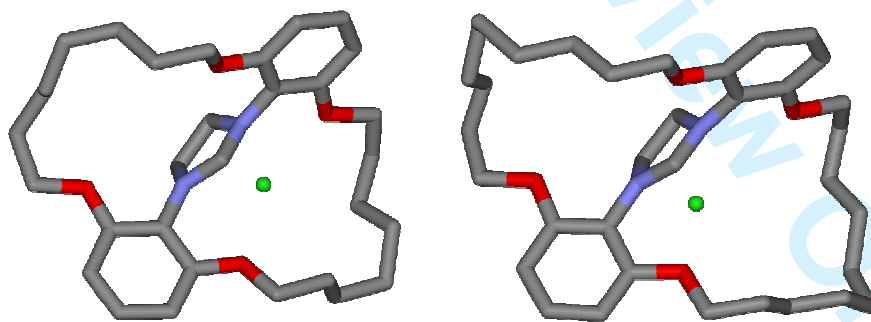


Figure 4. Comparison of the crystal structures of **1a** (left) and **1b** (right). Hydrogen atoms and solvent molecules are omitted for clarity.

### Axially chiral NHC-precursors **2**

The synthetic strategy for the formation of axially chiral imidazolium salts **2** was adopted from the route leading to non-chiral **1**. But instead of using two symmetric phenyl bridgeheads, one naphthalene bridgehead devoid of local  $C_2$ -symmetry was incorporated into the macrocycle to create axial chirality. 2,7-Dihydroxy-1-nitronaphthalene (**6**) was used as starting material, and the axially chiral salts **2** were obtained in racemic form (Figure 5).<sup>19</sup> For **2b**, an X-ray structural analysis was carried out (Figure 6) and the crystal contained both enantiomers.

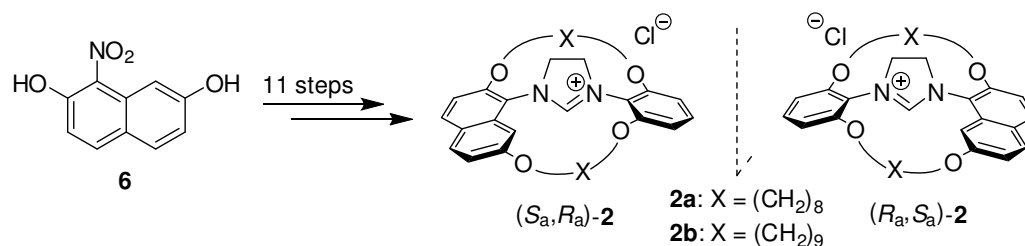


Figure 5. Synthesis of racemic axially chiral bimacrocyclic imidazolinium chlorides **2**.

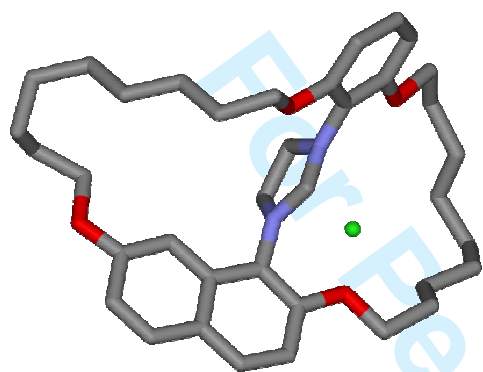


Figure 6. Crystal structure of **2b** (only the  $(S_a, R_a)$ -enantiomer is shown). Hydrogen atoms are omitted for clarity.

To apply the bimacrocycles **2** to enantioselective processes, the enantiomers need to be separated. As an interconversion of the enantiomers can occur by simple rotation of the imidazolinium ring with respect to the two bridgeheads, the question of the configurational stability of **2** had to be examined. This was done using helically chiral anions as stereodynamical probes. Association of enantiopure hexacoordinated phosphorus anions  $\Delta$ -TRISPHAT **7**<sup>23</sup> or  $\Delta$ -BINPHAT **8**<sup>24</sup> (Figure 7) to racemic **2** led to the formation of diastereomeric ion pairs that were examined by <sup>1</sup>H-NMR.<sup>19</sup>

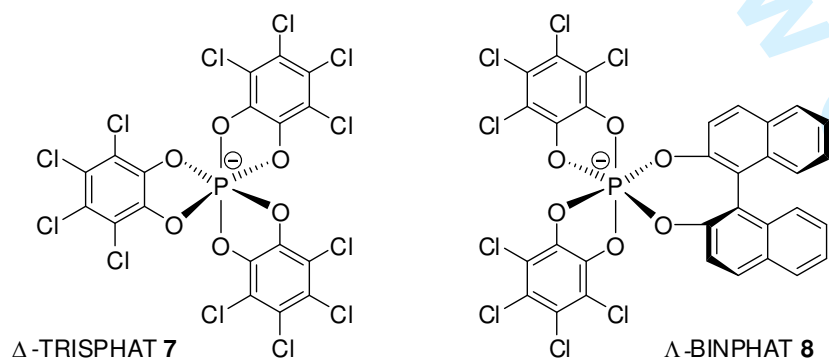


Figure 7. Helically chiral phosphorus anions.

While  $\Delta$ -TRISPHAT **7** induced only a small separation of the NMR signals,  $\Delta$ -BINPHAT **8** was more effective as a chiral NMR solvating agent. The integration of the separated signals indicated an imbalance in the diastereomeric population (for the diastereomeric ion pair prepared from **2b** and **8** the diastereomeric excess (d.e.) was 15% in  $CD_2Cl_2$  at room temperature). This imbalance was supposed to result from supramolecular diastereoselective interactions that may occur only with configurationally *labile* species (*Pfeiffer effect*<sup>25</sup>), causing the predominance of one diastereomeric ion pair in solution and

being a good probe for the lack of configurational stability of the cation.<sup>26</sup> As the stereoselective recognition among chiral ions is most pronounced in low polarity solvents,<sup>27</sup> the maximum diastereoselectivity with salts made of configurationally *labile* cations is achieved in low polar solvents and varies with modifications of the solvent polarity. The examination of the aforementioned diastereomeric mixture in deuterated solvents of different polarity indeed supported the configurational lability of **2b** (CDCl<sub>3</sub>: ε = 4.89, d.e. = 40%; C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>: ε = 8.42, d.e. = 17%; CD<sub>2</sub>Cl<sub>2</sub>: ε = 9.02, d.e. = 15%; C<sub>2</sub>D<sub>4</sub>Cl<sub>2</sub>: ε = 10.74, d.e. = 10%). Virtually identical results were obtained for the diastereomeric salts of the smaller bimacrocyclic **2a**.

These results proved that the barrier of rotation along the chiral axes in **2a** and **2b** is too small to allow their physical resolution at room temperature and the NHCs derived from **2** could not be applied to asymmetric catalysis. However, configurationally *stable* derivatives may be obtained by increasing the steric interactions along the chiral axes in order to enlarge the rotational barrier, e.g. by incorporation of sterically demanding substituents into the positions 4 and 5 of the imidazolium ring.

### Concave NHCs in nucleophilic organocatalysis

The mechanism for the thiamine-catalyzed benzoin condensation was established by Breslow in 1958 and it is based on the umpolung of a carbonyl carbon atom by the deprotonated thiazolium salt.<sup>1</sup> The scope of this reaction was expanded by Stetter in 1976, who reacted aldehydes with Michael-acceptors in the presence of thiazolium salts and base, yielding 1,4-diketones, 4-ketoesters or 4-ketonitriles (Stetter reaction).<sup>5a</sup> Chiral NHCs have successfully been applied as catalyst for asymmetric benzoin condensations and Stetter reactions, and thiazolium or triazolium salts are used as NHC-precursors for these reactions.<sup>5d</sup> In 2004, Glorius and Bode reported on the use of a sterically demanding imidazolium derived NHC as catalyst for the synthesis of  $\gamma$ -butyrolactones **13** from enals **9** and aldehydes **10** or ketones **11** (Figure 8). Either potassium *tert*-butoxide or DBU was used for the deprotonation of NHC-precursor **12**, and the preferred formation of *like-13* was observed using the NHC derived from **12** as catalyst.<sup>5b,5c</sup> However, in a recent publication,<sup>28</sup> the use of some thiazolium derived NHC catalysts has resulted in the predominant formation of *unlike-13*.

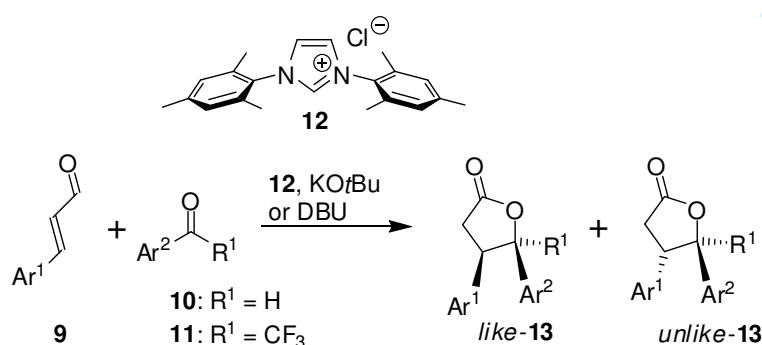


Figure 8. NHC catalyzed synthesis of  $\gamma$ -butyrolactones **13**.<sup>5b,5c</sup>

A reasonable mechanism was proposed for the reaction, involving the vinylogous umpolung of the  $\beta$ -carbon atom of the enal **9**, caused by nucleophilic attack of the NHC on its carbonyl carbon atom. The proposed catalytic cycle was supported by the observation of postulated intermediates by ESI mass spectrometry.<sup>29</sup> We have tested the concave NHCs derived from **1** as catalyst for this reaction, expecting to effect the diastereoselectivity with the bimacrocyclic structures. Different combinations of substrates **9** and **10** or **11** were examined, and lactones **13** could indeed be obtained using the concave NHCs derived from **1a** or **1b** by



deprotonation with DBU.<sup>22</sup> Unfortunately, the precatalysts **1** proved to be less effective in this reaction compared to **12**, and high loadings of **1** (25 mol%) were needed to produce reasonable amounts of products **13** with little stereoselectivity (*like:unlike*  $\cong$  1:1). While **1a** and **1b** showed the same reactivity and selectivity in most cases, an unexpected product was formed with precatalyst **1b** in the reaction of cinnamaldehyde (**9a**) with methyl 4-formylbenzoate (**10a**). While **1a** afforded the expected lactone **13a**, a cyclic hemiacetal **14** was obtained as the main product with **1b** (Figure 9).<sup>22</sup>

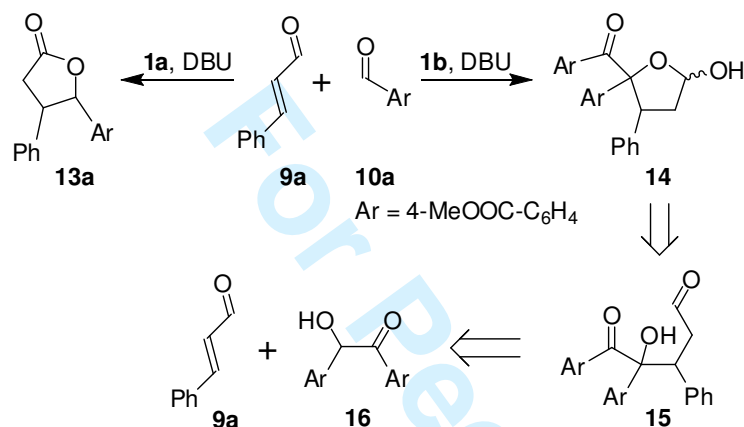


Figure 9. Reaction of cinnamaldehyde (**9a**) with methyl 4-formylbenzoate (**10a**) using NHC-precursor **1a** or **1b**.

An equilibrium between both anomeric forms (ratio 10:1) of **14** was observed in CDCl<sub>3</sub> at room temperature, with the hydroxyl and phenyl group being oriented *trans* in the major anomer, as could be deduced from the NOESY spectrum. The relative stereochemistry at the quaternary carbon atom could not be assigned undoubtedly. A molecule related to **14** has been reported to be produced from cinnamaldehyde (**9a**), acetaldehyde and fermenting baker's yeast,<sup>30</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 **14** implies the formation of benzoin **16**, whose anion reacts with the Michael-acceptor **9a**. The resulting hydroxyaldehyde **15** undergoes ring closure to hemiacetal **14** as the NMR spectra prove. Reasonable amounts of hemiacetal **14** were only obtained with precatalyst **1b**, and we suggest that these different reactivities result from the structural differences between **1a** and **1b** (Figure 4). The scope of this new reaction is currently under investigation in our laboratory.

### Concave NHC transition metal complexes

The bimacrocyclic NHC derived from **1a** was used as ligand for transition metal ions, and eight concave NHC complexes **17-24** were obtained (Figure 10).<sup>31</sup> Complexes **17**, **18**, **19** and **24** were characterized by single crystal X-ray analyses. Most of the complexes were synthesized by transmetalation from the NHC silver complex **17**, which is accessible in 86% yield by reaction of **1a** with silver(I) oxide. The use of NHC silver complexes as carbene transfer reagents is a popular method for the synthesis of NHC metal complexes, avoiding the handling of the sensitive free carbenes.<sup>32</sup> In contrast to the other complexes, palladium complex **19** was not accessible by transmetalation from silver complex **17** and could only be obtained in poor yield *via* the free carbene. The rhodium and iridium dicarbonyl complexes **22** and **23** were synthesized to investigate the electronic properties of the bimacrocyclic NHC ligand. The carbonyl stretching frequencies of respective complexes are a popular indirect measure of the ligands  $\sigma$ -donor strength.<sup>33</sup> A low stretching frequency (wavenumber) of CO

corresponds to strong  $\sigma$ -donation of the NHC. By using a linear fit procedure,<sup>33c</sup> the CO stretching frequencies of Ir(I)-NHC can be used to estimate Tolman's electronic parameter (TEP),<sup>34</sup> 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 NHCs are more electron donating than the most donating phosphines. Compared to frequently used NHCs, our new ligand was found to be significantly more electron donating.<sup>31a</sup>

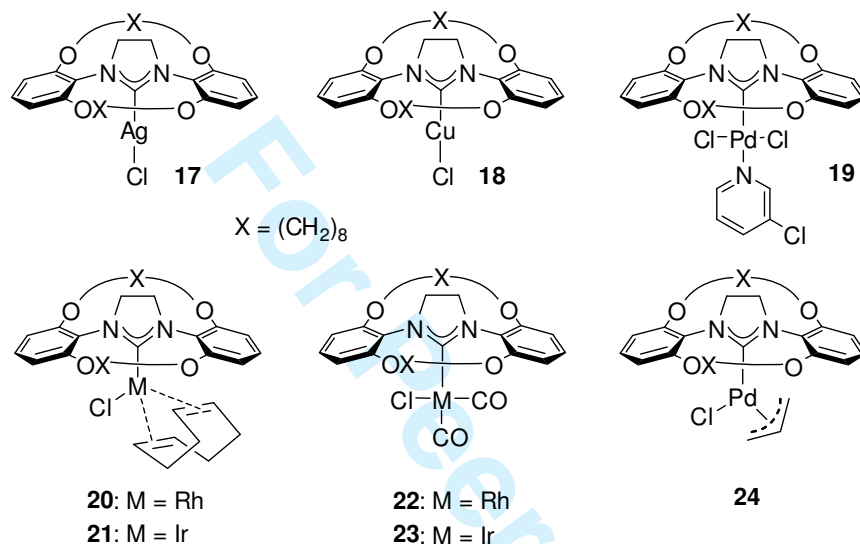


Figure 10. Concave NHC transition metal complexes.

Copper complex **18** proved to be reactive as catalyst for the cyclopropanation of styrene (**25**) and indene (**27**) with ethyl diazoacetate (EDA), but the diastereoselectivity was only slightly affected by the concave NHC ligand (Figure 11). Silver complex **17** was also tested as catalyst for this reaction, but only very low EDA consumption was observed as complex **17** decomposed under the reaction conditions.<sup>31a</sup>

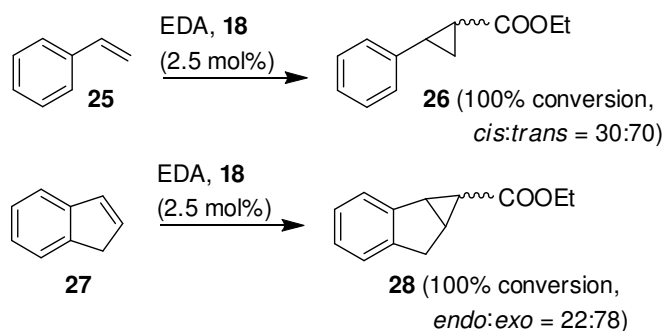


Figure 11. Cyclopropanation of styrene (**25**) and indene (**27**) with EDA using catalyst **18**.

Palladium complex **24**, accessible in 85% yield *via* transmetalation with allyl palladium chlorid dimer from silver complex **17**, was successfully applied as catalyst for Mizoroki-Heck and Suzuki-Miyaura cross-coupling reactions (Figure 12).<sup>31b</sup> While the use of aryl chlorides as coupling partners is nowadays established in the latter case,<sup>35</sup> the Mizoroki-Heck olefination of unactivated aryl chlorides is not trivial and mainly bromides and activated chlorides are successfully used in the reaction.<sup>36</sup> The olefinations were performed in tetrabutylammonium bromide as an ionic liquid at 140 °C (16 h reaction time). Using 1 mol% of catalyst **24**, good results were obtained in the reaction of activated and electronically neutral aryl bromides **29** with styrene (**25**), and also hindered 2-bromo-toluene afforded 72%

of the coupling product. Unfortunately, a decrease in yield was observed when analogous aryl chlorides **32** were used as the coupling partners. In contrast to these results, high yields were obtained in the Suzuki-Miyaura reaction of aryl chlorides **32** with 1-naphthalene-boronic acid (**31**) at low catalyst loading in short reaction times (0.2 mol% **24**, 2 h at 60°C).

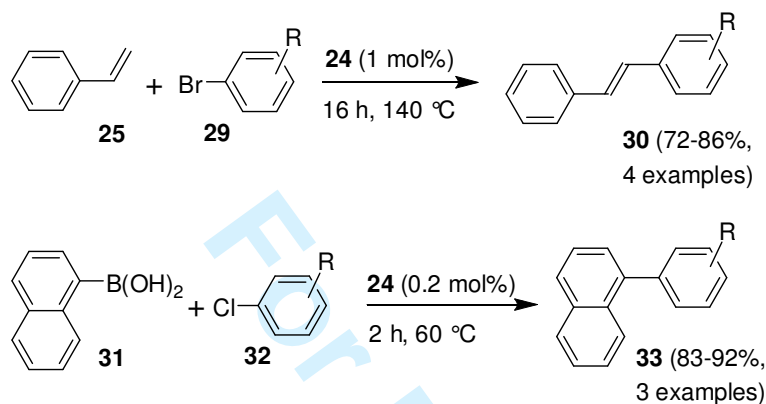


Figure 12. Mizoroki-Heck and Suzuki-Miyaura reactions using catalyst **24**.

Also axially chiral biaryls could be produced *via* Suzuki-Miyaura reactions using catalyst **24** (however, in racemic form). As the catalytic activity of the complexes **18** and **24** shows promise, we are currently investigating the feasibility to obtain configurationally *stable*, axially chiral NHC complexes derived from the *labile* NHC-precursors **2**<sup>19</sup> for **asymmetric catalysis**. We suggest that a tightly bound metal ion should increase the steric interactions along the chiral axes, resulting in resolvable chiral NHC complexes. Experiments in this vein are under way.

## Conclusion

Concave imidazolium ions **1** and **2** can readily be obtained as precursors to **concave** NHCs. These NHCs are active as nucleophilic catalysts and they can be used as ligands for transition metal catalysts. While stereoselectivities still have to be improved, a hitherto not observed hemiacetal **14** could be produced using one specific precatalyst (**1b**). As the catalytic activity of the concave NHCs and that of **respective** transition metal complexes shows promise, we are currently focusing on chiral modifications of the bimakrocyclic NHCs **for asymmetric catalysis**. In order to yield configurationally *stable* axially chiral imidazolium salts, *labile* cations **2** will have to be further modified. Alternatively, configurationally *stable* axially chiral NHC complexes might be obtained from the *labile* NHC-precursors **2**.

## References

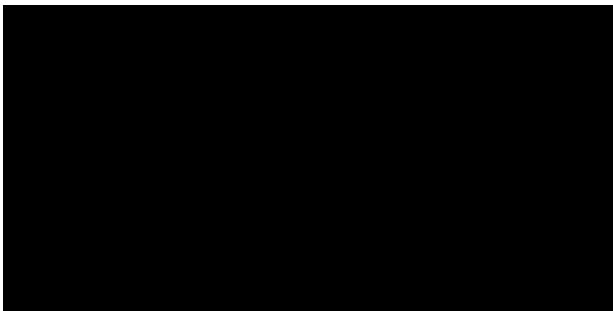
- <sup>1</sup> Breslow, R. *J. Am. Chem. Soc.* **1958**, *80*, 3719–3726.
- <sup>2</sup> Reviews on thiamine-dependent enzymes:
  - (a) Sprenger, G.A.; Pohl, M. *J. Mol. Catal. B* **1999**, *6*, 145–159;
  - (b) Duggleby, R. *Acc. Chem. Res.* **2006**, 550–557.
- <sup>3</sup>
  - (a) Arduengo, A.J.; Harlow, R.L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361–363;
  - (b) Arduengo, A.J.; Dias, H.V.R.; Harlow, R.L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534.

- 1  
2  
3  
4 (a) Arduengo, A.J.; Goerlich, J.R.; Marshall, W.J. *J. Am. Chem. Soc.* **1995**, *117*, 11027–  
5 11028.  
6  
7 (b) Arduengo, A.J.; Krafczyk, R.; Schmutzler, R.; Craig, H.A.; Goerlich, J.R.; Marshall, W.J.;  
8 Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523–14534.  
9  
10 (a) Stetter, H. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 639–648;  
11 (b) Burstein, C.; Glorius, F. *Angew. Chem. Int. Ed.* **2004**, *43*, 6205–6208;  
12 (c) Sohn, S.S.; Rosen, E.L.; Bode, J.W. *J. Am. Chem. Soc.* **2004**, *126*, 14370–14371;  
13 (d) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, 5606–5655.  
14  
15 (a) Grasa, G.A.; Kissling, R.M.; Nolan, S.P. *Org. Lett.* **2002**, *4*, 3583–3586;  
16 (b) Nyce, G.W.; Lamboy, J.A.; Connor, E.F.; Waymouth, R.M.; Hedrick, J.L. *Org. Lett.* **2002**,  
17 *4*, 3587–3590;  
18 (c) Singh, R.; Nolan, S.P. *Chem. Commun.* **2005**, 5456–5458.  
19  
20 Wanzlick, H.-W.; Schönherr, H.-J. *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141–142.  
21  
22 Öfele, K. *J. Organomet. Chem.* **1968**, *12*, P42–P43.  
23  
24 (a) Herrmann, W.A.; Köcher, C. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162–2187;  
25 (b) Herrmann, W.A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309;  
26 (c) Scott, N.M.; Nolan, S.P. *Eur. J. Inorg. Chem.* **2005**, 1815–1828.  
27  
28 (d) Nolan, S.P. (Ed.) *N-Heterocyclic carbenes in synthesis*, Wiley-VCH, Weinheim, **2006**.  
29  
30 (e) Glorius, F. (Ed.) *N-Heterocyclic carbenes in transition metal catalysis, Topics in*  
31 *Organometallic Chemistry, Vol. 21*; Springer, Berlin, **2007**.  
32  
33 Marion, N.; Diez-González, S.; Nolan, S.P. *Angew. Chem. Int. Ed.* **2007**, *46*, 2988–3000.  
34  
35 Öfele, K.; Herrmann, W.A.; Mihalios, D.; Elison, M.; Herdtweck, E.; Scherer, W.; Mink, J. *J.*  
36 *Organomet. Chem.* **1993**, *459*, 177–184.  
37  
38 (a) Weskamp, T.; Kohl, F.J.; Hieringer, W.; Gleich, D.; Herrmann, W.A. *Angew. Chem. Int.*  
39 *Ed.* **1999**, *38*, 2416–2419;  
40 (b) Scholl, M.; Ding, S.; Lee, C.W.; Grubbs, R.H. *Org. Lett.* **1999**, *1*, 953–956;  
41 (c) Huang, J.; Stevens, E.D.; Nolan, S.P.; Petersen, J.L. *J. Am. Chem. Soc.* **1999**, *121*, 2674–  
42 2678.  
43  
44 Kantchev, E.A.B.; O'Brien, C.J.; Organ, M.G. *Angew. Chem. Int. Ed.* **2007**, *46*, 2768–2813.  
45  
46 Altenhoff, G.; Goddard, R.; Lehmann, C.W.; Glorius, F. *J. Am. Chem. Soc.* **2004**, *126*, 15195–  
47 15201.  
48  
49 (a) Ma, Y.; Song, C.; Jiang, W.; Wu, Q.; Wang, Y.; Liu, X.; Andrus, M.B. *Org. Lett.* **2003**, *5*,  
50 3317–3319.  
51  
52 (b) Altenhoff, G.; Würtz, S.; Glorius, F. *Tetrahedron Lett.* **2006**, *47*, 2925–2928.  
53  
54 (a) Seiders, T.J.; Ward, D.W.; Grubbs, R.H. *Org. Lett.* **2001**, *3*, 3225–3228;  
55 (b) César, V.; Bellemin-Laponnaz, S.; Gade, L.H. *Chem. Soc. Rev.* **2004**, *33*, 619–636;  
56 (c) Suzuki, Y.; Yamauchi, K.; Muramatsu, K.; Sato, M. *Chem. Commun.* **2004**, 2770–2771;  
57  
58  
59  
60

- 1  
2  
3  
4  
5 (d) Ishida, Y.; Sasaki, D.; Miyauchi, H.; Saigo, K. *Tetrahedron Lett.* **2006**, *47*, 7973–7976;  
6  
7 (e) Kündig, E.P.; Seidel, T.M.; Jia, Y.; Bernardinelli, G. *Angew. Chem. Int. Ed.* **2007**, *46*,  
8 8484–8487.
- 9  
10  
11  
12  
13  
14  
15  
16  
17 Lünig, U. *Liebigs Ann. Chem.* **1987**, 949–955.
- 18  
19 Winkelmann, O.; Näther, C.; Lünig, U. *Eur. J. Org. Chem.* **2007**, 981–987.
- 20  
21 Winkelmann, O.; Linder, D.; Lacour, J.; Näther, C.; Lünig, U. *Eur. J. Org. Chem.* **2007**,  
22 3687–3697.
- 23  
24 (a) Lüthje, S.; Bornholt, C.; Lünig, U. *Eur. J. Org. Chem.* **2006**, 909–915;  
25 (b) Lünig, U.; Fahrenkrug, F. *Eur. J. Org. Chem.* **2006**, 916–923;  
26 (c) Liebig, T.; Abbass, M.; Lünig, U. *Eur. J. Org. Chem.* **2007**, 972–980.
- 27  
28 (a) Hadei, N.; Kantchev, E.A.B.; O'Brien, C.J.; Organ, M.G. *J. Org. Chem.* **2005**, 8503–8507.  
29 (b) Paczal, A.; Bényei, A.; Kotschy, A. *J. Org. Chem.* **2006**, *71*, 5969–5979.
- 30  
31 Winkelmann, O. *Ph.D. Thesis*, Christian-Albrechts-Universität zu Kiel, **2008**.
- 32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60
- 23 Tris(tetrachlorobenzenediolato)phosphate(V) anion:  
Lacour, J.; Ginglinger, C.; Grivet, C.; Bernardinelli, G. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*,  
608–609.
- 24 Bis(tetrachlorobenzenediolato)mono([1,1']binaphthalenyl-2,2'-diolato) phosphate(V) anion:  
Lacour, J.; Londez, A.; Goujon-Ginglinger, C.; Buß, V.; Bernardinelli, G. *Org. Lett.* **2000**, *2*,  
4185–4188.
- 25 (a) Pfeiffer, P.; Quehl, K. *Ber.* **1931**, *64B*, 2667–2671.  
(b) Norden, B.; Tjerneld, F. *FEBS Lett.* **1976**, *67*, 368–370.  
(c) Kirschner, S.; Ahmad, N.; Munir, C.; Pollock, R.J. *Pure Appl. Chem.* **1979**, *51*, 913–923.  
(d) Green, M.M.; Khatri, C.; Peterson, N.C. *J. Am. Chem. Soc.* **1993**, *115*, 4941–4942.  
(e) Owen, D.J.; VanDerveer, D.; Schuster, G.B. *J. Am. Chem. Soc.* **1998**, *120*, 1705–1717.  
(f) Hiraoka, S.; Harano, K.; Tanaka, T.; Shiro, M.; Shionoya, M. *Angew. Chem. Int. Ed.* **2003**,  
*42*, 5182–5185.  
(g) Vignon, S.A.; Wong, J.; Tseng, H.R.; Stoddart, J.F. *Org. Lett.* **2004**, *6*, 1095–1098.  
(h) Yeh, R.M.; Raymond, K.N. *Inorg. Chem.* **2006**, *45*, 1130–1139.
- 26 (a) Lacour, J.; Jodry, J.J.; Ginglinger, C.; Torche-Haldimann, S. *Angew. Chem. Int. Ed. Engl.*  
**1998**, *37*, 2379–2380.  
(b) Lacour, J.; Jodry, J.J.; Monchaud, D. *Chem. Commun.* **2001**, 2302–2303.  
(c) Vial, L.; Lacour, J. *Org. Lett.* **2002**, *4*, 3939–3942.  
(d) Desvergnès-Breuil, V.; Hebbe, V.; Dietrich-Buchecker, C.; Sauvage, J.-P.; Lacour, J.  
*Inorg. Chem.* **2003**, *42*, 255–257.  
(e) Jodry, J.J.; Frantz, R.; Lacour, J. *Inorg. Chem.* **2004**, *43*, 3329–3331.
- 27 (a) Hebbe-Viton, V.; Desvergnès, V.; Jodry, J.J.; Dietrich-Buchecker, C.; Sauvage, J.-P.;  
Lacour, J. *Dalton Trans.* **2006**, 2058–2065;

- 1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60
- (b) Bergman, S.D.; Frantz, R.; Gut, D.; Kol, M.; Lacour, J. *Chem. Commun.* **2006**, 850–852.
- 28 **Hirano, K.; Piel, I.; Glorius, F. *Adv. Synth. Catal.* **2008**, 350, 984–988. A possible explanation  
for the different diastereoselectivities is given in the supporting information.**
- 29 Schrader, W.; Handayani, P.P.; Burstein, C.; Glorius, F. *Chem. Commun.* **2007**, 716–718.
- 30 Bertolli, G.; Fronza, G.; Fuganti, C.; Grasselli, P.; Majori, L.; Spreafico, F. *Tetrahedron Lett.*  
**1981**, 22, 965–968.
- 31 (a) Winkelmann, O.; Näther, C.; Lüning, U. *J. Organomet. Chem.* **2008**, 693, 923–932;
- (b) Winkelmann, O.; Näther, C.; Lüning, U. *J. Organomet. Chem.* **2008**, 693, 2784–2788.
- 32 Lin, I.J.B.; Vasam, C.S. *Coord. Chem. Rev.* **2007** 251, 642–670.
- 33 (a) Herrmann, W.A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G.R.J. *Chem. Eur. J.* **1996**, 2,  
772–780;
- (b) Denk, K.; Sirsch, P.; Herrmann, W.A. *J. Organomet. Chem.* **2002**, 649, 219–224;
- (c) Chianese, A.R.; Li, X.; Janzen, M.C.; Faller, J.W.; Crabtree, R.H. *Organometallics* **2003**,  
22, 1663–1667;
- (d) Lavallo, V.; Mafhouz, J.; Canac, Y.; Donnadiou, B.; Schoeller, W.W.; Bertrand, G. *J.*  
*Am. Chem. Soc.* **2004**, 126, 8670–8671;
- (e) Herrmann, W.A.; Schütz, J.; Frey, G.D.; Herdtweck, E. *Organometallics* **2006**, 25, 2437–  
2448;
- (f) Frey, G.D.; Rentzsch, C.F.; von Preysing, D.; Scherg, T.; Mühlhofer, M.; Herdtweck, E.;  
Herrmann, W.A. *J. Organomet. Chem.* **2006**, 691, 5725–5738;
- (g) Leuthäuser, S.; Schwarz, D.; Plenio, H. *Chem. Eur. J.* **2007**, 13, 7195–7203.
- 34 Tolman, C.A. *Chem. Rev.* **1977**, 77, 313–348.
- 35 (a) O'Brien, C.J.; Kantchev, E.A.B.; Valente, C.; Hadei, N.; Chass, G.A.; Lough, A.;  
Hopkinson, A.C.; Organ, M.G. *Chem. Eur. J.* **2006**, 12, 4743–4748;
- (b) Marion, N.; Navarro, O.; Mei, J.; Stevens, E.D.; Scott, N.M.; Nolan, S.P. *J. Am. Chem.*  
*Soc.* **2006**, 128, 4101–4111.
- 36 (a) Herrmann, W.A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G.R.J. *Angew. Chem. Int. Ed.*  
*Engl.* **1995**, 34, 2371–2374.
- (b) Yang, C.; Nolan, S.P. *Synlett* **2001**, 10, 1539–1542;
- (c) Selvakumar, K.; Zapf, A.; Beller, M. *Org. Lett.* **2002**, 4, 3031–3033;
- (d) Zou, G.; Huang, W.; Xiao, Y.; Tang, J. *New. J. Chem.* **2006**, 30, 803–809;
- (e) Wang, C.; Liu, Y.; Peng, S.; Chen, J.; Liu, S. *J. Organomet. Chem.* **2007**, 692, 3976–3983.

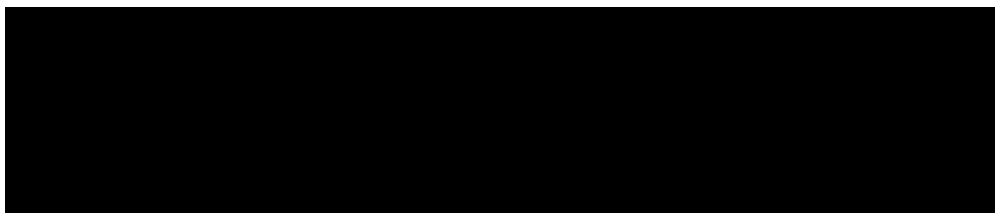
1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



51x26mm (150 x 150 DPI)

Peer Review Only

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

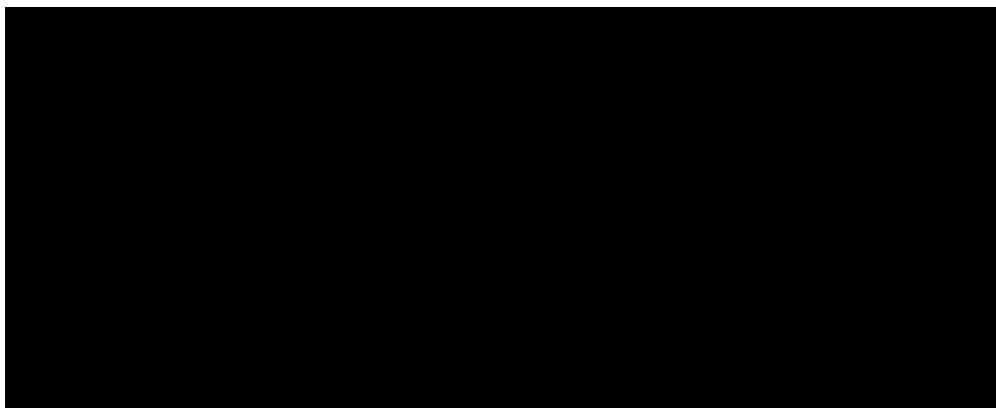


120x25mm (150 x 150 DPI)

Peer Review Only



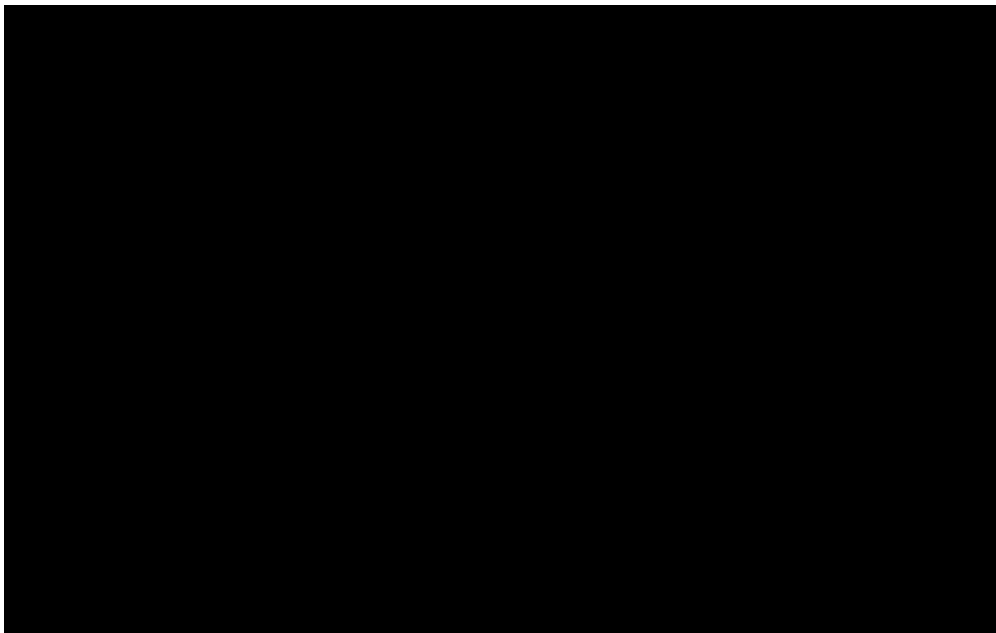
1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



125x50mm (150 x 150 DPI)

Peer Review Only

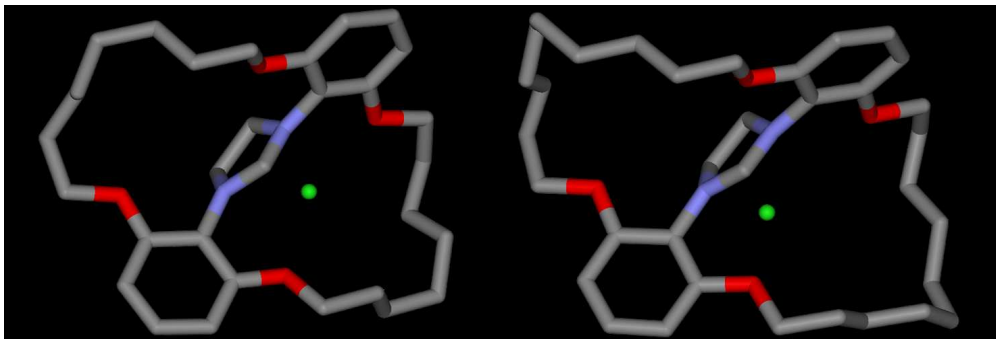
1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



181x114mm (150 x 150 DPI)

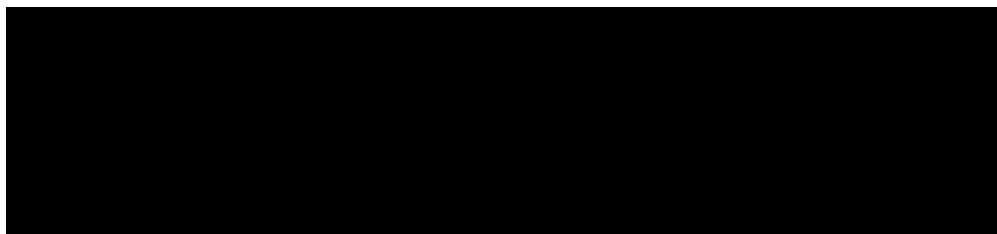
Review Only

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



251x85mm (150 x 150 DPI)

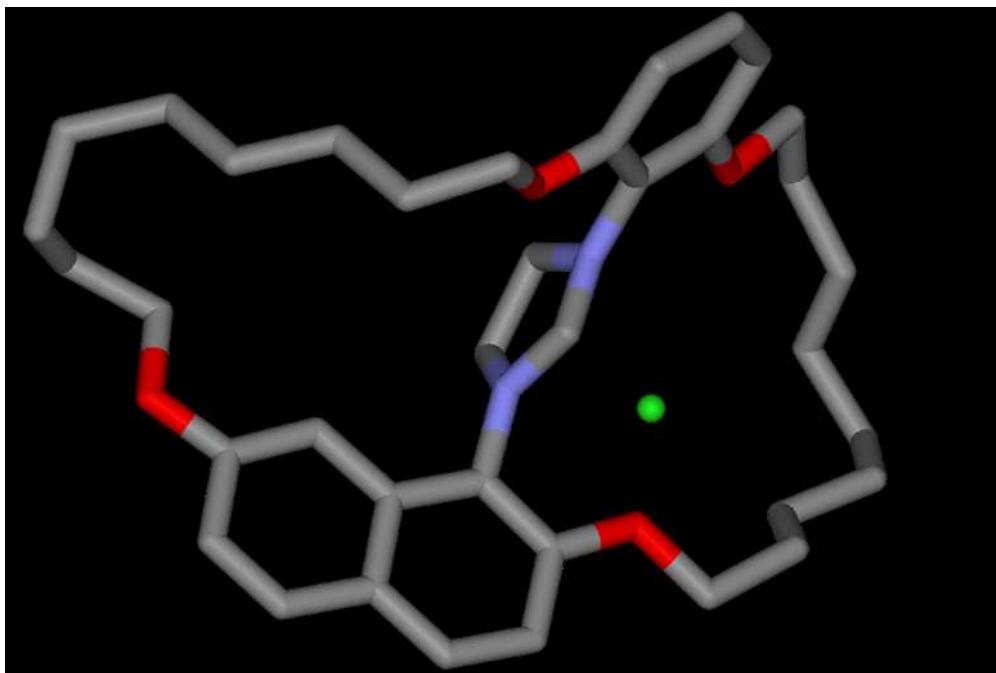
Peer Review Only



214x49mm (150 x 150 DPI)

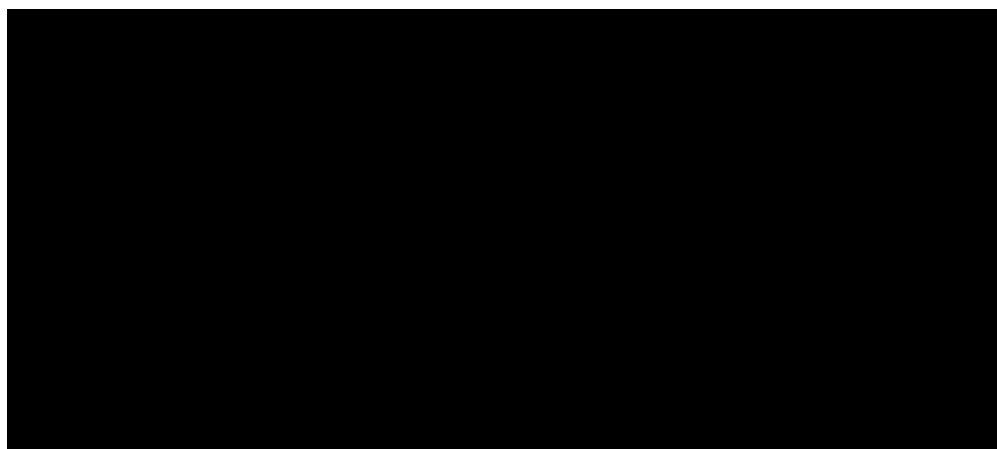
Peer Review Only

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



131x88mm (150 x 150 DPI)

view Only

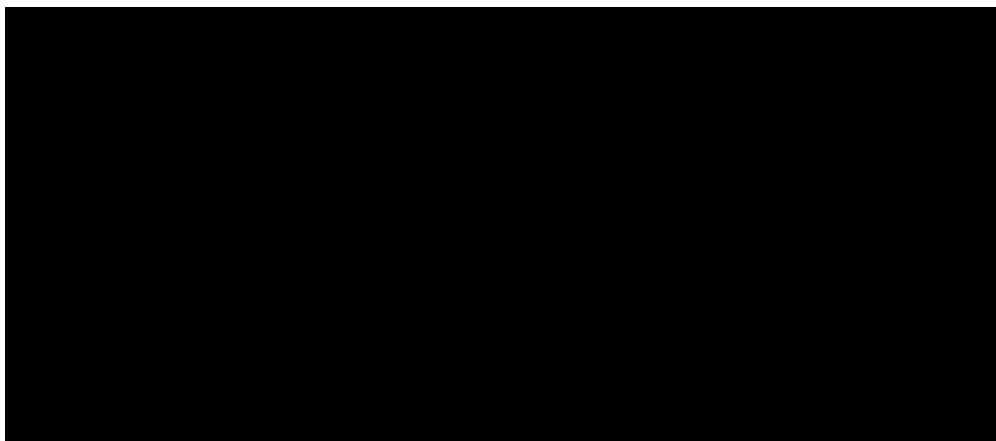


167x74mm (150 x 150 DPI)

For Review Only

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

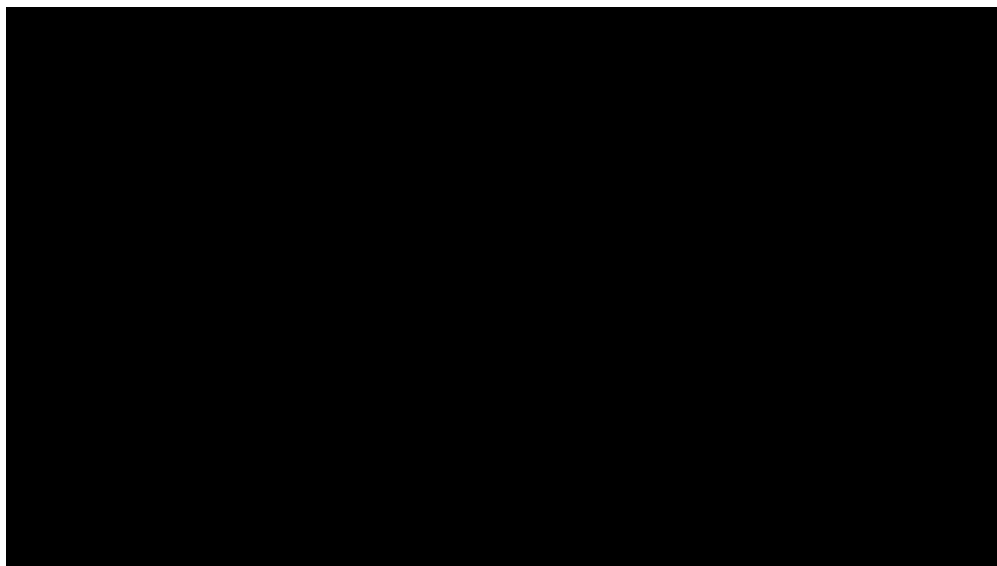
1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



157x69mm (150 x 150 DPI)

er Review Only

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

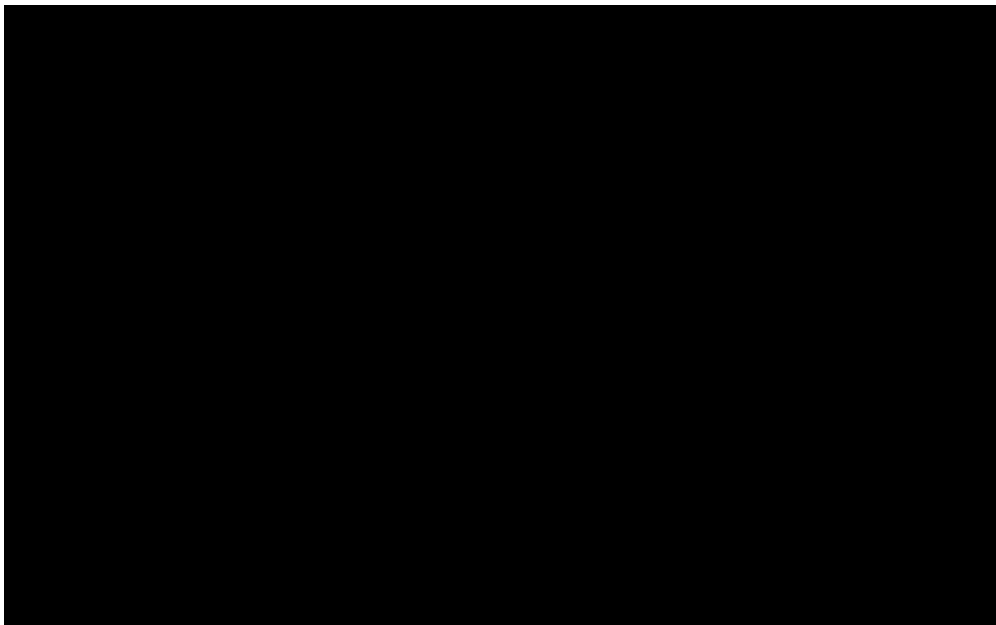


154x86mm (150 x 150 DPI)

Review Only



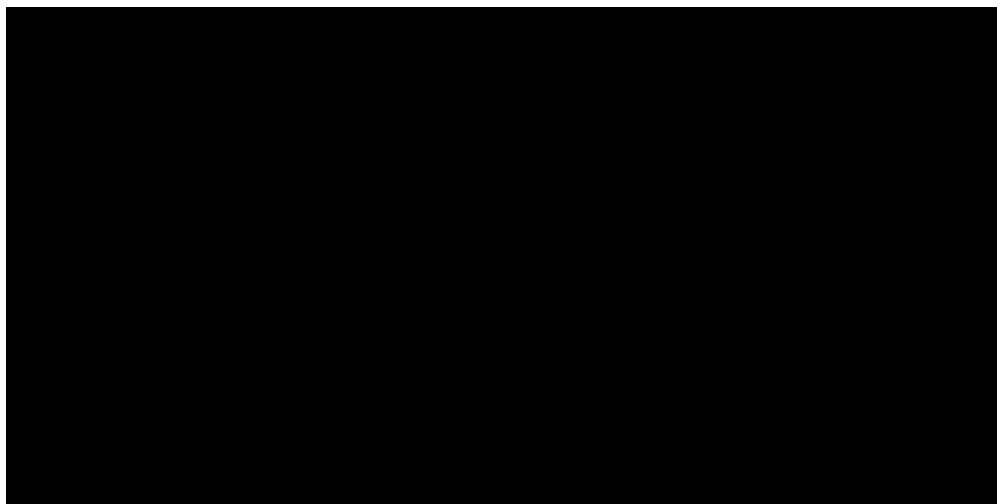
1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



178x111mm (150 x 150 DPI)

Review Only

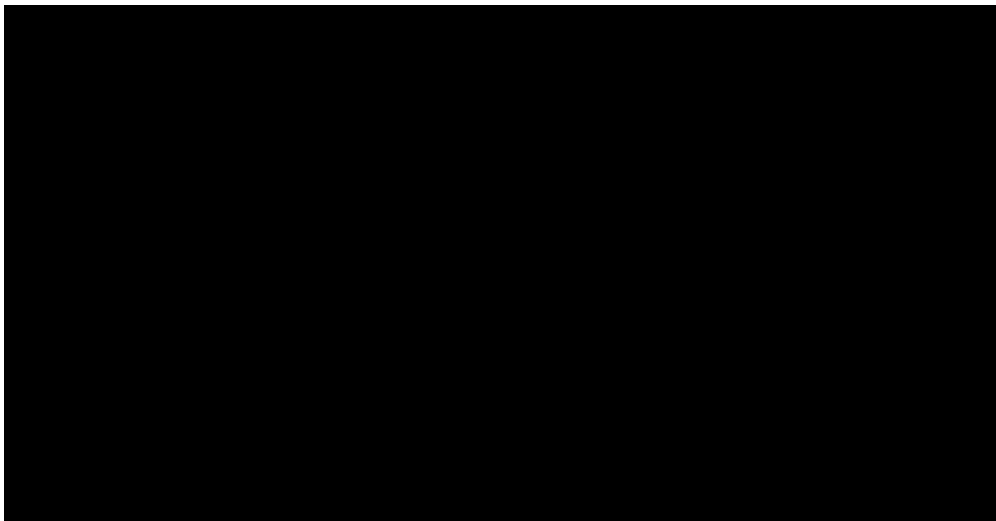
1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



136x68mm (150 x 150 DPI)

Review Only

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



159x82mm (150 x 150 DPI)

Review Only