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Amphiphilic Sugar Metal Carbenes: From Fischer Type to *N*-Heterocyclic Carbenes (NHCs)

Investigations on potential gelation and catalytic activities

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zur
Erlangung des Doktorgrades
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Rheinische Friederich-Wilhems-Universität Bonn

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September 2003 - July 2007

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Chimie Organique

Présentée par

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Pour obtenir le grade de
DOCTEUR de l'UNIVERSITE PARIS 6

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Soutenue le 10 Septembre 2007

devant le jury composé de :
M. le Prof. K.H. Dötz et M. le Dr. E. Rose. Directeurs de thèse
M. le Dr. J.-P. Djukic .et M. le Dr. P. Gros. Rapporteurs
Mme.le Prof. A. Proust et M. le Prof. K. Maier. Examinateurs

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Introduction

I Introduction

Organometallic chemistry is the study of structures bearing a metal carbon or metal heteroatom bond. It is probably one of the most studied parts in chemistry. Organometallics are a very broad field of compounds involving also living organism; as an example hemoglobin and myoglobin are porphyrins bonded to an iron atom. Organometallic compounds are also involved in the production of fine chemicals and pharmaceuticals.

One known organometallic compound is the ruthenium-binap complex synthesised by R. J. Noyori[1] and used in the preparation of anti-inflammatory drugs. The organometallic complex involved is used in catalytic amount. Catalysis is one of the themes that was recently rewarded with Nobel prices in 2001 and 2005.

In 2001 R. J. Noyori[1] and W. S. Knowles[2] shared a half price for catalysed chiral hydrogenation while K. B. Sharpless[3] got the other half price for his work on catalysed chiral oxidation reactions. In 2005 Y. Chauvin,[4] R. R. Schrock[5] and R. H. Grubbs[6] received the Nobel price for their work on the methatesis reaction methodology. This reaction involves a metal carbene and an olefin to form a new unsaturated structure. Metal carbenes are known since 1964 with the first publication of a tungstene carbene complex by E. O. Fischer,[10] but in the early 1990's carbene chemistry entered a new era with the first crystallisation of *N*-heterocyclic carbenes (NHC) by Arduengo.

N-heterocyclic carbenes have since then become popular ligands in organometallic and inorganic coordination chemistry. Because of their specific coordination chemistry, *N*-heterocyclic carbenes both stabilise and activate metal centers. In 1992/93 it was noted that NHC and phosphines are similar in terms of ligand properties, metal complex synthesis and coordination.[7]

[1] Noyori, R. Asymmetric catalysis: science and opportunities (Nobel Lecture) *Angew. Chem. Int. Ed.* **2002**, *41*(12), 2008-2022
[2] Knowles, W. S. Asymmetric hydrogenations (Nobel Lecture) *Angew. Chem. Int. Ed.* **2002**, *41*(12), 1998-2007
[3] Sharpless, K. B. Searching for new reactivity (Nobel Lecture) *Angew. Chem. Int. Ed.* **2002**, *41*(12), 2024-2032
[4] Chauvin, Y. Olefin metathesis: the early days (Nobel Lecture) *Angew. Chem. Int. Ed.* **2002**, *45*(23), 3741-3747
[5] Schrock, R. R.. Multiple metal-carbon bonds for catalytic metathesis reactions (Nobel Lecture) *Angew. Chem. Int. Ed.* **2002**, *45*(23), 3748-3759
[6] Grubbs, R. H. Olefin-metathesis catalysts for the preparation of molecules and materials (Nobel Lecture) *Angew. Chem. Int. Ed.* **2002**, *45*(23), 3760-3765
[7] Herrmann, W. A.; *Angew. Chem. Int. Ed.,* **2002**, *41*, 1290-1309

Self aggregation is a theme of everyday chemistry, wet soft solids like shampoo or toothpaste being well known examples.[8] Low molecular mass gelators that form aggregates are investigated as counterparts to formally used polymers. These amphiphilic molecules form aggregates in a solvent through forces that are not covalent bonds like in polymers, which make them more interesting. Recently, the groups of Dötz and Nolte were able to combine Fischer carbene complexes and low molecular mass gelators.[9]

NHC incorporated in a self-aggregating molecule should be the next logical step in order to combine amphiphilic structures and carbene chemistry.

[8] Sangeetha N. M., Maitra; U. *Chem. Soc. Rev.*, **2005**, *34*, 821-836
[9] Bühler, G., Feiters, M. C., Nolte, R. J. M., Dötz, K. H. *Angew. Chem. Int. Ed.* **2003**, *42*, 2494-2497

Background

II Background

II.1 Types of Carbenes

Transition metal carbene complexes or alkylidene complexes are described as molecules bearing one carbon atom connected to a metal by a double bond. These molecules will be then classified according to the metal, its oxidation state, and the substituents at the carbene center as either *Fischer*-Type[10,11] or *Schrock*-Type[12] carbenes. (Figure 1)

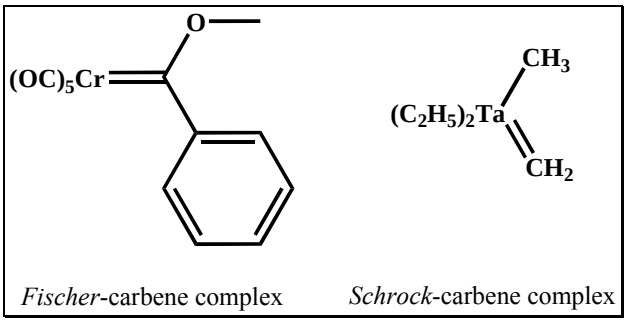


Figure 1: Examples of *Fischer* type and *Schrock* type carbene complexes.

To introduce the carbene complexes theme, and to understand the expectations from *N*-heterocyclic carbenes, a brief description of Fischer and Schrock carbenes is necessary. The molecular orbital diagrams in Figure 2 depict the bonding of Fischer (I), Schrock (II) and *N*-heterocyclic (III) carbenes. The will to have a NHC as carbene centre, instead of a Fischer type one, comes from the versatility it offers, such as a larger scope of metals to coordinate to (see II.1.3).

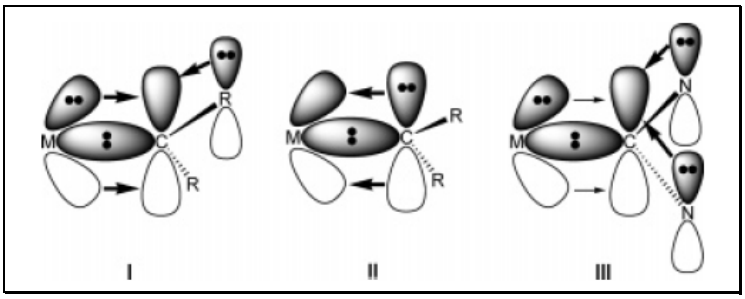


Figure 2: Molecular orbital diagrams of a Fischer (**I**), Schrock (**II**), and *N*-heterocyclic (**III**) carbene complex.

[10] Fischer, E. O.; Maasböl, O.; *Angew. Chem.* **1964**, *76*, 645.
[11] Fischer, E. O.; Maasböl, A.; *Angew. Chem.* **1973**, *85*, 618.
[12] Schrock, R. R.; *Acc. Chem. Res.* **1979**, *12*, 98.

In Fischer type carbenes low oxidation state metals are involved, resulting in high electron density on the d shell. A poor back donation from the metal to the carbene tends to lead to unstable carbenes. Ficher carbene complexes have an electrophilic character that can be seen with its resonance structures (see II.1). Contrary to this, the Schrock type carbenes are complexed to high oxidation level metals, meaning a lack of population on the d orbitals at the metal. The carbene carbon atom involves its p-electron shell in order to fill the d orbitals of the metal and form a bond. The study of its resonance structures leads the understanding of the nucleophilic character of this carbene (see II.1.2). The case of NHCs is explained in detail in section II.1.3.[13]

II.1.1 Fischer type carbene complexes

The first Fischer carbene complex was published in 1964 by E. O. Fischer und A. Maasböl.[10,11] Fischer carbenes form a σ bond to the metal and have an empty p orbital to accept electron density. The Fischer carbene carbon p orbital needs significant π-donating contribution from both metal and substituents. This feature is very important for the stability of these carbene complexes which is relayed by the experience that complexes with poor π-donor metals (early transition/high oxidation state) are unstable. On the other hand, complexes of late transition/low oxidation state metals tend to be significantly more stable. This specific structure gives the carbene carbon atom an electrophilic character. This can be rationalised with the mesomeric structures expressed in Figure 3.

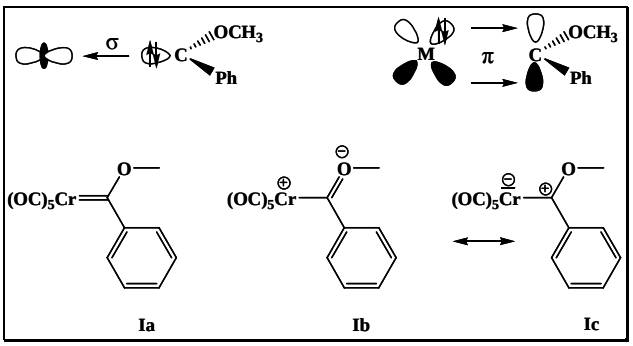


Figure 3: Possible Fischer carbene resonance structures.

The structure **Ic** (Figure 3) shows how the carbon center can be attacked by nucleophilic substances. It could be compared to carboxylic systems like esters or amides.

[13] Garrison, J. C ;. Youngs, W. J.; Chem. Rev. **2005**; *3976*.

This grew out R. Hoffmann's isolobal principle, which compares the frontier molecular orbitals from Fischer carbene complexes and carboxylic systems and states them as similar in terms of energy and symmetry.[14]

II.1.1.1 Reactivity

An interesting and most important feature of Fischer carbene complexes is the electrophilicity of the carbene carbon. This carbon behaves like a carbonyle type carbon, ideally positioned towards nucleophilic attack (Figure 4: **I**). The proton on the α position carbon has an enhanced acidity and can be deprotonated by a base, allowing modification of the side chain by reaction with an electrophile (Figure 4: **II**). Electrophiles can also react with heteroatoms (O, N) directly linked to the carbene (Figure 4: **III**). Finally carbonyl groups in the coligand sphere can undergo ligand exchange (Figure 4: **IV**).

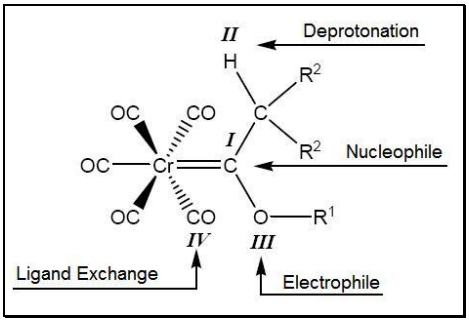


Figure 4: Reactivity of Fischer carbenes.

II.1.1.2 Synthesis of Fischer Carbenes

Among the several synthetic ways to prepare Fischer carbene complexes, the most widely used and still the easiest is the one originally reported by Fischer. It involves attack of an organolithium reagent on chromium hexacarbonyl producing an acylmetallate intermediate followed by alkylation on the oxygen atom. This preparation can be performed on open ended scale since most complexes are solid and can be purified by crystallisation. (Figure 5, *Synthetic Route A*)

[14] a) R. Hoffmann, *Science* **1981**, *211*, 995; b) R. Hoffmann, *Angew. Chem.* **1982**, *94*, 725; F. G. A. Stone, *Angew. Chem. Int. Ed.* **1984**, *96*, 85-96

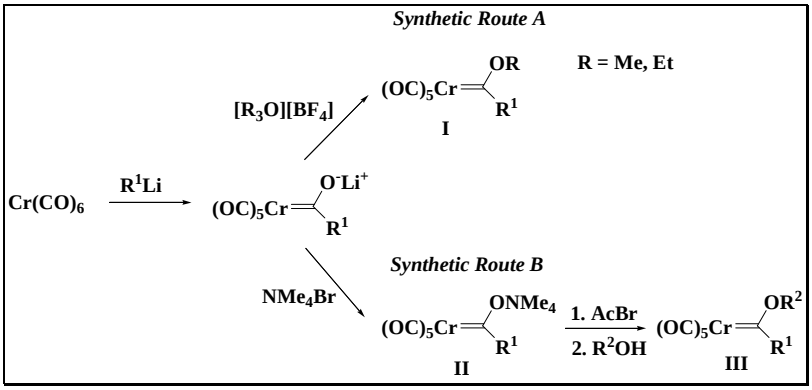


Figure 5: Original synthetic route to Fischer carbene complexes.

The identification of the fractions from the chromatography can be done on the basis of their color. The color of the complexes bearing alkoxy groups tend to be related to the hybridisation of the carbon atom connected to the carbene centre. Alkoxy carbene complexes with sp^3-carbons usually are yellow, those with sp^2-carbons are normally red and those with sp-hybridised carbon substituents have invariably an intense purple/black color. (Figure 6)

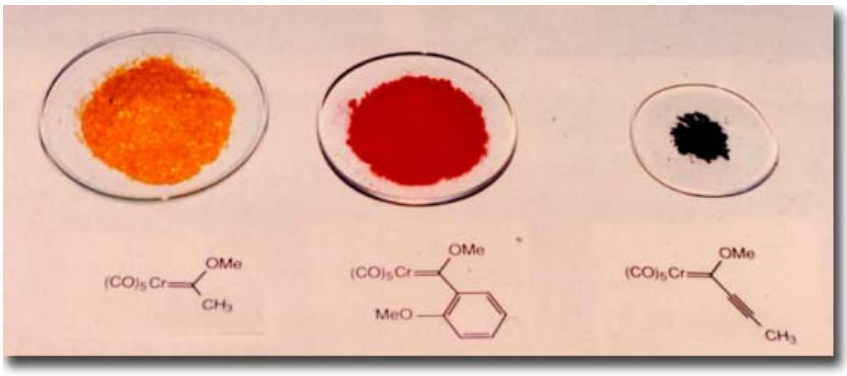


Figure 6: Color change depending on hybrididsation level.[15]

This class of reagents can be used in a large variety of reactions: benzannulation of unsaturated complexes with alkynes,[16] cyclopropanations, [2 + 2] cycloadditions, [3 + 2] cycloadditions, [4 + 1] cycloadditions, Ene reactions, Diels-Alder reaction,[17] Michael additions and aldol reactions[18] among others. It makes these reagents one of the most versatile reagent in the organometallic chemistry, which is reported in several reviews.[19,20,21]

[15] http://www.chemistry.msu.edu/faculty/wulff/myweb26/RESEARCH/carbenes.htm
[16] Doetz, K. H.; Stendel, J. Jr.; in Astruc D;; *Modern Arene Chemistry*, VCH-Wiley, Weinheim, **2002**, 250-296
[17] Doetz, K. H.; Boettcher, D.; Jendro, M.; *Inorg. Chim. Acta*, **1994**, *222*, 291-8.
[18] Wulff, W. D.; Anderson, B. A.; Toole, A. J.; Xu, Y.-C.; *Inorg. Chim. Acta* **1994**, *220*, 215-31
[19] a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreißl, F. R.; Schubert, M.; Weiss, K.; Transition Metal Carbene Complexes, VCH Weinheim, **1983**; b) Dötz, K. H.; *Angew. Chem. Int. Ed.*, **1984**, *96*, 573
[20] a) Wulff, W. D. in *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press : Greenwich, Conn, **1989**; Vol. 1; b) Wulff, W. D., in "*Comprehensive Organic Synthesis*", Trost, B. M.; Fleming, I., Eds., Pergamon Press, **1990**, Vol 5; c) Wulff, W. D. in *Comprehensive*

Another way to prepare Fischer carbene complexes is provided by the Semmelhack/Hegedus[22] route (Figure 7). This route is more preparative demanding and needs harder conditions to achieve the formation of the acyl metallate. Here, the chromium hexacarbonyl is reduced by the use of C_8K to dipotassium chromate(II) intermediate, which reacts with an acid chloride to give the acyl chromate. Finally, the reaction of the acyl chromate with e.g. methyl Meerwein salt yields the Fischer carbene complex.

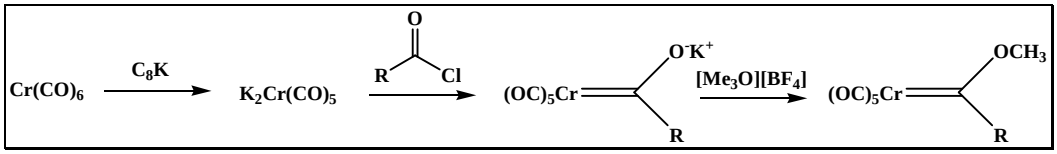


Figure 7: Semmelhack-Hegedus route to Fischer carbene complexes.

II.1.2 Schrock type carbene complexes

Schrock carbenes tend to bind well with early transition metals in high oxidation states. The high oxidation state will limitate the population of the d_π orbital on the metal, which leaves the path free for better π -donation from the filled p orbital of the carbene carbon atom to the d_π orbital of the metal. The repulsive effects inhibit the strength of the π-donation and overall lead to the destabilization of the metal-carbene carbon bond. Good substituents for Schrock carbene ligands are groups that are not π -donors such as alkyl groups. The structure **IIb** (Figure 8) shows the nucleophilicity of the carbon center in the carbene ligand.

Organometallic Chemistry II, Abel, E. W.; Stone, R. G. A. Wilkinson, G., Eds.; Pergamon Press, **1995**, *Vol. 12*, 469; d) Wulff, W. D., *Organometallics*, **1998**, *17*, 3116.

[21] a) Hegedus, L. S., *Tetrahedron*, **1997**, *53*, 4105; b) de Meijer, A.; Schirmer, H.; Duetsch, M., *Angew. Chem. Int. Ed. Engl*., **2000**, *39*, 3964. c) Dötz, K. H.; Tomuschat, P.; *Chem. Soc. Rev*., **1999**, *28* 187; d) Herndon, J. W.; *Coord. Chem. Rev*., **1999**, *181*, 177; e) "Metal Carbenes in Organic Synthesis", Dörwald, F. Z.; Wiley-VCH, **1999**; f) Bernasconi, C. F., *Chem. Soc. Rev*., **1997**, *26*, 299; g) M. Doyle in "Comprehensive Organometallic Chemistry II", E. W. Abel; F. G. A. Stone; G. Wilkinson, Eds., Pergamon Press, 1995, Vol 12; h) Harvey, D. F.; Sigano, D. M., *Chem. Rev*., **1996**, *96*, 271

[22] a) Öfele, K.; *Angew. Chem*. **1968**, *80*, 1032; b) Rees, C. W.; von Angerer, E.; *J. Chem. Soc., Chem. Commun.* **1972**, 420; c) Semmelhack, M. F.; Lee, G. R.; *Organometallics* **1987**, *6*, 1839; d) Imwinklried, R.; Hegedus, L. S.; *Organometallics* **1988**, *7*, 702; e) Schwindt, M. A.; Lejon, T.; Hegedus, L. S.; *Organometallics* **1990**, *9*, 2814; f) Schwindt, M. A.; Miller, J. R.; Hegedus, L. S.; *J. Organomet. Chem.* **1991**, *413*, 143

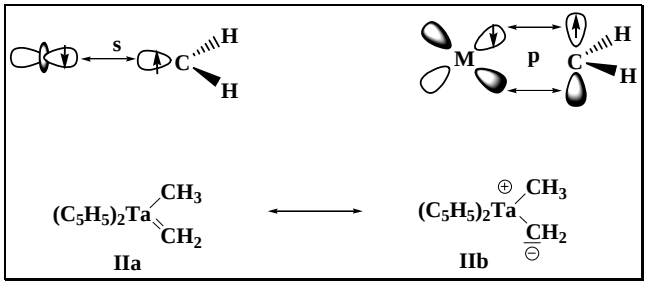


Figure 8: Resonance form for Schrock carbene complexes.

With regard to the isolobal principle these carbene complexes are similar to ylides/ylenes and represent an alternative to Wittig reagents.[23] An example for these structures is the Tebbe reagent[24], it is used in the methylenation of various carboxylic products like aldehydes, esters or amides. The methyl transfer reagent in this case is the Schrock type carbene $Cp_2Ti{=}CH_2$.

II.1.3 *N*-Heterocyclic Carbenes

II.1.3.1 Structure

Carbenes are neutral species, with six electrons in their valence shell[25], and are able to adopt two different geometries: linear or bent. The linear *sp*-hybridized carbene has its two p_x, p_y orbitals degenerated (Figure 9). This degeneracy can be broken when the carbene undergoes any external pressure that forces it to bend. This force will not affect the orbital p_y, which will stay unchanged, but the orbital p_x is stabilised and has its energy lowered, to get a more s-type character (Figure 9). Consequently the p_x will be known as σ and p_y as π orbital. The two lone electrons could form four possible electronic configurations: with one electron in both σ and p_π orbital assigning the carbene a triplet state ($^3B_1$), or with the pair located in either the σ ($^1A_1$) or the p_π ($^1A_1$) orbital, resulting in a singlet state. One last case is also possible with one electron in the σ and one in the p_π, as for $^3B_1$ state, but with antiparallel spins, which makes it a singlet state ($^1B_1$). (Figure 10)

[23] Wittig, G.; Geißler, G.; *Liebigs Ann. Chem.* **1953**, *44*, 580.
[24] Tebbe, F. N.; Parsall, G. W.; Reddy, G. S.; *J. Am. Chem. Soc.* **1978**, *100*, 3611.
[25] Bourrissou, D.; Guerret, O.; Gabbaï F, P.; Bertrand, G.; *Chem. Rev.,* **2000**, *100*, 39.

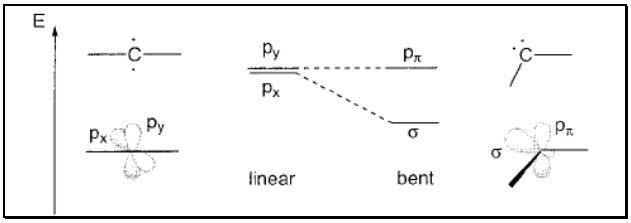


Figure 9: Relationship between the carbene bond angle and the nature of the frontier orbitals.

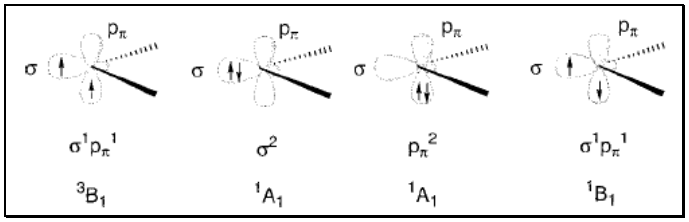


Figure 10: Electronic configurations of carbenes.

The reactivity of carbenes can be understood because of their ground state spin multiplicity, a singlet state carbene with a free orbital and one filled with a pair of electrons can be seen as amphiphilic, potentially able to be attacked by either a nucleophile or an electrophile.[26] With a single electron in each orbital, triplet state carbenes are regarded as di-radicals. The ground state multiplicity is related to the orbital's energy; Hoffmann[27] showed that the bigger the gap between the σ and p_π orbital is, the more the carbene will be in singlet state configuration, while a low energy gap will induce a triplet state carbene. With these informations, electronic and steric effects can now be analysed.

II.1.3.2 Electronic Effects

II.1.3.2.1 Inductive Effects

The electronic properties of a substituent will affect the energy gap between the σ and p_π orbitals. As understood previously the more the gap is increasing the more the singlet state is favored, and opposite the more the energy difference is diminished the more the carbene will adopt a triplet state. As recently reconfirmed[28], σ electron donating groups will reduce the energy gap thus facilitating the triplet state, while an σ electron withdrawing group will stabilise the σ orbital, enhancing its *s* character, and leave the p_π unchanged. In this case, the energy gap between the two orbitals is then increased favouring a singlet state carbene.

[26] Schuster, G. B.; *Adv. Phys. Org. Chem.* **1986**, *22*, 311.
[27] Gleiter, R.; Hoffmann, R.; *J. Am. Chem. Soc.*, **1968**, *90*, 1475.
[28] Irikura, K. I.; Goddard, W. A. III; Beauchamp, J. L.; *J. Am.Chem. Soc.* **1992**, *114*, 48.

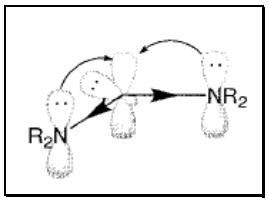


Figure 11: Electronic effects in diaminocarbene.

II.1.3.2.2 Mesomeric Effects

As with inductive effects, substituents with mesomeric effects can affect the state of the carbene as well.[29] π electron donating groups, such as halides, amine derivatives or phosphines are predicted to give bent structures, and π electron withdrawing groups (e.g. boron derivatives, silicon derivatives) are meant to give linear or quasi-linear structures.[1,30] The π orbitals will then interact and as seen in Figure 12, a π donating group will stabilise the p_π, with its lone pair, forming two new molecular orbitals, a bonding one and a non-bonding one, increasing the gap between the HOMO and LUMO orbitals, i.e. favouring the singlet state.

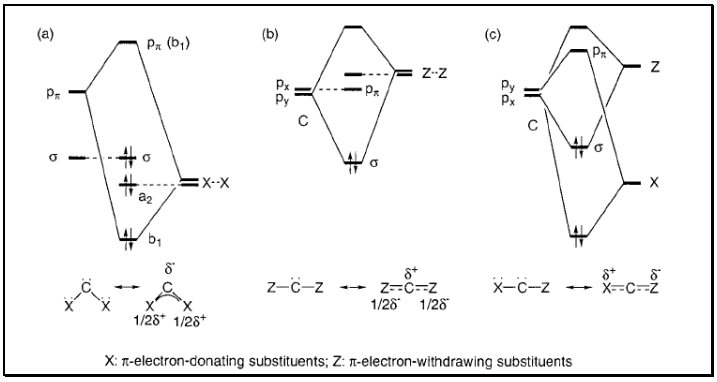


Figure 12: Perturbation orbital diagrams showing the influence of the mesomeric effects.

In the case of a π withdrawing group, interaction takes place at p_y orbital, perpendicular to the plan, leaving the p_x unchanged and then breaking the $p_{x,y}$ degeneracy, leading to a singlet state.

[29] a) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W.; *J. Am. Chem.Soc.* **1968**, *90*, 1485; b) Baird, N. C.; Taylor, K. F.; *J. Am. Chem. Soc.* **1978**, *100*, 1333.
[30] a) Schoeller, W. W.; *J. Chem. Soc., Chem. Commun.* **1980**, 124; b) Pauling, L.; *J. Chem. Soc., Chem. Commun.* **1980**, 688.

II.1.3.3 Steric Effects

Steric congestion around the carbene center is known to stabilise this center,[31] but the more hindered it is, the more it broadens the angle around the carbene carbon, therefore favouring the triplet state (Figure 13).

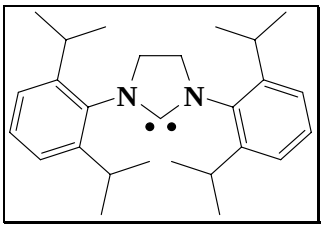


Figure 13: 1,3-Bis(2,6-diisopropylphenyl)-imidazolidin-2-ylidene. (SIPr).

It is understandable that a singlet state carbene is easier to stabilise than a triplet one. The carbon has naturally three out of four possibilities to acquire a singlet state. Then, combining the desired electronic effects previously described lead to the desired carbene. Imidazole provides two σ electron withdrawing groups and at the same time two π electron donating groups, in place of the nitrogens. The closed and rigid five-membered ring provides a good obstacle for preventing the linearisation of the carbene, even for bulky substituents. Finally, the delocalisation in the aromatic system makes the N-heterocyclic carbene a well-stabilised conjugated base. As a conclusion NHCs are stable and easy to handle carbenes.

II.1.3.4 *N*-Heterocyclic Carbenes and their metal coordination

II.1.3.4.1 Reactivity

In 1970, Wanzlick showed that imidazolium salts could be deprotonated by using a highly hindered base (e.g. KO^{t}Bu).[32] In 1991, Arduengo managed to obtain the first crystalline free carbene structure, using two adamantyl groups as substituents on the nitrogens[33] (Figure 14). *N*-Heterocyclic carbenes have been of popular interest because of their specific coordination chemistry (they both stabilise and activate metal centers).

[31] Gilbert, B. C.; Griller, D.; Nazran; A. S. *J. Org. Chem.*, **1985**, *50*, 4738.
[32] Wanzlick, H. W.; Schönherr, H. J.; *Liebigs Ann. Chem.*, **1970**, *731*, 176.
[33] Arduengo, A. J. III; Harlow R. L.; Kline M.; *J. Am. Chem. Soc.* **1991**, *113*, 361.

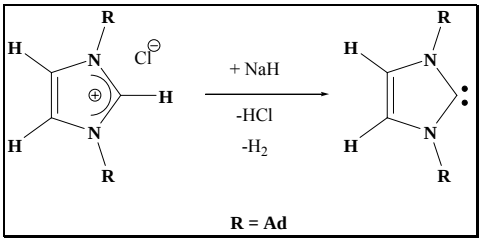


Figure 14: The first stable crystalline structure with adamantyl as substituent on nitrogens.

NHCs multiple features, like their lower toxicity than phosphines, make them the ligands of choice for catalysis. They are easily removable from organic reaction mixtures and no excess of ligand is needed. Some ligands are air and room temperature stable, which makes them easy to handle. Electron rich phosphanes and carbenes are similar in terms of metal coordination, ligand properties and metal complex synthesis, but in terms of bonding NHCs are superior to phosphines.[34] The wide range of metals that they can coordinate to, provide great opportunities. The carbon metal bond is longer compared to any of the Fischer or Schrock type carbenes, because of their low backbonding, giving them the possibility to rotate around the metal carbene-carbon bond.[35] Back donation from the metal to the ligand is believed to be minor;[36] however, recent theoretical and structural evidence[37,38] has suggested that π back-donation is larger than previously admitted. The degree of back-donation is dependent upon the metal in question. While the degree of π-back donation may come to a question, it is generally accepted that it is smaller than the π back-donation of Fischer carbenes.

II.1.3.4.2 Formation

Nowadays some *N*-heterocyclic precursors are commercially available, essentially because they are easily accessible. It all started in the early 1960's when Wanzlick realised that the stability of carbenes could be enhanced by the presence of amino substituents. His attempt to synthesise a 1,3-diphenylimidazolidin-2-ylidene by thermal elimination of chloroform unfortunately yielded only the dimeric electron-rich olefin.[39] (Figure 15)

[34] Huang, I.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P.; *Organometallics* **1999**, *18*, 2370.
[35] Herrmann, W. A.; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.
[36] Green, J. C.; Scurr, R. G.; Arnold, P. L.; Cloke, F. G. N.; *Chem. Comm.* **1997**, *20*, 1963.
[37] Nemcsok, D.; Wichmann, K.; Frenking, G.; *Organometallics* **2004**, *23*, 3640.
[38] a) Frison, G.; Sevin, A.; *J. Phys. Chem. A* **1999**, *103*, 10998; b) Frison, G.; Sevin, A.; *J. Organomet. Chem.* **2002**, *643-644*, 105; c) Frison, G.; Sevin, A.; *J. Chem. Soc., Perkin Trans. 2* **2002**, 1692.
[39] a) Wanzlick, H. W.; Kleiner, H. J.; *Angew. Chem. Int. Ed.*. **1961**, *73*, 493; b) Wanzlick, H. W.; *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 75; c) Wanzlick, H. W.; Esser, F.; Kleiner, H. J.; *Chem. Ber.* **1963**, *96*, 1208.

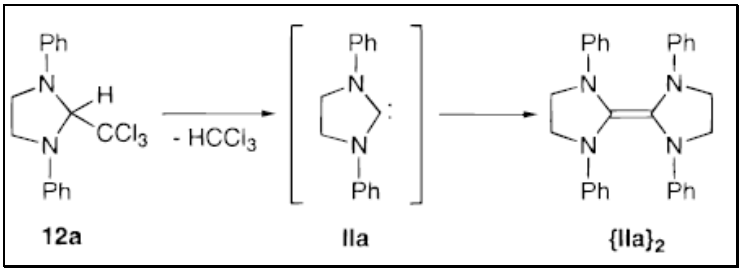


Figure 15: Wanzlick's first attempt to synthesise a free *N*-heterocyclic carbene.

A decade later, Wanzlick again showed that imidazolium salts **13a**,**b** (Figure 16) could be deprotonated by potassium *tert*-butoxide to afford the corresponding imidazol-2-ylidenes **IIIa**,**b** (Figure 16).[40] Following this work, Arduengo was able to obtain the first crystal structure of a stable carbene,[33] obtained after deprotonating 1,3-di(1-adamantyl)imidazolium chloride with sodium or potassium hydride in the presence of catalytic amounts of KO^{t}Bu.

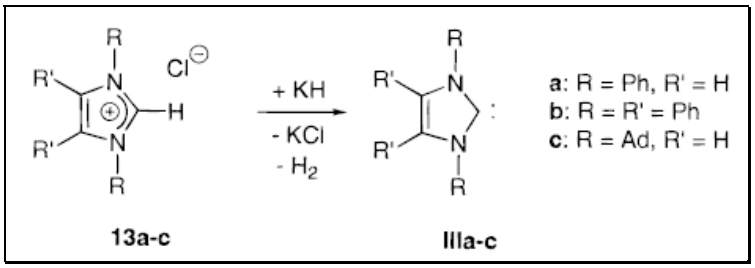


Figure 16: Synthesis of the first isolable free carbenes.

An easy access to these carbene precursors is provided by the condensation of glyoxal, two equivalents of a primary amine and formaldehyde to yield a symmetrical imidazolium salt. An unsymmetrical variation could be obtained with two different amines, or in a successive alkylation of the imidazole anion.[41] These precursors could be deprotonated using different methods. Widely used is the "ammonia method" described first by Herrmann[42] involving liquid ammonia with or without amines or polar aprotic solvents. A large variety of deprotonating agent can be used from metal hydrides to carboxylates, amides and alkoxides and from low temperature to 0°C. (Figure 17)

[40] a) Wanzlick, H. W.; Schönherr, H. J. *Liebigs Ann. Chem.* **1970**, *731*, 176. b) Schönherr, H. J.; Wanzlick, H. W. *Chem. Ber.* **1970**, *103*, 1037. c) Similar results were obtained in the triazole series: Walentowski, R.; Wanzlick, H. W. *Z. Naturforsch.* **1970**, *25b*, 1421.
[41] a) Wallach, J.; *Ber. Dtsch. Chem. Ges.,* **1925**, *15*, 645; b) Gridnev, A. A.; Mihaltseva, I. M.; *Synth. Commun.* **1994**, *24*, 1547; c) Arduengo III, A., J., (E. I. Du Pont de Nemours & Compagny), US 5.077.414 A2, **1992** ; WO 91/14678 [*Chem. Abstr.* **1992**, *116*, 106289e].
[42] Herrmann, W. A.; Köcher, C.; (Hoechst AG), DE 1961090.8 A1, **1996** ; EP 0721950 ; WO 97/34875 [*Chem. Abstr.* **1997**, *127*, 318962v].

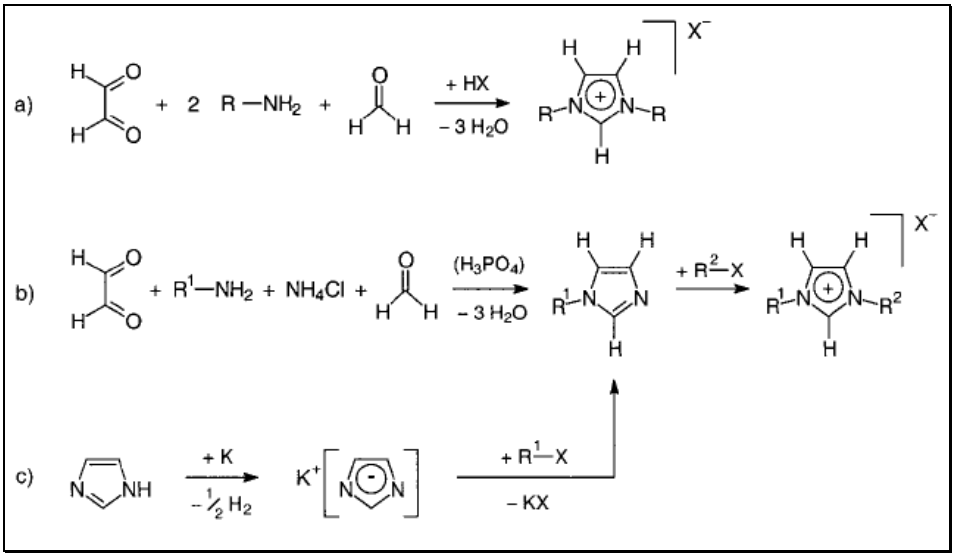


Figure 17: Different access to NHC carbene precursors.

In 1993, Kuhn developed another interesting approach relying on the reduction of imidazol-2(3H)-thiones with potassium in boiling THF.[43] (Figure 18)

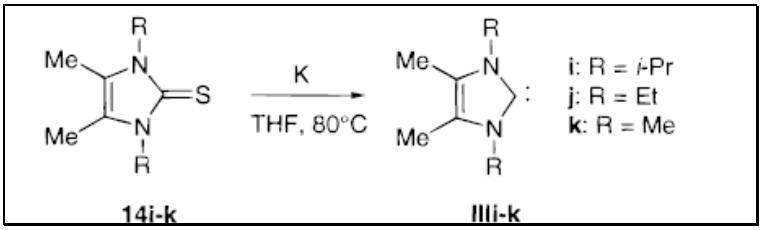


Figure 18: Reductive approach to NHCs by reduction of imidazole-2-thiones.

Finally , Enders reported in 1995 the first commercially available NHC carbene. The 1,2,4-triazol-5-ylidene IVa (Figure 19) is obtained by thermal elimination (80 °C) of methanol in vacuo (0.1 mbar) from 5-methoxy-1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazole **15a** (Figure 19) in quantitative yield.[44]

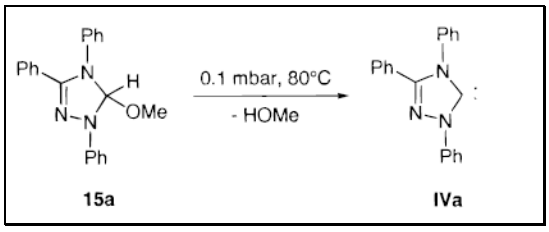


Figure 19: The first commercially available *N*-heterocyclic carbene.

[43] Kuhn, N.; Kratz, T.; *Synthesis* **1993**, 561.
[44] Enders, D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J. H.;Melder, J. P.; Ebel, K.; Brode, S.; *Angew. Chem., Int. Ed. Engl.***1995**, *34*, 1021.

Wang and Lin first demonstrated that the use of Ag_2O was a very powerful way to form a useful class of transfer reagents.[45]. The silver NHC carbene complexes could be obtained in high yields and transferred to different metals such as gold or palladium in good yields.

Examples of the variety of the metals that can be attached to NHCs are shown in Figure 20.

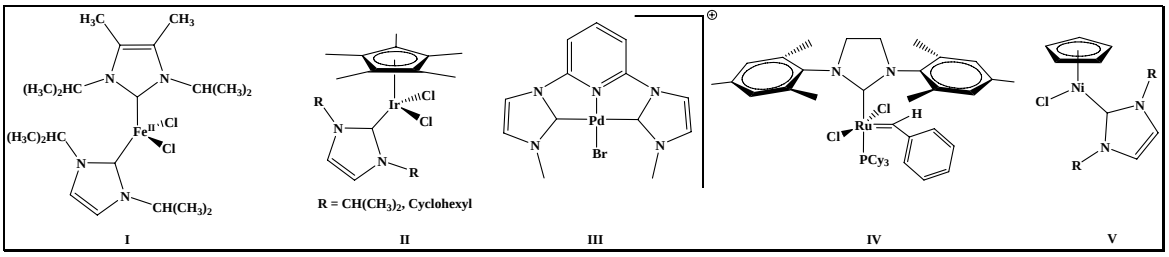


Figure 20: Variety of metal fragments accepted by NHC.

A large scope of metals can be complexed with NHCs, including iron, iridium, palladium, ruthenium and nickel.[46] Carbon-hydrogen bonds can be activated with an iridium complex (Figure 20, II).[47] An iron complex (Figure 20, I) can control atom transfer radical polymerisation (ATRP).[48] Palladium complexes are used in cross-coupling chemistry (Figure 20, III),[49] ruthenium type catalysts of the latest generation are used for olefin methatesis (Figure 20, IV).[50]

II.2 Gels

II.2.1 Introduction

The area of self aggregating molecules has kept on growing since it became known that they can be involved in various areas, such as drug delivery substances[51,52] or tissue

[45] Wang, H. M. J.; Lin, I. J. B.; *Organometallics*, **1998**, *17*, 972.
[46] a) Voges, M. H.; Romming, C.; Tilset, M.; *Organometallics* **1999**, *18*, 529; b) Abernathy, C. D.; Cowley, A. H.; Jones, R. A.; *J. Organomet. Chem.*, **2000**, *596*, 3.
[47] a) Prinz, M.; Grosche, M.; Herdtweck, E.; Herrmann, W. A.; *Organometallics,* **2000**, *19*,1692; b) Prinz, M. *Dissertation*,Technische Universität Müchen, **2001**.
[48] Louie, J.; Grubbs, R. H.; *Chem. Commun.,* **2000**, 1479.
[49] a) Peris, E.; Loch, J. A.; Mata, J.; Crabtree, R. H.; *Chem. Commun.* **2001**, 210; b) Loch, J. A.; Crabtree, R. H.; *Pure Appl. Chem.* **2001**, *73*, 119.
[50] a) Chatterjee, A. K.; Grubbs, R. H.; *Org. Lett.*, **1999**, *1*, 1751; b) Chatterjee, A. K.; Morgan, J. P.; Scholl, M.; Grubbs, R. H.; *J. Am. Chem. Soc.*, **2000**, *122*, 3783; c) Trnka, T.; Grubbs, R. H.; *Acc. Chem. Res.*, **2001**, *34*,18.
[51] Xing, B.; Yu, C. W.; Chow, K. H.; Ho, P. L.; Fu, D.; Xu, B. *J.Am. Chem. Soc.* **2002**, *124*, 14846.
[52] Tiller, J. C.; *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 3072

engineering.[53] In the case of biological studies, the problem of non-degradation of polymers is always present, but gelator molecules can avoid this problem while their aggregation consists of non convalent bonding (hydrogen bonding, π-stacking, van-der-Waals interaction), and therefore are more easily degradable. Flory defined a gel as "a colloidal dispersion that behaves itself as a solid, during the time scale of the experiment".[54] A gel is formed when a known amount of substance (0.1-10 wt %) is solved in, most of the cases, a hot solvent and while cooling adopt a macroscopic structure that leaves the complete volume of solvent encaged in the newly built gel network. A simple test for gels is to turn the vial upside down and see if the gelated solvent stays on top (Figure 21).

Figure 21: Upside down test for gelation.

II.2.1.1 Primary structure

The gelation process is thought to arise from nanostructure aggregation and can be assimilated to protein's primary, secondary and tertiary structure. As a reminder, protein primary structure is a succession of amino acids where the terminal amine functionality is not involved in a peptide bonding. Gelation itself is the delicate art of the balance between hydrophilic and hydrophobic interactions, the will of solvation and at the same time of aggregation. While hydrogen bonding can be the driving force in most gelation cases, they will not help in an aqueous medium where aliphatic interaction can take the duty back, but salt interactions or metal-metal interactions can also help.

[53] Lee, K. Y.; Mooney, D. J.; *Chem. Rev.* **2001**, *101*, 1869.
[54] Flory, P. J.; *Faraday Discuss.* **1974**, *57*, 7.

II.2.1.2 Secondary structure

The secondary structure is defined as the morphology of the aggregates which can be shapped as micelles, vesicles, fibers, ribbons or sheets. Compared to this, the secondary structure of proteins is caused by saturation of all hydrogen bondings. A peptide will fold itself to obtain the most favoured structure by using hydrogen bonding. Micelles are fluid species formed at the critical micelles concentration (CMC) which depends on the structure of the molecule. Above this concentration point, the micelles might form ellipsoidal micelles and further on rods. Rodlike monomer functionalised with complementary donor and acceptor groups on opposite sides and chemically different surfaces first assembles into tapes via recognition of the donor and acceptor groups. The chirality is then translated into the twist of the tape, resulting in different affinities for the solvent. This leads to a helical curvature of the tape. Several models have been submitted to explain the formation of the secondary structure.[55,56,57,58] Bagchi and Nandi,[58] as an example, argued that the formation of a helical structure in mono- or bilayers is driven by interactions of chiral centers. Their calculations of the effective pair potential between two molecules showed that the minimum energy conformation in the case of racemic pairs leads to a nearly parallel alignment. For an enantiomeric pair, the repulsion would lead to a twist in the alignment up to 45° provoking a helical structure. Those calculations support and explain the observed results.

II.2.1.3 Tertiary structure

The tertiary structure is based on the interaction between the formed aggregates, and determines if a gel is formed or not. Long flexible fibers are physically more suited to entrap solvents than small ones.[54] The tertiary structure arises from the interaction between the fibers forming entangled fibers and interconnected networks. It can be again compared to proteins where the tertiary and quaternary structures result from the fitting of the fibers together. According to Pozzo et al. the most important factor in the gelation process is the cooling rate. Depending upon the driving force of the crystallization, a gel or a solid phase in equilibrium with the liquid solvent is obtained.[59] From a very low cooling rate (0.005°C/min), one would

[55] Aggeli, A.; Nyrkova, I. A.; Bell, M.; Harding, R.; Carrick, L.; McLeish, T. C. B.; Semenov, A. N.; Boden, N.; *Proc. Natl. Acad. Sci.* **2001**, *98*, 11857.
[56] Israelachvili, J. N.; *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: New York, **1991**.
[57] Schnur, J. M.; *Science* **1993**, *262*, 1669.
[58] Nandi, N.; Bagchi, B.; *J. Am. Chem. Soc.* **1996**, *118*, 11208.
[59] Lescanne, M.; Colin, A.; Mondain-Monval, O.; Fages, F.; Pozzo, J. L.; *Langmuir* **2003**, *19*, 2013.

obtain a mixture between solvent, gelified parts and solid parts, while with a faster rate up to 20°C/min a gelation test can be successful with a complete homogeneous structure. (Figure 22)

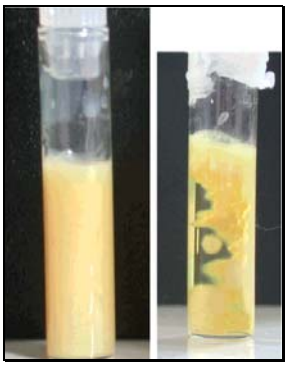


Figure 22: Visible effect of the cooling rate on the degree of gelation (only part of the solvent is trapped, right photo).

In another work, Liu investigated the effect of an additive to the gelation process.[60] The study focused on ethylene/vinyl acetate copolymer (EVACP) as additive and showed not only that it helps to gel a solvent, but also permits to understand part of the mechanism of gelation, concluding that the tertiary structure relies on crystallographic mismatch branching.

II.2.2 Examples of Hydrogelators

In order to understand which directions can be taken in the investigation it is good to know what motifs can generally promote gelation. As said earlier, the possibility to have gelation is narrowly linked to the ability of the molecule to balance between precipitation or crystallisation and solvation. In water, structures bearing a hydrophilic group, which provide solubility, and a hydrophobic group, promoting aggregation, are likely to be hydrogelators. So far, it is admitted that not only one but several types of construction motifs can lead to a gelator structure. Amphiphiles, bolaamphiphiles, sugar or steroid based systems are the most common gelators structures.

[60] Liu, X. Y.; Sawant, P. D.; Tan, W. B.; Noor, I. B. M.; Pramesti, C.; Chen, B. H.; *J. Am. Chem. Soc.* **2002**, *124*, 15055.

II.2.2.1 Amphiphiles

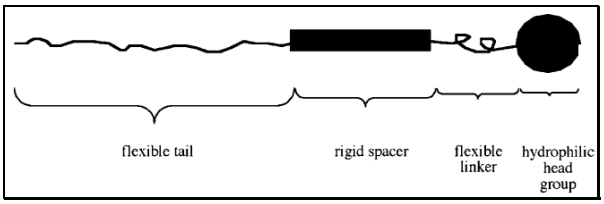


Figure 23: Description of an amphiphilic molecule.

In the early works from Kutinake which were focused on describing the morphology of amphiphiles that would lead to gels, it is shown that the aggregate morphology could be controlled by appropriated designed structures.[61] According to Kutinake's group, the basic structure contains a hydrophilic head group, a rigid segment and a flexible tail. (Figure 23) The flexible tail is usually an alkyl chain but functional groups like vinyl groups and esters have also been mentioned. Starting the work with diphenylazomethine as rigid segment, they first investigated the influence of the flexible tail length. They stated that molecules bearing up to C_6 chain length would not form aggregates, while those bearing seven to more methylene groups would form stable layers. They also found out that a branched tail would not provide aggregation. The investigation next focused on the rigid segment, which they showed to be the second most important factor for the morphology. The diphenyl derivatives studies showed that too much bending is not advantageous for molecular ordering. Following their morphology results: "from pre-rods to rods", they claimed that polyoxoethylene or anionic phosphate are better than ammonium salts as hydrophilic head. As a conclusion they assure that self-assembly is not achieved without flexible tail, rigid segment and hydrophilic group.

II.2.2.2 Bolaamphiphiles (two-headed amphiphiles)

Bolaamphiphiles are named after a South American weapon made of two balls connected by a string called "bola". The main difference between bolaamphiphiles and conventional ones is the aggregate morphology. In the case of long linkers these molecules could fold into two parts and adopt another aggregation modus like micelle, vesicle or lamella. (Figure 24) Shimizu and co-workers have thoroughly explored bolaamphiphiles with

[61] Kunitake, T.; Okahata, Y.; Shimomura, M.; Yasunami, S.;Takarabe, K. *J. Am. Chem. Soc.* **1981**, *103*, 5401

a variety of head groups including nucleotides[62,63,64] amino acids[65,66] and sugars,[67,68] that form both gels and fibers. The short linked bolaamphiphiles show concentration dependency to form gels or fibers.

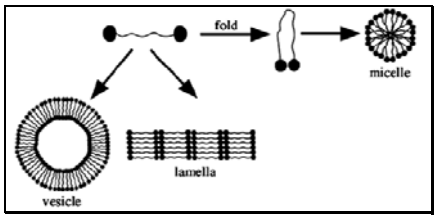


Figure 24: Description of bolaamphiphile aggregation models.

II.2.2.3 Carbohydrates

Similarly, Fuhrhop[69] investigated amide properties on gelation, saying that if the head group of amphiphiles are chiral and contain an amide bond, than helical fibers and gels may be formed as a kind of vesicular or micellar solutions. He reveals that the hydrogen bond between the amide groups is responsible for this rearrangement. The work focused on *n*-alkylgluconamides, using different electron microscopy techniques and differential scanning calorimetry (DSC), they relayed the idea that only chiral substances would produce helical fibers, because the crystallisation range is too slow and would form enantiopolar crystals instead. Shinkai and co.[70] have also worked on sugar derivatives, because the carbohydrate family provides a large variety of skeletons. His work focused on pyranose form from glucose, galactose and mannose, with alkyl chains and aminophenyl moiety. They provide three different interactions, hydrogen bonding, hydrophilic interactions and π-π stacking. Gronwald[71] and Shinkai showed the importance of π-π stacking interaction compared to the role of the nitro group in nitrobenzylidene modified monosaccharides. The glucopyranose derivatives were able to gel polar solvents, such as alcohols and water, where the solvent molecules can play a hydrogen bonding donor and acceptor, revealing therefore the importance of the π-π stacking effect. Finally he compared gluco-, manno- and

[62] Iwaura, R.; Yoshida, K.; Masuda, M.; Ohnishi-Kameyama, M.;Yoshida, M.; Shimizu, T.; *Angew. Chem., Int. Ed.* **2003**,*42*, 1009.
[63] Iwaura, R.; Yoshida, K.; Masuda, M.; Yase, K.; Shimizu, T.; *Chem. Mater.* **2002**, *14*, 3047.
[64] Shimizu, T.; Iwaura, R.; Masuda, M.; Hanada, T.; Yase, K.; *J.Am. Chem. Soc.* **2001**, *123*, 5947.
[65] Kogiso, M.; Hanada, T.; Yase, K.; Shimizu, T.; *Chem. Commun.***1998**, 1791.
[66] Kogiso, M.; Ohnishi, S.; Yase, K.; Masuda, M.; Shimizu, T.; *Langmuir* **1998**, *14*, 4978.
[67] Nakazawa, I.; Masuda, M.; Okada, Y.; Hanada, T.; Yase, K.; Asai,M.; Shimizu, T.; *Langmuir* **1999**, *15*, 4757.
[68] Shimizu, T.; Masuda, M.; *J. Am. Chem. Soc.* **1997**, *119*, 2812.
[69] Fuhrhop, J. H.; Schnieder, P.; Rosenberg, J.; Boekema, E.; *J. Am.*Chem. Soc. **1987**, 109, 3387.
[70] Jung, J. H.; Shinkai, S.; Shimizu, T.; *Chem. Eur. J.* **2002**, *8*, 2684.
[71] Gronwald, O.; Shinkai, S.; *J. Chem. Soc., Perkin Trans. 2,* **2001**, 1933.

galactopyranose hydrogen bonding length[72] to understand why one sugar moiety structure would gelate one solvent and the other one not. He concluded that, as the bonds were not so different from one carbohydrate to another; the difference in gelation should be due to a structural preference in the molecular aggregation.

II.2.2.4 Organometallic gelators

In 2003 the Dötz[9] group successfully synthesised a gelator of a new type. (Figure 25) The insertion of a pentacarbonyl chromium Fischer carbene fragment in place of an amide lead to a new molecule with enhanced organic solvent gelation properties.

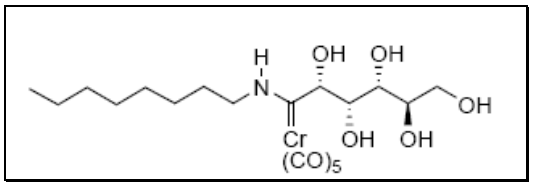


Figure 25: The first organometallic gelator for organic solvents.

Based on a known gelator,[73] *N*-*n*-octyl-D-gluconamide, the metal complex derivative showed to be suited to form gels in dichloromethane, chloroform, benzene and toluene, and also looses at the same time its solubility in water. The interest to synthesise this molecule came from the isolobality of the chromium carbene moiety to the carbonyl group.

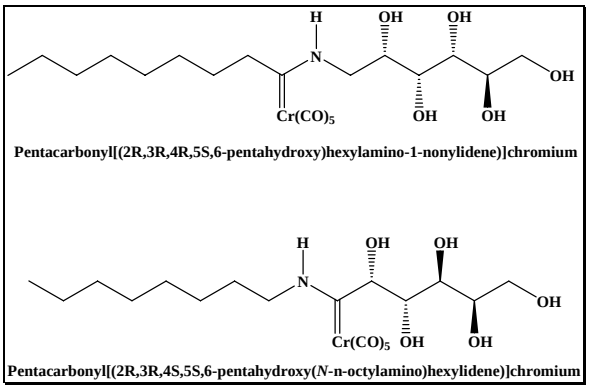


Figure 26: Variations on the orignal gelator.

[72] Yoza, K.; Ono, Y.; Yoshihara, K.; Akao, T.; Shinmori, H.; Takeuchi, M.; Shinkai, S.; Reinhoudt, D. N.; *Chem. Commun.***1998**, 907.
[73] Hafkamp, R. J. H., Feiters, M. C., Nolte, R. J. M.; *J. Org. Chem.***1999**, *64*, 412.

In further studies from the Dötz group, the main structure would undergo different change, like a change of the sugar motif[74] and the position of the nitrogen on the carbene functionality[75]. All of the modifications retained the gelation abilities. (Figure 26)

II.2.2.5 Others gelators

There are also other classes of gelator molecules and as an example the wide class of steroid-based molecules is suited for gelation. It was in 1997 that Weiss and coworkers discovered the first low molecular mass organo gelator based on cholesterol.[76,77,78] In cholesterol containing gelators it is the covalently bound cholesteryl group that induces directional self-association through weak van der Waals interactions.

[74] Zschoche, F., *Diplomarbeit*; Universtät Bonn, **2003**.
[75] Klawonn, T., *Diplomarbeit*; Universtät Bonn, **2003**.
[76] Žinić, M., Vögtle, F., Fages, F.; *Top Curr Chem*, **2005**, *256*, 39.
[77] Terech P., Weiss R. G.; *Chem Rev*, **1997**, *97*, 3133.
[78] Abdallah D. J., Weiss R. G.; *Adv Mater*, **2000**, *12*, 1237.

Aim of the Work

III Aim of the work

The aim of the work was to incorporate a new carbene functionality into the main gelator structure. While the important role of the amide moiety in the formation of aggregates, mostly due to its ability to provide hydrogen bonding, was recognized, because whether it is in an azasugar or an aminoalkyl motif the gelation properties were retained. The starting point in this thesis was to explore the combination of the former works as a new "urea-type" imidazole carbene study. The replacement of the Fischer motif with an imidazole gives the opportunity to incorporate imidazole-2-ylidenes chemistry and to discover the effects of this structural change on the sol-gel chemistry. (Figure 27)

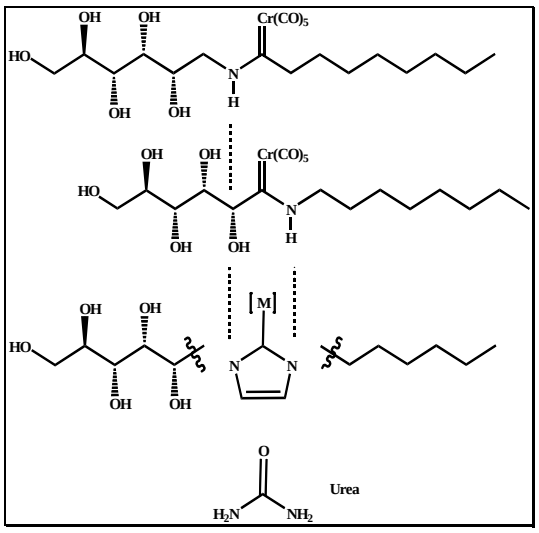


Figure 27: Original idea of the project.

The imidazol-2-ylidene chemistry would provide the possibility to coordinate a larger range of metals than the one available with the Fischer carbene chemistry. It should provide easier access to target molecules, the organometallic step (often limiting one in terms of yield) are to be the last ones in the synthetic route. The structures are thought to be more robust and would not need low temperature protocols. Despite the changes in structure and the physical properties that would be brought to the main original design, one would keep in sight to have gelation abilities. The combination of new coordination metal chemistry and gelation ability should broaden perspectives and permit exploration of a new field in organometallic chemistry. Of course since we apply new chemistry, the aim is first to synthesise a new library of amphiphilic structures. Their gelation abilities or their catalytic properties would be next investigated.

Results and Discussion

IV Results and Discussion

IV.1 Strategy

The whole work has to be considered as a screening of different methods to transform a Fischer carbene complex into an imidazole moiety to provide a new variety of amphiphilic structures. The work was planned as follows: at first a direct replacement of the carbene fragment, then followed in a second approach by the separaration of the imidazole motif from the carbohydrate part with different linkers.

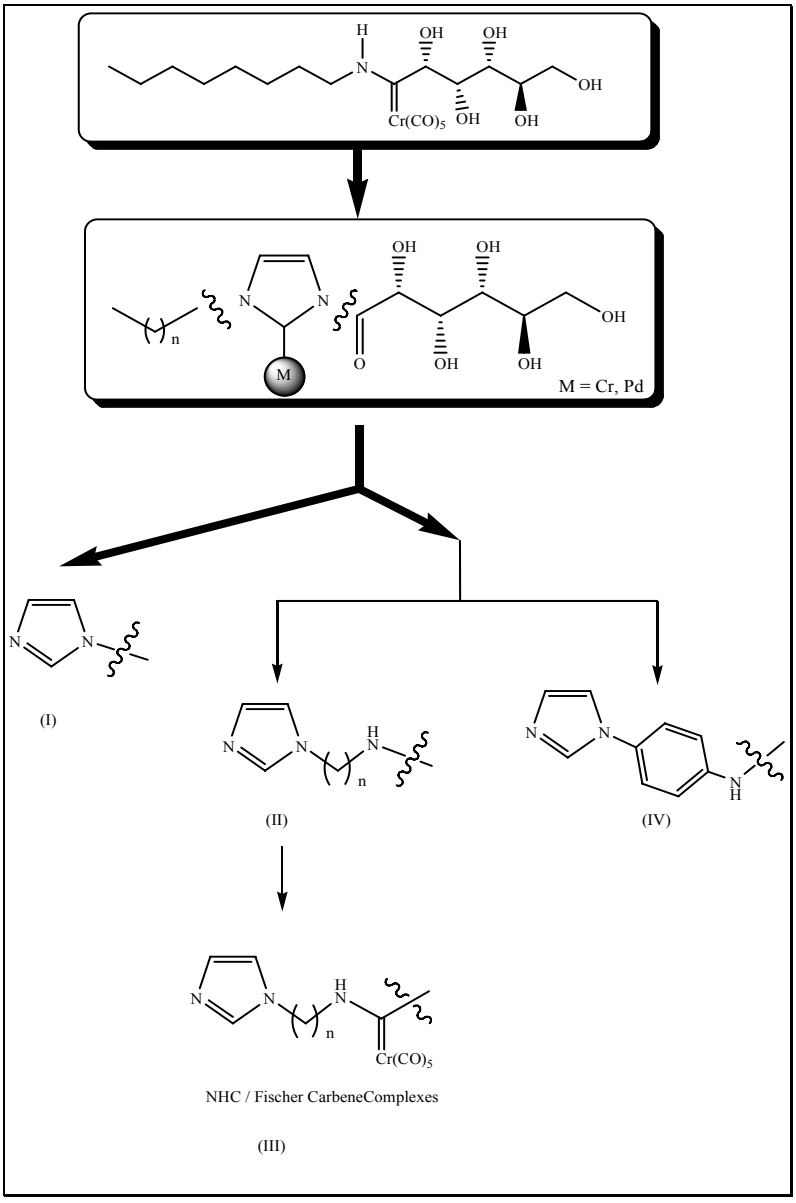


Figure 28: Starting point and road map for the incorporation of an NHC in a known gelating system.

In details, this includes firstly (I) a road where the imidazole should be interconnected between the carbohydrate with an amide type bond and a lipophilic chain. Secondly (II), the imidazole is to be separated from the glucose part by an alkyl chain, thirdly (III), a structural analogue is to bear an *N*-Heterocyclic Carbene (NHC) and a Fischer type carbene moiety. And finally (IV) a 1,4-phenylene ring was employed (Figure 28).

IV.2 Precedent work

Established by the Dötz group in 2003, the first organometallic gelator based on sugar proved gelation of various organic solvents.[9,79] As this work is related to the investigation of physical properties of a new type of carbene, it should be first determined which basic structure is the most convenient. According to other investigations of the same working group, glucose appears to be a better gelator agent than mannose or galactose and is also the most affordable. Concerning the metal, chromium and tungsten have similar effects on gelation, but the yields are the determining factor in favour of chromium.

IV.3 Road I: Synthesis of glucoimidazol-2-ylidene alkyls

IV.3.1 Retrosynthetic studies

In the first route the target molecule does not bear any spacer. The determining step in this case is the formation of the metal complex precursors. The metal complex formation (Figure 29) should occur via transmetalation after formation of a silver carbene complex.[45]

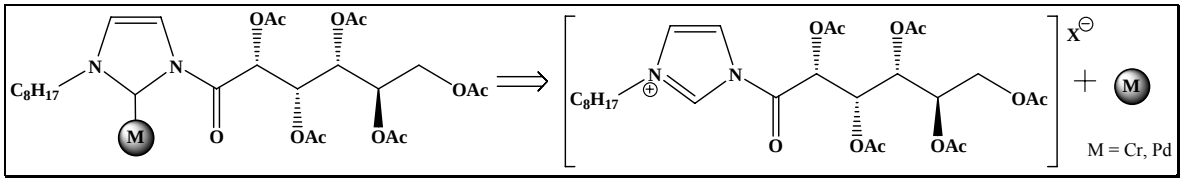


Figure 29: Retrosynthesis of the imidazol-2-ylidene carbene complex.

The formation of the imidazolium salt (Figure 30) should occur by N-acylation with gluconic acid chloride. The similarity of this structure with *N,N'*-carbonyldiimidazole (CDI)[80] could

[79] Bühler, G.; *Dissertation*, Universtät Bonn, **2004**.
[80] Vaidyanathan, R.; Kalthod, V. G.; Ngo, D. P.; Manley, J. M.; Lapekas, S. P.; *J. Org. Chem*, **2004**, *69*, 2565.

make it difficult to achieve it because of the weakness of the newly formed nitrogen acyl bond. CDI is a well known substrate to achieve carboxylic acids and amide formation.

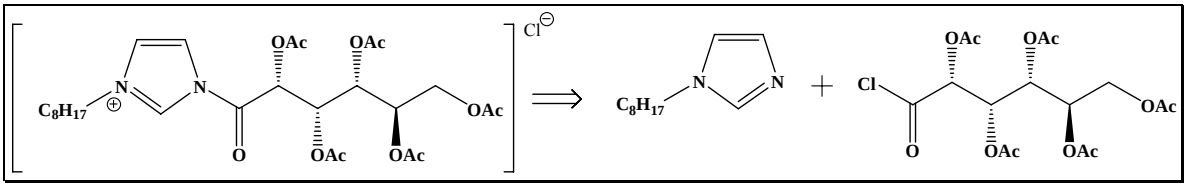


Figure 30: Formation of the imidazolium precursor.

The *N*-alkyl imidazole moiety could be achieved with another nucleophilic substitution (Figure 31).

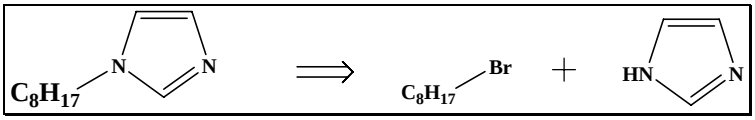


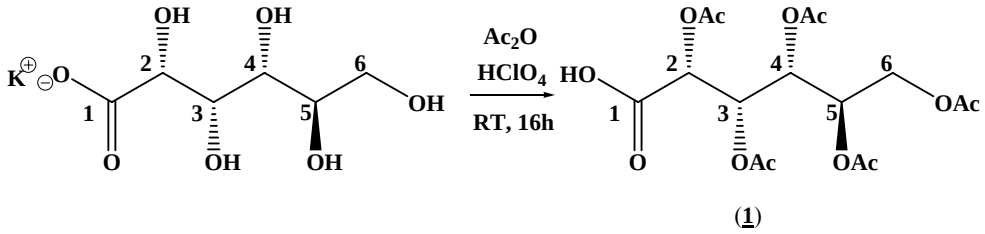
Figure 31: Retrosynthetic view of the alkylation of the imidazole moiety.

IV.3.2 Synthesis of the complexes following the road I

IV.3.2.1 Synthesis of 2,3,4,5,6-penta-*O*-acetyl gluconic acid (**1**)

The main part of every structure that has been synthesised is the carbohydrate functionality. Because of precedent work and because it has been shown as the most appropriate from the sugar library, the work is focused only on the glucose in its acyclic form.

As a precaution with respect to the various reaction conditions during the synthesis of the target molecules its protection and deprotection should be considered. The main reason to protect the hydroxyl functionalities is to enhance the solubility of the sugar. There are several possibilities to protect hydroxyl functions such as acetals, esters or ethers. The one that has to be chosen is the one which is versatile enough to be used in either organic or organometallic routes. The acetyl groups offer good yields in protection and can easily be removed under mild basic conditions such as ammonia in methanol.



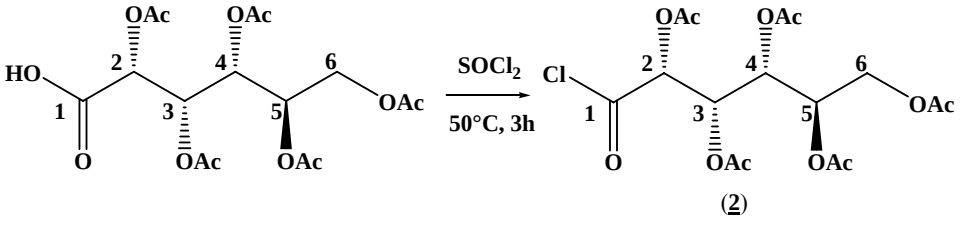
(**1**)

Scheme 1: Synthesis of 2,3,4,5,6-penta-*O*-acetylated D-gluconic acid (**1**).

Following the literature procedure,[81] acetic anhydride is activated with perchloric acid. The perchloric acid has to be given carefully so that the reaction mixture temperature does not exceed 10°C. The potassium salt of the gluconic acid is then given in small portions. The reaction is stirred overnight and then quenched with a water/ice mixture followed by the extraction of the aqueous phase with dichloromethane; the organic phase is then dried over magnesium sulfate. The concentration of the organic phase will afford a yellow oil. The dissolution of this oil in toluene will help to get rid of the traces of acetic acid. The crude substance is recrystallised from diethyl ether and petroleum ether to afford a white solid with up to 74% yield.

IV.3.2.2 Synthesis of 2,3,4,5,6-penta-*O*-acetyl-D-gluconic acid chloride (**2**)

Again the previous work[81] gives an appropriate scheme to synthesise the acid chloride derived from the carboxylic acid. The use of thionyl chloride gives the desired product at 50°C reaction temperature (Scheme 2). Care has to be taken to have only dried flasks and distillated solvents. Traces of water would react with the product to reproduce the starting material. The reaction must be performed under inert conditions in a fuming hood due to the formation of hydrogen chloride. The concentration of the product is initiated with a water pump and the crude product is then dried under low pressure.



(**2**)

Scheme 2: Synthesis of 2,3,4,5,6-penta-*O*-acetylated-D-gluconic acid chloride (**2**).

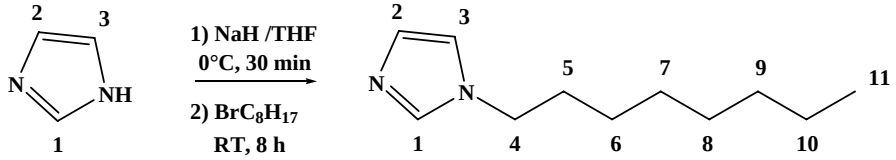
[81] Straub, W.; *Dissertation* **1995**, Universität Bonn.

The crude product is recrystallised from distillated solvents, in this case diethylether and petrol ether. The off-white solid is recovered with yields up to 87%. The product as a dried powder is not very sensitive to air but to moisture.

The obtained NMR spectra (^{1}H, ^{13}C) of the product do not differ too much form those of the starting material. The proton NMR shows a disappearance of the hydroxyl hydrogens, but these are exchangeable protons, and can not be seen under protic solvent conditions, so this is not a proof. The carbon spectrum shows in contrary evidence of the formation of the product because of the shift of carbon number 2 (Scheme 2) from 70.1 ppm to 76.6 ppm.

IV.3.2.3 Synthesis of *N*-*n*-octylimidazole (**3**)

The *N*-alkylation is performed according to a slightly modified literature from RajanBabu,[82] in which the bromooctane reacts with the imidazolate anion formed after deprotonation with sodium hydride (Scheme 3).



(**3**)

Scheme 3: Synthesis of *N*-*n*-octylimidazole (**3**).

The use of THF instead of DME is mainly due to laboratory causes. THF is a usual solvent and easily dried. DME is a chelating solvent so its use would enhance the basicity of sodium hydride by chelating the sodium cation. A known equivalent system is THF / TMEDA, which would also chelate the alkaline metal. Eventually the system without TMEDA proved to be as efficient and gives yields up to 83%. The formation of the imidazolate anion is the determining step, so all precautions have to be taken to avoid the presence of water until the end of the reaction. The sodium hydride suspended in 60% in mineral oil, is cleaned with some distillated petroleum ether and a white powder is obtained when dried under vacuum. The white power is then solved with THF. After addition of the bromide and TMEDA to the reaction mixture, the reaction is stirred for eight hours. The final

[82] Clyne, D. S.; Jin; J.; Genest, E.; Gallucci, J. C.; RajanBabu, T. V.; *Org. Lett.,* **2000,** *2*, 1125.

addition of water destroys the unreacted sodium hydride. The yellow oil recovered is purified by silica gel chromatography, and the product is obtained with 83% yield.

IV.3.2.4 Formation of the metal complex precursor

The next step is the formation of the imidazolium salt from the reaction of the gluconic acid chloride **2** and *N*-octylimidazole **3** (Figure 32).

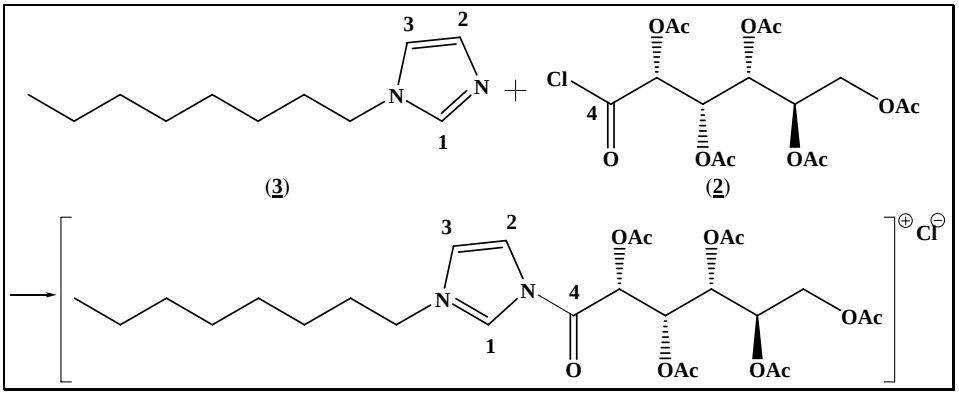


Figure 32: Investigation on 3-*N'*-octyl-1-*N*-(2R,3R,4R,5S,6-penta-*O*-acetylhexanoyl)imidazolium chloride.

The targeted structure presented in Figure 32 seems to be labile because of the nitrogen-acyl bond, which is used in CDI for amide or ester formation.[80] The isolation of the pure product could not be achieved, but NMR spectra and mass spectrometry of the crude reaction have identified the intermediate.

No matter whether the reaction is conducted in dichloromethane at room temperature, or by refluxing the system, there was no isolation of the salt possible. Apparently the salt is formed, but is not stable enough to be isolated. As no isolation is possible NMR and mass spectra from the crude reaction mixture were measured to characterise the salt. The best solvent to dissolve the crude mixture was acetone-D_6. In most cases imidazole protons resonate shifts between 7 and 8-9 ppm. The formation of a salt would definitely shift the signal of the proton in position 1 (Figure 32) to lower field. The appearance of a chemical shift at 11.05 ppm (Figure 33) is a hint, the correlation of the integration with two signals at 8.02 and 7.88 ppm (1 proton to 1 to 1) is a second hint. Figure 33 reveals those significant shifts along with the original three signals of the starting material can be seen.

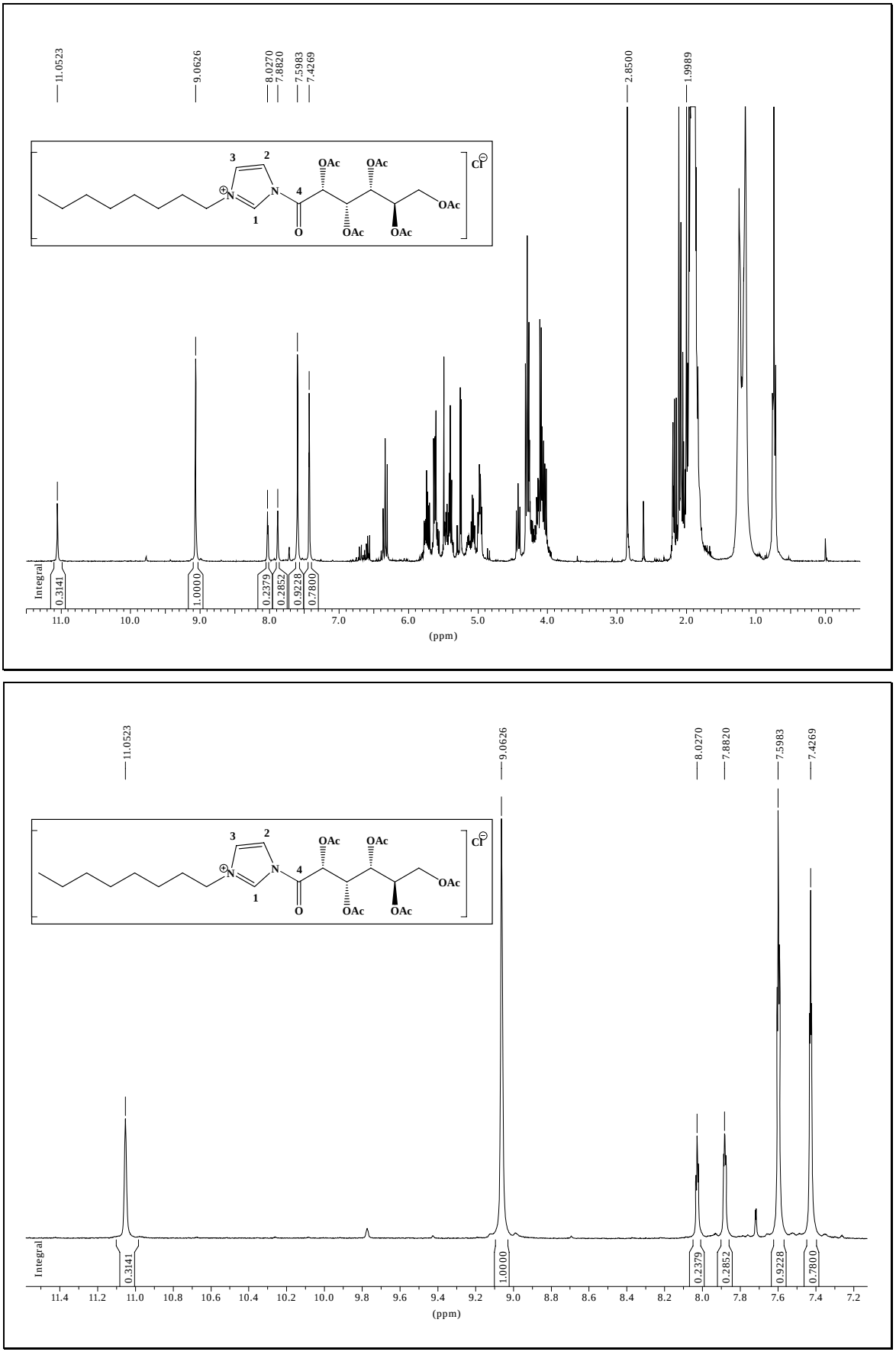


Figure 33: ^{1}H NMR spectra of the crude product of the imidazolium chloride intermediate.

The integration shows a 1 to 3 ratio between what is thought to be the imidazolium salt and the starting material, which would mean a 25% product formation. The proton NMR is not sufficient for the identification of the salt intermediate. The carbon NMR (Figure 34) should also give specific signals. If the complex is formed then two different separate patterns have to be present in the aromatic region. Two sets of signals can be seen, one set at 135.6; 124.1 and 119.3 ppm and another set for the starting material at 123.8, 122.5 and 120.4 ppm. The carboxylic acids region shows a small signal at 169.1 ppm which could be attributed to the amide carbon signal. (Figure 34)

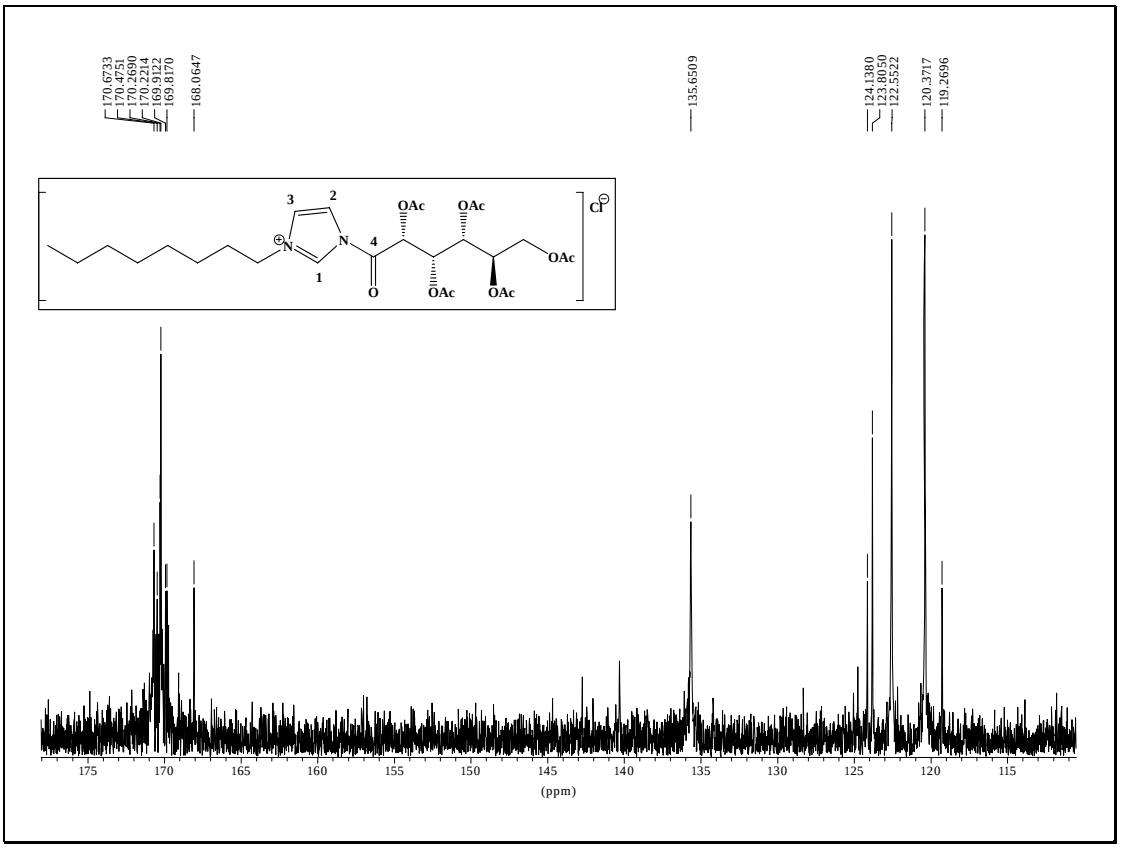


Figure 34: ^{13}C NMR spectrum of the crude product of the imidazolium chloride intermediate.

Further support the existence of this intermediate is provided by mass spectrometry. As it is thought that the complex is not stable enough, the mildest conditions should be used. Under FAB (matrix: mNBA) conditions (Figure 35), the signal at 569.2 m/z definitely confirms the presence of the salt.

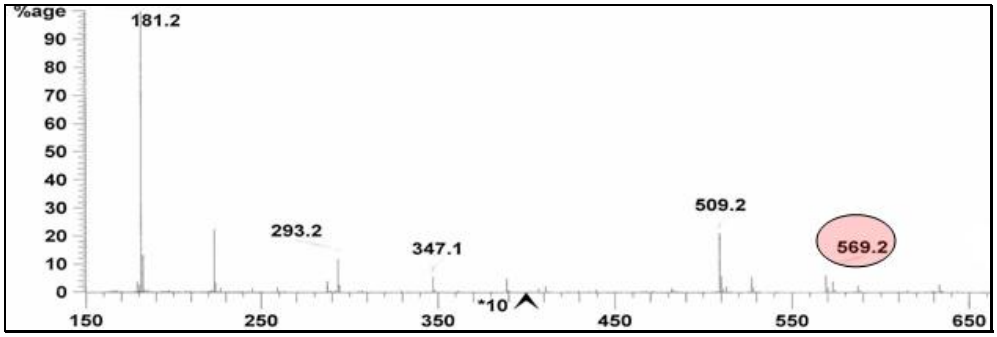


Figure 35: Mass (FAB: mNBA) Presence of the cation of the intermediate imidazolium.

The mass spectrum also shows fragments that further support the presumed structure. The peak at m/z = 509.2 (2%) could match the loss of a first protective group (OAc: m/z 59), then at m/z = 293.2 (10%) a loss of m/z = 296 results from cleavage of 4 protective groups, the CH_2 group and two CH groups. Finally, the basis peak at m/z: 181.2 (100) matches perfectly the loss of the glucose part, affording *N*-octylimidazole as [M+H]. It is now established that the alkylation occurs, but the product can not be isolated, so the next step is to investigate an in situ formation of the metal complex.

IV.3.2.5 Synthesis of the metal chromium complex

As the formation of the precursor of the carbene complex is now established, the preparation of the desired complex can be investigated. According to literature[32] the newly formed imidazolium salt can be deprotonated using a base to yield the free carbene, ready to complex various metals[83] (Figure 9). Wanzlick used sodium hydride to free the first carbene. The most acidic proton is definitely the one at carbon number one, but the use of a hydride could also interfere with the acetyl protective groups. A milder base was found in 1993 when Arduengo synthesised the first silver imidazol-2-ylidene complexes.[84] Silver complexes are quite easy to prepare and well suited for transmetalation. The prepared salt is dissolved in dichloromethane at room temperature and left to stir overnight in the presence of silver oxide (Ag_2O) following Lin and Wang's procedure.[45] All silver salts are sensitive to light and the silver carbene is no exception.

[83] Herrmann, W. A.; *Angew. Chem. Int. Ed.*, **2002**, *41*, 1290.
[84] Arduengo, A. J., III; Dias, H., V., R. ; Calabrese, J., C.; Davidson, F.; *Organometallics*, **1993**, *12*, 3405

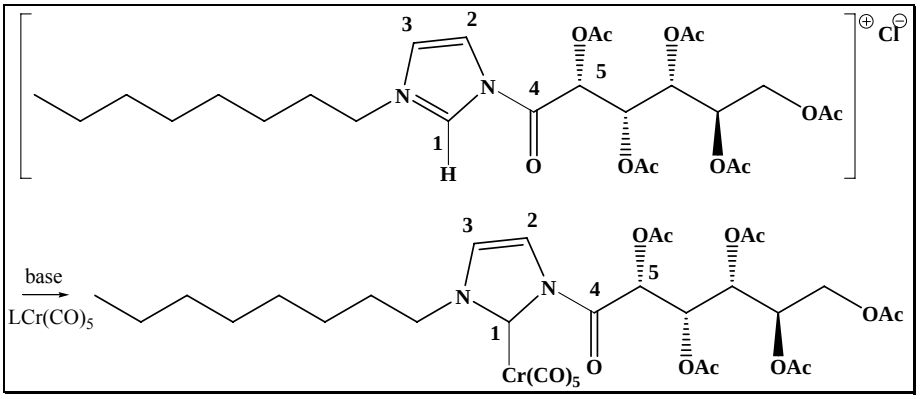
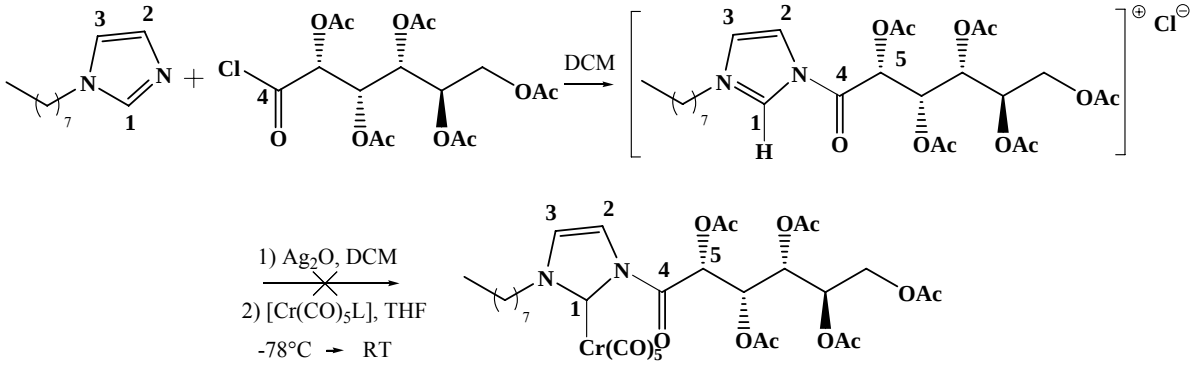


Figure 36: Pentacarbonyl[3-N'-octyl-1-N-(2R,3R,4R,5S,6-penta-O-acetylhexanoyl)-2,3-dihydro-imidazol-2-ylidene]chromium.

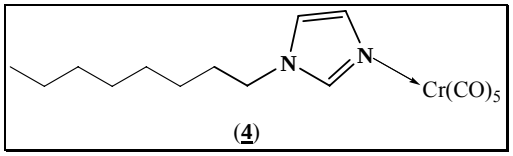
After formation of silver hydroxide (AgOH), the second silver atom will complex to the free carbene. The so formed silver hydroxide attacks then a second molecule of imidazolium salt and releases one molecule of water. Silver(I)oxide is the most used silver base reagent because the reaction is very easy to monitor; it is insoluble in dichloromethane whereas the silver carbene complexe is. The transmetalation ease of silver carbenes will allow it to be exchanged for chromium (Scheme 4).



Scheme 4: In situ preparation of the chromium carbene complex.

When the reaction between the imidazolium salt and the silver oxide is over, the new silver carbene complex should react with the chromium pentacarbonyl source. In THF the original cyclooctene chromium pentacarbonyl complex undergoes a ligand exchange between cyclooctene and THF. The temperature is an important factor because if this ligand exchange might occur at -20°C, a too high temperature would make the complex unreactive. The ligand exchange is indicated by a color change of the solution from yellow to orange. The main and only product recovered is indeed a chromium pentacarbonyl species, but the lack of signals in the range of 4 to 5 ppm in the ^{1}H-NMR spectrum and no signal at 190 ppm in the ^{13}C-NMR

spectrum just means that the carbohydrate functionality has been lost. The presence of a pentacarbonyl chromium pattern can only be understood as a coordination between the metal and the nitrogen formally bearing the sugar side chain, as depicted in Scheme 5. The mass spectrometry also confirms the formation of **4**.



Scheme 5: pentacarbonyl[1-*N*-octyl-3-*N'*-imidazole-2-ylidene]chromium (**4**).

The appearance of this compound **4** (Scheme 5) as only isolobale main product confirms that the imadazolium salt intermediate undergoes an amide cleavage rather than deperotonation followed by complewation to give the desired chromium complex.

IV.3.3 Conclusion

The salt intermediate is most probably too instable because of the nitrogen-acyl bond. An alternative possibility is incorporating a spacer between the imidazole and the carbonyl group. This strategy is followed in the chapter IV and chapter VI. There, the influence of alkyl chains and benzene rings as spacers is investigated.

IV.4 Road II: Synthesis of Imidazol-2-ylidene complexes with alkyls spacer

IV.4.1 Retrosynthetic studies

In that approach, the determining step will be the formation of the new amine. The metalation of the carbene or the formation of the imidazolium salt should be carried out as described before, including the use of silver oxide as a metal transfer agent (Figure 37),

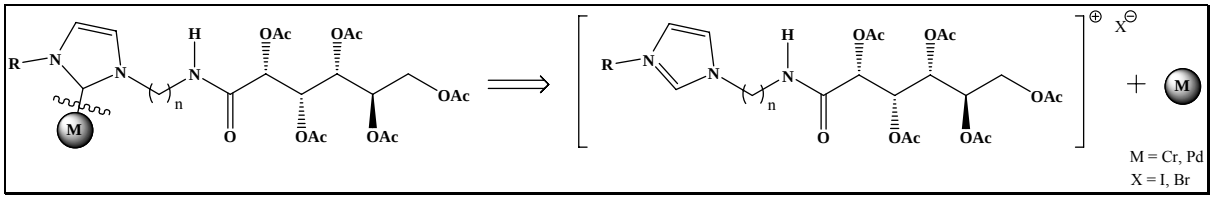


Figure 37: Retrosynthetic approach for the metalation step.

and the alkylation of the last free nitrogen of the imidazole (Figure 38). The preceeding step is

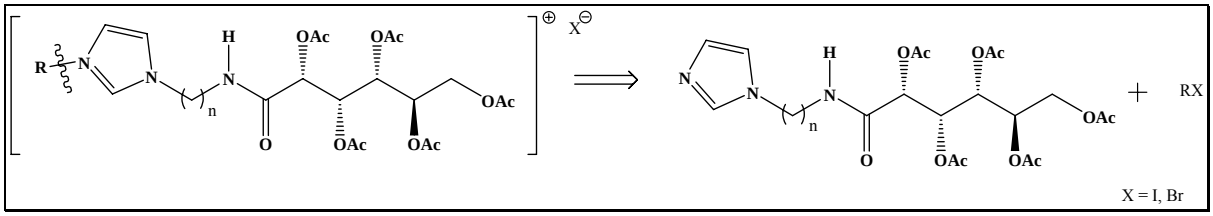


Figure 38: N-acylation of the gluconic amide functionnalised imidazole.

a classic amide formation between a *N*-alkylaminoimidazole and the gluconic acid chloride (**2**) previously described (Scheme 2).

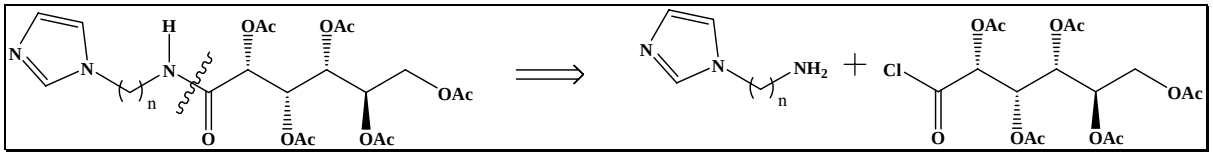
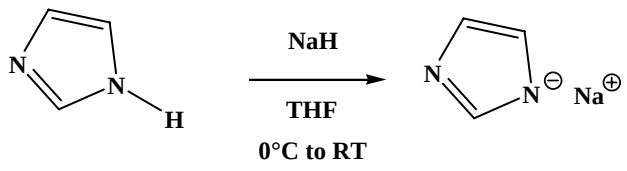


Figure 39: Proposed approach for the amide formation.

The most of the work will be spent on the design of the amine. There could be several ways to reach this amine. To avoid the formation of any symmetrical bi-functionalised imidazole, every investigation should be based on the use of a metal imidazolate. Whether the deprotonation should occur with potassium or sodium hydride will not influence the outcome (Scheme 6). The use of potassium has been quickly put aside because of its more dangerous handling in comparison to sodium hydride.

IV.4.2 Synthesis of the complexes following the road II

IV.4.2.1 Synthesis of sodium imidazolate



Scheme 6: Formation of the imidazolate intermediate.

Despite the fact that the imidazolium salt has not been isolated, its description was important because it was used in every different functionalisation process.

To attach the amine functionnality on the imidazolate, protected amines or synthetic equivalents such as phthalimide, amino alcohols and nitriles have to be used. (Figure 40)

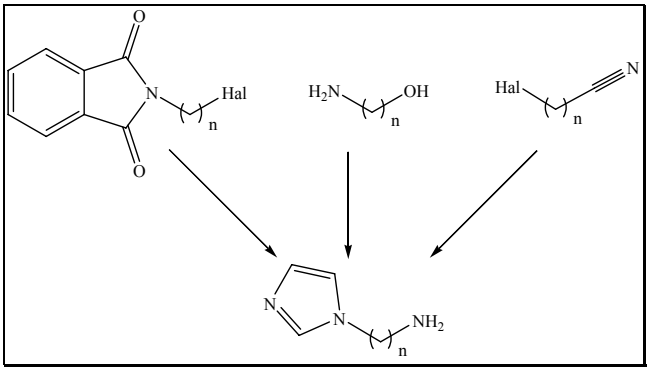
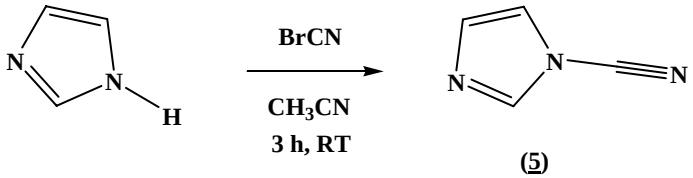


Figure 40: Investigations on the formation of the *N*-aminoalkylimidazoles.

In a first approach, it is thought to try to keep the imidazole center as close as possible to the sugar moiety. The idea to be as close to the original system presented in Figure 28 is still valid. The first spacer that comes in mind is one methylene unit. The (1*H*-imidazol-1-yl)methanamine[85] used to be commercially available but at an excessive price. Therefore an idea was to start from bromocyanide, react it with imidazole and reduce the produt to the amine.

IV.4.2.2 Synthesis of imidazole-1-carbonitrile[86] (**5**)



Scheme 7: Formation of imidazole-1-carbonitrile (**5**).

Following the literature procedure a solution of imidazole dissolved in acetonitrile (30 ml) is prepared and then bromocyanide in acetonitrile was added. The solution was stirred at room temperature to yield white needle-like crystals in 48% yield. The product decomposes on exposure to light. A first hint to find out if the product was formed is the appearance of a small signal at 104 ppm in the ^{13}C-NMR spectrum, the ^{1}H-NMR spectrum will not give further information because no protons were added to the structure.

[85] Popowycz, F.; *Bioorg. Med. Chem. Lett.* **2001**, *11*, 2489.
[86] McCallum, P., B., W.; Weavers, R., T.; Grimmett, M., R.; Blackman, A., G.; *Aust. J. Chem*., **1999**, *52*, 159.

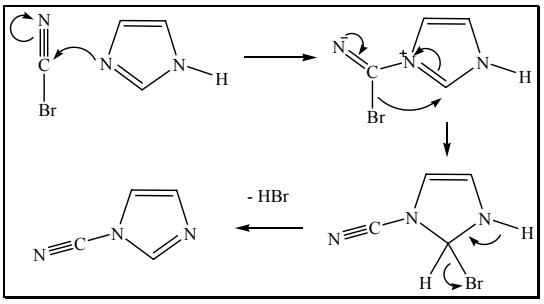
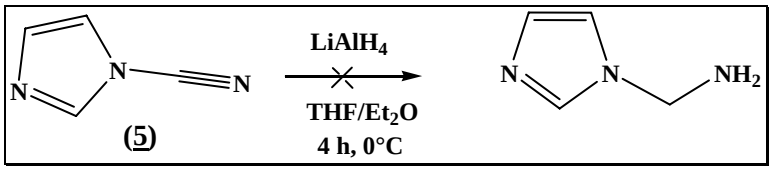


Figure 41: Suggested mechanism by Blackman.

Blackman and coworkers submitted a mechanism for the N-nitrile bond formation, (Figure 41) saying that it can only occur if a nitrogen lone pair is available and if the substituent on the second nitrogen is a proton. If it is not the case one ends up with a brominated nitrogen and liberation of HCN. The obtention of the nitrile function on the nitrogen does now allow the reduction to the primary amine.

IV.4.2.3 Synthesis of imidazole-1-methylamine

Following literature[87] the use of lithium aluminium hydride is an efficient way to reduce a nitrile to an amine. Two equivalents are needed; one hydride attacks the carbon center of the nitrile while the nitrogen from the nitrile complexes a molecule of AlH_3. The reaction is performed at 0°C for four hours; the solution is then quenched carefully with water. The addition of water to the unreacted hydride has to be done at 0°C because of exothermic formation of dihydrogen.



Scheme 8: Attempted synthesits of imidazole-1-methylamine.

Lithium aluminium hydride species is available as a grey powder which forms a suspension either in THF or Et_2O. In both cases the reaction does not occur.

[87] Mislow, K.; Hellman, H.; *J. Am. Chem . Soc.,* **1951***, 73,* 242.

The formation of a methylene group and an amine is expected, in the NMR spectra it should result in the appearance of one new signal for the methylene group between 3.80 and 5 ppm, and one new signal for the amine protons. The methylene hydrogens should be low fielded because of the presence of the nitrogen atoms on each side. The amine protons might exchange with the solvent and therefore can disappear in the ^{1}H-NMR spectrum, depending on temperature. The ^{13}C-NMR should show a new signal in the range of 50 to 60 ppm for the newly formed CH_2 group. Unfortunately in none of the experimental attemps these signals could be observed (Figure 42).

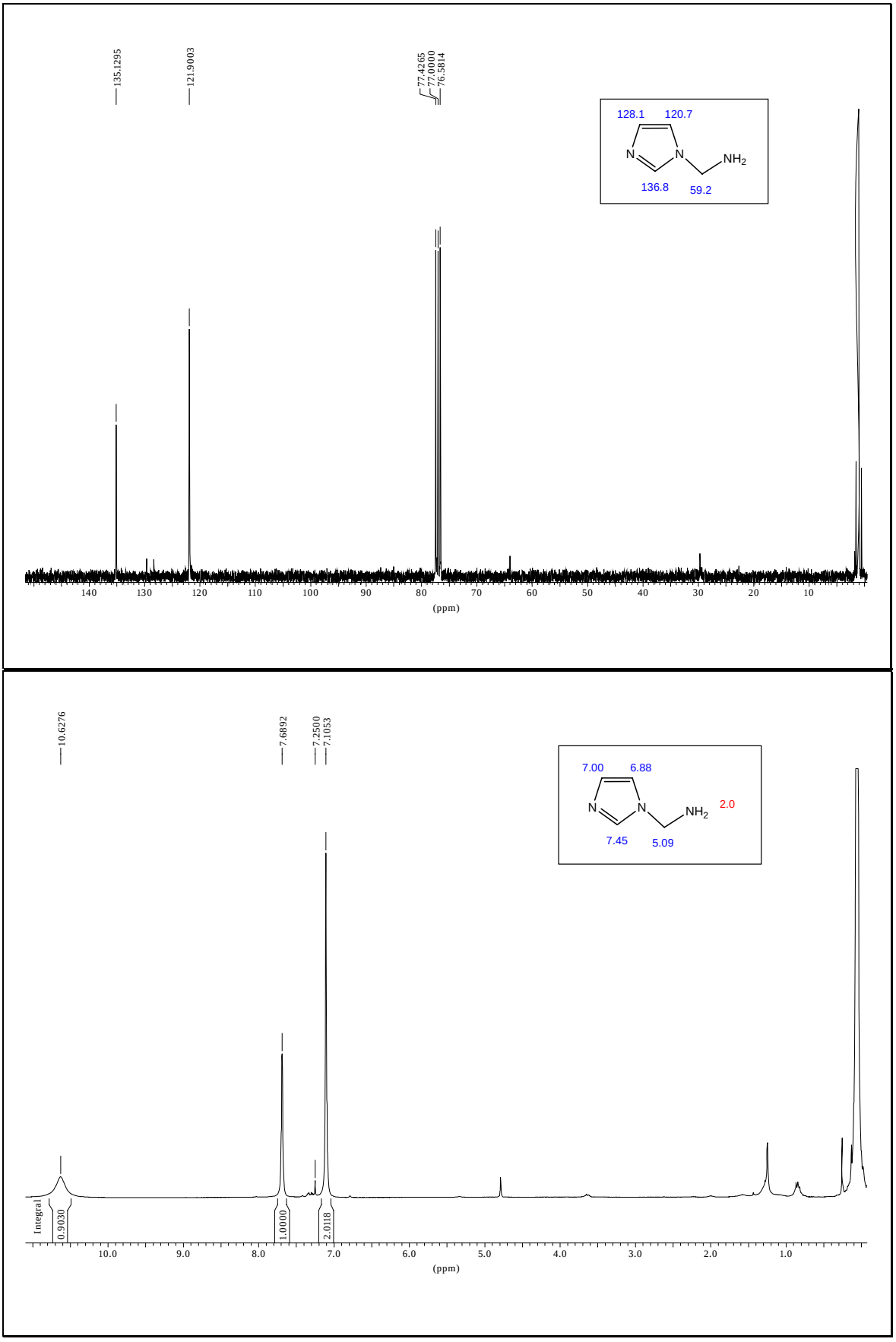


Figure 42: ^{1}H-NMR and ^{13}C-NMR investigation on crude product of the attempted reduction of imidazol-1-carbonitrile (in box: predicted signals).

In the ^{1}H NMR spectrum it is visible that in the aromatic region just two signals are present (Figure 42, lowest picture). The first one at 7.10 ppm corresponds to 2 protons, and the second one at 7.69 ppm to one proton, which is in accordance with a symmetrical system. If it is symmetrical it is probably imidazole, and the last signal at 10.63 ppm, integrating for one proton, follows this theory, being the N-H proton from imidazole. The ^{13}C NMR spectrum shows only two signals for imidazole but no new signal in the methylene range.

The most probable reaction is the formation of the first nitrile aluminium intermediate, the hydride would attack the carbon atom from the nitrile, followed by the rearomatisation of the system, leading to imidazole and most probably HCN or any other derivatives.

It is easy to conclude that if the shortest alkyl amine is not easy to obtain, the next approach should include a longer spacer to put some distance between the amide and the imidazole. For economic reasons the work focused on six, seven or eight methylene groups. Shorter chains proved to be too expensive and as long as one does not have a proper and efficient synthetic route, then the work should be based first on longer chains. In previous work made in the Dötz group the optimal balance was found with an octyl alkyl chain.[79] As we expect the sugar amide system to be crucial for the aggregation, the length of the spacer should not be of a too big influence.

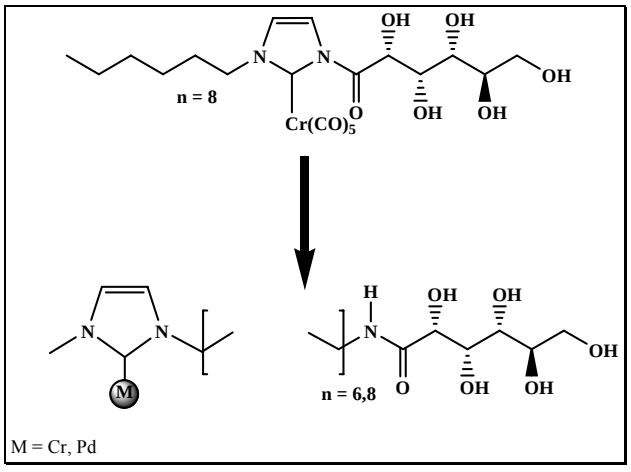


Figure 43: Projected view of an alkyl spacered complex.

As described earlier (Figure 40), three methods retained the attention to form the desired amine. Aminoalcohols (Figure 44 A) will be first investigated. The substitution on the carbon bearing the hydroxyl functionality implies that this OH group is transformed into a

good leaving group. Since the molecule bears a free primary amine, its protection is necessary. In a second view, the Gabriel method (Figure 44 B) will be investigated. Starting from phthalimide alkyl halides, as synthetic equivalents to an amino functionality, the imidazole will substitute the halide and the new molecule will undergo reduction to free the amine. Finally, the nitrile method (Figure 44 C), shown previously (Scheme 8), will be applied again to see if with longer alkyl chains the dissociation of the molecule to give back imidazole still occurs.

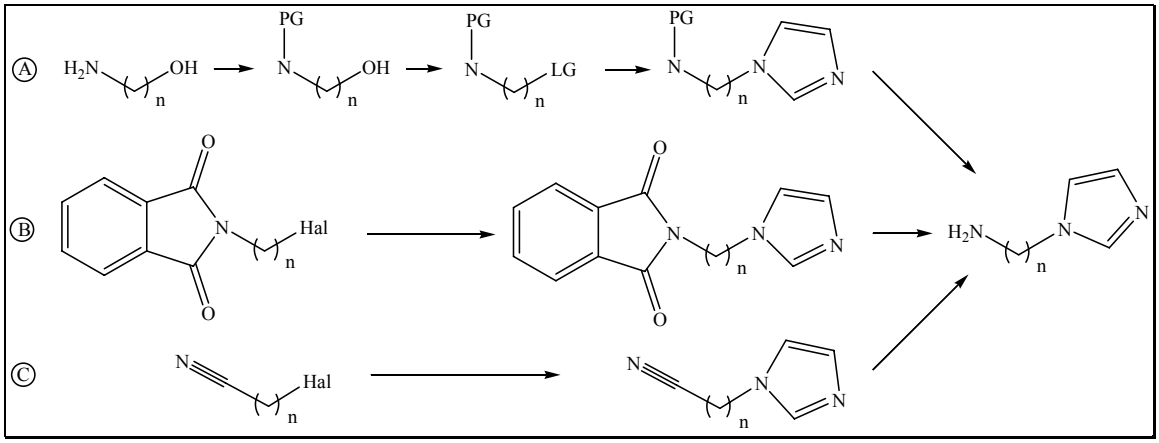


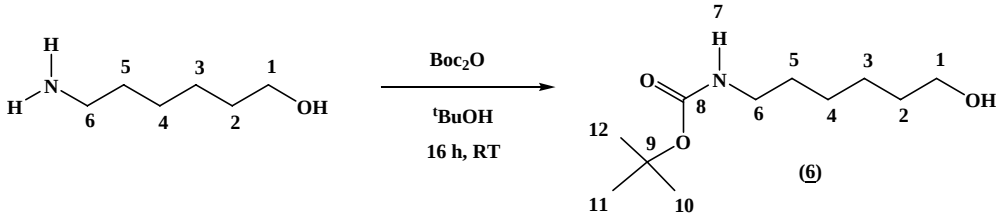
Figure 44: A) Aminoalcohol route; B) Gabriel synthesis; C) Nitrile route to N-aminoalkylimidazole.

The decision on which to choose one route or another will depend on the access and the yield of the reactions.

IV.4.2.4 Synthesis of *N*-aminoalkylimidazole

IV.4.2.4.1 *Amino alcohol strategy*

IV.4.2.4.1.1 Synthesis of *tert*-butyl 6-hydroxyhexyl carbamate (**6**)



Scheme 8: Boc protection of the amine functionality on 6-aminohexanol (**6**).

Following the literature[88], the protection can proceed under acidic conditions. The di-tert-butylcarbonate (Boc_2O) is activated and then attacked by the nucleophilic amine to yield the protected amine and *tert*-butyl hydrogen carboxylic acid. The crude product is purified over silica gel column chromatography. A light yellow oil is obtained. This oil crystallises at low temperature overnight in the freezer.

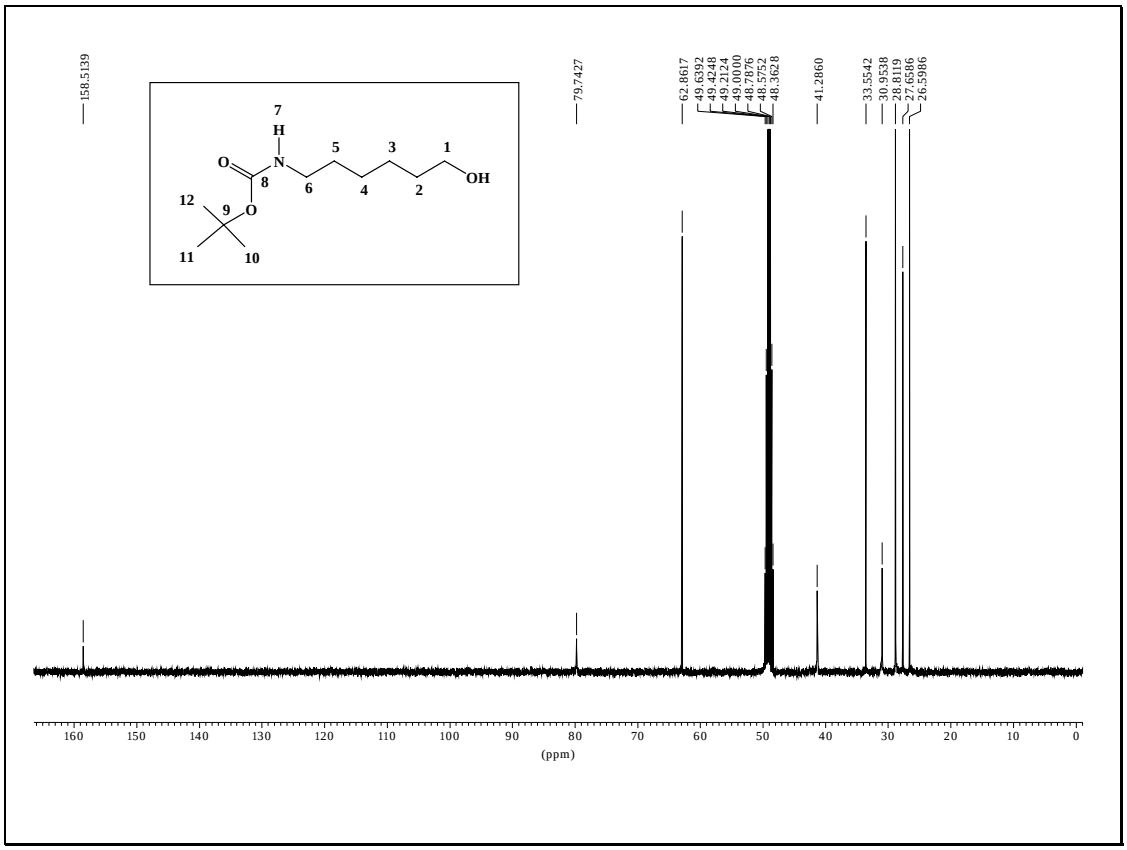


Figure 45: ^{13}C NMR from the Boc-protected aminoalcohol product.

The carbamate would provide a carbonyl signal and a quarternary carbon signal (C_9) in the ^{13}C NMR (Figure 45). The presence of these two signals at 158.5 and 79.7 ppm are the proof of the presence of the carbamate on the molecule. The protection now achieved with up to 98% yield, it is thought on how to substitute the imidazole to the hydroxy function. The hydroxy groups will have to be transformed to optimise its leaving property. To provide a better leaving group two possiblities are offered: an halogenation or a triflate (Figure 46).

[88] Strazzolini, P.; Melloni, T.; Giumanini, A., G.; *Tetrahedron* **2001**, *57*, 9033

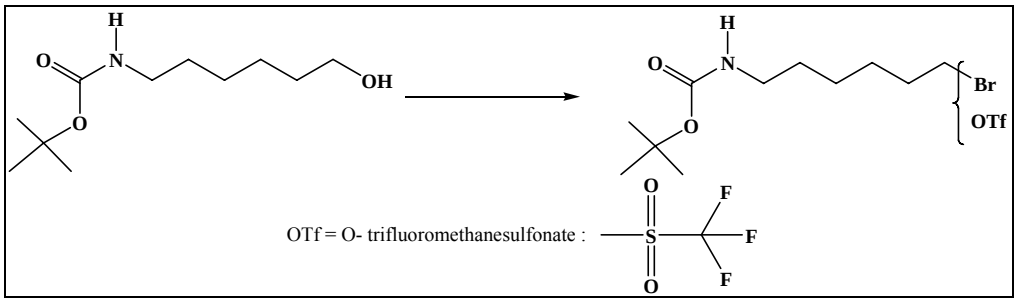
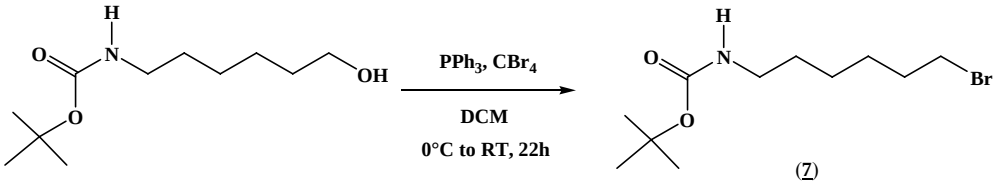


Figure 46: Nucleophilic substitution of hydroxyl group tested.

According to the litterature,[89] the formation of a triflate using triflic anhydride and a base should proceed smoothly but after several attempts this method did not prove to be very efficient. Even if the product might have been formed, a second carbon signal in the ^{13}C-NMR spectrum at 119.7 ppm appeared (the range where the quarternary carbon from the triflate is expected) but it was not possible to isolate the desired product. It is known that silica gel can be a bit acidic, and towards such group one can easily think that the triflate could be cleaved, but as long as triflate compounds are stable enough to be purified over column chromatography; it should not be the reason.[90] The next investigation was focused on the halide route.

IV.4.2.4.1.2 Synthesis of *tert*-butyl 6-bromohexyl carbamate (7)



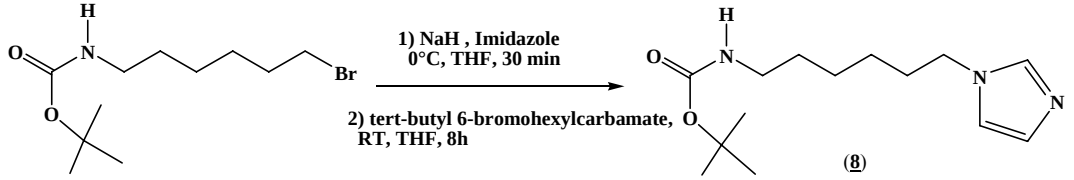
Scheme 9: Hydroxyl-bromide exchange formation on the terminal carbon position (7).

Following the literature protocol,[91] the alcohol and the tetrabromomethane (CBr_4) are dissolved in dichloromethane. The triphenyl phosphine (PPh_3) is given to the reaction mixture over a period of twenty minutes (Scheme 9). The tetrabromomethane activates the triphenylphosphine, and the oxygen from the alcohol will attack the phosphorus to generate an oxyphosphonium intermediate. The oxygen is then transformed into a leaving group, and an S_N2 displacement by the halide takes place, leaving the brominated species and the

[89] a) Patel M.; *Bioorg. Med. Chem. Lett.*, **1999**, *9*, 3217. b) Kogen, H.; Toda, N.; Tago, K.; Marumoto, S.; Takami, K.; Ori, M.; Yamada, N.; Koyama, K.; Naruto, S.; Abe, K.; Yamazaki, R.; Hara, T.; Aoyagi, A.; Abe,Y.; Kaneko,T.; *Org. Lett.,* **2002**, *4*, 3359.
[90] Grakauskas, V.; Baum, K..; Beard, C. D.; *J. Org. Chem.*, **1973**, *38*, 3673.
[91] Bauer, E. B.; Hampel, F.; Gladysz, J. A.; *Organometallics*, **2003,** *22,* 5567.

phosphane oxide. The candidate for the nucleophilic substitution with imidazole, obtained with up to 96%, is then ready.

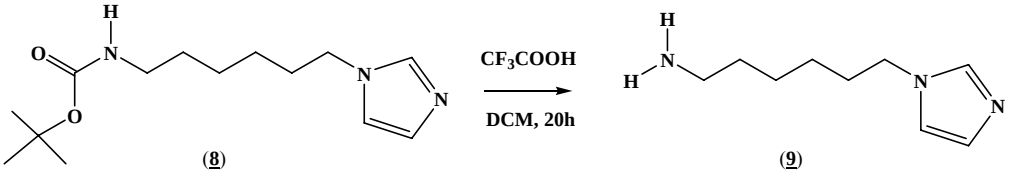
IV.4.2.4.1.3 Synthesis of *tert*-butyl 6-(1H-imidazol-1-yl)hexylcarbamate (**8**)



Scheme 10: Formation of imidazole alkyl carbamate (**8**).

As mentioned earlier, the reaction will take place between the imidazolate anion (Scheme 6) and the brominated species. The reaction is left to run eight hours to have optimum results. The crude product is purified via column chromatography to yield up to 83% of the product **8**. After three steps the protected amine is obtained and the last step to obtain the amine **9** is to cleave off the Boc group.

IV.4.2.4.1.4 Synthesis of 6-(1H-imidazol-1-yl)hexyl-1-amine (**9**)



Scheme 11: Deprotection of (**8**) to obtain the free amine (**9**).

Using the traditional method, meaning trifluoroacetic acid, the BOC group will be removed (Scheme 11). This acidic medium leads to the rearrangment of the carbamate to release carbon dioxide, isobutene in the gas phase and the free amine. The reaction mixture has to be neutralised with a two molar sodium carbonate solution. The product is obtained with only 17% yield.

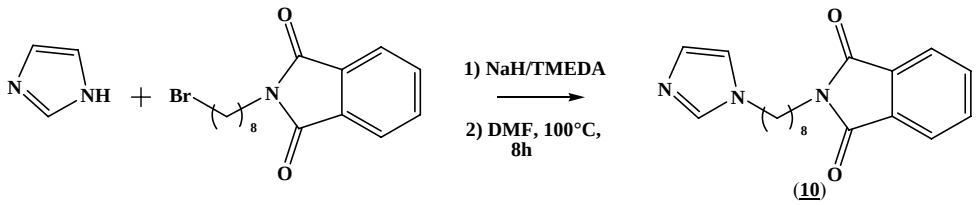
IV.4.2.4.1.5 Conclusion

To conclude on this route, the four steps amino alcohol strategy does not prove any high efficiency essentially due to the last step. The overall yield is not high (13%) mostly

because of the deprotection step, which does not seem to work as expected. Due to the low yields the next idea was to use the Gabriel method.

IV.4.2.4.2 *Gabriel Synthesis strategy*

IV.4.2.4.2.1 Synthesis of 2-(8-(1H-imidazol-1-yl)octyl) isoindoline-1,3-dione (**10**)



Scheme 12: 2-(8-(1H-imidazol-1-yl)octyl)isoindoline-1,3-dione formation (**10**).

In an attempt to synthesise the free amine with a higher yield, the Gabriel synthesis for primary amines is applied. The commercially available 8-bromooctylphthalimide permits to work directly on the substitution step. The imidazolate (Scheme 6) formed after use of sodium hydride and TMEDA in DMF directly attacks the carbon bearing the halide to yield the product **10** (Scheme 12). The reaction was performed at 100°C for 8h.[92] As expected the product was obtained in good yields (>98%) after purification over silica gel column chromatography.

IV.4.2.4.2.2 Synthesis of 8-(1H-imidazol-1-yl)hexyl-1-amine (**11**)

To access the free amine from **10** there are two often used possibilities, the principle is the same, a nucleophilic substance will attack the electrophile carbons at the base of the indole group. Either a treatment with an aqueous sodium chloride solution or hydrazine should convert the phthalimide to the amine. (Figure 47)

[92] Wright, W. B., Jr.; Press, J. B.; Chan, P., S.; Marsico, J. W.; Haug, M., F.; Lucas, J.; Tauber, J.; Tomcufcik , A., S.; *J. Med. Chem.*, **1986**, *29*, 523.

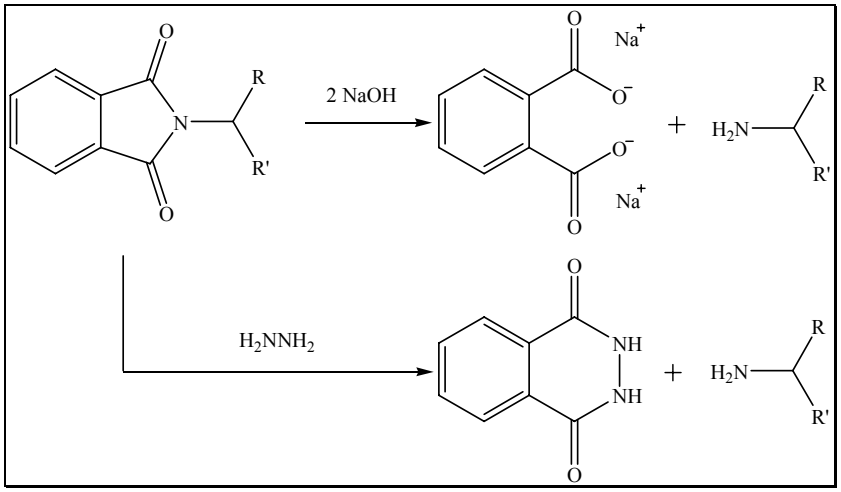
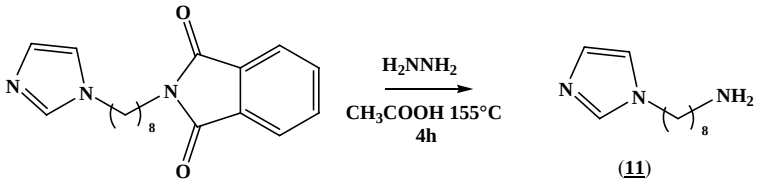


Figure 47: Primary amine formation following the Gabriel synthesis method.

According to the literature the hydrazinolysis should be the method of choice. Despite the fact that hydrazine is more dangerous to handle than a solution of sodium hydroxide, the reaction was performed at 155°C in acetic acid for four hours. (Scheme 13)



Scheme 13: 8-(1H-imidazol-1-yl)octylamine formation (**11**).

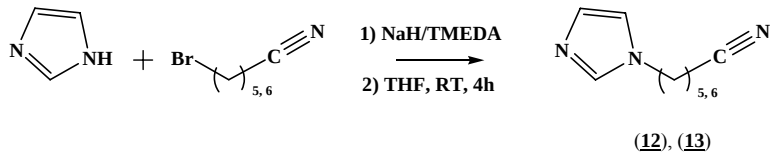
After four hours and a basic treatment in the work up, the free amine is obtained with 42% yield. The basic treatment transforms the ammonium salt into the free amine. As seen in Figure 47, the hydrazine attacks the electrophilic carbon atoms of the phthalimide to form 2,3-dihydrophthalazine-1,4-dione and the primary amine.

IV.4.2.4.2.3 Conclusion

This road seems definitely to be superior to the amino alcohol strategy with only two steps and a better overall yield of 42%. The third synthetic entry, the nitrile strategy, offers the advantage to avoid working with hydrazine.

IV.4.2.4.3 *Nitrile strategy*

IV.4.2.4.3.1 Synthesis of 5-(1H-imidazol-1-yl)hexane nitrile (**12**)



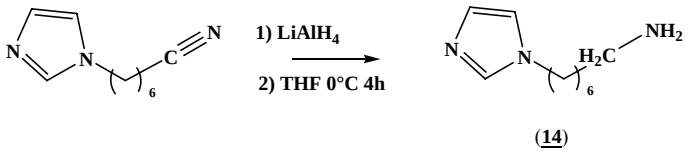
(**12**), (**13**)

Scheme 14: 6-(1H-imidazol-1-yl)hexyl-nitrile (**12**) and 7-(1H-imidazol-1-yl)hexyl-nitrile (**13**) formation.

In the last attempt to improve the obtained results on the formation of the amine, the reduction of nitriles was investigated. Firtsly the cyanoalkylimidazole was synthesised by nucleophilic substitution of imidazole with 7-bromoheptylnitrile (Scheme 14). The reaction was tested, for availability reasons, with both hexane and heptane nitriles, both providing the equivalent results. After purification over silica gel column chromatography, the best yield is obtained with the bromohexylnitrile with 90% (**12**) while the bromoheptylnitrile would give 85% (**13**).

Following the literature protocol the nitrile is now reduced to the amine using lithium aluminium hydride ($LiAlH_4$).

IV.4.2.4.3.2 Synthesis of 7-(1H-imidazol-1-yl)heptan-1-amine (**14**)



(**14**)

Scheme 15: 7-(1H-imidazol-1-yl)heptan-1-amine formation (**14**).

$LiAlH_4$ is the reducing agent of choice to provide amines starting from nitriles. The hydride attacks the carbon center from the nitrile functionality; the resulting product is then complexed with the remaining AlH_3. This operation will occur two times, in order to get a methylene group. The free amine is freed when the reaction is quenched carefully with water (Scheme 15). The reaction would give up to 90% yield.

One way to find out if the product is formed is to look for the disappearance of the nitrile signal in the ^{13}C-NMR spectrum (Figure 48) and the formation of a methylene signal.

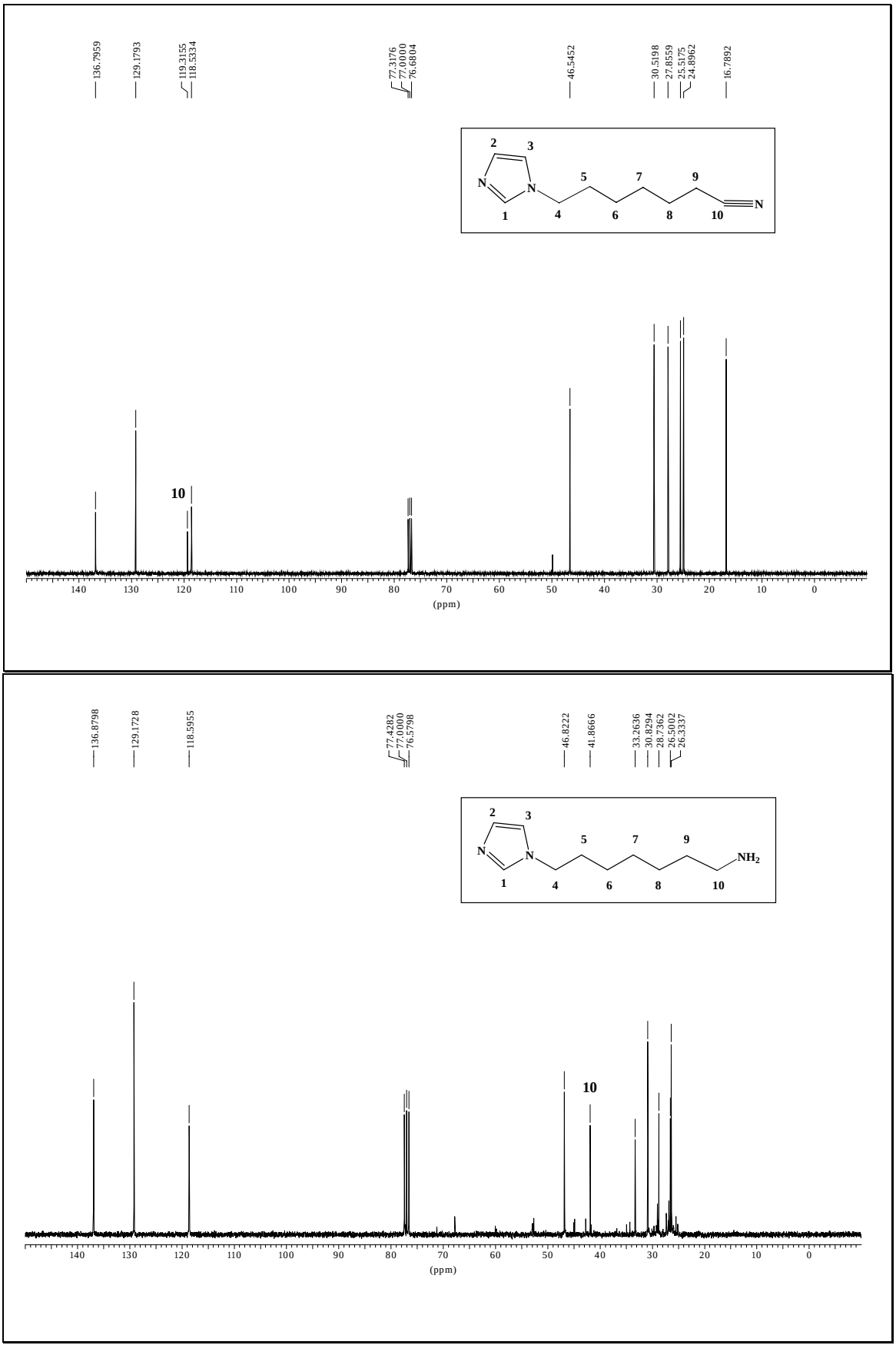


Figure 48: Evidence of the reduction of the nitrile functional group.

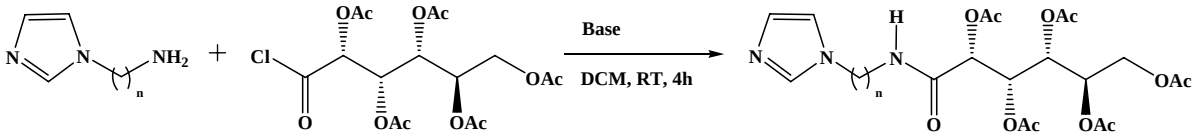
In Figure 48 the carbon 10 has been highlighted, proving that the nitrile group has been reduced. In the spectrum of the starting material **13** (Figure 48, up) the signal arises at 119.3 ppm, while in the product **14** (Figure 48, down) this signal has disappeared and a new signal has arisen at 41.8 ppm. This new methylene signal is slightly shifted downfield, compared to a normal methylene group of an alkyl chain, because of the new amine functionality nearby.

IV.4.2.4.2.3 Conclusion

With only two reaction steps, the ω-cyanoalkylimidazole reduction method has proven to be the most efficient of the three with an overall yield of 76% in the case of heptylamine (**14**) and 81% in the case of hexylamine (**9**). Its easy handling method and good overall yield, dictated this as the method of choice for the further formation of amines.

IV.4.2.5 Synthesis of *N*-(7-(1H-imidazol-1-yl)heptyl)-2,3,4,5,6-penta-O-acetyl-D-glucon amide (**15**)

The synthetic method to amines now established, the next step is to connect it to the sugar unit to build the amphiphilic molecule, we have originally thought of (Scheme 15).



Scheme 15: The *N*-[7-(1H-imidazol-1-yl)heptyl)-2,3,4,5,6-penta-O-acetyl-D-glucon amide (**15**) and (**16**) formation.

According to known methods for amide formation, the amine is solved in dichloromethane and the acid chloride would be dropwise added to the reaction mixture. The primary amine initially forms an intermediate with the acid chloride in which the nitrogen is positively charged. Consequently a base is used, if theoretically a second equivalent of amine should play this role; an additive base is often used. A problem of this reaction is the formation of hydrochloric acid. As known for its basic properties, pyridine is the base of choice because its conjugated acid will form a salt with the remaining chloride anion and avoid the gas formation. The results obtained were as average between 40% and 60% yield.

The test was also made with another base, triethylamine, also used in amide formation. The reaction using triethylamine did not prove to be more efficient with a yield of 54%. So the two bases are equivalent for this reaction. The average result is hard to understand, the potential traces of water in the solvent could turn the acid chloride into its precursor the carboxylic acid, but no traces of starting material can be found. The carboxylic acid is considered unreactive towards amide formation in comparison to the acid chloride. The column chromatography would provide only the product in the yields previously mentioned and pyridine. No starting material can be found, which probably means that the conversion is complete.

Another problem caused by the formation of an amide is the E/Z isomerisation. The amide can adopt two different configurations. (Figure 49)

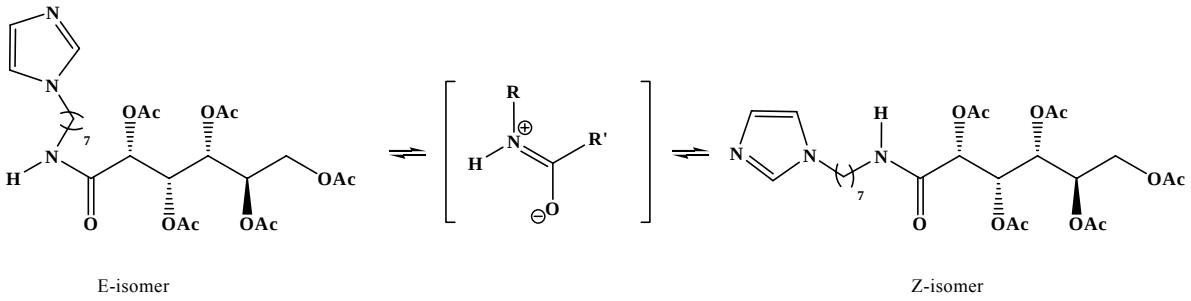


Figure 49: Possible isomeric structures.

The configuration is determined at the intermediate state, the formation of these two isomers will be seen by NMR. To go from one isomere to the other, one needs to rotate around the nitrogen - carbon bond. What makes the isomerisation to occur is the conjugation of the nitrogen lone pair with the carbonyl group, which would fix the configuration on E or Z. The energy difference needed to obtain an isomerisation is very low, so the molecule can rotate easily around the carbon - nitrogen axis. The NMR spectroscopy will give an average result and will often show one set of signals for the molecule, if the energy barrier is small.

To depict this isomerisation effect, the Figure 50 presents two substances that are anlaysed latern where the formation of these products is visible. On the Figure 50 left is showed the imidazolium salt **26** and on the figure 50 right is presented the complex **37**.

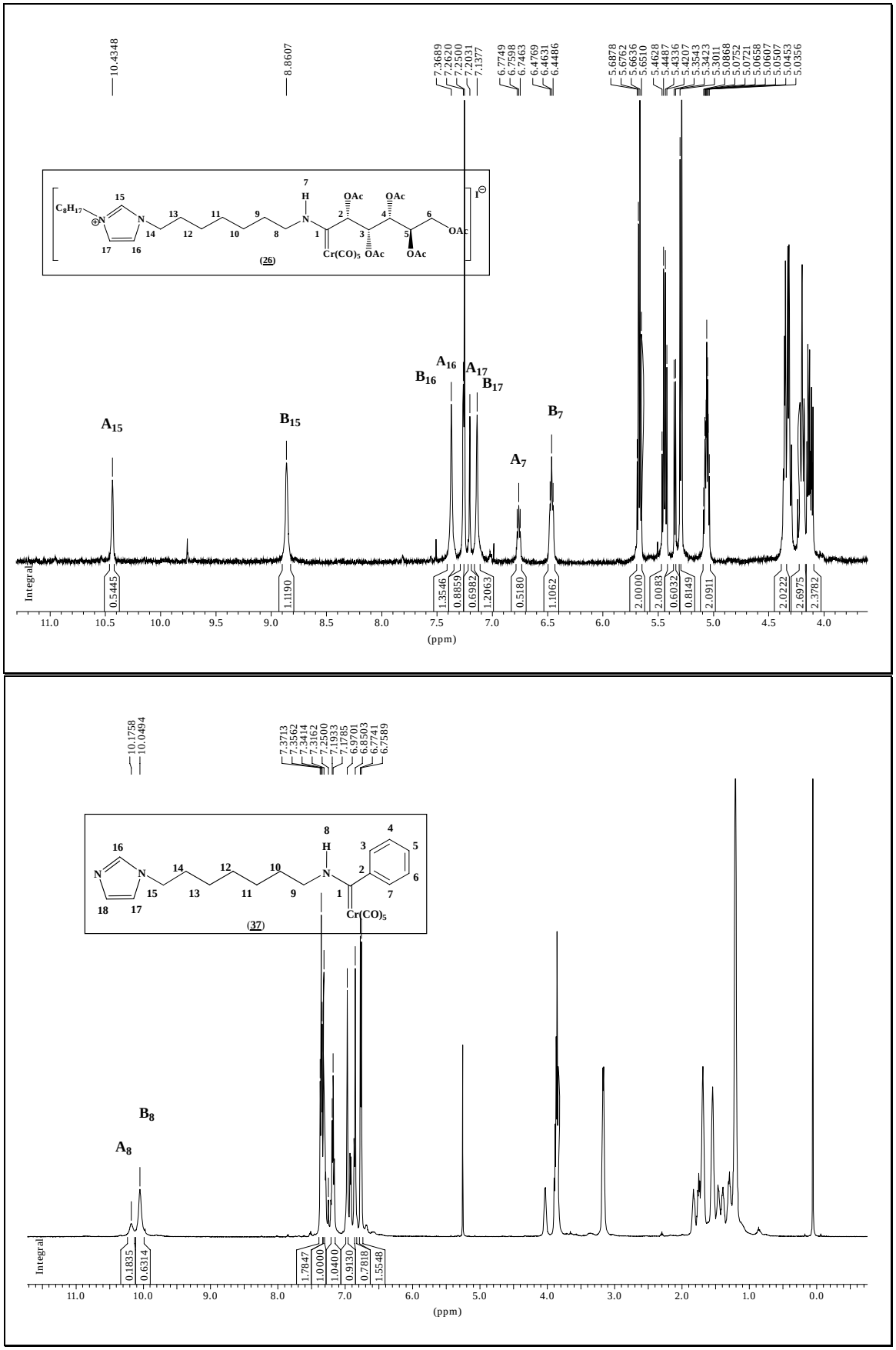


Figure 50: Examples of visible E/Z isomerisation effect on compounds **26** and **37**.

The different compounds can be easily identified in the NMR spectra but not attributed.In the upper example presented in Figure 50, the two E/Z systems can be identified with their respective integration, here marked A and B. It is noted that in the sugar reagion this effect is not visible where every signal integrates for one proton. On the bottom picture from Figure 50, the effects is still but less visible. The amide proton of the complex **37** is the only trace of this effect.

In the precise case of **15** that we are studying, the energy difference between the two states must be low, which always the case for amides. In fact one sees only one set of signals (Figure 51) but this E/Z differentiation occurs at this stage so it is the reason why it was important to mention it now.

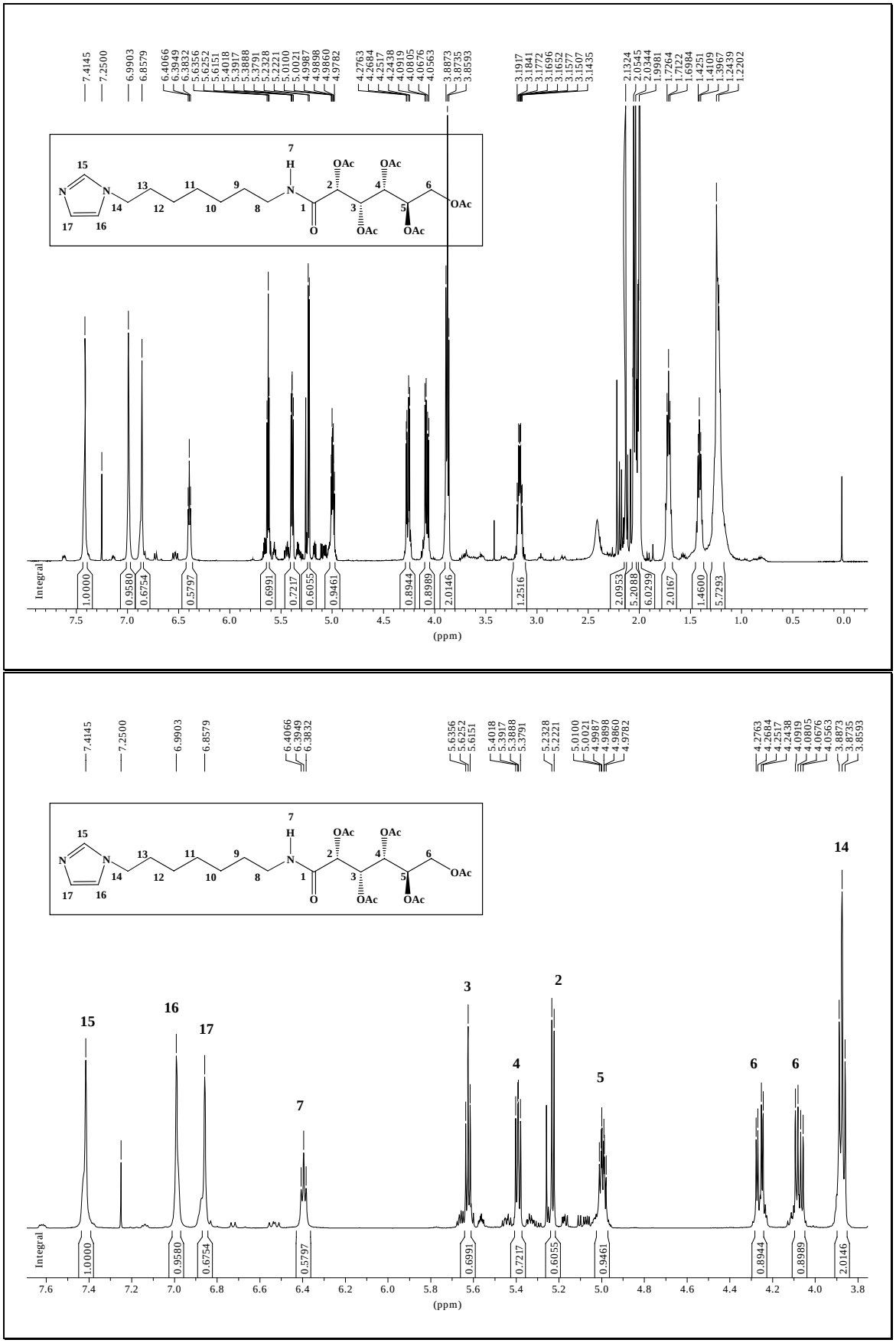


Figure 51: [1]H NMR spectra from molecule (**15)**.

One can see on Figure 51 that the explained difference of energy is low enough to have free rotation over the carbon - nitrogen bond. That the reason why only one set of signal can be seen. Even if one could argue that under the main signals in the sugar region there are other signals, they are not significant because too small, and the proton 7 is definitely alone. This proton 7 is also the proof that the amide has been formed and will come with the shift of a signal in the ^{13}C NMR from 162 ppm (to the acid chloride) to 165 ppm (Figure 52).

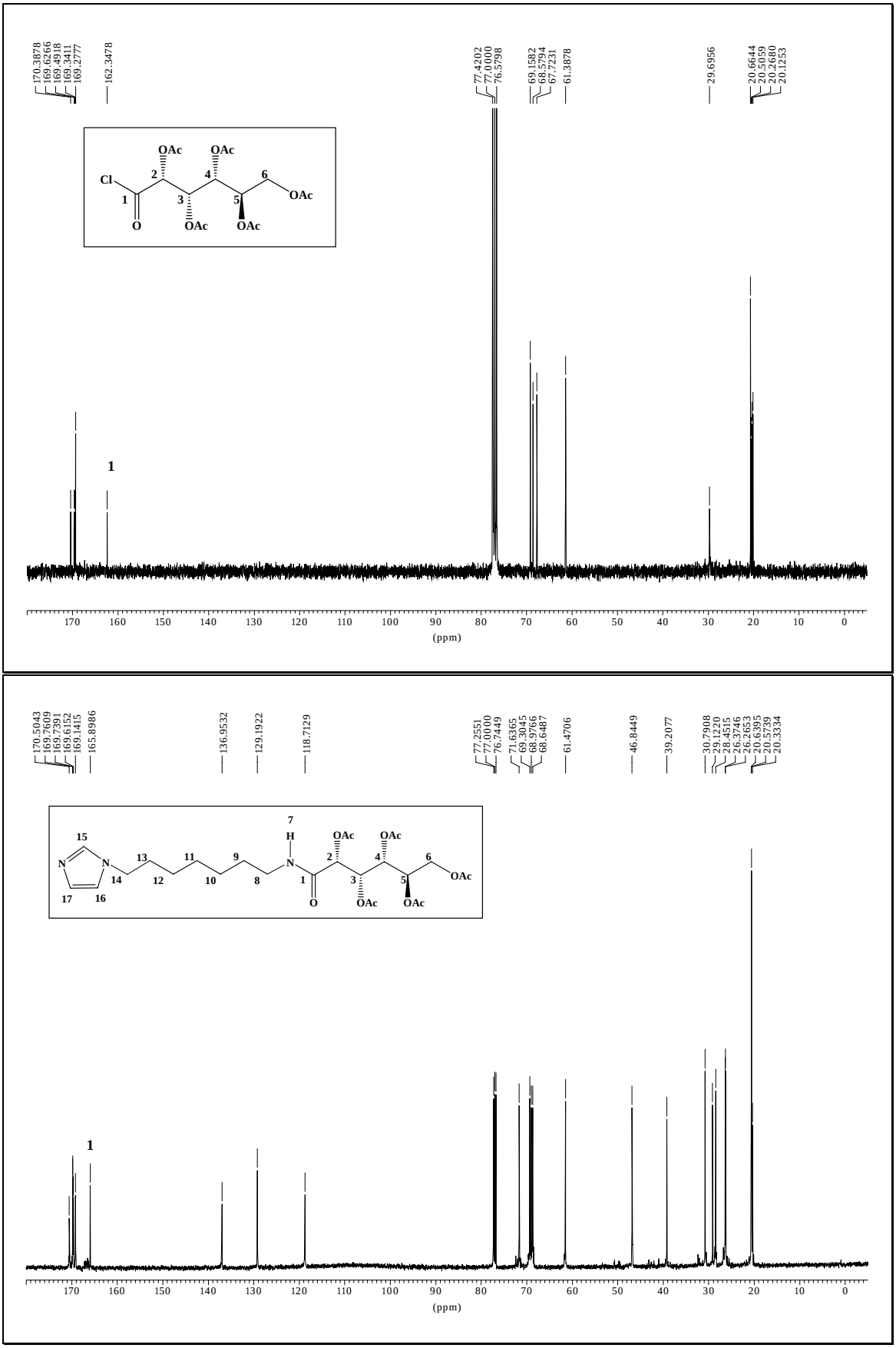
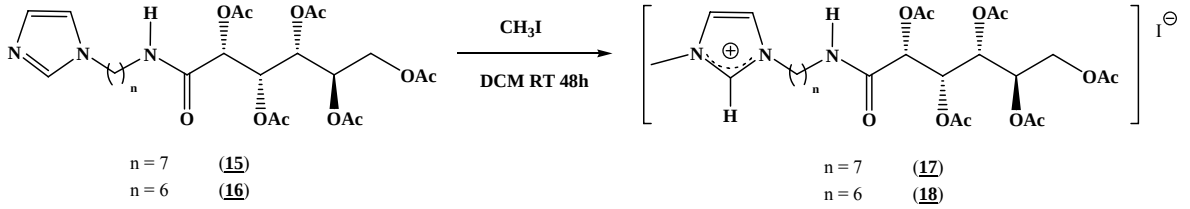


Figure 52: ^{13}C NMR: shift of carbonyl carbon signal in **15** compared to **2**.

With the molecule now bearing an imidazole, alkyl spacer and the hydrophilic protected sugar part, the next stage is to bring in the metal to the structure.

IV.4.2.6 Synthesis of 1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamido)heptyl]-3-*N'*-methylimidazolium iodide (**17**)



Scheme 16: 1-N-[7-N"-(2R,3R,4R,5S,6-penta-O-acetyl-hexanoylamino)heptyl]-3-N'-methylimidazolium iodide formation (**17**) and (**18**).

In order to form the *N*-heterocyclic carbene the imidazole moiety must be first quarternized. Following Rajanbabu's[82] alkylation method, the molecule is to be stirred for forty-eight hours at room temperature with methyliodide (Scheme 16). Methyliodide is a well known and very efficient alkylating agent. The reaction though needs a large excess of methyl iodide to achieve good yields (20 eq.). The product is obtained with up to 99% yield. The purification over silica gel column chromatography is not necessary and will definitely drop the yields, because of the nature of the product; most of it would just stay on the top of the column or decompose. Actually the excess of methyl iodide can be removed under the low pressure vacuum, and the crude substance is then washed with petrol ether.

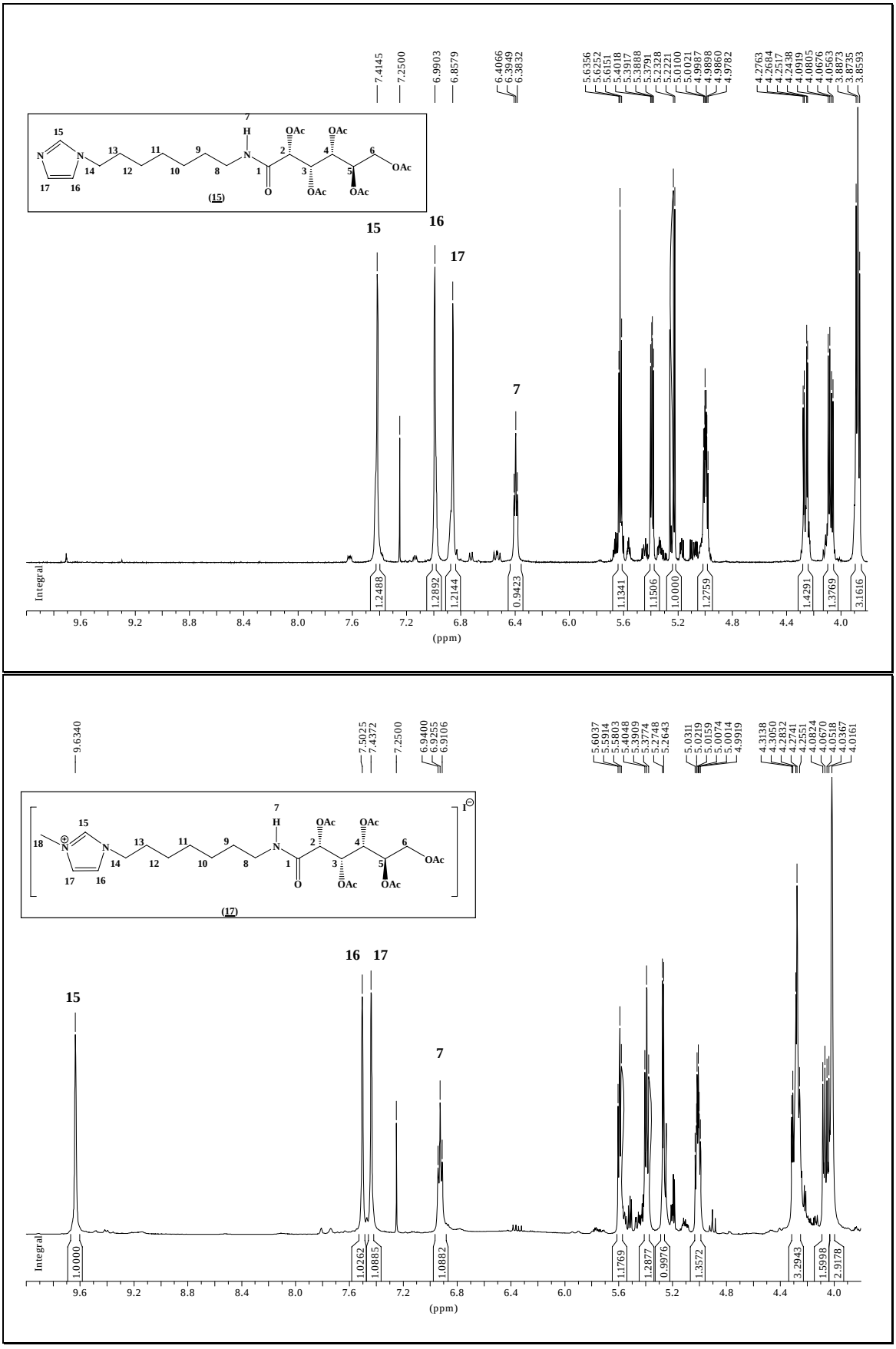


Figure 53: ^{1}H NMR: shift of imidazolium salt **17**.

As soon as the imidazole moiety is quaternized, the electron density in the heterocyclic ring is changed. The hydrogen on the central carbon, will have less electron density and then obtain a very acid character. In the ^{1}H-NMR acidic protons, because of the low electron density around the centre bearing them, are low fielded. As one can see on Figure 53, the shift of proton 15 has been importantly changed. The rest of the molecule does not seem to be affected. Of course one must see the appearance of three protons of the newly brought methyl group at 4.10 ppm. 4.10 ppm is actually high shifted for a methyl group, but the presence of nitrogen, which drags electrons, as neighbour introduces a change in its behaviour.

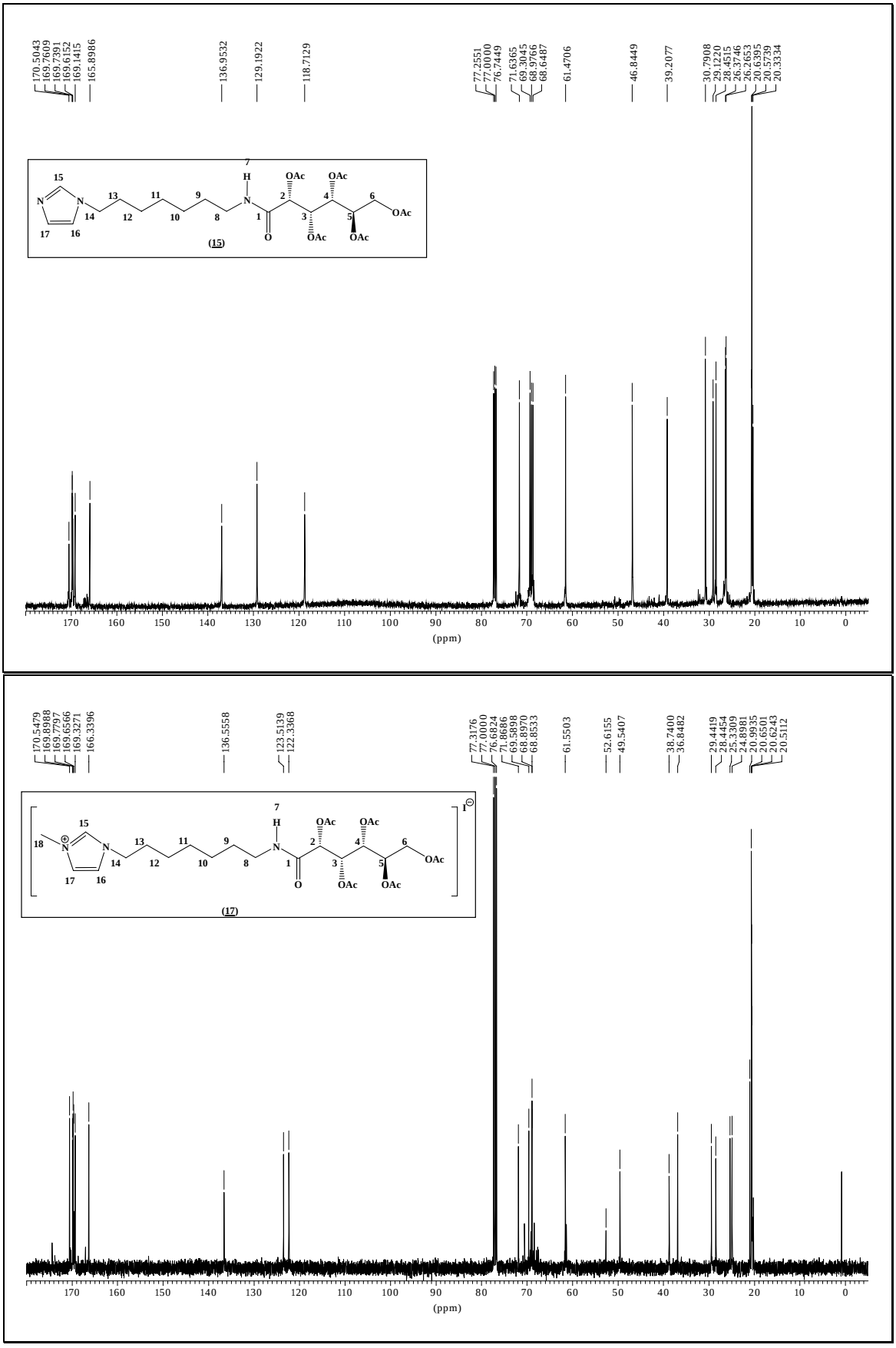
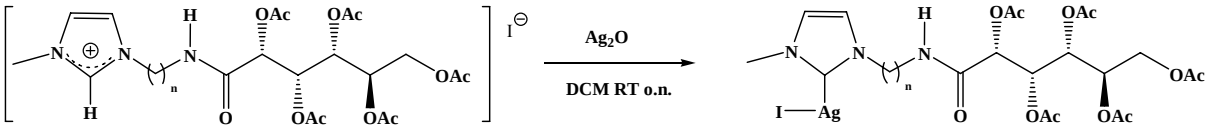


Figure 54: ^{13}C NMR: shift of imidazolium salt (**17**).

This methylation also has an influence on the ^{13}C-NMR (Figure 54). Interestingly, the three signals for the imidazole, in the 130 ppm range, do not change too much; maybe the two unsaturated carbons will have now similar shifts. The carbon atom number 14 does not move at all. The effective alkylation can be seen at 36.8 ppm where a new signal has appeared and the DEPT 135 spectrum differentiates it from the other signals as only primary carbon in this range.

The formation of the imidazolium salt compound is now achieved; the next step will then be the metalation of the complex. That is where the N-heterocyclic chemistry takes all its importance. In comparison to Fischer carbene chemistry, the whole backbone of the structure has been synthesised without any special precautions (i.e. inert atmosphere). With such a synthetic route one can now build, theoretically, a larger variety of metal complexes than with classic Fischer carbene structures.

IV.4.2.7 Synthesis of [1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamido)heptyl]-3-*N'*-methyl-2,3-dihydro imidazol-2-ylidene]silver(I)iodide (**19**)



n = 7 (**17**)
n = 6 (**18**)

n = 7 (**19**)
n = 6 (**20**)

Scheme 17: [1-N-[7-N''-(2R,3R,4R,5S,6-penta-O-acetyl-hexanoylamino)heptyl]-3-N'-methyl-2,3-dihydroimidazol-2-ylidene] silver(I)iodide (**19**) and (**20**) formation.

According to different papers,[83] the deprotonation of the acidic protons can be done by several different bases. Sodium hydride, catalysed with potassium *tert*-butoxide or potassium hydride could be too basic for the system, some protons on the sugar part on the amide, or the protective groups might not tolerate a too basic medium. That is why following Lin and Wang[45] mild silver oxide procedure was immediately thought of. The use of silver oxide will form a new metal complex which will be an excellent transmetalation complex for the next step. The silver oxide can be seen in two parts: silver (δ^+) and silver oxide (δ^-) species. (Figure 55) The formally negatively charged silver oxide moeity deprotonates the acidic proton and

forms silver hydroxide, while the remaining formally positively charged silver coordinates to the free carbene.[93]

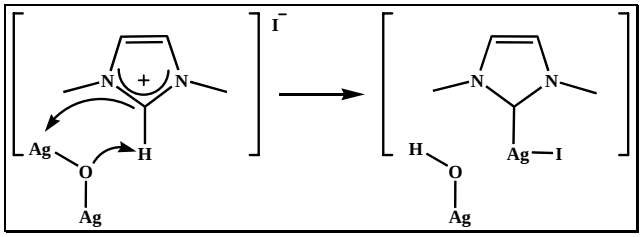


Figure 55: First step in the formation of the silver carbene (mechanism proposed after personal talk with Dr. Mangeney and coworkers).

The newly formed silver hydroxide can still react with another imidazolium salt. The reaction would lead to the formation of water and a second silver carbene complex. That is the reason why in most publications is found a 0.5 equivalent of silver oxide to the salt ratio. The reaction is easy to follow because silver oxide is not soluble in a solvent like dichloromethane. Its solution is a hint that the reaction is proceeding.[93] After workup (filtration over celite), the crude dark brown complex can be obtained in up to 98% yield.

The nature of silver complexes themselves makes it difficult to characterise them. As transfer reagent complexes they are very reactive and thus also very sensitive. Some silver complexes can be purified, crystallised and are characterised,[93] but in the case of the sugar complexes they have been too labile to survive more than filtration over celite. Their light sensitivity adds to the preacaution to be taken to handle them. The first hint for the formation of the complex is the disappearance of the acidic proton at 10 ppm in the ^{1}H-NMR spectrum, which means that the imidazolium cation has been successfully deprotonated. The ^{13}C-NMR spectrum reveals the presence of a new signal at 178.6 ppm that can be attributed to the carbene signal because it comes with the disappearance of the central imidazole carbon signal at 137 ppm. The silver carbene peaks are not so often visible in mass spectrometry but in the case of the hexyl alkyl spacer (**20**) the mass spectrum shows silver complex peaks. The mass spectrometry was done under FAB conditions, with mNBA (m-nitro benzyl alcohol) as matrix. Three interesting signals were spotted, the first signal and basis peak at m/z = 570.2 gives a hint on the presence of the free carbene. A second signal at m/z = 676.2 (10) can be interpreted as the silver carbene complex without its halide. There is lastly a peak at 1247.5

[93] Pytkowicz, J.; Roland, S.; Mangeney, P.*; J. Organomet. Chem.* **2001**, *631*, 157.

m/z that can be attributed to a silver complex bearing two NHC ligands. It has already been reported that the silver complex formation could depend on the solvent.[94] What is to be seen is that the dimerisation of the molecule is avoided.[95] (Figure 56)

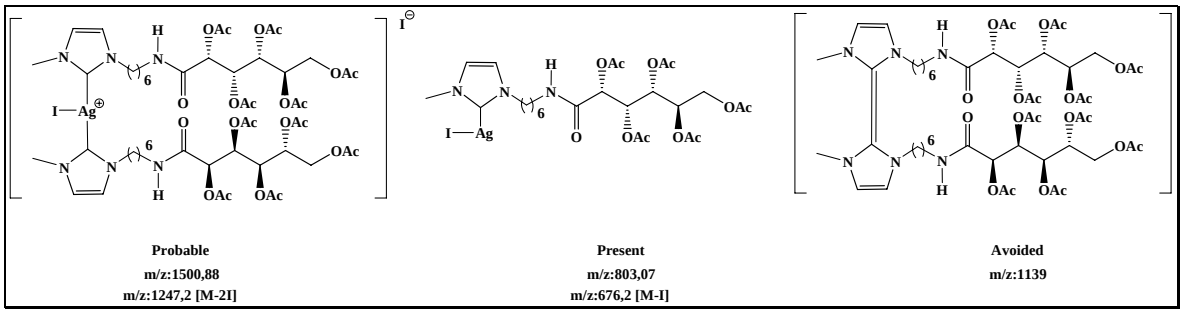
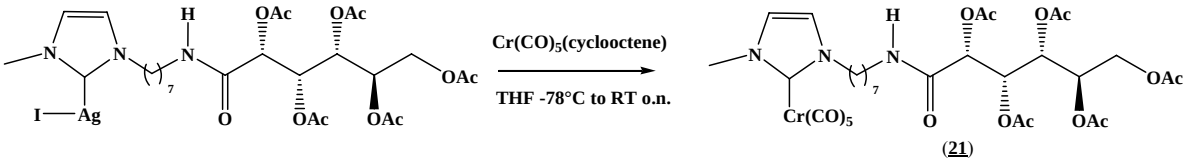


Figure 56: Possible silver carbene complexes found in mass spectrometry.

Now that the formation of silver carbene complexes, mono- or di-carbene, has been successfully established, the next step will involve the metal transfer.

IV.4.2.8 Synthesis of Pentacarbonyl[1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoyl amido)heptyl]-3-*N'*-methyl-2,3-dihydro imidazol-2-ylidene]chromium (**21**)

The choice of the metal was decided very early, the first organometallic gelator is based on chromium, so to have a point of comparison the first NHC sugar complex should also be based on chromium. The coordinative sphere around the metal is thought of being of great importance in the gel formation that is why a library of other metal complexes to synthesise, even if it can be seen as a chemical synthetic challenge, is not the first aim at the moment.



Scheme 18: NHC pentacarbonyl chromium complex formation (**21**).

With the chromium complex to be studied, the first precautions should be taken. The chromium pentacarbonylcyclooctene complex is the metal source of choice, because it can be

[94] De Frémont, P.; Scott, N. M.; Stevens, E. D.; Ramnial, T.; Lightbody, P. C.; Macdonald, C. L. B.; Clyburne, J. A. C.; Abernethy, C. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 6301.
[95] Hahn, F. E.; Wittenbecher, L.; Le Van, D.; Fröhlich, R.; *Angew. Chem. Int. Ed.* **2000**, *39*, 541.

prepared in large quantities in the laboratory and is easily be stocked. Cyclooctene is a very labile ligand, and traces of hexacarbonylchromium are always found after stock of the substance. Unfortunately, chromium hexacarbonyl is not reactive enough to be set in a reaction with the silver carbene complex. THF is a solvent of choice, it quickly substitutes the cyclooctene ligand and the newly THF formed complex is stable in solution. The exchange can be monitored by a colour change of the solution. The pentacarbonyl cyclooctene complex is yellow; the THF one is light orange. The exchange occurs already at low temperature, that is the reason why, a first flask containing the silver carbene complex is prepared and the complex is solved in THF and precooled at -78°C, in a second one, the chromium pentacarbonyl complex is solved with -78°C precooled THF. The THF chromium solution is then as soon as possible transferred to the silver carbene complex solution. The precautions are designed to lower the exchange of THF with cyclooctene, and to maximise the chances of reaction with the silver carbene complex. The reaction can be also easily monitored just by seeing the precipitation of silver halides. The IR spectroscopy could not be of a great interest before the purification of the product, because of the presence of hexacarbonylchromium, which will hide any other signals. The purifications are done over silica gel column chromatography with dichloromethane and methanol and afford a yellow solid with an average of 40% (for $(CH_2)_6$ bridge, **22**) and 65% (for $(CH_2)_7$ bridge, **21**) yields respectively.

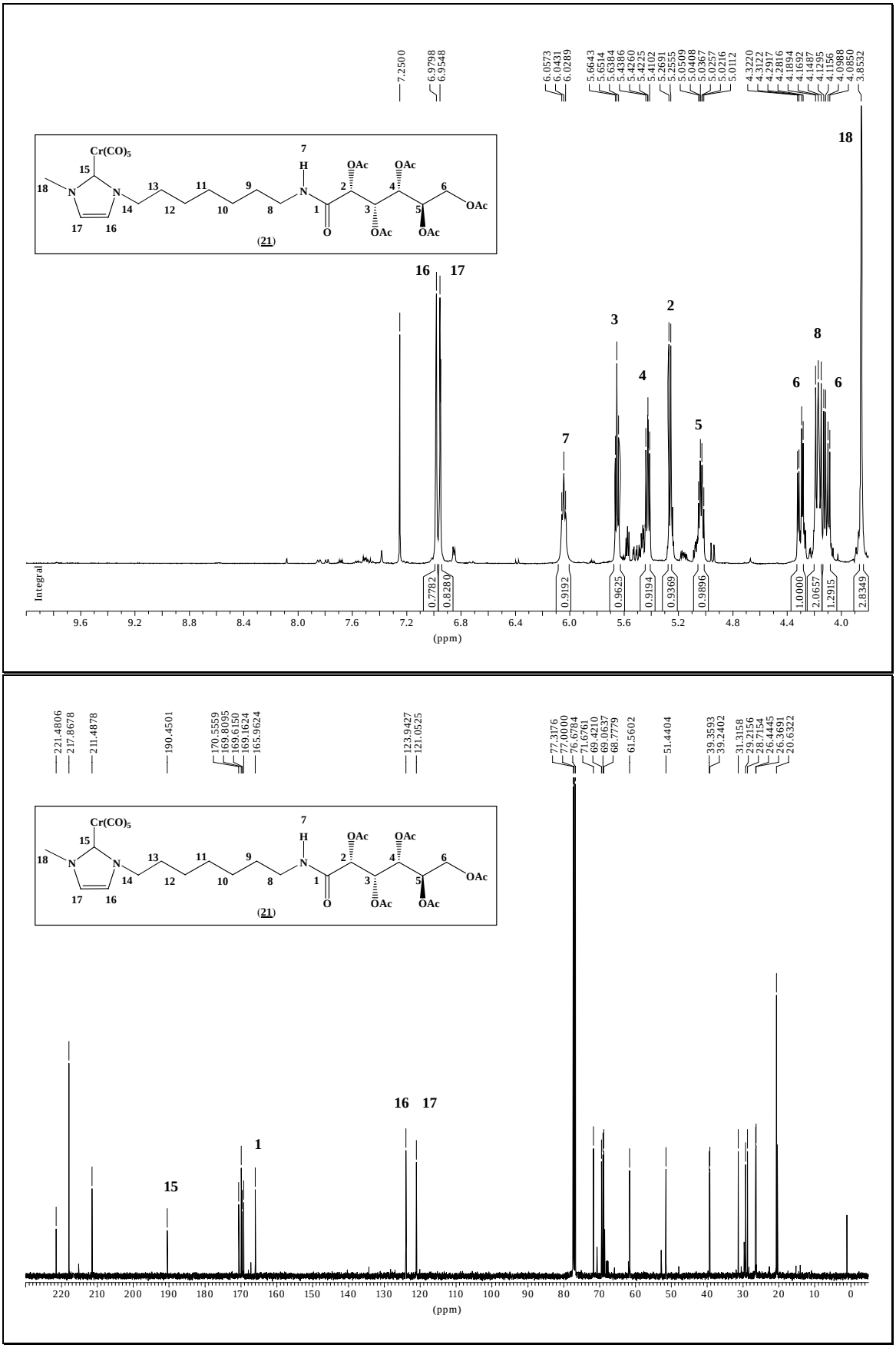


Figure 57: ^{1}H-NMR (upper picture) and ^{13}C-NMR (lower picture) evidences of the chromium complex formation (**21**).

The first evidence in the ^{1}H-NMR spectrum that the chromium carbene complex is formed is that the imidazole moiety now only exhibits two protons. The acidic proton, formally on position 15, has been removed by the silver oxide action, and then the silver itself was exchanged for the chromium. The ^{1}H-NMR (Figure 57, up) shows also the presence of the amide proton (7) and the sugar part (3, 4, 5, 6). The ^{13}C-NMR (Figure 57, down) provides several new signals; first of all at 190.5 ppm the new designed carbene carbon (C_{15}). The carbene carbon signal in the silver complex was seen at 178 ppm which corresponds to a shift of 12 ppm. The carbonyl carbons from the pentacarbonyl moiety exhibit also characteristic signals in the ^{13}C-NMR spectrum. In chromium hexacarbonyl the metal coordinates to six ligands, which results in an octahedral symmetry. As one ligand has been exchanged the symmetry is disturbed (Figure 30).

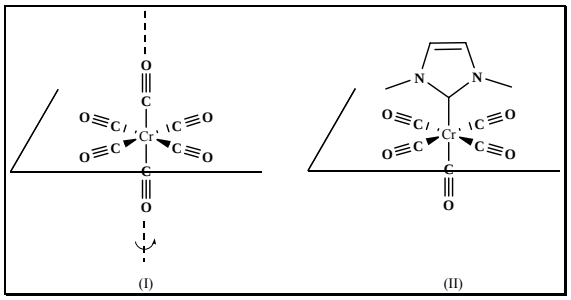


Figure 58: Symmetry disturbance in the chromium coligand sphere resulting in different ^{13}C-NMR signals.

In the case of chromium hexacarbonyl (Figure 58, I) every carbonyl ligand is equivalent so it is expected to see only one signal (at 211 ppm; Figure 57, right). In the case of the NHC complex (Figure 58, II), it is understandable that the four planar carbonyl groups are equivalent, but the last carbonyl group is trans to the carbene, so it is expected to have a signal for one carbonyl and one for the four other carbonyl ligands. As expected, two different signals at 221.5 ppm and 217.9 ppm can be seen (Figure 57, bottom). The integration of signals in ^{13}C NMR spectrum is not significant, but to equivalent carbon, such consideration is a hint. The correlation between the smaller carbonyl signal at 221.5 ppm and the one at 217.9 pm gives a 1 to 4 ratio, just as expected.[96] Of course if the symmetry is disturbed, other analytical methods could prove the formation of the substance. As explained by Cotton,[97] complexes of the type $LM(CO)_5$ (M = Cr is exposed) have a C_{4V} symmetry and show three different bands in the IR spectra, the two A_1 and one E. After investigation on the force constants Cotton found out that actually the B_1 band, even if not infrared active in such

[96] Tafipolsky, M.; Scherer, W.; Öfele, K.; Artus, G.; Pedersen, B.; Herrmann, W. A.; McGrady, G. S.; *J. Am. Chem. Soc.* **2002**, *124*, 5865.
[97] Cotton, F.; A; Kraihanzel, C., S.; *J. Am. Chem. Soc.* **1962**, *84*, 4432.

symmetry, could be present. The mechanical coupling of the CO stretching in the ligand could enable the B_1 to gain intensity. This incident implies a degeneracy of the $A_{1\text{-}2}$ and the E bands. All the NHC-$Cr(CO)_5$ complexes should exhibit two or three bands which consist of a medium A_1 a strong E ($A_{1\text{-}2}$) and sometimes a B_1 band. The Infrared (FTIR) spectrum in Figure 59 confirms what Cotton predicted.

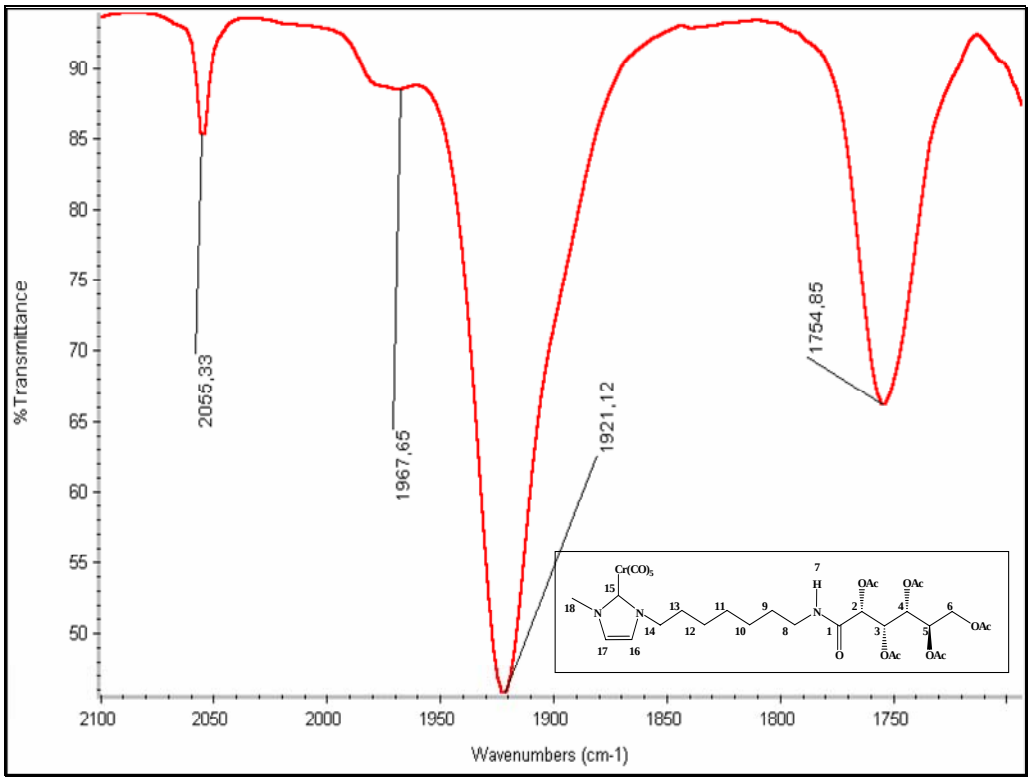


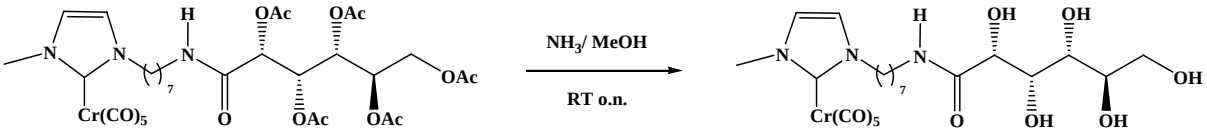
Figure 59: FTIR spectrum of **21** resulting from the carbonyl dissymmetry around the metal center.

The spectrum shows without a doubt the presence of a pentacarbonyl chromium complex, the bands correspond to the typical pentacarbonyl structure, with signals at 2055 cm^{-1} (m, A_1), 1921 cm^{-1} (vs, E). As reference the chromium hexacarbonyl structure exhibits a signal at 1980 cm^{-1} (vs) in dichloromethane, solvent used for the spectrometry. The signal at 1754 cm^{-1} corresponds to the carbonyl groups from the protective acetyl groups.

IV.4.2.9 Synthesis of Pentacarbonyl[1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-hydroxy-hexanoyl amido)heptyl]-3-*N'*-methyl-2,3-dihydro-imidazol-2-ylidene]chromium (**23**)

IV.4.2.9.1 *Synthesis*

As said above, the protecting groups will be now removed in order to facilitate the formation of aggregates. The formation of hydrogen bondings should be the main driving force.



(**21**) (**23**)

Scheme 19: Deprotection of the glucose subunit under basic conditions (**23**).

Under basic conditions, ammonia in methanol, the acetyl groups will be attacked leaving the hydroxy groups free.[79] The reaction time can be long because of the five protective groups. Some molecules are first fully deprotected and others just partially. The best monitoring method is TLC. The product is a recovered as light yellow solid after column chromatography. The eluent mixture must be polar enough, without MeOH in the eluent mixture the product will not move on the silica gel. After several tests the best mixture is found to be dichloromethane (80%) and methanol (20%). The problem of such polar eluents is that it also drags lots of normally unwanted by-products from the column which always affect the analytics.

IV.4.2.9.2 *Discussion*

The main problem will be the analytical investigations. Theses molecules are not easily soluble in common deuterated solvents, the only execption being MeOD. The drawback from such a solvent in the presence of exchangeable protons is that the signals of most protons will disappear. In the ^{1}H-NMR spectrum the amide proton then disappears and so do the five hydroxy protons. Even if the signals are detected the attribution is very relative. The determining analytic is the ^{13}C NMR spectrum, because the NMR solvent does not affect it, and the IR spectrum that will show the disappearance of the acetyl groups in combination

with mass spectrometry datas. The ^{1}H-NMR spectrum shows however the important signals, such as the two imidazole proton signals at 7.30 ppm and 7.27 ppm. The alkyl chain signals are detected at 1.84, 1.54 and 1.45 ppm and the disappearance of the methyl group signals for the acetyl protecting groups can be seen. The signals for the sugar part and the methylene groups connected to the imidazole and amide functionality in the 4 to 5 ppm range have no clear shape to be cleary distinguished. The protons on the glucose are expected to be in that range because the acetyl protecting moiety was electron withdrawing, which means that it would drain the electron density shifting the protons at each of the five carbons atoms from the gluconic part to higher field, which was the case found earlier.

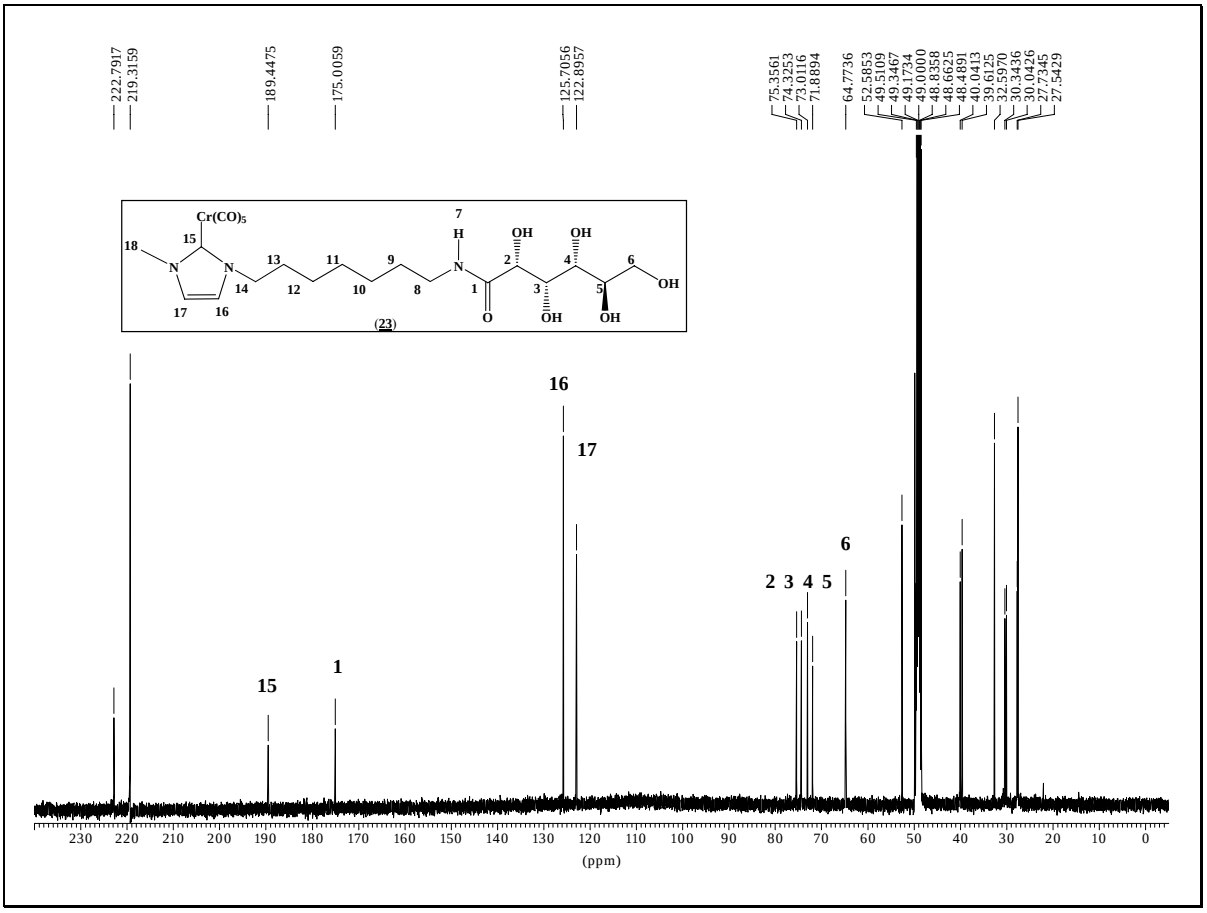


Figure 60: ^{13}C NMR spectrum from the deprotected product (**21**).

The loss of the five signals at 180 ppm and at 25 ppm for the methyl groups compared to **21** prove the deprotection. The FTIR spectrum shows the disappearance of the characteristic acetyl group at 1754 cm^{-1} shown previously in Figure 59. Figure 61 shows the difference before and after the deprotection.

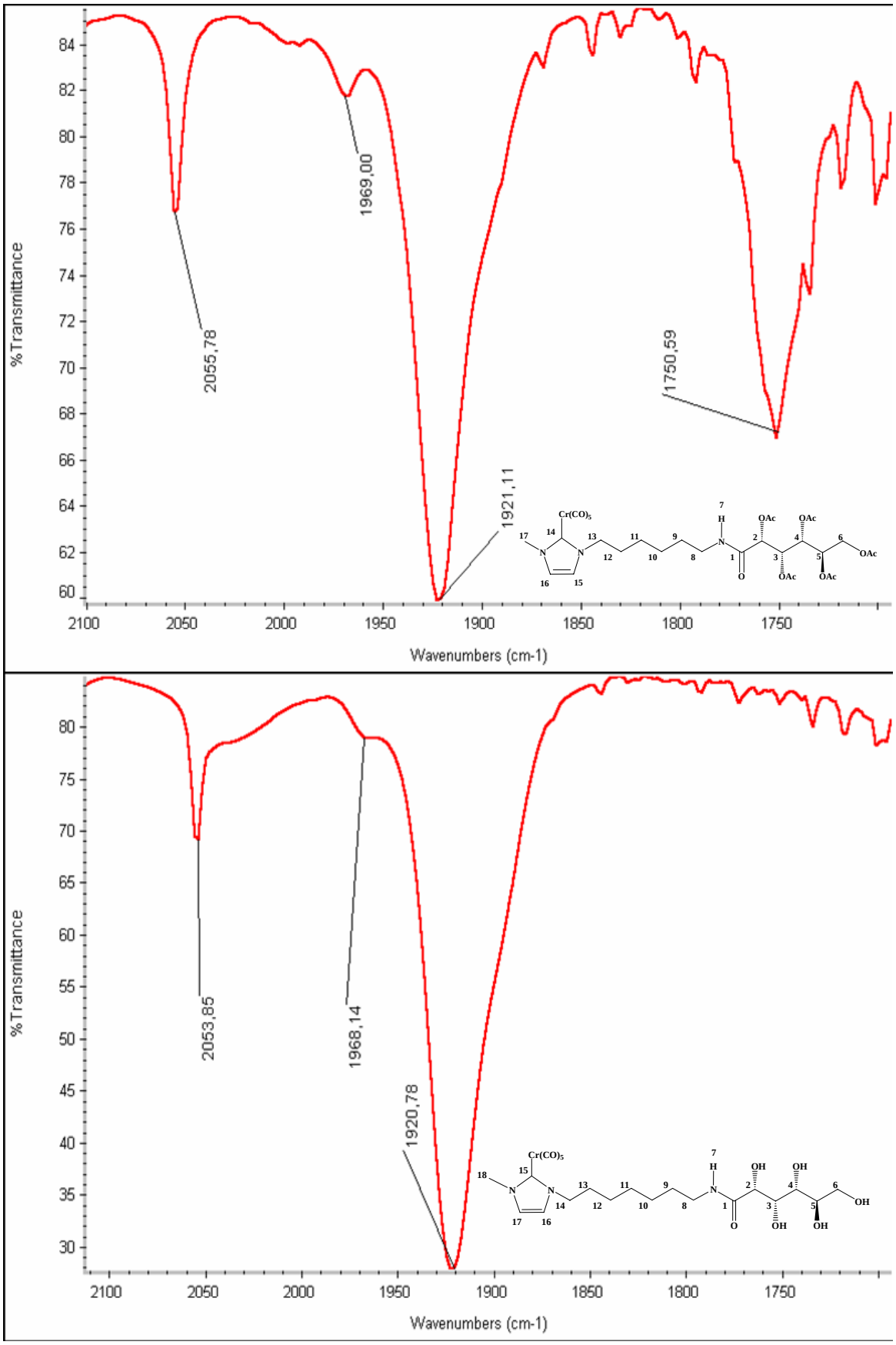


Figure 61: FTIR spectrum of the protected and deprotected carbene complexes (**22**, up; **23**, down).

The formation of the product is finally confirmed by the mass spectrum showing a peak at m/z = 564.1293, with the ESI method in negative modus, which corresponds to the molecule without one proton.

Now that the synthesis of the first of this new class of amphiphilic molecules is achieved, it has to be evaluated if the balance between hydrophilicity and lipophilicity provides gelation. All tests have to be carried out under argon atmosphere. The first tests are made with a concentration of 5 weight percent. (It means that for a 100% weight sample, 5% of this weight corresponds to the total amount of gelator in the sample) The behaviour of the substance was tested on a large panel of solvents.

	MeOH	CH_3CN	DMSO	DMF	CH_2Cl_2	$CHCl_3$	CCl_4	Et_2O	C_6H_6	Tol	cy-Hex	PE	*n*-Hex
Behaviour	S	P	S	S	S	S	P	P	P	P	P	P	P

Table 1: Behaviour of chromium carbene **23** in different solvent (5 wt %) (P = Precipitation; S = Solution).

In Table 1, the solvents are ordered according to decreasing polarity. On the first view, it is obvious that the molecule seems to be too polar, showing no or poor solubility in low polar solvents (*n*-hexane, benzene, toluene), while more polar solvents like MeOH or CH_2Cl_2 simply dissolve it. The deprotected carbene complex with six CH_2 methylene bridge, was deprotected, but the NMR done in D_2O despite the pattern of a pentacarbonyl and imidazole visible could not used to describe the product because of scale problem, the chemical shifts do not fit to the structure.

IV.4.2.9.3 *Conclusion*

According to the first results showed here, it is clear that the balance between hydrophilicity and lipophilicity has not been found. Compared to the original carbene gelator the main difference is the change of the carbene position. The Fischer carbene was in the middle of the structure making it a real amphiphile, but the first attempt (see chapter **IV.3.**) to replace the Fischer carbene by an NHC was not succesful. The introduction of a spacer between the imidazole moiety and the sugar part turns it more into a bolaamphiphilic system. The carbonyl and the hydroxy groups on the sugar and the carbonyl groups on the metal might form hydrogen bonds; it would mean then that the lipophilic part could be not big

enough to counter this effect. The first solution to it is to enhance the lipophilic effect, which means to change the length of the alkyl chain.

This tuning of the molecule is based on the skeleton of N-[7-(1H-imidazol-1-yl)heptyl)-2,3,4,5,6-penta-O-acetyl-D-glucon amide (**15**). With a known synthetic procedure the molecules should be achieved quickly.

IV.4.2.10 Synthesis of 1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamino)heptyl]-3-*N'*-"alkyl"-imidazolium "halide"

IV.4.2.10.1 *Synthesis*

As previously explained the starting material of the synthesis is the amide (**15**), the same procedure is applied to achieve the formation of imidazolium salts with a C_2, C_4, C_8 and C_{16} alkyl chain. (Figure 62)

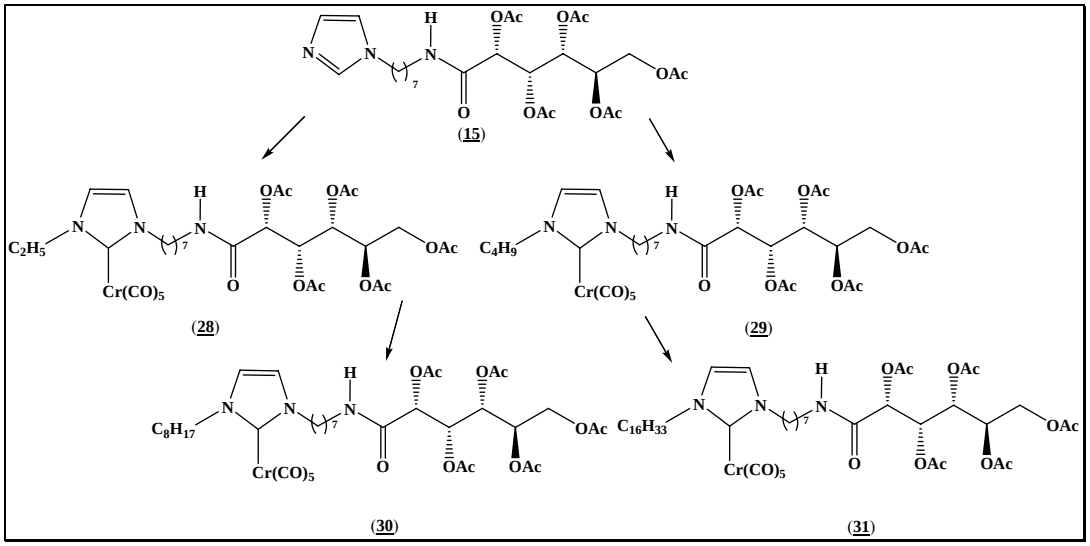
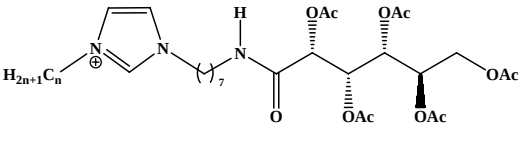


Figure 62: Controlled evolution of the lipophilicity in the imidazolium chromium carbene complex.

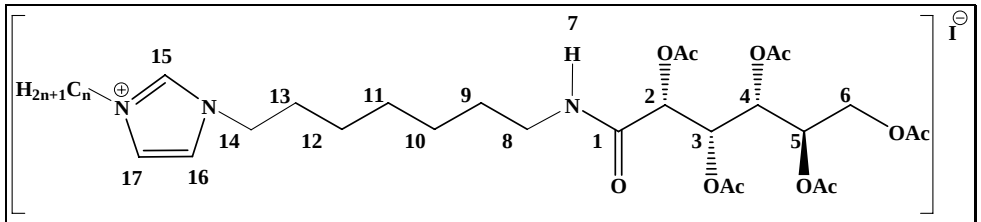
The preparation of the imidazolium salts will follow the same protocol as the one shown in Scheme 16. The imidazole amide **15** is dissolved in the smallest possible amount of dichloromethane and 20 equivalents of the alkyl halide are then given to the reaction. The first attempts were made with bromide as halide, because it is easily available. Ethyl bromide, butyl bromide and hexadecyl bromide give the differents salts with average to good yields, decreasing as the chain would grow in length. (Figure 63)



	A⁻	Yield	A⁻	Yield	
C_2H_5	Br^-	70%	I^-	99%	(**24**)
C_4H_9	Br^-	56%	I^-	91%	(**25**)
C_8H_{17}			I^-	99%	(**26**)
$C_{16}H_{33}$	Br^-	44%	I^-	93%	(**27**)

Figure 63: Imidazolium salt with different alkyl chain lengths yields.

Octyliodide gave good yields (99% yield in the best case). Following this result, all reactions were again performed with the corresponding alkyl iodides. The expected results were achieved, with a nearly complete efficiency (Figure 63). As shown in Figure 64, the first hint of the success of the reaction will be seen in the ^1H NMR. It expected again to have low field shifted protons because of the salt formation.



	Proton N°15	Proton N°16	Proton N°17	Proton N°7	$C_nH_{2n+1}CH_2$-N	
Starting Material	7.42	6.98	6.84	6.56	-	
C_2H_5	10.1	7.46	7.43	6.70	4.32	(24)
C_4H_9	10.2	7.43	7.33	6.70	4.33	(25)
C_8H_{17}	10.3	7.40	7.28	6.70	4.10	(26)
$C_{16}H_{33}$	10.25	7.40	7.27	6.70	4.10	(27)

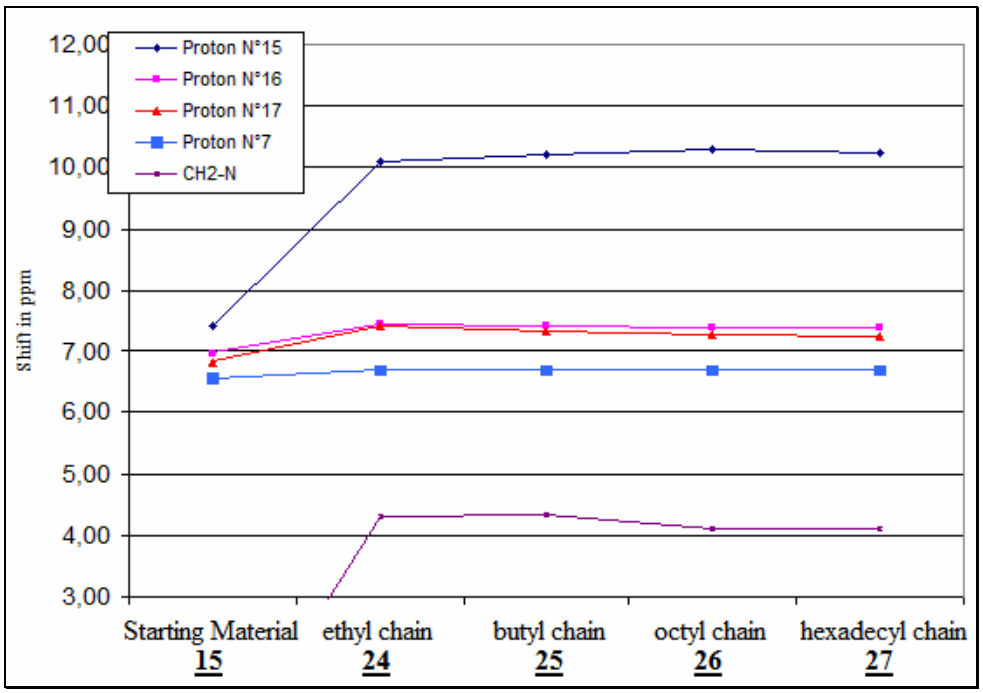


Figure 64: Evolution of the shift (in ppm) of the most important protons in $CDCl_3$.

IV.4.2.10.2 *Discussion*

The most influenced proton is, of course, the proton on position 15 (Figure 64). From 7.42 ppm it is shifted to a very acidic type shift of 10.3 ppm average, which seems not to be depending on the alkyl chain length substituent. The two other protons on the imidazole part are also affected but not as much as the proton number 15, they are shifted of a 0.5 ppm average. The proton number 7, as known as the amide proton, is hardly changed from the starting material to the products and has an average shift of 6.70 ppm. This value indicates

that the sugar part is still connected to the imidazolium salts. At last, the appearance of a signal at 4 ppm is very important. It shows that a methylene group is now connected to the nitrogen, its very low field shift is a result of the poor electron density at the imidazole ring. 3.8 ppm could have been expected for a methylene connected on a nitrogen (example: the protons on methylene number 14 in the starting material are at 3.85 ppm). The difference in the shift from 4.30 ppm to 4.10 ppm between the first two salts **24** and **25** and the two others **26** and **27** can be attributed to a higher inductive effect due to the longer chain, even if the inductive effects are quite relative. In the ^{13}C-NMR spectrum the appearance of a new signal at 40 ppm is the proof of the connection of a new methylene group, from the alkyl substituent, and a nitrogen on the imidazole (Figure 65). Again, the shift difference between the four new substances on the methylene group can be attributed to the inductive effect.

That is where the NHC chemistry is easier than the Fischer carbene chemistry to obtain such structures. The ligand structure can be obtained after several organic steps leaving the metal step as the last one. The metal complexes are now formed with the previously shown "silver route" (Chapter **IV.4.2.7**).

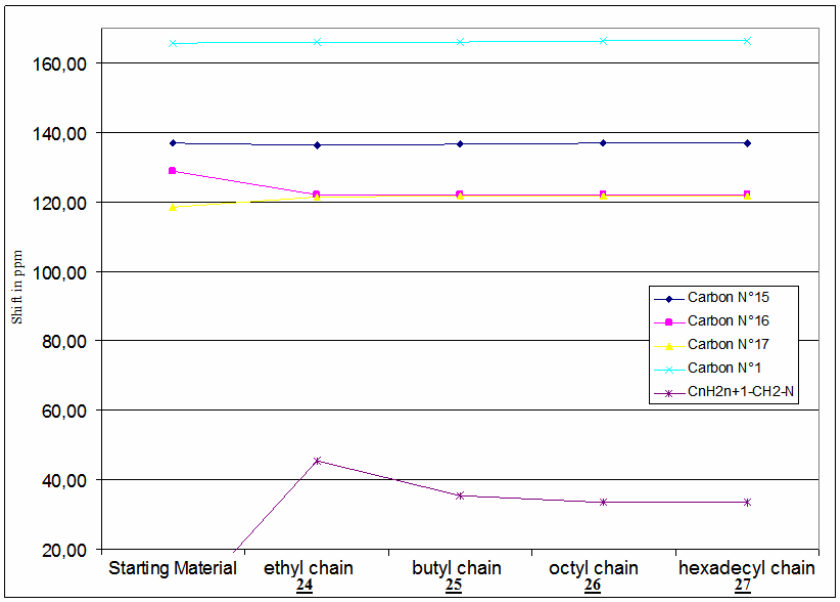
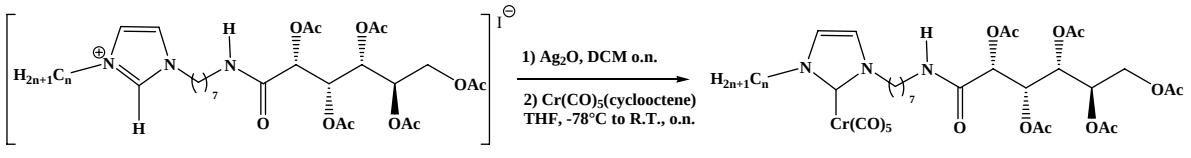


Figure 65: ^{13}C-NMR carbon shift comparison between the different imidazolium salts formed.

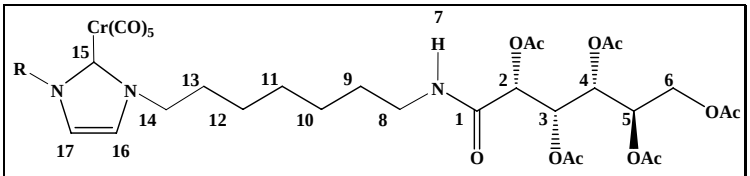
IV.4.2.11 Synthesis of Pentacarbonyl[1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoyl amino)heptyl]-3-*N'*-"*alkyl*"-2,3-dihydro-imidazol-2-ylidene]chromium



C_2H_5 : (**24**) C_2H_5 : (**28**)
C_4H_9 : (**25**) C_4H_9 : (**29**)
C_8H_{17} : (**26**) C_8H_{17} : (**30**)
$C_{16}H_{33}$: (**27**) $C_{16}H_{33}$: (**31**)

Figure 66: General adopted route to the NHC chromium pentacarbonyl carbene systems **28** - **31**.

The formation of the new chromium complexes involves two organometallic steps. The first one is the formation of the silver carbene complex that will be used as metal transfer reagent. Convinced previously by the light sensitivity of these complexes and because of the average yields (see chapter **IV.4.2.7**), the decision was taken to make one reaction out of two reaction steps. To prevent decomposition of the silver intermediate because of light exposure and purification, the chromium carbene complex formation is immediately set after the accepted time to generate to the silver carbene complex (eight hours) is over. As a reminder the two steps reaction gave a 65% x 65% = 42% overall yield for compound **21**.

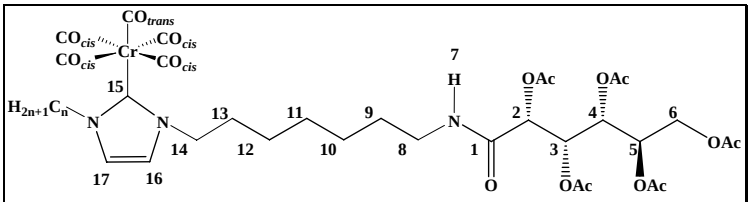


R	CH_3	C_2H_5	C_4H_9	C_8H_{17}	$C_{16}H_{33}$
Yield for 1 step strategy (exception of CH_3)	42%	54%	38%	46%	46%
	(**21**)	(**28**)	(**29**)	(**30**)	(**31**)

Figure 67: Yields for the complexes **28** to **31** generated by the "one-pot" strategy.

In Figure 67, it is shown that in most cases this "one-pot" strategy has improved the yield. After formation of the silver complex, the resulting dark brown solution is filtered over celite, to remove excess or unreacted material. After concentration under low pressure, the dark crude product is dissolved in precooled THF (-78°C), and a THF solution of $Cr(CO)_5$(cyclooctene) is added. This new protocol gives higher yields and saves time between

the silver complex analytics and the synthesis of the chromium complexes. It also reduces the risk of decomposition of the silver complex due to light exposure.

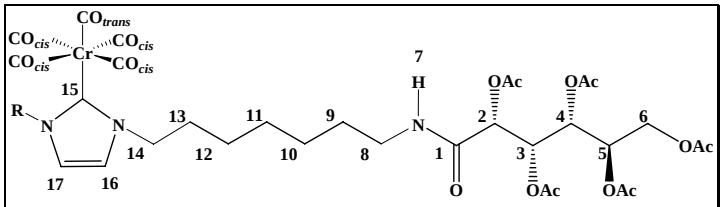


	Carbon N° 15	Carbon CO trans	Carbon CO cis	Carbon N° 1	C_nH_{2n+1}-CH_2-N	
Starting Material (Average Value)	137	-	-	166	37.5	(**15**)
C_2H_5	189.3	221.6	217.7	165.9	39.3	(**28**)
C_4H_9	187.4	221.8	217.3	165.7	39.3	(**29**)
C_8H_{17}	189.4	221.7	217.7	165.9	39.3	(**30**)
$C_{16}H_{33}$	189.5	221.6	217.7	165.9	39.2	(**31**)

Figure 68: ^{13}C-NMR shift (in ppm) evolution for complexes **28** to **31** of the most important carbon signals in $CDCl_3$.

The analytical data shown in Figure 68 indicate the formation of the different complexes with an important shift in the ^{13}C NMR spectrum of the carbon atom number 15 compared to the starting material **15**, which changes its behaviour from an aromatic carbon to a metal carbene carbon. The signal at 189 ppm (187 ppm for complex **29**) is typical for a *N*-heterocyclic carbene, the two sets of signals at 221 ppm and 217 ppm found in every complex show the presence of the pentacarbonyl chromium moiety with the expected *cis*/*trans* pattern.

This *cis*/*trans* behaviour of the carbonyl groups is also seen in the IR spectra, which one are summarised in Figure 69; it reveals also the familiarity between all the newly formed complexes (**28**, **29**, **30**, **31**) and the original complex (**21**).



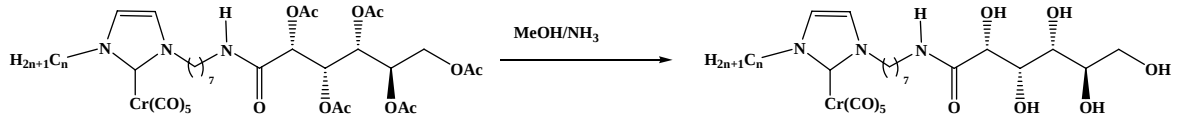
R	A_1	E	B	Acetyl	
CH_3	*2055*	*1921*	*1899*	*1754*	(**21**)
C_2H_5	2053	1920	1897	1751	(**28**)
C_4H_9	2054	1921	1894	1751	(**29**)
C_8H_{17}	2055	1920	1899	1754	(**30**)
$C_{16}H_{33}$	2055	1920	1899	1754	(**31**)

Figure 69: IR data prooving the similarities of the new complexes to the first synthesised.

The last step of the synthesis involves the deprotection of the hydroxyl groups.

IV.4.2.12 Synthesis of Pentacarbonyl[1-*N*-[7-*N''*-(2R,3R,4R,5S,6-pentahydroxy-hexanoyl amino)heptyl]-3-*N'*-"*alkyl*"-2,3-dihydro-imidazol-2-ylidene]chromium

IV.4.2.12.1 *Synthesis*



C_2H_5 : (**28**)
C_4H_9 : (**29**)
C_8H_{17} : (**30**)
$C_{16}H_{33}$: (**31**)

C_2H_5 : (**32**)
C_4H_9 : (**33**)
C_8H_{17} : (**34**)
$C_{16}H_{33}$: (**35**)

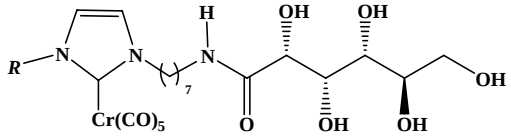
Figure 70: General adopted route to free hydroxy chromium pentacarbonyl NHC complex systems **32** to **35**.

The new established library of complexes is to be tested as low molecular mass gelators after the deprotection of the gluconyl hydroxy groups. All the new complexes should be more hydrophobic than the complex **21**, hoping then to find the right balance between hydrophilicity and hydrophobicity. As seen before, the deprotection occurs under mild conditions with a saturated solution of ammonia in methanol. All new complexes are obtained

with an average yield of 13% to 36%. These low yields can be attributed to the partial deprotection of complexes or decomposition.

As said before, the deprotection of the complexes is accepted when in the ^{13}C-NMR spectra no more acetyl protecting groups signals are detected, the FTIR spectra leave also a signal free zone where formally the signals of the acetyl groups were found and the mass spectra confirme the formation of each system.

IV.4.2.12.2 *Discussion*



Solvent / R	MeOH	CH_3CN	DMSO	DMF	DCM	$CHCl_3$	CCl_4	Et_2O	Benz	Tol	cy-Hex	PE	n-Hex	
CH_3	*S*	*P*	*S*	*S*	*S*	*S*	*P*	*P*	*P*	*P*	*P*	*P*	*P*	(21)
C_2H_5	S	P	S	S	S	S	**P**	**P**	**P**	**P**	**P**	P	P	(32)
C_4H_9	S	P	S	S	S	S	**P**	**P**	**P**	**P**	**P**	P	P	(33)
C_8H_{17}	S	P	S	S	S	S	**P**	**P**	**S**	**P**	**P**	P	P	(34)
$C_{16}H_{33}$	S	P	S	S	S	S	**S**	**S**	**S**	**S**	**S**	P	P	(35)

P = Precipitate
S = Solution
G = Gel

Figure 71: Behaviour of **32**, **33**; **34** and **35** in different solvent (5% wt).

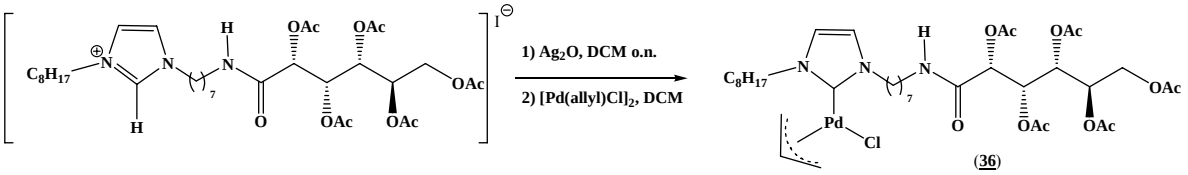
The results in Figure 71 reveal that no gelation occurs. In terms of behaviour two groups of complexes can be distinguished, bearing a small (**32**, **33**) or a medium (**34**) to long alkyl chain (**35**). Whether the system has been synthesised with C_1 (**21**), C_2 (**32**), or C_4 (**33**) units the results are the same: solvation in polar solvents and precipitation in less polar ones. Starting from C_8 (**34**) it is seen that aromatic solvents prove solvation and no more precipitation. This tendency is underlined by the behaviour of the C_{16} (**35**) complex which dissolves in all chlorinated and aromatic solvents. Unfortunately, no gelation abilities can be found. The change in the behaviour is still interesting to interpret. It seems that rather the length of the hydrophobic "tail" has an influence on the gelating/non-gelating ability, whereas the sugar moiety may not be the strongest force in the aggregating mode in this case. It is no

doubt that hydrogen bonding can take place in such a structure, but at least is is not driving the aggregation strongly enough to promote gelation. It also means that the environment the metal center, whatever is its role in the aggregation, did not help to form a structure rigid enough.

From this conclusion, it is thought to reintroduce the metal close to the rigid glucoamide part. We have seen along this path that the alkyl spacer is not able to achieve the gelation goal. The idea is now to add a phenyl spacer, which will minimize the distance between the metal centre and the hydrophilic "head". Parallel to this, a new investigation has to be done: to find out if the imidazole metal complex can be incorporated in a known gelator system. Also a palladium complex is synthesised to see if catalysis is possible with such an amphiphilic structure.

IV.4.2.13 Synthesis of Bis-[1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamino) heptyl]-3-*N'*-octyl-2,3-dihydro-imidazol-2-ylidene]palladium(II)chloride (**36**)

IV.4.2.13.1 *Synthesis*



Scheme 20: Palladium (II) complex (**36**) synthesis.

Following the same general method as previously shown, the palladium complex will be synthesised via the silver carbene complex method. Following literature from Mangeney,[98] a mono carbene palladium allyl chloride complex can be prepared using this "silver route". According to this publication, the product can be obtained with good yields.

IV.4.2.13.2 *Discussion*

After several synthetic attempts, the yields in the case of this amphiphilic structure were quite impressively reduced in comparison to the published structure. The main difference between the complex, shown in Scheme 20, and the one from work of Mangeney

[98] Mangeney, P.; Roland, S.; Audouin, M.; *Organometallics* **2004,** *23,* 3075.

and coworkers is that the substituents on the imidazole moiety are less hindering (Figure 72). This deficit in steric congestion seems to lead to another structure. In this case, the decisive hint will be given by the mass spectroscopy. The presence of the carbene signal in the ^{13}C-NMR spectrum, at 177.9 ppm is a in of dicator for the formation of the bis carbene complex **36**. The FAB-MS spectrum does not show the expected signal for a mono carbene complex, but shows a palladium bis carbene chloride cation peak instead, as a first fragment, followed by a bis carbene palladium signal (m/z: 1507.7). The most probable structure that the metal complexe adopts is *trans*, which leads to understand the presence of a single signal in ^{13}C-NMR for the carben carbon, the structure being more or less symmetrical as represented in Figure 72.

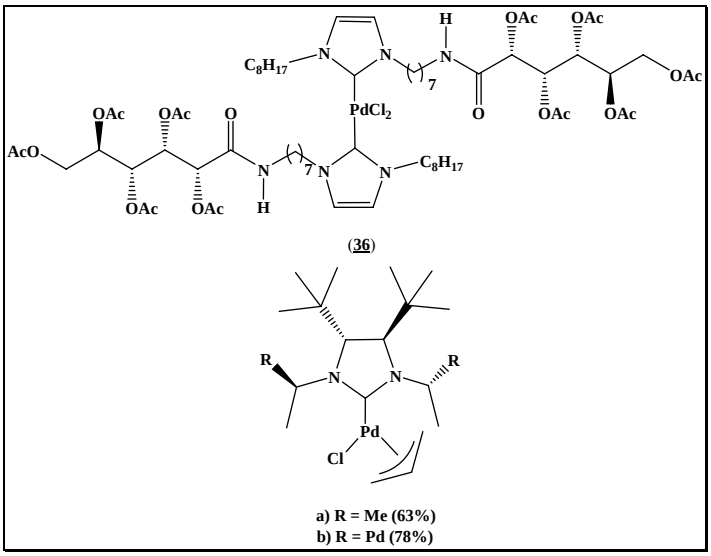


Figure 72: Palladium (II) complex (**36**) obtained compared to Mangeney's published work.

The yield of **36** in this reaction is 13%.

IV.4.2.13.3 *Applications*

The synthesis of this complex was made to see if in the molecular environment of a sugar and long alkyl chain palladium catalysis could take place. Some attempts have been made in Suzuki coupling reaction.

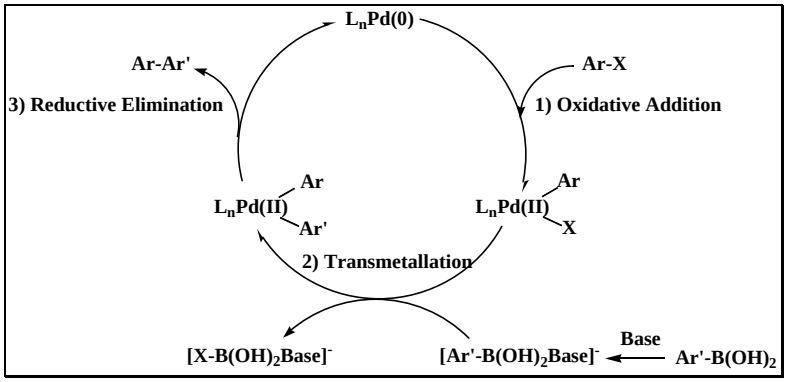


Figure 73: General mechanism for Suzuki cross coupling reaction.

IV.4.2.13.3.1 Introduction - The Suzuki cross coupling reaction

As like other palladium-catalysed cycles, the Suzuki coupling starts with an oxidative addition on the metal centre. To realise this step a palladium (0) is required, but in the complex **36**, the oxidation number of the palladium is (II) and must therefore be reduced before it enters the catalytic cycle (Figure 73). An excess of boronic acid is then given to the reaction medium to reduce the metal centre, at the same time it will give a quantity of homocoupling product that will not be higher than the catalyst weight percent.

The first step is the oxidative addition, admitted as the limiting step, where the metal centre will insert into between the aryl carbon atom and the halide or pseudo halide.

In a second step, the transmetalation occurs; the halide on the metal centre will be exchanged against the organic rest coming from the boronic acid. In the precise case of the Suzuki coupling, the boronic acid partner must be activated. The base generates a boronate species which then reacts with the metal centre.

Finally, the quickest step takes place. The reductive elimination will combine the two organic substrates on the metal into one and free a reduced metal complex. After this operation the metal recovers its original oxidation state (0) and can be then reintroduced in the catalytic cycle while the product of cross coupling is obtained.

IV.4.2.13.3.2 Examples

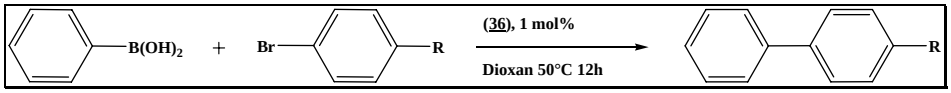


Figure 74: Suzuki coupling general attempt with the complex **36**.

The catalytic tests were followed by GCMS, which is an instant analysis of the reaction. The substance is separated over a column chromatography while being carried through the column by an inert gas. Each product is then analysed by mass spectrometry. The tests were made on activated and unactivated substances and without catalyst. In order to make time comparison possible the reactions were monitored after twelve hours. The results are shown in Table 2.

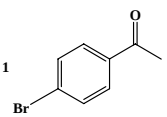
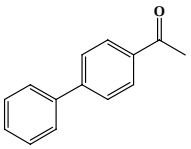
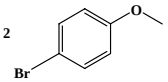
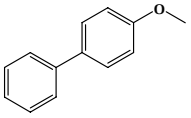
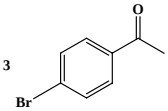
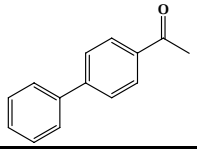
entry	substrates	product	time	cat.	temperature	conv.
1			12 h	0	50°C	-
2			12 h	1 mol %	50°C	up to 8%
3			12 h	1 mol %	50°C	up to 95%

Table 2: Results for Suzuki coupling.

In entry 1 (Table 2), the catalyst is absent and it can be seen that the reaction does not take place (blind test). When the palladium catalyst is given to the system, the formation of the bi-aryl molecules takes place. The entries 2 and 3 (Table 2) show that the catalyst is efficient for activated species, with conversion up to 95%. Activated species are molecules that will, because of the electronic structure, favour the oxidative step. The carbonyl group (in 4-bromoacetophenone, entries 1 and 3, Table 2) is electron withdrawing, which means that it will assist the C-Br cleavage, therefore helping the oxidative step. The methoxy group (in 4-bromoanisole, entry 2, Table 2) has the opposite effect. As the oxidative addition is accepted to be the limiting step in the catalytic cycle, non activated species will hinder this step providing an explanation for the low yields for entry 2 (table 2).

IV.4.3 Conclusion

This palladium amphiphilic complex seems to be catalytic active despite its large dimension. While the result for unactivated substrates is low, it might be optimised during further invetigations. The steric congestion provocated by a *trans* complex could have led to no catalytic results.

IV.5 Road III: Synthesis of hetero-bimetallic bis carbene complexes

IV.5.1 Retrosynthetic studies

Due to the fact that the previously prepared amphiphilic NHC comlexes did not show any gelation abilities, the investigations were now focused on the possibility of incorporating a NHC type carbene on a known gelating structure. Starting from the first known organometallic gelating complex, the incorporation of an imidazole moiety should prove no difficulty as shown in Figure 75.

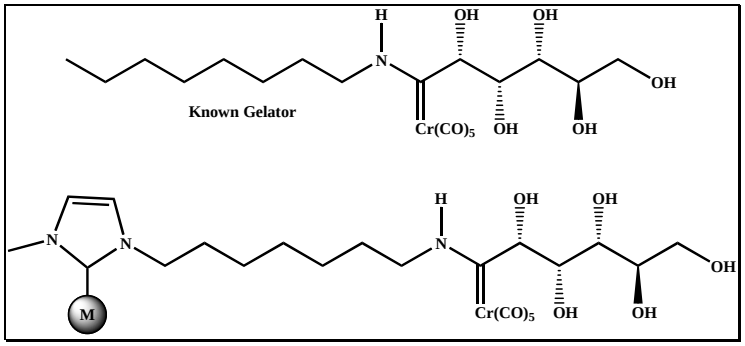


Figure 75: Investigation on the potential of bis-hetero-carbene type complexes.

As presented in Figure 76, the molecules could be built via the Fischer carbene complexes, following the same method as presented before. The last step is the complexation of the metal to the imidazolium precursor. This occurs after transmetalation between the desired metal and the silver carbene complex formed in-situ.

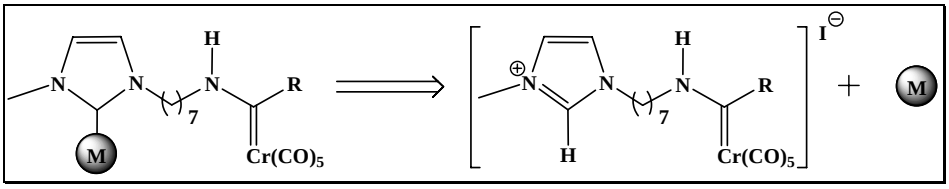


Figure 76: Formation of the bimetallic bis carbene complexes.

To obtain the precursors of these bimetallic complexes, the method of choice is the methylation of imidazole with methyliodide, as previewed in Figure 77.

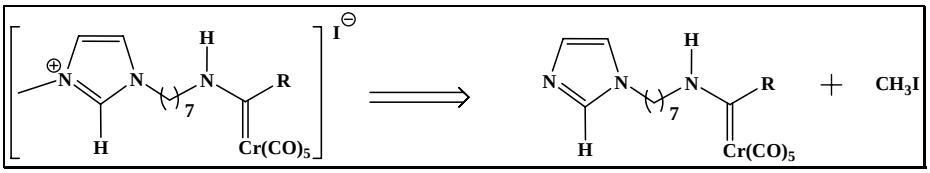


Figure 77: Quarternisation of an imidazole amine Fischer carbene complex.

To connect these two different types of carbenes, the most suitable synthesis is probably the formation of an amino Fischer carbene complex. This can be proceeded through the reaction of a methoxy carbene complex and an imidazole amine. (Figure 78)

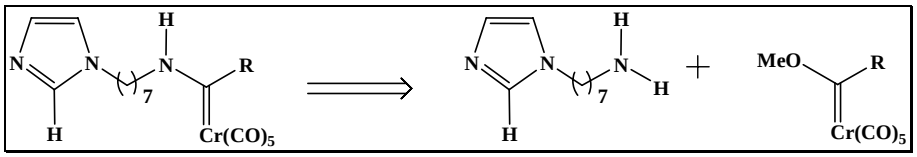


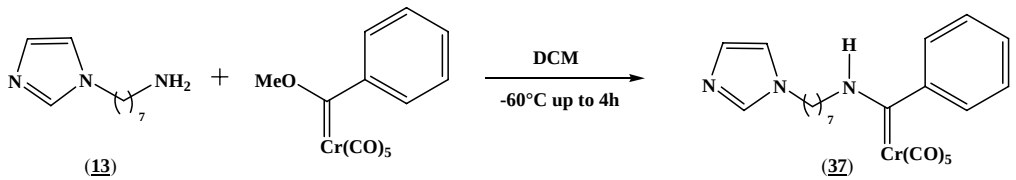
Figure 78: Synthons for the amide formation.

According to precedent work[79], the preparation of the amino Fischer carbene gluconyl complexes can be achieved with good yields. As a first attempt, the test is to be done on a simple system to avoid any loss of material, due to the difficult conditions of the formation of the Fischer carbene complex derived from the gluconic acid.

IV.5.2 Synthesis of the complexes following the road III

IV.5.2.1 Synthesis of Pentacarbonyl[7-(1-N'-imidazole)-N-heptylamino]benzylidene chromium (**37**)

IV.5.2.1.1 *Synthesis*



(**13**) (**37**)

Scheme 21: Synthesis of imidazole alkyl phenyl amino chromium carbene complex (**37**).

Following the adopted working group protocol[79], the previously synthesised amine **13** is given to a solution of the methoxy carbene complex in dichloromethane at -60°C. The system is left to stir at -60°C for several hours, only monitored by colour change and TLC. The phenyl methoxy carbene complex is a red solid, which turns the solution red; the formation of the amide will change the colour of the reaction from deep red to intense yellow. The colour is never a proof but a hint. The reaction can be finished after having given the amine to the reaction mixture or up to four hours after.

The nucleophilic attack of the amine group on the electrophilic carbene centre yields the amide complex with 62%. The free nitrogen on the imidazole does not interfere in the reaction because it is not nucleophilic enough in comparison to the amine. The purification over silica gel in a cooled column affords a yellow orange solid.

IV.5.2.1.2 *Discussion*

The presence of the amide proton can be immediately seen in the ^{1}H-NMR spectrum, this proton number 8 behaves like a very acidic proton. Its shift at 9.80 ppm betrays the presence of an electron withdrawing group, which is the pentacarbonyl chromium group. In the ^{13}C-NMR spectrum the carbene carbon signal is very weak but still can be seen at 279.6 ppm. The presence of a double set of carbonyl signals at 223.5 ppm and 217.3 ppm adds to the theory that a pentacarbonyl chromium system is present on the molecule. The FTIR spectrum shows bands at 2055 cm^{-1}, 1974 and 1930 cm^{-1} proving again the existence of a

pentacarbonyl chromium system, and its difference with the starting material (bands at 2063 (A_1) and 1953 (E) cm^{-1}) seals its evidence (Figure 79). The mass spectroscopy adds also a last clue with the peak at m/z = 462.1 for $[M+H]^+$.

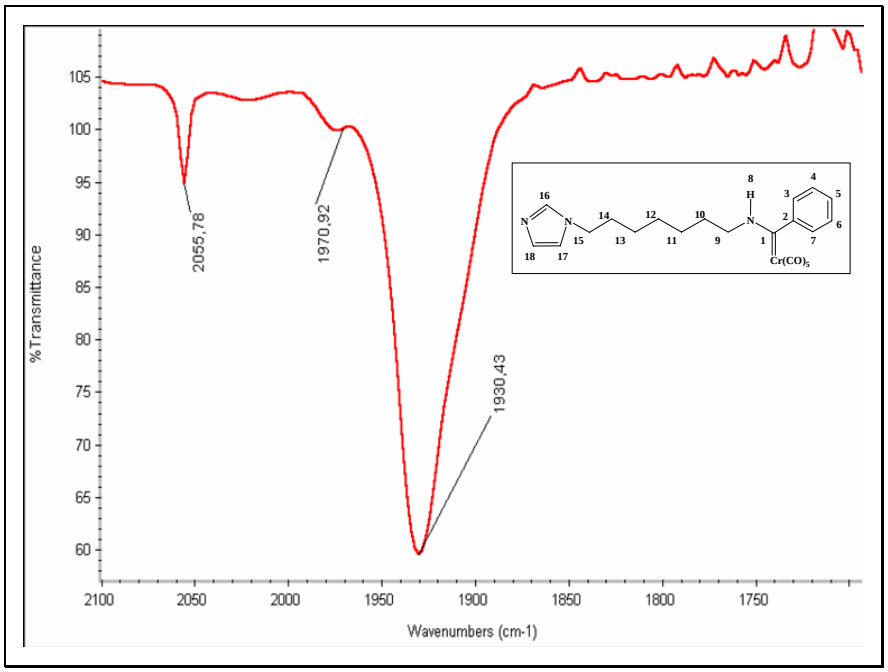
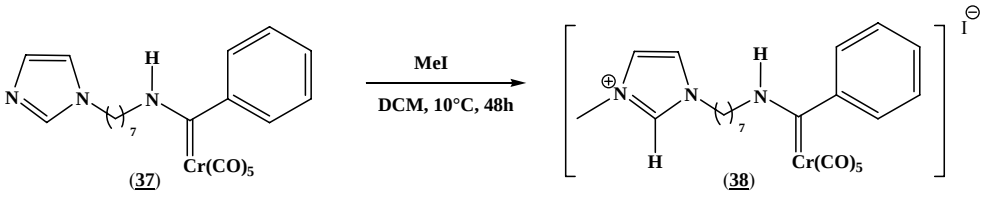


Figure 79: FTIR spectrum of the complex (**37**).

With the imidazole now attached to the Fischer carbene, the inherent chemistry of this heterocycle can be investigated.

IV.5.2.2 Synthesis of [Pentacarbonyl[7-[3-N'-(methyl)imidazolium]N-heptylamino (benzylidene)]chromium]iodide (**38**)

IV.5.2.2.1 *Synthesis*



Scheme 22: Synthesis of the imidazolium salt (**38**).

Following the same method as used before (see chapter **IV.4.2.6**); the product is dissolved in dichloromethane and left to react with an excess of methyl iodide for 48 hours.

The reaction should be done at maximum 10°C. At lower temperatures, the reaction is extremely slow, while at higher temperature, the carbene complex decomposes.

Again, if the complex has to be cleaned by column chromatography the yield will dramatically drop, because of the very polar nature of the molecule. The reaction is usually over 90% conversion, but always contaminated with traces of methyl iodide. After the chromatography the yield drops to 35%, so depending on the purity of the previous amine **13**, the work can be continued with or without purification, because methyl iodide does not interfere with the next steps.

From the analytics, the FTIR spectrum for **38** shows the presence of the pentacarbonyl carbene system (Figure 80). The bands are nearly the same as on complex **37** which means that the metal complex is still present.

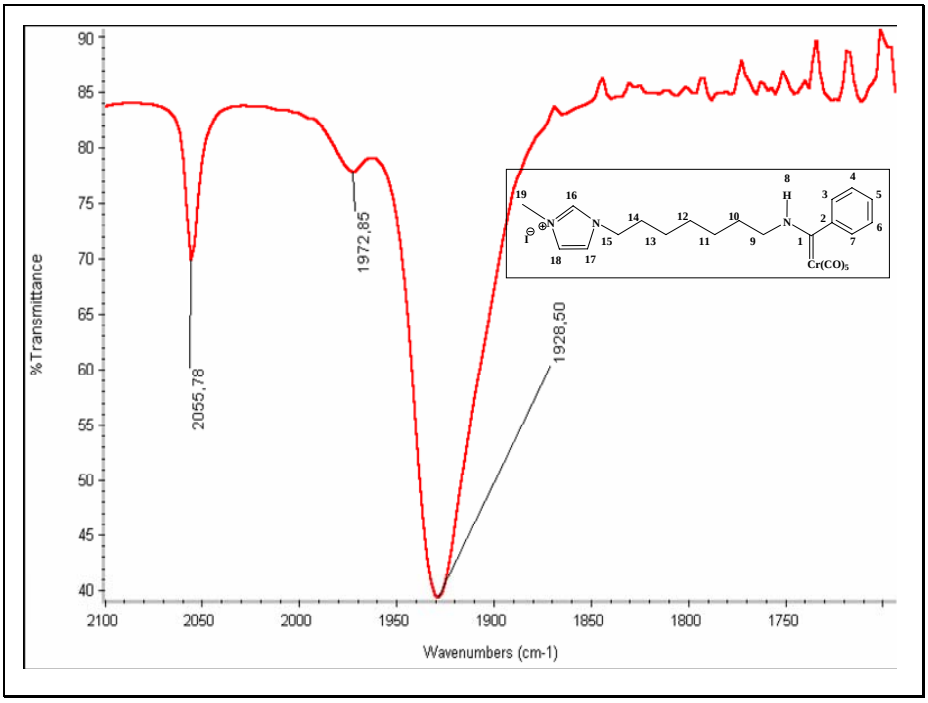


Figure 80: FTIR spectrum of the imadazolium salt, the complex was not affected by the reaction.

IV.5.2.2.2 *Discussion*

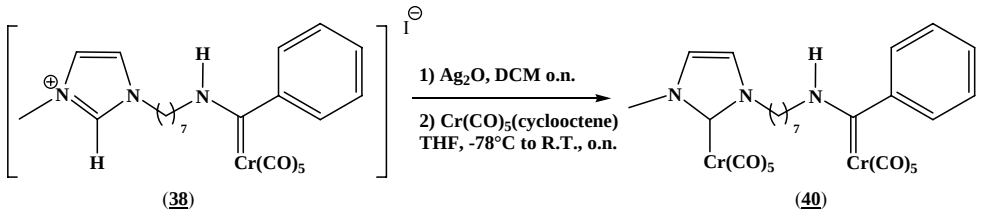
The first hint of the formation of the complex is, as seen earlier in complex **17**, the shift of the acidic proton of the imidazole group in the ^{1}H-NMR spectrum. The new shift is at 9.99 ppm. A look at the ^{13}C-NMR spectrum also gives several indications on the formation of

the desired product: a first signal at 273.1 ppm shows the presence of a Fischer carbene. In addition to this two signals at 219.4 and 213 ppm are found, with a 1/4 ratio typical for carbonyl groups of a pentacarbonyl metal complex. Finally the most important signal is at 32.5 ppm; it is the only signal that does not have the same phase with the alkyl methylenes in DEPT135 experiment. It means that this signal corresponds to a low fielded primary (or tertiary) carbon group: here this is the newly added methyl group. Mass spectrum shows a peak at m/z = 476.2 which is the mass of the cation.

It is accepted now that the salt is formed under the described conditions.

IV.5.2.3 Synthesis of Pentacarbonyl-7-[pentacarbonyl(1-N-(methyl)-2,3-dihydro-imidazol-2-ylidene)chromium]N-heptylamino(benzylidene)]chromium (**40**)

IV.5.2.3.1 *Synthesis*



(**38**) (**40**)

Scheme 23: Synthesis of the homo-bi-metallic hetero-bis-carbene system (**40**).

To obtain the structure **40** presented in Scheme 23, the in-situ method seen before with silver andtallation in one step is used. To obtain the best results, the first step is left to run overnight protected from light and just filtered. Immediately after the filtration over celite, the dichloromethane is removed under low pressure. The crude product is then dissolved in precooled THF (-60°C) and then left to react with the $Cr(CO)_5$(cyclooctene) complex. As previously mentioned the chromium cylcooctene complex is given as a solution in THF. The complete reaction sequence gives an overall yield of 12%.

IV.5.2.3.2 *Discussion*

Two different reasons can be given as explanation for the very low yield. First, I have reported that in the case of such molecules each step has an average of 65% yield which leads to an overall yield of 42% (see chapter **IV.4.2.11**). 42% is supposed to be an average yield that the reaction can yield. The reason why the yield is even lower than 42% in this case refers

to the second point. The second point is that the molecule **39** (Figure 81) offers a metal carbene moeity ($Cr(CO)_5$) and at the same time also a carbene transfer reagent (AgX). The NMR study from the crude silver complex step shows several signals. As said earlier, in order to improve the yields due to the lability of silver carbene complexes, no purification was done, just a simple filtration. The crude ^{13}C-NMR spectrum showed then several sets of peaks in the range of "metal-carbonyls" between 215 ppm and 220 ppm, and also in the Fischer-carbene carbon (carbon number 1, Figure 81) range (280 ppm). In the window where the silver NHC carbene (carbon number 16, Figure 81) complex signal is expected, two signals can be seen. The first one is at 190 ppm and the second one at 182 ppm. The signal of the starting material **38** can be immediately excluded because its carbon number 16 (Figure 81) gives a signal at 132 ppm. Since the former complexes (complex **19**, **20**) have shown a silver carbene carbon signal at 178 ppm, the peak at 182 ppm seems reasonable. The mass spectrum will give a hint that the complex is formed and has two ligands attached to the silver with an m/z = 1059.3. This m/z value corresponds to two ligands and one silver atom, no iodide is observed.

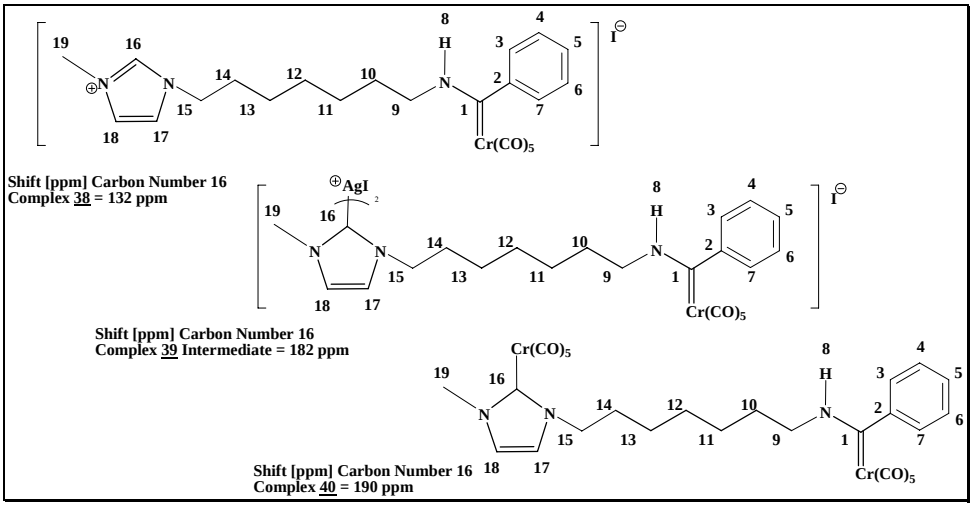


Figure 81: Comparison between the different shifts of the carbon number 16 signal.

One theory is that the signal at 190 ppm (^{13}C-NMR spectrum) belongs already to the bis chromium complex **40**. This would mean that the silver complex is formed and reacts immediately with another molecule. At the same time, the presence of the signal at 182 ppm in solution let to think that this silver complex is stable enough to be seen and identified. The crude mass spectrum revealed a signal at m/z = 670 which corresponds to the bis chromium complex **40**. To be sure that this second carbene signal at 190 ppm belongs to the bis

chromium system, the second step, where cyclooctene chromium pentacarbonyl is given, is done. This additional equivalent of chromium will be transferred to the silver carbene complex in solution, and yield the desired bis carbene complex **40**.

After purification over silica gel column chromatography, a yellow solid is recovered with, as said earlier, 12% yield. The ^{13}C-NMR spectrum is depicted in Figure 82.

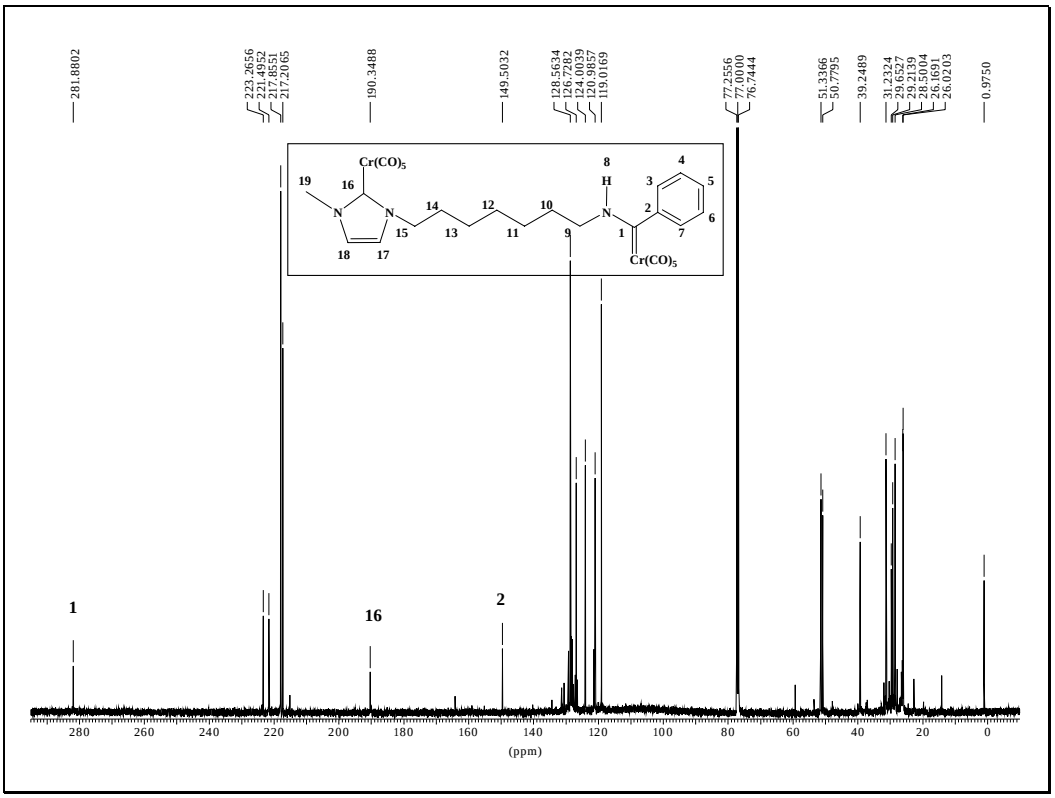


Figure 82: ^{13}C NMR spectrum of the bis carbene complex (**40**).

This synthesis is a success in several aspects. First, the achievement of a hetero-bis-carbene-homo-bi-metallic complex, shown in Figure 82, means that the proposed strategy works. The cohabitation of the two carbene complex units is undoubtfully seen here with the presence of a carbene carbon signal at 282 ppm (carbon number 1: Fischer type carbene carbon signal) and the one at 190 ppm, being carbon number 16 (NHC carbene signal). With this spectrum, it is possible to predict the spectrum of the silver carbene complex **39**, because the signal from complex **40** can be removed from the crude NMR spectrum of the reaction revealing then the signals for **39**. A prediction of the silver complex **39** ^{13}C-NMR spectrum can be sorted out, because mass spectrometry test revealed its presence in the crude reaction (scheme 23).

The result demonstrates with no doubt that the signal at 182 ppm (Figure 81) belongs to the silver carbene complex **39**. Then the signal at 278.9 ppm is assigned to the Fischer carbene carbon number 1 and its pentacarbonyl pattern is seen at 221.4 (CO_{trans}) and 217.1 (CO_{cis}) ppm. Again the attribution is made from deduction of the product and starting material spectra, in the reaction shown in Scheme 23 from the crude NMR after the first step.

Interestingly the FTIR spectrum does not show a difference between the two different types of chromium pentacarbonyl systems. The Figure 55 shows the IR bands of the complex **40**.

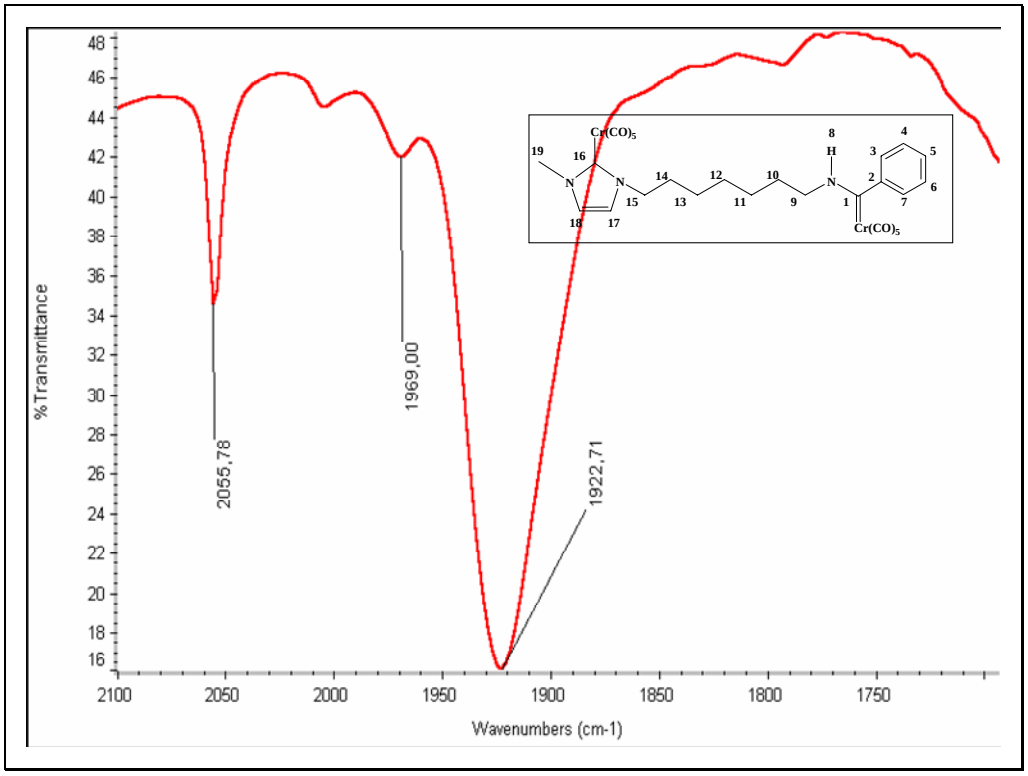


Figure 83: FTIR of the bis chromium complex **40** in dichloromethane.

In Figure 84 the two IR spectra of complexes **21** (Figure 84, up) and **38** (Figure 84, down) are compared. **21** is an NHC chromium pentacarbonyl complex and **38** is the NHC salt precursor of **40**. The bands have the same pentacarbonyl pattern, the 1754 cm^{-1} band is not to be taken in consideration, while complex **40** does not carry a sugar moiety and this band corresponds to the carbonyls of the acetyl protecting groups.

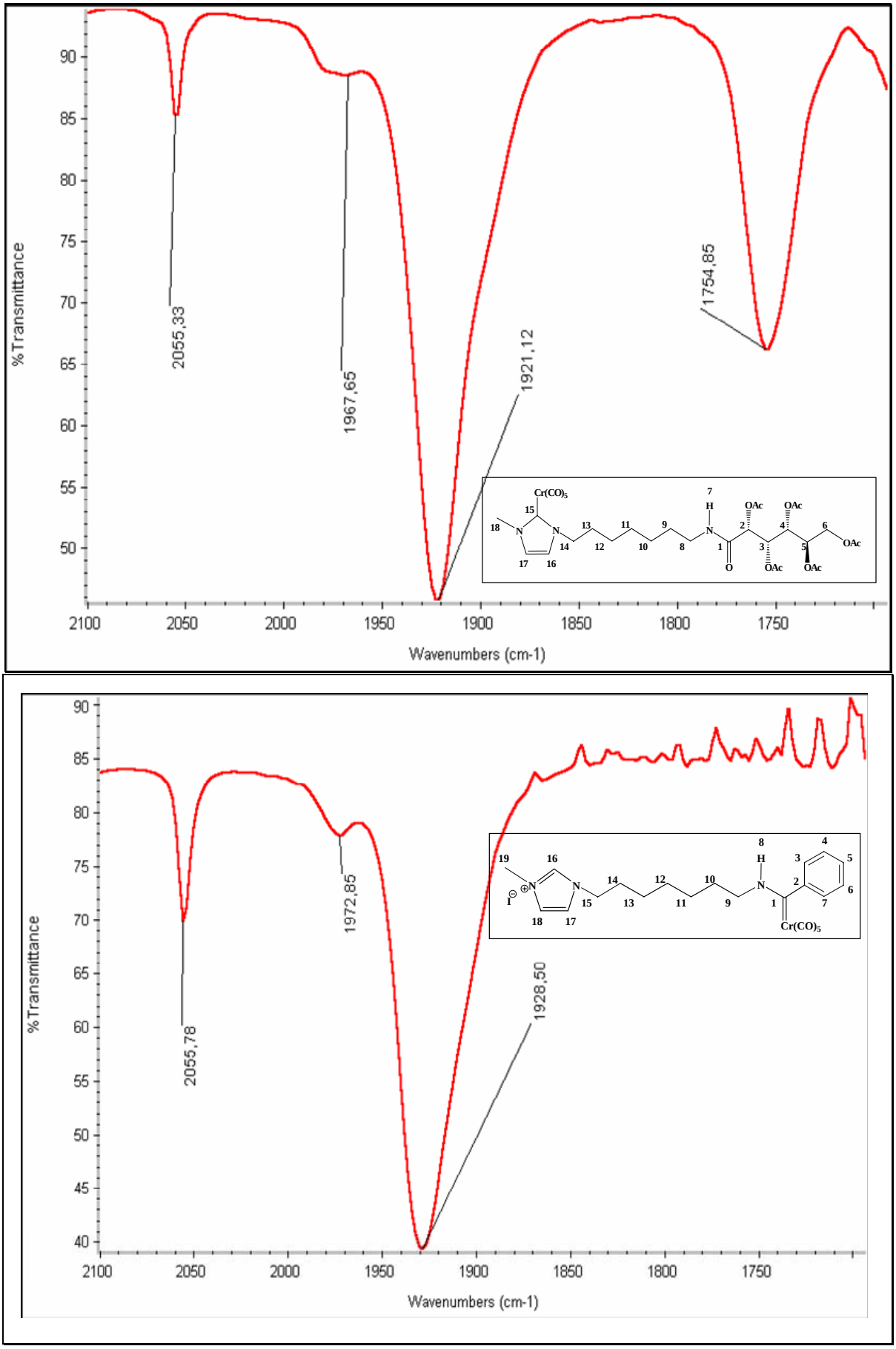


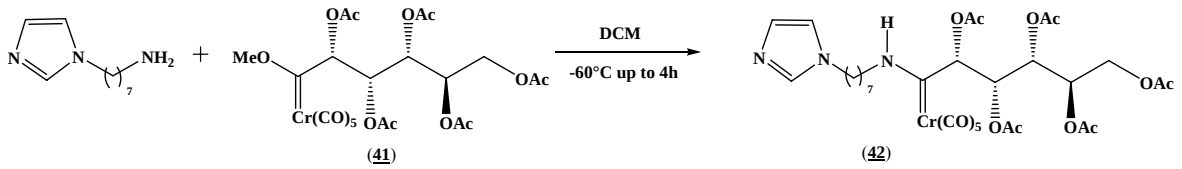
Figure 84: Comparison of the two types of chromium pentacarbonyl pattern taken separately

The Figure 84 shows that the FTIR spectrum of **40** (Figure 83) could have been expected, in terms of pattern. Unfortunately, this method cannot be used to monitor the formation of such complexes because: as seen in Figure 82 the E band at 1922 cm^{-1} does cover most probably both E bands from each pentacarbonyl structure, despite the visible difference shown in Figure 84. Even the secondary derivative does not provide a differenciation.

The second positive point in this synthesis is that now the road to the bis carbene complex bearing a glucose moiety is clear.

IV.5.2.4 Synthesis of *N*-1H-Imidazol-1-yl[pentacarbonyl-[7-heptylamino(2R,3R,4R,5S,6-penta-*O*-acetyl hexylidene)]chromium] (**42**)

IV.5.2.4.1 *Synthesis*



Scheme 24: Synthesis of the amino carbene complex (**42**)

The experience in the formation of the complex **37** (Scheme 22) is the starting point of this synthesis. The methoxy carbene complex **41** has been prepared according to the "Hegedus route" (see **II.1.1.2** Figure 7)[22]. The previously synthesised amine **13** is given to a solution of the methoxy carbene complex **41** in dichloromethane at -60°C. The system is left to stir at -60°C for up to 4 hours, only monitored by color change (ret to yellow) and TLC. The reaction can be finished after having given the amine to reaction or up to four hours after.

The nucleophilic attack of the amine group on the electrophilic carbene centre will yield the amide complex with 37%. The purification over silica gel in a cooled column affords a yellow orange solid.

IV.5.2.4.2 *Discussion*

The relevant signals can be spotted in the ^{13}C-NMR spectrum without a problem (Figure 85). The presence of the signals at 268 ppm (carbene carbon signal number 1) and at 222 and 217 ppm (identified as the metal carbonyl signals) prove the presence of a Fischer carbene on the structure. The original signal for the carbene carbon atom in the starting material **41** is at 355 ppm, so no confusion with product signal is possible. Three signals at 137, 132 and 119 ppm correspond to the three carbon atoms 15, 16, and 17 of the imidazole (Figure 57). Other very important signals to see are the five carbon signals from the acetyl protecting groups. Their presence between 168 and 170 ppm confirm that the sugar part is present. The fact that they can be individually counted proves that no partial deprotection occurred during the reaction. The FTIR spectrum shows the same pattern as the starting material with bands at 2057 (m, A_1); 1974 (sh, B_1); 1930 (vs, E) and 1751 cm^{-1} (m, Acetyl). The mass spectrometry (ESI, positive, MeOH) shows a peak at m/z = 796.2 which corresponds to the mass of **42** plus one proton.

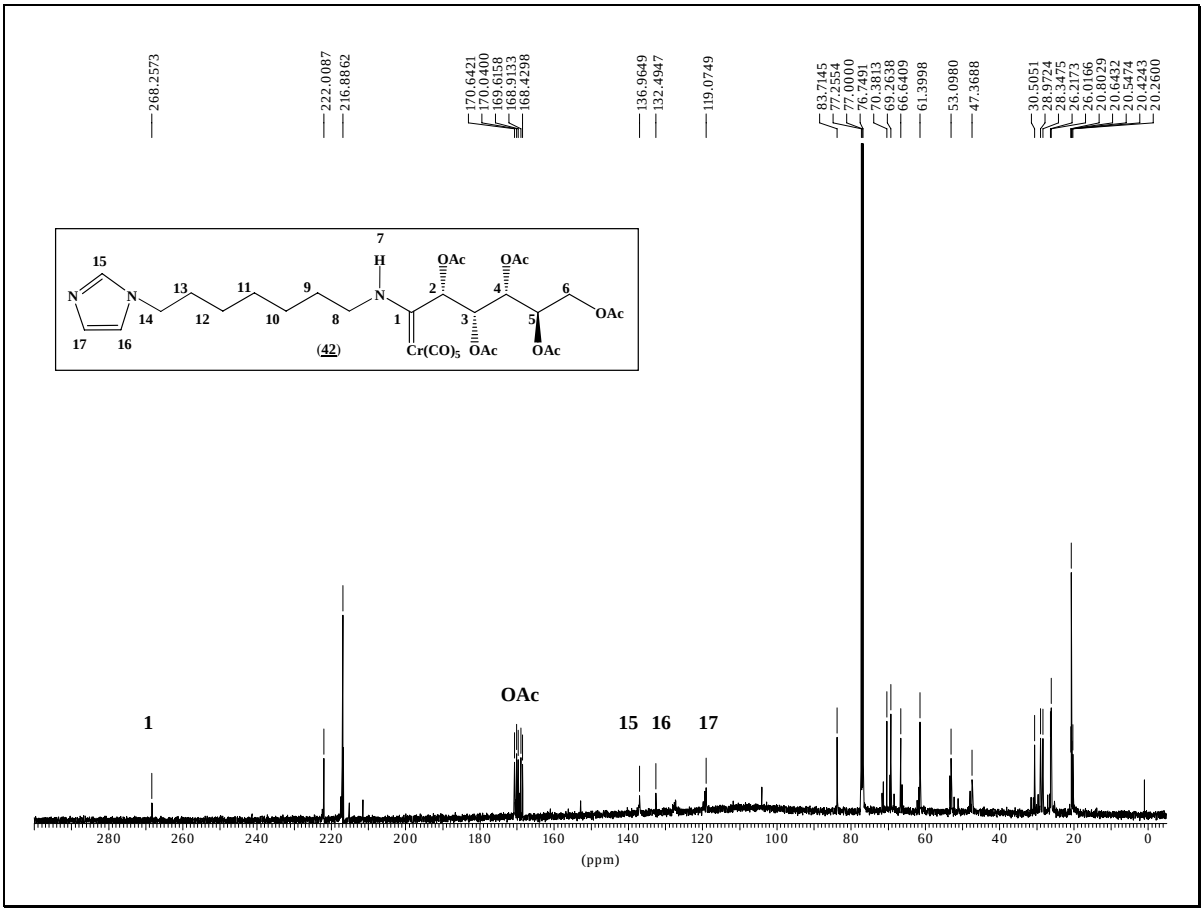
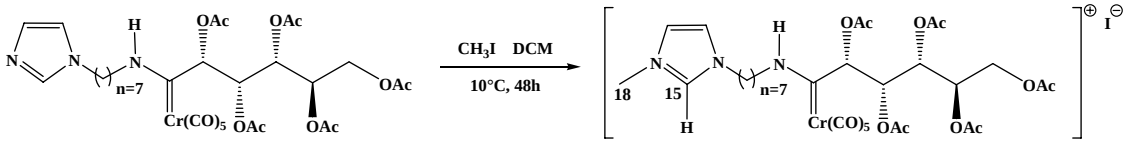


Figure 85: ^{13}C-NMR spectrum of the complex **42**

The next steps in the synthesis are the methylation of the complex on the imidazole moiety, and then the formation of the bis metal complex.

IV.5.2.5 Synthesis of [*N'*-methyl-*N*-1H-imidazolium[pentacarbonyl[7-heptylamino (2R,3R,4R,5S,6-penta-*O*-acetyl-hexylidene)]chromium]iodide (**43**)

IV.5.2.5.1 *Synthesis*



(42) (43)

Scheme 25: Synthesis of the imidazolium salt (**43**)

The approved method of quaternisation of the imidazole (see chapter **IV.4.2.6**) is applied with success to the complex, offering a yellow orange oil with 86% yield.

IV.5.2.5.1 *Discussion*

In this case, the analysis focuses on the question if all important signals are still present in the NMR spectrum after the reaction. The first hint is given by the ^{1}H-NMR spectrum, which reveals a very acidic proton at 9.93 ppm. This signal reflects again the quaternarisation of the imidazole, yielding a very low fielded shift for the proton bore by the carbene carbon (position 15 on Figure 86). The information is consolidated by the ^{13}C-NMR spectrum which shows a new signal at 36.8 ppm. This signal can only be attributed to the new methyl substituent (position 18 on Figure 86) by comparison with the DEPT 135 spectrum (Figure 86, down). This is the only signal that does not phase with the alkyl chain methylene groups.

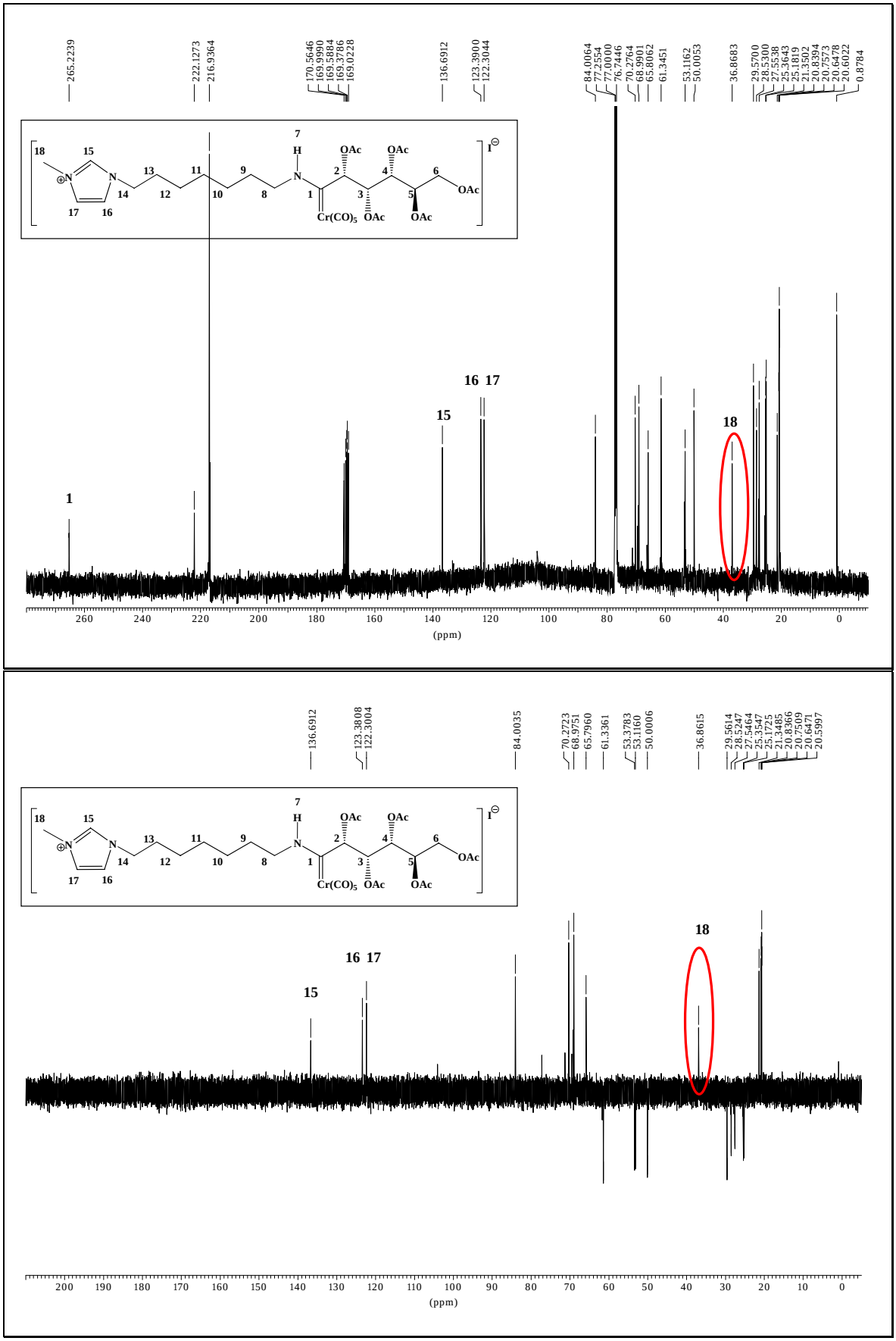
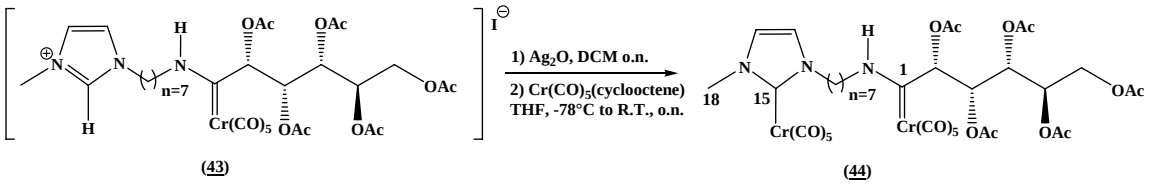


Figure 86: ^{13}C-NMR (up) and DEPT 135 (down) spectra hinting the methylation of the imidazole

The quite low shift of the substituent number 18 for a methyl group is due to the nearby presence of an nitrogen atom. The mass spectrometry in FAB mode reveals the cation of the product at m/z = 760.3. FTIR is again not relevant of any changes but helps to secure that the pentacarbonyl system is still present, bands at 2057 (m, A_1), 1972 (sh, B_1), 1924 (vs, E) and 1751 (m, acetyl) cm^{-1}.

IV.5.2.6 Synthesis of {[Pentacarbonyl(*N'*-methyl-2,3-dihydro-*N*-imidazol-2-ylidene) chromium] pentacarbonyl[7-heptyl-amino(2R,3R,4R,5S,6-penta-*O*-acetyl-hexylidene)] chromium} (**44**)

Continuing with the synthetic strategy, the formation of the metal chromium complex is done, according to the silver / chromium "one pot" method (see **IV.4.2.11**). The reaction equation for the formation of complex **44** can be seen on Scheme 26.



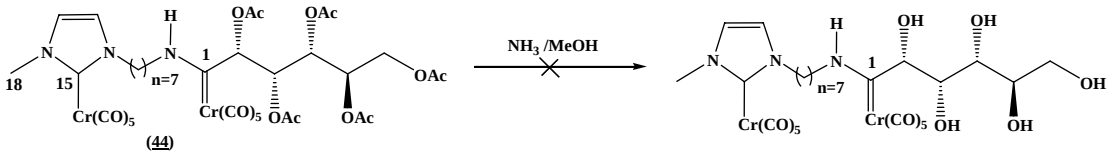
Scheme 26: Synthesis of the chromium pentacarbonyl complex (**44**).

This time, the reaction affords 23% yield, but the different fractions obtained by column chromatography are not clean, traces of hexacarbonyl chromium and solvents make the interpretation difficult. A deeper investigation is then needed to see the product. The ^{1}H-NMR spectrum is too weak to see the product.

The ^{13}C-NMR shows the important signals at 266 ppm for the Fischer carbene carbon, a signal at 190.5 ppm for the NHC carbene carbon. The presence of the acetyl protecting groups is proved by the signals between 170 and 169 ppm and also at 21, 20 ppm for the carbonyl groups and the methyl groups respectively. These signals are weak, and therefore other analytical methods are needed to characterise completely the molecule. The FTIR spectrum shows bands at 2056 (m, A_1), 1923 (vs, E) and 1751 (m, acetyl) cm^{-1}, proving the presence of pentacarbonyl structure and of the acetyl groups. The band at 1980 cm^{-1} shows also that hexacarbonyl chromium is present, which is probably the reason why the spectra

cannot be resolved. A mass spectrum gives the assurance that the complex is built with a peak at m/z = 951.2.

IV.5.2.7 Investigation on the synthesis of {[pentacarbonyl(N'-methyl-2,3-dihydro-N-imidazol -2-ylidene)chromium][pentacarbonyl(7-heptyl-amino(2R,3R,4R, 5S,6-pentahydroxy-hexylidene))]chromium}



Scheme 27: Attempted deprotection of the complex **44**.

The deprotection method has already proved its efficiency (see **IV.4.2.9**). In this case, even after several attempts the product was not obtained. A whitish solid stuck to the glass was recovered after concentration of the recovered fractions. Unfortunately, this white solid was not soluble in any deuterated solvent therefore no analytic measurements could be achieved for the resulting substance. It is difficult to predict the reason why the reaction did not proceed. In the previous step the continuous presence of hexacarbonyl chromium in every analytics was mentioned, which can come from a possible degradation of the product (**44**). The reaction might then not take place if the product is already lacking stability. The speculations on why the reaction failed are even more difficult as no analytics could be achieved from the resulting substance.

This result gives no hope for gelation ability tests and the first reason is obviously that the product is not obtained. In a second view, it can be easily understood that with an unstable substance any further investigations on any gelation abilities would be difficult.

IV.5.3 Conclusion

Using the adopted method shown before (see chapter **IV.4**) a new class of ligands was synthesised with low to average yields. This permits to have molecules bearing two different types of carbenes on the same structure and also two different types of metal coordinated to each of these carbenes (**40**). This implies a new broad field of investigations combining the chemistry of Fischer carbenes with the versatility of the *N*-heterocyclic carbenes.

The difficulties encountered in the formation of an analogue complex, just additionally bearing a NHC complex unit, to the one published by the Dötz working group[9] leaves the influence of a NHC metal complex on a known gelator structure unclear.

Another concept was studied, in which the general structure is again changed. A phenyl ring is used as a spacer instead of an alkyl chain. The addition of an aromatic spacer probably changes the behaviour of the molecule by adding π-stacking ability to the molecule, but it also permits to rearrange the molecule order having the imidazole moiety again between hydrophilic head and hydrophobic tail.

IV.6 Road IV: Synthesis of "aromatic spacer complexes"

IV.6.1 Retrosynthetic studies

To incorporate an aromatic ring between the imidazole and the hydrophilic part, the shortest and easiest method is to use commercial products. The use of 4-(1*H*-Imidazol-1-yl)aniline lead to the formation of an amide derivated from gluconic acid chloride (**2**) which can be quarternised afterwards (Figure 87).

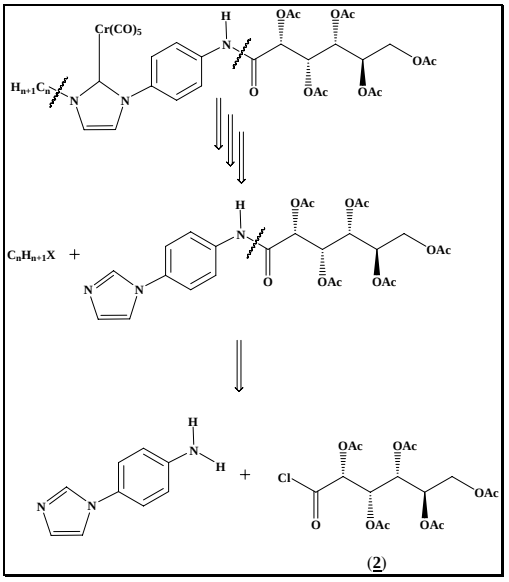


Figure 87: Retrosynthesis for an aromatic spacer complex.

The step where the metal should be implemented into the structure is equivalent to previous studies. It starts with the imidazolium salt formation, followed by silver carbene

complex formation with Ag_2O and transmetalation with a chromium source. This method permits to obtain a precursor for alkylation of a similar type as seen before. A simple alkylation with alkyl halides is predicted.

For this pathway to the imidazolium salt a familiar route is used: an N-alkylated imidazole moiety is quaternised in a nucleophilic substitution with an alkyl halide (Figure 88).

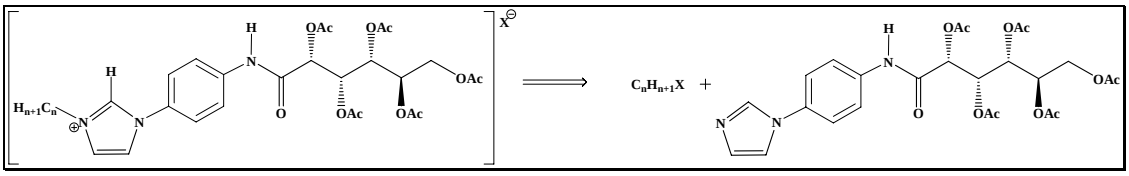


Figure 88: Approach to an imidazolium salt.

To get to the amide synthon, the gluconic acid chloride **2** is again used as the starting material. The other reagent of the reaction, the 4-(1*H*-imidazol-1-yl)aniline is commercially available (Figure 89).

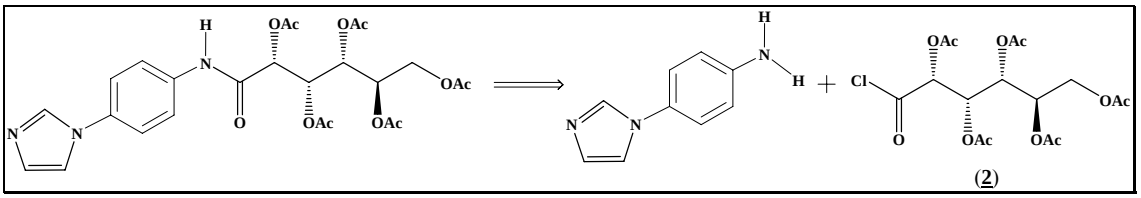
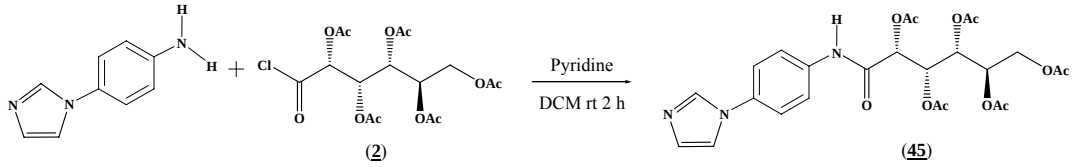


Figure 89: Proposed approach to the amide synthon.

IV.6.2 Synthesis of the complexes following the road IV

IV.6.2.1 Synthesis of *N*-1H-[(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamido)-1,4-phenylene] imidazole (**45**)

The first reaction in this synthetic route is the formation of the aryl spacer carbohydrate compound (**45**, Scheme 28). The access to the amide formation is analogue to what is previously reported (**IV.4.2.5**), i.e. the nucleophilic amine attacks the gluconic acid chloride **2** in the presence of a base.



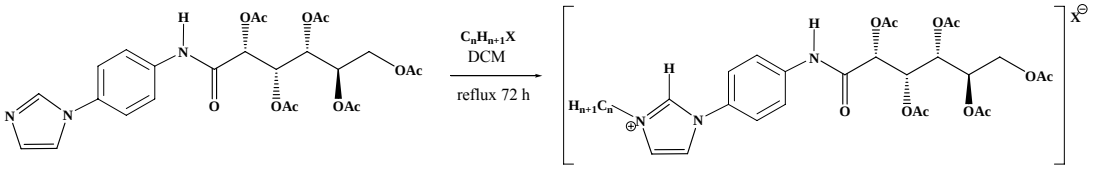
Scheme 28: Synthetic formation of the amide **45**.

Both starting materials are given in an equimolar ratio. The attack of the amine functionality on the gluconic acid chloride releases hydrochloric acid. The use of pyridine, as a base, reduces this formation. The product is obtained as a white solid after purification over column chromatography giving a 64% yield. The aniline derivative gives in this case an equivalent yield as in the case of the primary amine (see **IV.4.2.5**). The aromatic amine could have been less nucleophilic due to the nitrogen lone pair delocalised in the aromatic ring, but the result does not support this tendancy. The purification of this substance is of high importance because the starting material, 4-(1*H*-Imidazol-1-yl)aniline, has nearly the same retention factor and reactivity as the product. If not separated the amine reacts the same way as **45** in the following step of the synthesis, making it extremely difficult to separate the by products formed from the rest of the substance and interfering with the yields and the reactions.

IV.6.2.2 Synthesis of *N'*-"alkyl"-*N*-1H-[(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamino) - 1,4-phenylene]-imidazolium "halide" (**46; 47**; **48**)

The previous experiences (**IV.4.2.12.1**, Figure 70) showed that the longest alkyl chains have the biggest influence on the solubility of these types of amphiphiles. According to Kutinake's work[99] a long flexible tail is needed, methyl, ethyl and butyl groups do not follow this requirement, so to counter the balance of the hydrophilic part it is decided to start directly to work with $C_{12,}$ C_{14} and C_{16} chains.

[99] Kunitake, T.; Okahata, Y.; Shimomura, M.; Yasunami, S.;Takarabe, K.; *J. Am. Chem. Soc.* **1981**, *103*, 5401.



(**45**)

(**46**) R = $C_{12}H_{25}$; X = I

(**47**) R = $C_{14}H_{29}$; X = Br

(**48**) R= $C_{16}H_{33}$; X = I

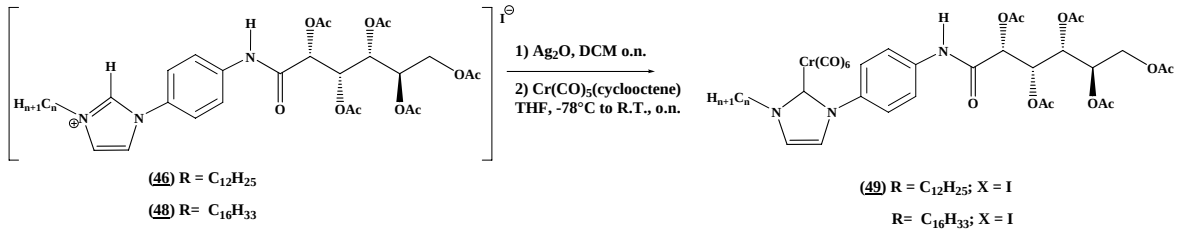
Scheme 29: Fomation of the different aryl spacer imidazolium salts.

The preparation of the imidazolium salts follows the same general procedure. The starting material (**45**) is dissolved in dichloromethane, then a large excess of the alkyl halide is given to the reaction. Longer alkyl chains are less reactive than methyl iodide so the reaction temperature of the system is raised to the boiling reflux point. After 72 hours the salts are obtained in average yields. In fact the products can be achieved with up to 99% in the case of **46** and **48** but these yields depend on the purity of the starting material. After the reaction, the product is purified by the addition of petrol ether in which the alkyl halides are soluble but not the product. The crude product NMR spectra reveal the purity of the product. In the worst case in which the product is not clean enough and a column chromatography is needed the yields can drop down to 36% for **46** and 12% for **48**. As mentioned earlier (**IV.5.2.2**), depending on the purity of the precursor **45** a simple filtration column over silica gel can be done with dichloromethane eluating the starting material followed by addition of methanol to obtain the pure product with moderate yield.

In the case of **47** the product is obtained with 12% yield only, the conversion is never complete and even after several additional hours of reaction time, no improvements on conversion is seen. This difference can be explained by a closer look at the leaving group. The "$C_{14}H_{29}$" halide was only commercially available as bromide, while the other chains areavailable as iodide. A similar effect has already been seen and experienced (**IV.4.2.10,** Figure 62). Since iodide is the best leaving group, in the halide class, it makes iodo substrates the best candidates in the nucleophilic substitution. Because of the low yield for compound **47**, resulting in low quantity of the desired product, further work on the intermediate chain length C_{14} has been stopped at this stage.

IV.6.2.3 Synthesis of Pentacarbonyl{*N'*-dodecyl-*N*-[(2R,3R,4R,5S,6-penta-O-acetyl-hexano ylamino)-1,4-phenylene]-2,3-dihydro-imidazol-2-ylidene}chromium (**49**)

After the synthesis of the imidazolium salts **46** and **48**, the same procdure (see **IV.4.2.11**) was used to form the chromium pentacarbonyl complexes (**49**) (Scheme 30).



Scheme 30: Formation of chromium pentacarbonyl complex **49** via transmetalation.

The formation of the chromium NHC complex through deprotonation of **46** with silver(I)oxide followed by a metal transfer with a chromium source afforded a yellow solid with 31% yield. The product shows all expected signal patterns in the NMR experiments. ^{1}H-NMR spectroscopy shows only two signals for the metal coordinated imidazole moiety at 7.07 and 6.98 ppm. The most indicative signs are again seen in the ^{13}C-NMR spectrum. The signal at 192.5 ppm gives a hint at the formation of a carbene complex, supported by the presence of the distinctive carbonyl group signals at 221 and 217 ppm. The five signals between 170 ppm and 169 ppm reveal the presence of acetyl protecting groups, meaning the carbohydrate part is present and still protected, its own signals appear in at 71 to 61 ppm. The signal at 164 ppm belongs to the amide carbonyl group, and the signals between 130 and 120 ppm confirm the presence of the aryl spacer. The FTIR spectrum shows the typical bands for a pentacarbonyl system with a medium signal at 2053 cm^{-1} (m, A_1) and a very strong one at 1924 cm^{-1} (vs, E), the presence of the acetyl protecting groups can be again seen at 1753 cm^{-1} (m, Acetyl). Finally the mass spectrometry in FAB mode with mNBA as a matrix seals the presence of the complex with a peak at m/z = 908.3 corresponding $[M+H]^{+\bullet}$.

The same procedure as used above is applied to the precursor C_{16} chain alkylated salt **48**. The silver oxide (Ag_2O) deprotonates the acidic hydrogen atom on the imidazole moiety and then forms a silver carbene complex (see Figure 55). The silver is then exchanged by the chromium to obtain the new metal complex. The reaction is monitored by FTIR, which shows

the typical IR bands pentacarbonyl chromium pattern that we are used to (see Figure 90) but the mass spectrum of the crude mixture did not show a trace of the product.

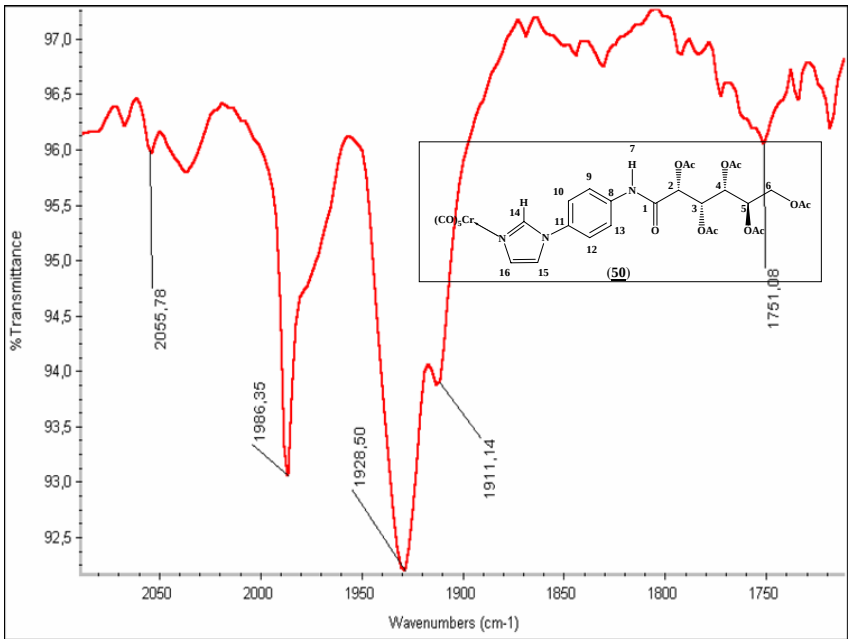


Figure 90: FTIR spectrum of the crude mixture.

After the separation over silica gel chromatography, two fractions were collected and analysed. The main fraction will be discussed here. The yellow solid obtained shows in a FTIR spectrum again the typical bands of chromium pentacarbonyl complexes and of the acetyl protecting groups signal (see Figure 91).

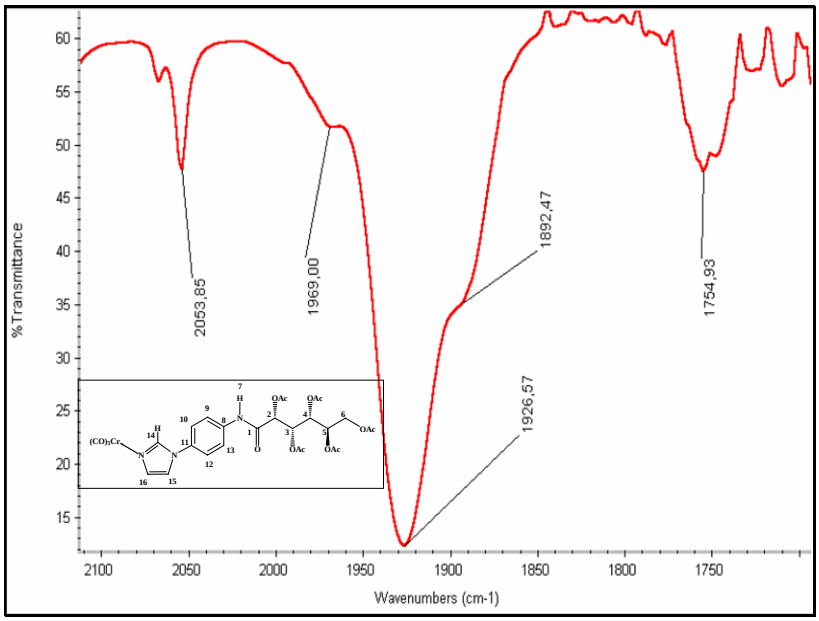


Figure 91: FTIR spectrum of the main fraction.

However, the NMR spectra reveal something unexpected. The ^{1}H-NMR (Figure 92, upper picture) shows three signals in the aromatic region that can be attributed to the imidazole moiety. These three signals should not be present in the case of a functionalised NHC carbene complex. The absence of the protons for the C_{16} alkyl chains means that the system is not quarternised anymore. The small signals in the upfield region of the spectrum have been integrated to show that the amount of protons does not reach the value of 33, which is awaited for the alkyl chain.

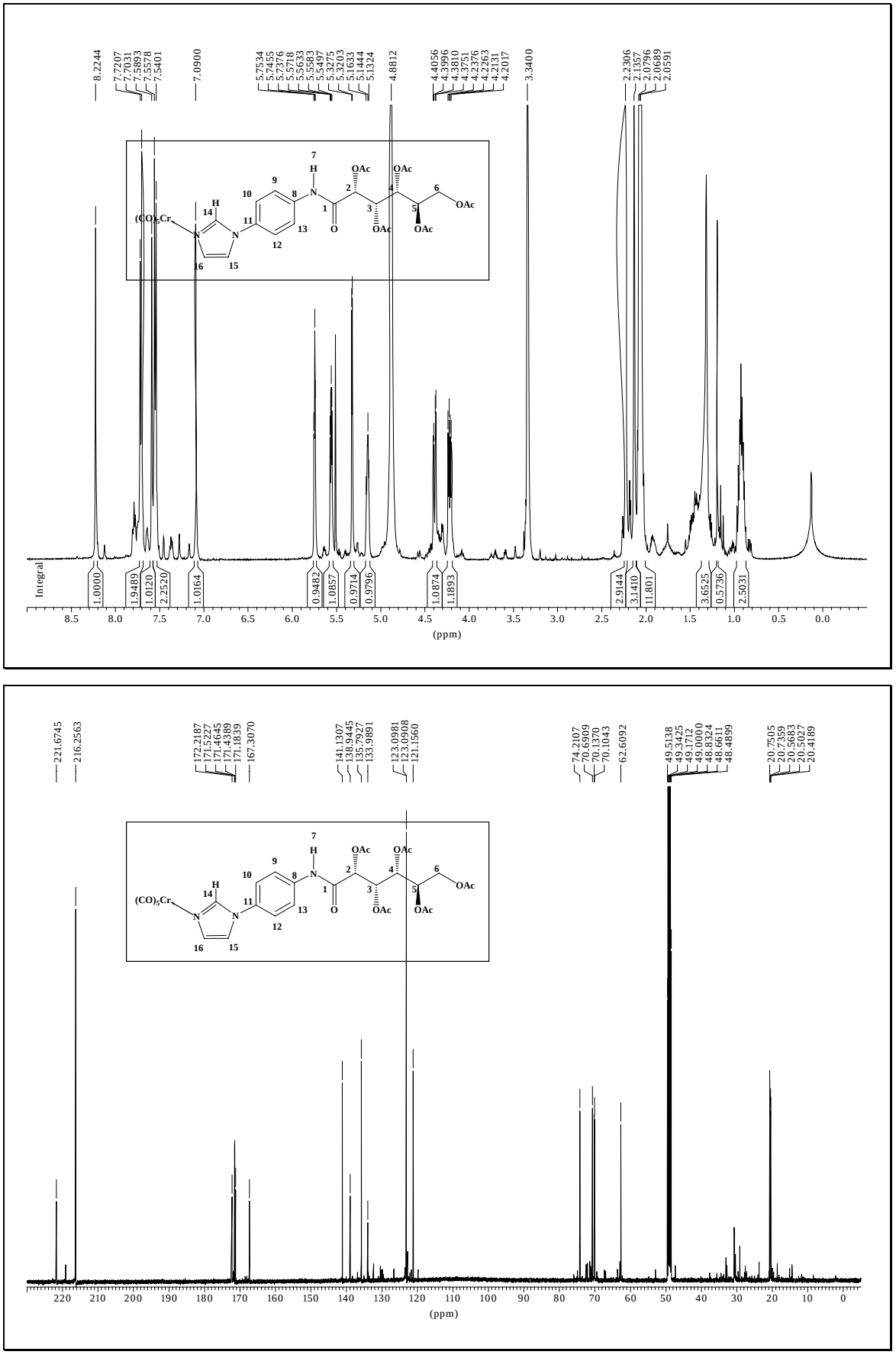


Figure 92: Investigations of the product from the main fraction.

A look at the ^{13}C-NMR spectrum helps to understand what happened (Figure 92, lowest picture). The signal at 190 ppm is not present, which means that there is no NHC. But the presence of two signals above 210 ppm proves that a pentacarbonyl complex is still present. The sugar part is still present on the structure like the signals for the amide at 167 ppm and the signals of the acetyl protecting groups between 169 and 170 ppm can attest. The five signals around 70 ppm are the signals for the glucose skeleton. Again, no signals for the fifteen methylene groups of the alkyl chain can be seen. Out of this, a structure can be drawn (**50** Figure 93), which supports the spectroscopic evidence. The mass spectrum does confirm the formation of this product with a peak of m/z 739.1.

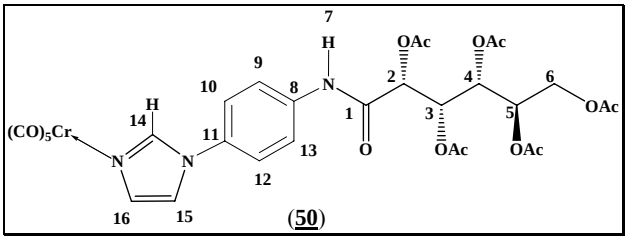
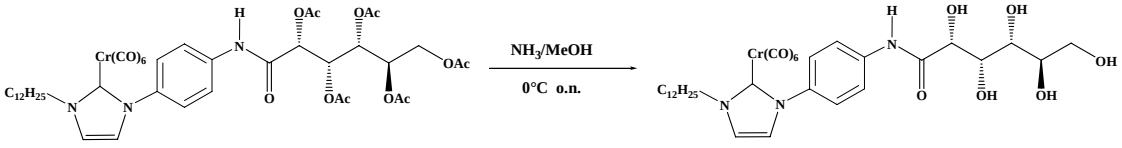


Figure 93: Side product of the reaction.

Two hypotheses are advanced for the formation of the product. The first is that **45** is still present, after purification of the product **48**, leaving a quantity of unacylated product ready to react with the chromium source. A second is that the deprotontion did not occur and the alkyl exchanged itself with the chromium source.

IV.6.2.4 Synthesis of Pentacarbonyl{*N'*-dodecyl-*N*-[(2R,3R,4R,5S,6-pentahydroxy-hexanoyl amino)-1,4-phenylene]-2,3-dihydro-imidazol-2-ylidene}chromium (**51**)



Scheme 31: Synthesis of complex **51** after removal of acetyl protecting groups from **49**

The deprotection of the complex **49** occurs under the same conditions as before (see **IV.4.2.9**). The use of a saturated solution of ammonia in methanol permits the removal of the acetyl protective groups in a mild way (Scheme 31). The reaction affords a light yellow solid in 68% yield after purification over silica gel column chromatography.

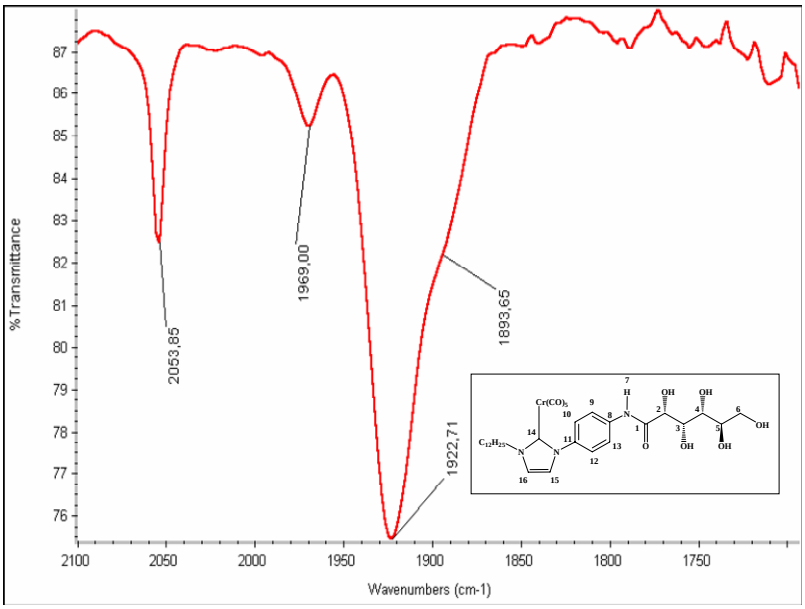


Figure 94: FTIR spectrum of the complex **51**

A first hint, for the success of the reaction can be seen with the FTIR spectroscopy (Figure 94). Since the intensive band for the acetyl groups is missing, the sugar part has been deprotected. The pentacarbonyl band set is still present, so the structure seems to be holding its metal carbonyl system. The ^{13}C-NMR spectrum shows signals at 222.7, 216 and 192 ppm, providing evidence that the carbene and chromium pentacarbonyl are still present.

IV.6.2.4.1 *Applications*

After the formation of the complex **51**, the gel tests were tempted with this complex. The results are presented in table 3.

	MeOH	CH_3CN	DMSO	DMF	CH_2Cl_2	$CHCl_3$	CCl_4	Et_2O	C_6H_6	Tol	cy-Hex	PE	*n*-Hex
Behaviour	S	P	S	S	P	P	S	P	P	P	S	-	G

Table 3: Behaviour from molecule **51** in different solvent (5 wt %)

Two interesting facts can be seen. Compared to the complexes **32** to **35** (Figure 70), there is a change of behaviour in chlorinated solvents. The complexes **32** to **35** are soluble in dichloromethane and chloroform, which is not the case for **51**. The precipitate recovered lead to the interpretation that the structure seems to have become less polar. The second and more interesting point is that a gel is formed in *n*-hexane. The first test is made with 5% wt and lead

to a complete gelation of the solvent. With 1% wt the system leads to a partial gelation of the solvent (see **II.2.1.3** Figure 22).

In order to understand the formation of the aggregates, TEM (Transmission Eletron Microscopy) pictures are recoded.

TEM spectroscopy is a technique using an electron beam that will be projected through the material.[100] A beam of highly focused electrons are directed toward a thin sample (<200 nm) dried in high vacuum. A sample is composed of the product to analyse (here the gel) laid on a copper grid. These highly energetic electrons interact with the atoms in the sample producing characteristic radiation and particles providing information for materials characterization. Information is obtained from both deflected and non-deflected transmitted electrons, backscattered and secondary electrons, and emitted photons.[101]

IV.6.2.4.2 *Results*

The images obtained are images of the aggregated structure in a solvent free environment, due to the high vacuum phase. The aggregation in the gel phase could be then slightly different. Removing the solvent might give a clean picture of the aggregates forming the network. On Figure 95, a first picture of the sample is shown, taken with light microscopy. It displays the material being equally reparted on the grid.

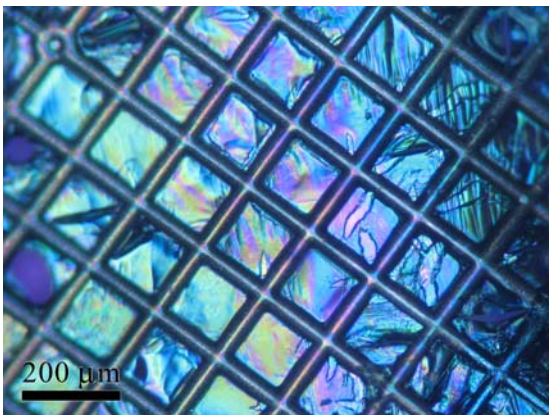


Figure 95: Picture of **51** under light microscopy

[100] http://www.tf.uni-kiel.de/matwis/amat/def_en/backbone.pdf
[101] http://cmm.mrl.uiuc.edu/techniques/tem.htm

The pictures in Figure 96 show in different scales the material in TEM spectroscopy.

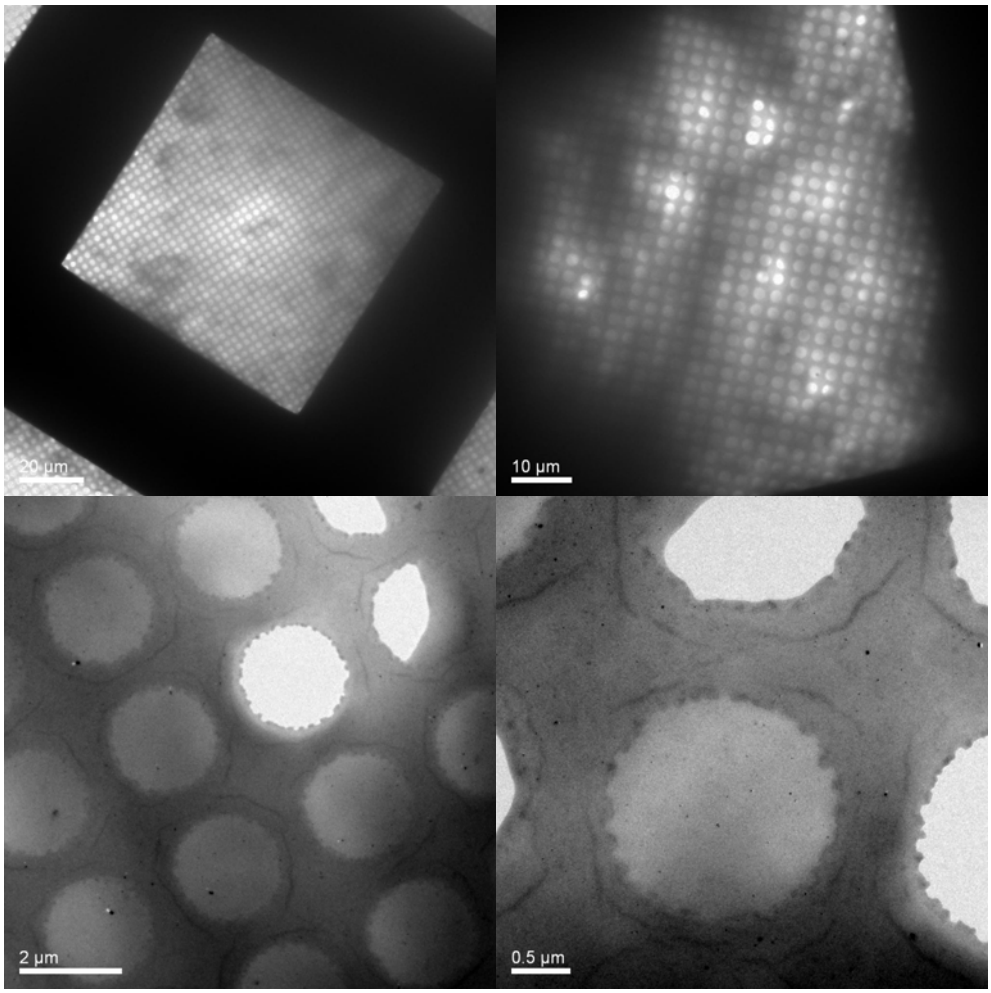


Figure 96: Zoom in on the material from 20 µm to 0.5 µm

The structure of the gel is not resolvable; the material behaves itself like a thin layer (film). No fibers can be seen, which makes the interpretation of the aggregation impossible. The structure depends on the gelator aggregating with the solvent molecules. As the molecule could form a gel in only one solvent, the possibilities of seeing another type of aggregation and than fibers through microscopy tests are reduced. Such pictures might originate from too much material laid on the copper grid but in this case (as seen in the picture in the lower left corner of Figure 96) the grid holes are still visible, which means that the layer of product is not too thick. An EDX (Energy Dispersive X-ray Spectroscopy) experiment is conducted to be sure that it is the complex **51** that leads to this aggregation. EDX analysis is used in conjunction with TEM and is not a surface analysis technique. An electron beam strikes the surface of a conducting sample. The energy of the beam is typically in the range of 10-20 keV. This causes X-rays to be emitted from the point of the material hit by the beam. By

moving the electron beam across the material an image of each element in the sample can be acquired giving information on the elemental composition of the material under examination.[102]

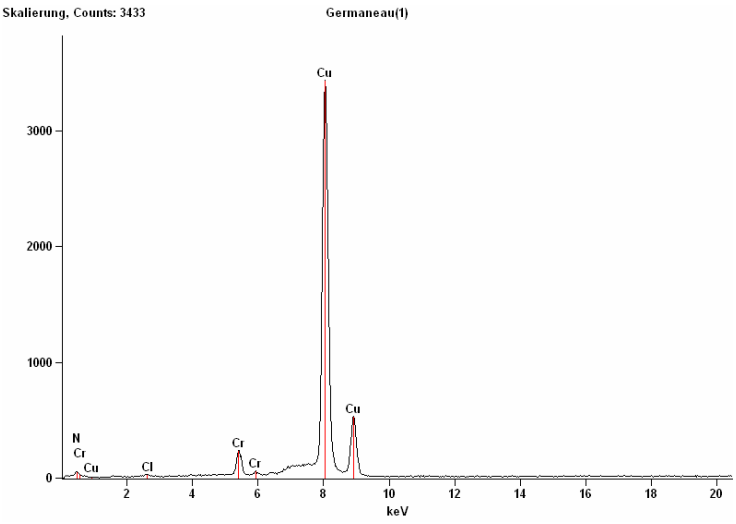


Figure 97: EDX experiment of sample of molecule **51**

The EDX picture (Figure 97) shows without any doubt, that the chromium complex is the gelator. The high amount of copper (Cu) is caused by the grid itself. The lack of visibility of fibers makes it impossible to elaborate an aggregation model.

IV.6.2.4.3 *Discussion*

In order to elucidate the role of the metal fragment in the aggregation properties of chromium carbene complex **51** the study was extended to the imidazolium precursors **46** and **48**. Salts are also known to be gelators[76] but in the case of the chromium carbene complexes synthesis (e.g. **51**) the salts are intermediates and when the complex is formed the salt is replaced by the metal species, which means that the abilities whatever they are might be lost from salt to metal complex.

	MeOH	CH_3CN	DMSO	DMF	CH_2Cl_2	$CHCl_3$	CCl_4	Et_2O	C_6H_6	Tol	cy-Hex	PE	*n*-Hex
46	S	S	S	S	S	S	S	P	S	P	P	P	P
48	S	S	S	S	S	S	S	P	S	S	P	P	P

Table 4: Behaviour of molecules **46** and **48** in different solvents (5 wt %).

[102] http://www.uksaf.org/tech/edx.html

Table 4 shows that these salts are not efficient in gelation of solvents. The salts and the metal complex **51** show some distinct differences. While chlorinated solvents dissolve the salts, again the metal complex remains undissolved. In the case of toluol the salts behave different: **48** is soluble while **46** stays insoluble.

IV.6.3 Conclusion

The synthesis of aromatic ring spacer complexes suceeded with very different results. The chosen synthetic method has shown its reliability starting from amide **45**, the desired imidazolium salts **46**, **47** and **48** were synthesised. The yields can be very good to very low if a column chromatography is needed, making the most important step the formation of the amide **45**. The alkylating agents could easily be separated from the reaction mixture.

The formation of the metal complex **50** according to the silver carbene route has again proven to be efficient, leaving the reason for the failure of the formation of the C_{16} chain chromium complex unclear. A solubility problem of the salt **48** might be the reason.

The complex **51** has proven gelation in *n*-hexane, unfortunately the gel structure could not be resolved due to the aggregation mode. These results tend to show that the balance between hydrophilicity and hydrophobicity is delicate but near.

Concluding Remarks and Outlook

V Concluding Remarks and Outlook

The work presented herein describes in detail in four parts the investigations on the formation of a new class of amphiphilic *N*-heterocyclic carbene complexes.

Chapter **IV.3**: Study on the one to one replacement of a Fischer carbene complex by an *N*-heterocyclic carbene on a known system.
Chapter **IV.4**: Synthetic approach on new analogue complexes with alkyl chains used as spacer.
Chapter **IV.5**: Formation of homo bi-metallic hetero-bis carbene complexes.
Chapter **IV.6**: Synthesis of phenyl ring spacered *N*-heterocyclic carbene complexes.

Through this report were described all attempts and achievements in the development of a new class of amphiphilic *N*-heterocyclic carbene ligands. The formal replacement of a Fischer type carbene, present in the original amphiphilic structure on which the work is based,[9] by a more versatile NHC moiety proved to be difficult. The problem could be solved by using different spacers between the hydrophilic head and the hydrophobic tail of the complex. (e.g. **51** Figure 98)

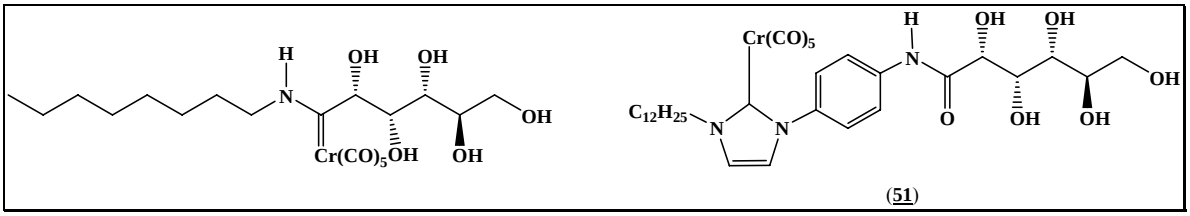


Figure 98: From Fischer carbene complex[9] to new NHC equivalent.

The direct installation of an NHC in place of a Fischer complex was not achieved due to the low stability of the intermediate, even if this intermediate was shown to be formed. (Figure 99)

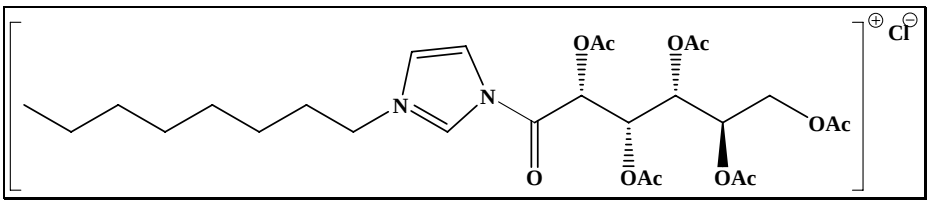


Figure 99: First approach to a new class of amphilic structure bearing NHC.

This issue led to a second approach where the use of a spacer between the carbene centre and the hydrophilic head was necessary. A complete new family of amphiphilic systems bearing NHC chromium carbenes (**23**, **32**-**35**, **51**) could be accessed, using a very efficient protocol based on a transmetalation strategy via silver(I) oxide. This protocol permits to obtain the new class of complexes under mild conditions. (Figure 100)

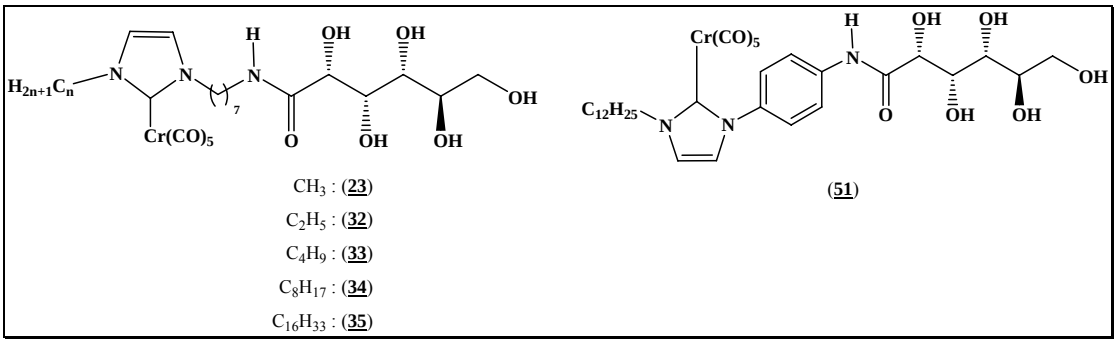


Figure 100: New NHC carbene complexes with alkyl and phenyl spacers.

The complexes **23**, **32**-**35** did not gelate any of the solvents studied, meaning that the metal must be part of the rigid structure to play its role in the aggregation. Through the transmetalation route, involving silver (I) carbene complexes, compounds **23**, **32**-**35** were obtained in yields from 38% to 69%.

The alkyl spacered system permitted to have access to new structures. Among those compounds were new homobimetallic hetero-bis-carbene complexes. In an attempt to combine the known Fischer carbene chemistry that has led to the gelation of chlorinated and aromatic solvents and of NHC chemistry some new complexes incorporating these two types of carbenes could be synthesised. (**39**, **40**, **44** Figure 101)

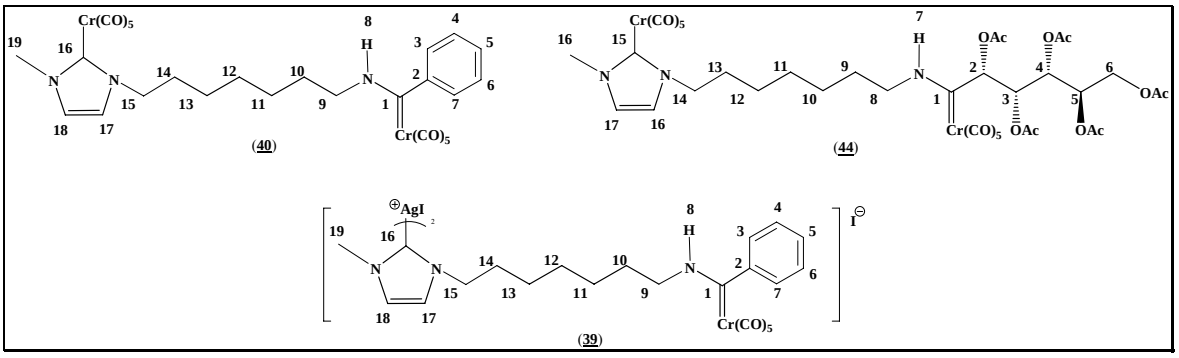
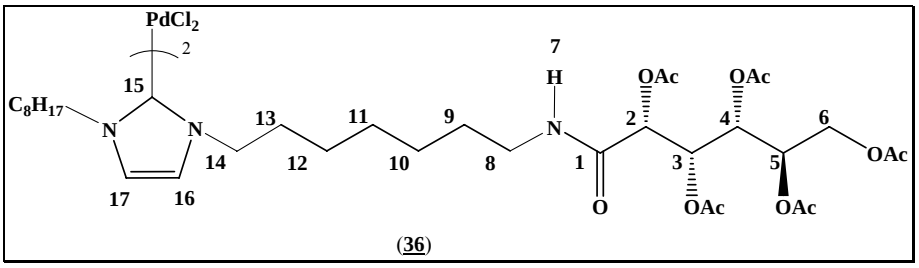


Figure 101: Examples of new hetero-bis-carbene bimetallic complexes.

The combination of two different metals in the same molecule (**39**) offers new opportunities for bimetallic chemistry.

The transmetalation with silver complexes does not narrow the versatility of NHC complexes. As shown in this work both chromium (0) and palladium (II) complexes can be formed. (Figure 102)

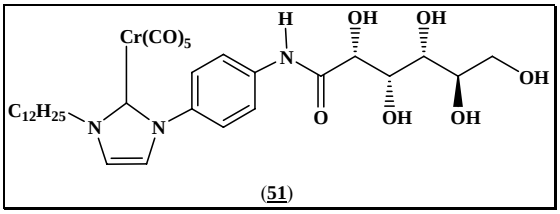


(**36**)

Figure 102: A new palladium (II) complex suitable for Suzuki coupling.

Examples of catalytic activities with complex **36** showed that its amphiphilic ligand allows a Suzuki reaction to be run catalytically under mild conditions, despite its sterical bulk, having up to 95% conversion.

Finally, phenylene spacered complexes were synthesised, with good to average yields, and their gelation abilities have been investigated systematically. Among a series of protic and aprotic polar and non polar solvents test, n-hexane was the only solvent to form a gel Even if only one solvent could form a film gel in the presence of 5 wt % of chromium carbene complex **51**. (Figure 103)



(**51**)

Figure 103: A new NHC amphiphilic carbene complex providing gelation abilities.

The perspectives, that the general synthetic methodology offers, broaden the field of future investigations. (Figure 104)

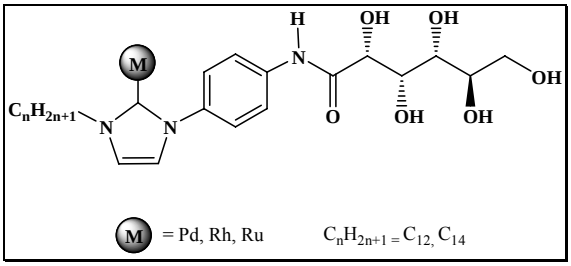


Figure 104: Expectation on further developments for amphiphilic NHC complexes.

The goal of building a structure that could gelate solvents and at the same time is versatile enough to be used in catalytical palladium chemistry is within reach.

V Zusammenfassung und Ausblick

Diese Arbeit beschreibt in vier Kapiteln detailliert die Untersuchungen zur Darstellung einer neuen Klasse von amphiphilen N-heterocyclischen (NHC) Carbenkomplexen:

Kapitel **IV.3**: Untersuchungen zum Ersatz einer Fischer-Carbenkomplexeinheit durch einen NHC-Carbenliganden in einem bekannten Carbenkomplex-System.
Kapitel **IV.4**: Synthetischer Ansatz zu einem neuen analogen Carbenkomplex mit Alkylketten -Spacer.
Kapitel **IV.5**: Bildung von homo-bimetallischen Hetero-Biscarben-Komplexen.
Kapitel **IV.6**: Synthese von NHC-Carbenkomplexen mit einem Benzenring als Spacer.

In der vorliegenden Arbeit wurden die Arbeiten im Zusammenhang mit der Entwicklung einer neuen Klasse von amphiphilen NHC-Carbenliganden beschrieben. Der formale Ersatz der Fischer-Carbeneinheit in einen amphiphilen Carbencomplex durch eine vielseitigere NHC-Einheit erwies sich als schwierig. Dieses Problem konnte aber durch den Einbau verschiedener Spacer zwischen dem hydrophilen Kopf- und dem hydrophobien Schwanzteil gelöst werden (z. B. **51**, Abbildung 98).

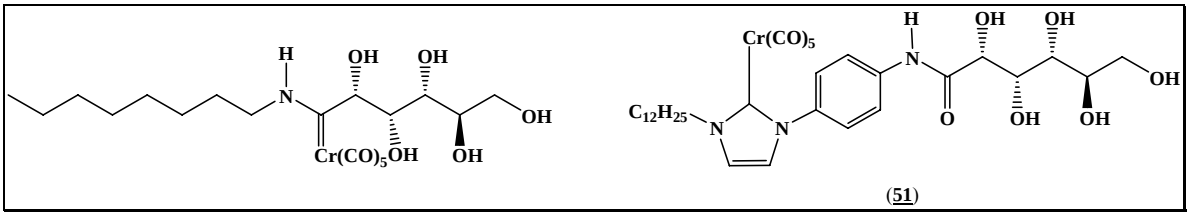


Abbildung 98: Von einem Kohlenhydrat-Fischer-Carbenkomplex[9] zu einem neuen NHC-Analogon.

Der direkte Einbau eines NHC-Liganden anstelle einer Fischer-Carbeneinheit wurde aufgrund der geringen Stabilität der dabei durchlaufenen Zwischenstufe nicht erreicht; es könnte jedoch auch wenn gezeigt werden, dass sich diese Zwischenstufe bildet (Abbildung 99).

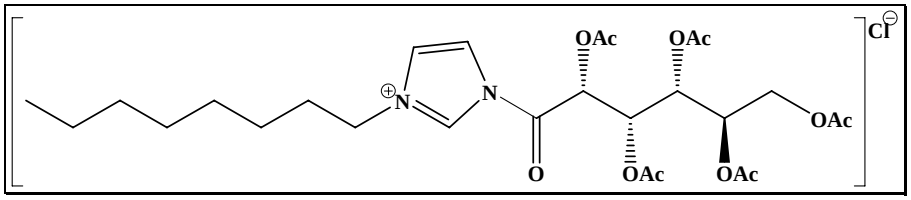


Abbildung 99: Erster Zugang zu einer neuen Klasse von amphiphilen NHC-Liganden.

Dieses Problem führte zu einem zweiten synthetischen Ansatz, in dem der Einsatz eines Spacers zwischen der Carbeneinheit und dem hydrophilen Kopfteil nötig wurde. Es gelang, eine neue Familie von amphiphilen Systemen mit NHC-Chromcarbenkomplexen (**23**, **32**-**35**, **51**) herzustellen, wobei ein sehr effizientes Verfahren unter Benutzung von Silber(I)oxid angewandt wurde. Dieses Verfahren erlaubt es, die neue Klasse von Komplexen unter milden Reaktionsbedingungen zu erhalten (Abbildung 100).

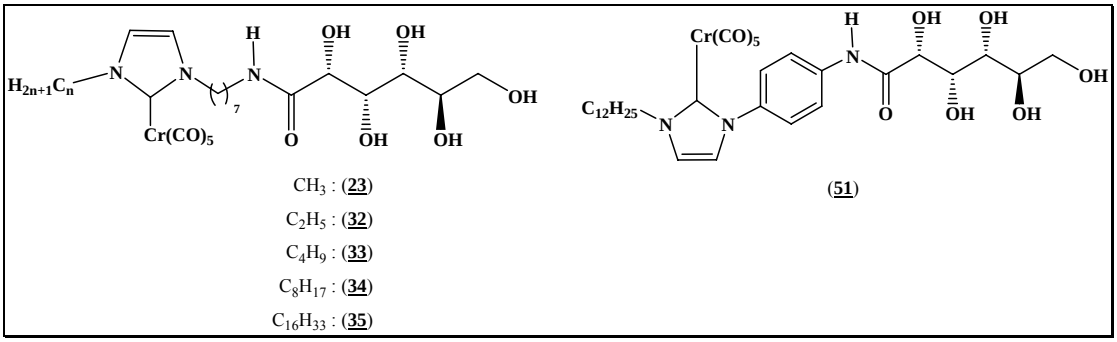


Abbildung 100: Neue NHC-Carbenkomplexe mit Alkyl- und Phenyl-Spacern.

Die Komplexe **23** und **32**-**35** zeigten keine Gelierungseigenschaften; das bedeutet, dass das Metal Teil der starren Struktur sein muss, um eine Rolle bei der Aggregation zu spielen. Durch die Transmetallierungsroute, in der Silber(I)carben-Komplexe als Vorläufer eingesetzt werden, wurden die Verbindungen **23** und **32**-**35** in Ausbeuten von 38% bis 69% erhalten.

Die Molekülsysteme mit Alkyl-Spacern erlaubten den Zugang zu neuen homo-bimetallischen Hetero-Biscarben-Komplexen. Sie konnten beim Versuch erhalten werden, die bekannten, zur Gelierung von organischen Lösungsmitteln führenden Fischer-Carbenkomplexe mit *N*-heterocyclischen Carbenen zu kombinieren (**39**, **40**, **44**; Abbildung 101).

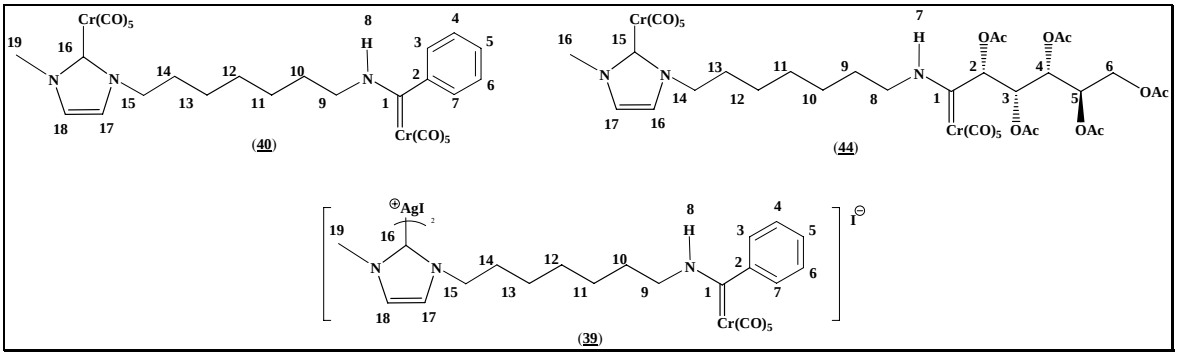


Abbildung 101: Beispiele für neue homo-bimetallische Hetero-Biscarben-Komplexe.

Die Kombination von zwei verschiedenen Metallen im selben Molekül (**39**) bietet neue Möglichkeiten für bimetallische Komplexe.

Die Transmetallierung von Silber-Carbenkomplexen engt die Zugangsmöglichkeiten zu NHC-Komplexen keineswegs ein. Wie gezeigt werden konnte, sind sowohl Chrom(0)- als auch Palladium(II)-Komplexe durch diese Strategie erhältlich (Abbildung 102).

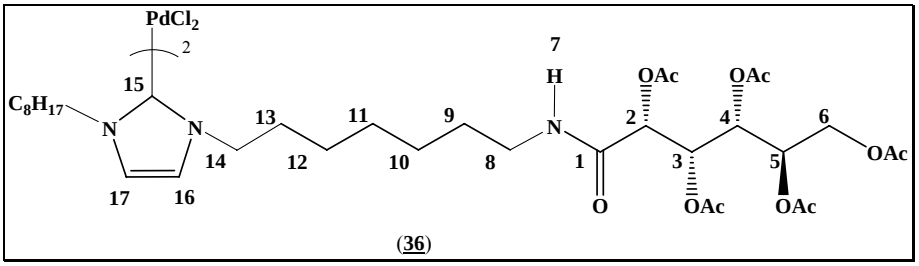
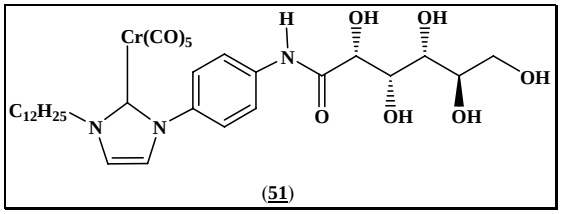


Abbildung 102: Ein neuer Palladium(II)-Komplex für die Suzuki-Kupplung.

Katalytische Mengen des Komplexes **36** ermöglichen trotz dessen recht großen amphiphilen Liganden bei der Suzuki-Kupplung eine Umwandlung von bis zu 95%.

Schließlich konnten die aromatische Spacer aufweisenden NHC-Komplexe in mäßigen bis guten Ausbeuten synthetisiert und deren Gelierungseigenschaften systematisch untersucht werden. Auch wenn nur ein einziges Lösungsmittel geliert werden konnte, so wurde doch der Weg zur optimalen Struktur eines potenten organometallischen amphiphilen NHC-Gelators aufgezeigt (Abbildung 103).



(**51**)

Abbildung 103: Ein neuer gelierender amphiphilischer NHC-Komplex.

Die Aussichten, die die erarbeitete allgemeine Synthesestrategie zu den NHC-Carbenkomplexen anbietet, erweitert die Möglichkeiten bei den zukünftigen Untersuchungen zu amphiphilen NHC-Komplexen (Abbildung 104).

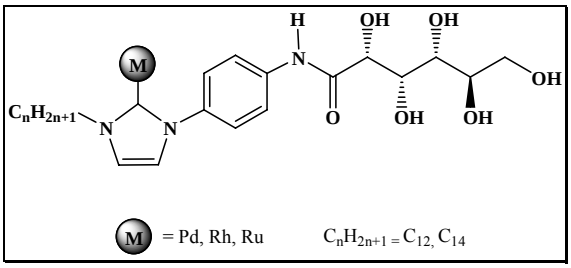


Abbildung 104: Möglichkeiten für die zukünftige Entwicklung von amphiphilen NHC-Komplexen.

Das Ziel, eine zur Gelierung von Lösungsmitteln befähigte Struktur aufzubauen, die außerdem vielseitig genug ist, um in Palladium-katalysierten Reaktionen genutzt zu werden, ist nun in Reichweite gerückt.

V Abstract

Le travail présenté ici décrit, en détail, en quatre parties, les recherches effectuées afin de synthétiser une nouvelle famille de complexes N. hétérocycliques carbéniques amphiphiles.

Chapitre **IV.3**: L'étude sur le remplacement d'un complexe carbénique de type N-hétérocyclique en lieu et place d'un système carbénique de type Fischer.
Chapitre **IV.4**: Une approche synthétique sur l'utilisation d'une chaîne alkyle comme espaceur pour la formation de nouveaux complexes.
Chapitre **IV.5**: La synthèse de complexes de type homobimetallique hétéro-bi-carbenes.
Chapitre **IV.6**: La synthèse de complexes de type N hétérocyclique carbene utilisant un phényle comme espaceur.

Ce rapport décrit toutes les tentatives et réussites dans le développement d'une nouvelle famille de ligands amphiphiles de type N hétérocyclique carbene. Le remplacement direct du carbene de Fischer, présent dans la structure originale sur laquelle le travail est basé,[9] par un plus versatile groupe NHC est apparu difficile. Ce problème a pu être résolu par l'utilisation de différents espaceurs placés entre la tête hydrophile et la partie hydrophobe du complexe. (c. f. **51**, figure 98)

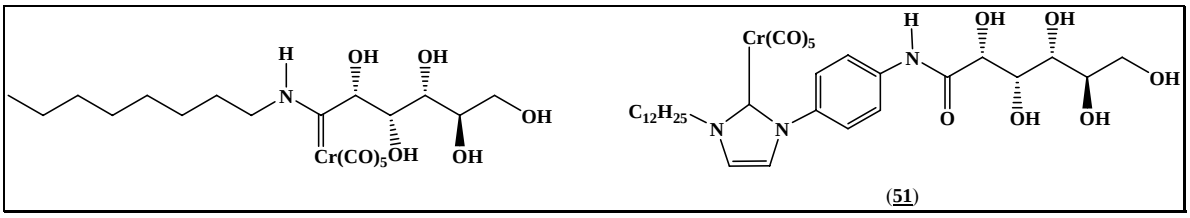


Figure 98 : Le complexe de Fischer de départ[9] et un nouvel équivalent de type NHC.

L'incorporation directe d'un NHC à la place d'un carbene de Fischer n'a pas pu être effectuée dû à l'instabilité de l'intermédiaire ionique, même si la présence de cet intermédiaire a été prouvée. (Figure 99)

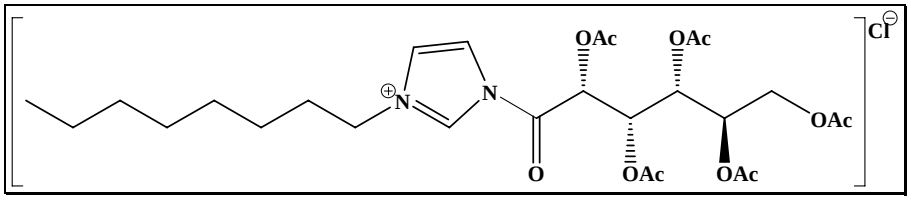


Figure 99 : Première approche pour la formation d'une nouvelle classe de carbenes amphiphiles.

Ce résultat dicta une seconde approche où l'utilisation d'un espaceur entre le centre carbénique et la tête hydrophile fut nécessaire. Une complète nouvelle famille de systèmes amphiphiles comportant un carbene de type NHC du chrome (**23**, **32**-**35**, **51**) fut donc accessibles, utilisant une méthode très efficace à base d'oxyde d'argent (I). Ce protocole a permis d'obtenir une nouvelle classe de complexes du chrome utilisant des conditions douces (Figure 100).

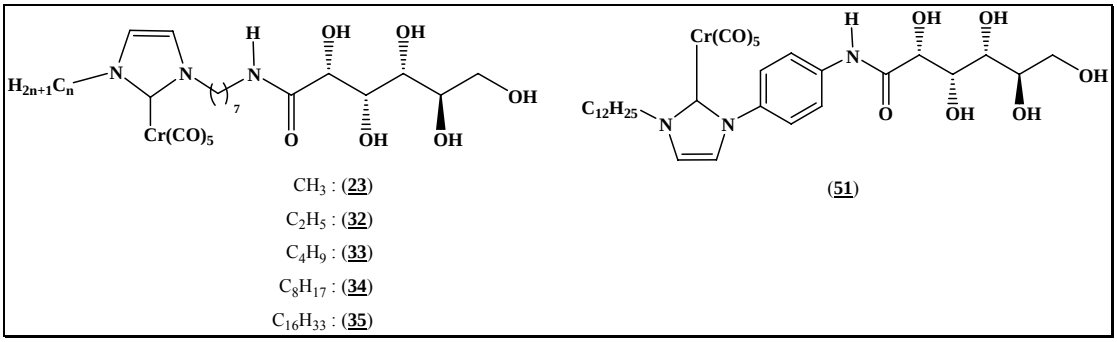


Figure 100 : De nouveaux complexes carbéniques avec chaîne alkyle et phényl comme espaceurs.

Les complexes **23**, **32**-**35** n'ont pas formé de gels dans aucun des solvants testés, montrant que le métal doit certainement faire partie de la partie rigide de la molécule pour jouer son rôle dans l'agrégation. Utilisant cette méthode de transmetallation, à base de complexes de carbenes d'argent (I), les molécules **23**, **32**-**35** ont été obtenues avec des rendements échelonnés entre 38 % et 69 %.

Les systèmes comportant une chaîne alkyle comme espaceur ont permis d'atteindre de nouvelles structures. Parmi celles-ci sont les nouveaux complexes homobimetallic hétéro-bicarbéniques. Dans une étude portant sur la combinaison possible de la chimie des carbenes de Fischer, qui a mené à la formation de gels des solvants organiques, avec la chimie inhérente aux complexes incorporant des carbenes types NHC, ces nouvelles molécules comportant deux types de carbenes différents ont été synthétisées. (**39**, **40**, **44** ; Figure 101)

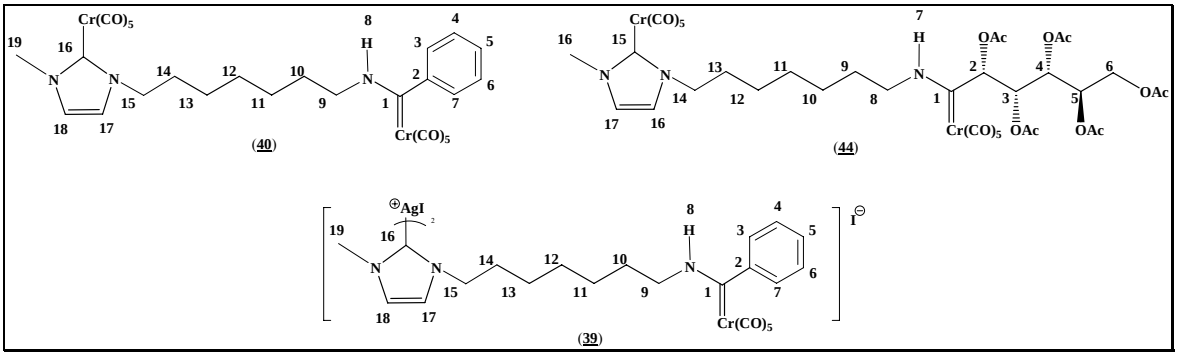


Figure 101 : Exemples de nouveaux complexes hétéro-biscarbène bimétalliques.

La formation de complexes ou cohabitant deux métaux différents (**39**) peut ouvrir de nouvelles perspectives dans le domaine de la chimie bimétallique.

La transmétallation avec les complexes d'argent ne limite pas la versatilité des complexes à base de NHC. Comme a pu l'être démontrer dans ce rapport aussi bien des complexes du chrome (0) que du palladium (II) ont pu être synthétisé. (Figure 102)

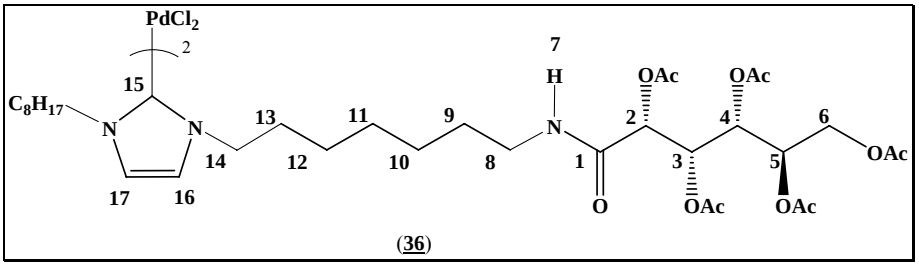


Figure 102 : Un nouveau complexe du palladium (II) utilisable pour la réaction de Suzuki.

Des exemples d'activité catalytique avec le complexe **36** montrent que le caractère amphiphile du ligand permet l'achèvement de réactions de type Suzuki de façon catalytique, malgré sa gêne stérique, ayant jusqu'à 95 % de conversion.

Enfin, des complexes avec des espaceurs aromatiques ont été synthétisés, avec de bon à très bons rendements, et leurs capacités à geler des solvants ont subies une étude systématique. Même si seul en combinaison avec un solvant le complexe **51** a pu donner naissance à un gel, la structure optimum ne devrait pas être très différente de celle de **51**. (Figure 103)

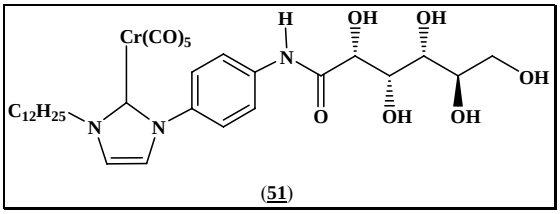


Figure 103 : Un nouveau complexe de type NHC ayant la capacité de former des gels.

Les perspectives que cette méthode synthétique générale apporte, permettent de penser à plusieurs nouvelles structures possibles dans le cadre de nouvelles études. (Figure 104)

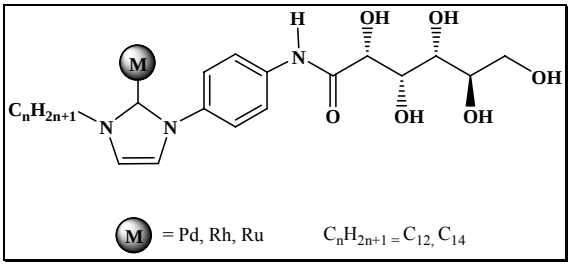


Figure 104 : Projection sur de nouveaux développements pour des complexes amphiphiles de type NHC.

Le but de synthétiser une structure qui pourrait donner naissance à des gels dans plusieurs solvants ans également avoir des propriétés lui permettant d'être utilisé, en combinaison avec du palladium, en catalyse est désormais envisageable.

Résumé :

La récente découverte de nouvelles molécules organiques permettant la formation de gel dans différents solvants provoque l'intérêt et profiterait de la présence de complexe carbénique dérivé de l'imidazole.

Les gels sont devenus depuis la fin d'années 90 un sujet d'intérêt, car ils peuvent être utilisés dans de nombreux domaines tels la synthèse, la séparation, les matériaux, l'électronique moléculaire, la catalyse, la livraisons ou modification d'agents de peinture, d'encres, d'entretiens, de cosmétiques ou de polymères. Suite à la découverte en 2003 de complexe organométallique amphiphile du chrome ayant les mêmes propriétés de formation de gel en milieux organiques, le travail s'oriente autour de l'optimisation de la structure originale avec le remplacement du carbene de Fischer présent sur la molécule originale par un carbene de type *N*-hétérocyclique (NHC). La formation des gels est déterminée par l'agrégation au niveau des molécules entre elles ou avec des molécules de solvants. Cette agrégation permet la formation de structures supramoléculaires qui sont constituées de fibres de matériaux encageant des molécules de solvants. Ces fibres enlacées entre elles peuvent donner naissance à d'autres fibres de tailles plus importantes et hélicoïdales. À la différence des autres matériaux et polymères, les gels ne sont construits que sur des interactions non covalentes (liaisons hydrogènes, π-staking, interactions type Van der Waals), ce qui permet de faire repasser le complexe à l'état solide ou en solution suite à l'ajout d'un cosolvant, sans rompre aucune liaison, permettant rapidement et simplement de séparer le complexe du milieu réactionnel. L'apport de carbenes de type NHC est attrayant, car permettraient d'ouvrir d'autres horizons en termes de métaux. Les complexes de type NHC permettent en opposition aux carbenes de Fischer la complexation d'un plus grand de métaux par exemple le palladium, le ruthénium, le rhodium, etc.

La synthèse de carbenes amphiphiles dérivés de l'imidazole devrait donc pouvoir élargir les possibilités de synthèse dans le milieu des gels. La formation de fibres hélicoïdales pouvant apporter une chiralité supramoléculaire, la possibilité de séparer le complexe du milieu réactionnel et enfin la possibilité de faire de la catalyse en milieu gel sont les centres d'intérêts qui ont amenés à cette étude.

Experimental Part

VI Experimental Part

All organometallic reactions were performed under argon atmosphere and in previously dried vessels.
Dichloromethan was distilled over calcium hydride, methanol over magnesium and tetrahydrofuran over sodium. Diethylether was distilled over calcium chloride and petrol ether over lithium aluminium hydride. All distillated solvents were kept dried by using 4 Å molecular sieves.
All temperatures mentioned are temperatures measured from oil, water or cooling bath.

All organometallic compounds were purified over silica gel in chromatography column equipped with a cooling mantle under argon atmosphere.
The silica gel is provided by *Merck*, Type 60 (0.063 - 0.200 mm). All silica gel was dried under low pressure and flushed with argon several times before use.
TLC are of Type 60 F254, purchased directly from *Merck*.
The detection of products spots on TLC can be made possible by the use of the Seebach reagent medium prepared with 6 ml of sulfuric acid, 94 ml of water, 2.5 g molybdatophosphoric acid and 1.0 g cer(IV)sulfate (a.k.a. Seebach-reagent).

- FTIR - Spectroscopy

All IR spectra were measured with a *Nicolet Magna 550* FT-IR-Spectrometer in sodiumchloride cuvettes.

Abbreviations for intensities of IR Bands
w: weak
m: medium
s: strong
vs: very strong
sh: shoulder

- NMR - Spectroscopy

All ^{1}H- and ^{13}C-NMR spectra were measured on DPX-300, DPX-400 or DRX-500 machines from *Bruker* at room temperature. All deuterated solvents were used as received.

Abbreviations for intensities of ^{1}H-NMR signals
s: singulet
d: doublet dd: doublet of doublets etc.
t: triplet
m: multiplet
br s: broad signal

- Mass - Spectroscopy

Mass spectra were collected at the *Rheinischen Friedrich-Wilhelms-Universität Bonn* with different machines. Electron Ionisation (EI-MS)) spectra were made with a MS 50 (70eV) from *Kratos,* the Positiv-Ion Fast Atom Bombardment-experiments spectra (FAB) were obtained from a Concept 1H machine from *Kratos*. Meta-Nitrobenzylalcool (mNBA) is used as matrix in the FAB technique. The value between brackets (XX) is the relative intensity of the desired peak in comparison to the basis peak. Some complexes could only be seen in an Electron-Spray-Ionisation apparatus coupled with a *Fourier*-Transform-Cyclotron-Resonance-Mass-spectrometer (ESI-FT-ICR-MS) from *Bruker*. This machine could be used under supervision from the working group of Dr. C. A. Schalley in the *Kekulé-Institut für Organische Chemie und Biochemie der Universität Bonn*. For these experiments the substances were dissolved in methanol;

- TEM - Spectroscopy

The transmission elctron microscopy machine unsed in *Institut für Anorganische Chemie der Universität Bonn* is an *EM 400-STEM* und *CM 30 ST-STEM* from *Phillips*.

Abbreviations

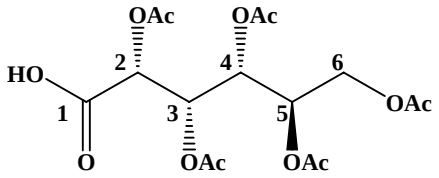
- δ: chemical shift
- ^{1}H: proton NMR
- ^{13}C: carbon NMR
- a.k.a.: also known as
- Boc_2O: Di-*tert*-butyl dicarbonate
- CMC: critical micelles concentration
- °C: degree Celsius
- cm^{-1}: wave number
- CDI: carbondiimidazole
- CH_2: methylene group
- DCM: dichloromethan
- DEPT: distorsionless enhancement by polarisation transfer
- DME: dimethoxyethane
- DMF: dimethylformamide
- DMSO: dimethylsulfoxide
- E/Z: entgegen/zusammen (opposite/together)
- EDX: energy dispersive X-ray spectroscopy
- EI: electron ionisation
- ESI: electro spray ionisation
- Et_2O: diethylether
- EVACP: ethyl/vinyl acetatecopolymer
- FAB: fast atom bombardment
- g: gramm
- G: gel
- GCMS: gas chromatography mass spectroscopy
- h: hour
- Hz: Frequency
- IR/FTIR: Fourrier transform infrared
- J: coupling constant
- KO^tBu: potassium *tert*-butoxide
- L: ligand
- M^+: molucular ion
- M: molecular mass
- m/z: mass to charge ratio
- ml: milliliter
- min: minute
- *m*NBA: *meta*-nitrobenzylalcohol
- MS: mass spectroscopy
- NHC: N-heterocyclic carbene
- NMR: nuclear magnetic resonance
- o.n.: overnight
- OAc: O-acetyl
- OTf: O-trifluoromethansulfonate
- P: precipitate
- ppm: parts per million
- PE: petrol ether
- Rf: retention factor
- rt: room temperature
- S: solution
- TEM: transmission electron microscopy
- THF: tetrahydrofuran
- TLC: thin layer chromatography
- TMEDA: tetramethylethylenediamine

General Procedure for Suzuki cross coupling.

General considerations: Reactions were performed under standard Schlenk conditions under an atmosphere of argon; cesium carbonates and dioxane were purchased from Acros and used as bought. All catalytic reactions were performed according to the following general procedure: catalyst (1 mol %) and $CsCO_3$ (2.0 equivalents) were dried under vacuum for 15 minutes and then mixed under an inert atmosphere of argon in a small schlenk tube equipped with a side argon flow. Dioxane (10 mL) was added, the boronic acid (1.5 equivalent) injected and then the second substrate (1 equivalent) injected.

2,3,4,5,6-penta-*O*-acetyl gluconic acid (**1**)

To a 70 mL solution of acetic anhydride at -10°C, 7 mL of perchloric acid are added dropwise, while adding the system should not exceed 0°C. 10 g (42.27 mmol) of gluconic acid, potassium salt, are given in four portions. The reaction mixture is left to run overnight at room temperature. The yellowish solution is then quenched with a 300 mL ice/water mix. The system is extracted three times with 50 mL of DCM. The combined organic phase is dried over magnesium sulfate, filtrated and concentrated under low pressure. The product can be recrystallised from Et_2O/PE to afford a white powder with 74% yield (9.42 g).



(**1**)

Yield : 74%

Formula : $C_{16}H_{22}O_{12}$

Mass : 406.3 g mol^{-1}

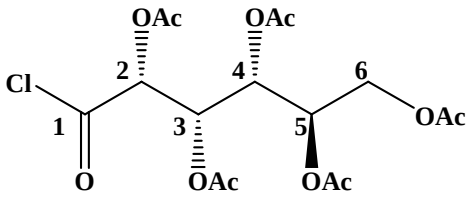
^{1}H-NMR (300 MHz, $CDCl_3$): δ[ppm] = 7.33 (OH, br s, 1H); 5.60 (H_3, dd, $^3J_{3-2}$ = 4.0 Hz, $^3J_{3-4}$ = 4.9 Hz, 1 H); 5.48 (H_4, dd, $^3J_{4-3}$ = 5.0 Hz, $^3J_{4-5}$ = 6.1 Hz, 1H); 5.28 (H_2, d, $^3J_{2-3}$ = 3.8 Hz, 1H); 5.06 (H_5, ddd, $^3J_{5-4}$ = 6.0 Hz, $^3J_{5-6a}$ = 4.2 Hz, $^3J_{5-6b}$ = 5.6 Hz, 1H); 4.28 (H_{6a}, dd, $^3J_{6a-5}$ = 4.1 Hz, $^2J_{6a-6b}$ = 12.2 Hz, 1H); 4.10 (H_{6b}, dd, $^3J_{6b-5}$ = 5.5 Hz, $^2J_{6b-6a}$ = 12.2 Hz, 1H); 2.16; 2.06; 2.05; 2.02 (-OC(O)CH_3, s, 15H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 170.6; 170.1; 169.9, 169.8; 169.7; 169.6 (-COOH, -OC(O)CH_3); 70.1 (C-2); 69.3, 68.6, 68.5 (C_3, C_4, C_5); 61.5 (C_6); 20.7; 20.6, 20.5; 20.3; 20.2 (-OC(O)CH_3).

EI-MS (70eV): calc. for $C_{16}H_{22}O_{12}$ m/z: 406.3387; found m/z = 389 (2) $[M\text{-}OH]^+$, 361 (3) $[M\text{-}COOH]^+$.

2,3,4,5,6-penta-*O*-acetyl-gluconic acid chloride (**2**)

9.42 g (23.2 mmol) dried penta-O-acetyl gluconic acid **1** is dissolved in 50 mL of thionyl chloride and stirred for three hours at 50°C. The light yellow solution is first concentrated with a water pump and then dried under low pressure. The product can be recrystallised from an absolute Et_2O/PE mix to afford a white powder with 87% yield (8.59 g).



(**2**)

Yield : 87%

Formula : $C_{16}H_{21}ClO_{11}$

Mass : 424.7 g mol^{-1}

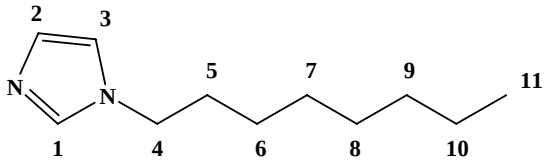
^{1}H-NMR (300 MHz, $CDCl_3$): δ[ppm] = 5.74 (H_3, dd, $^3J_{3-2}$ = 3.4 Hz, $^3J_{3-4}$ = 4.9 Hz, 1H); 5.48 (H_4, dd, $^3J_{4-3}$ = 4.9 Hz, $^3J_{4-5}$ = 6.3 Hz, 1H); 5.46 (H_2, d, $^3J_{2-3}$ = 3.4 Hz, 1H);5.05 (H_5, ddd, $^3J_{5-4}$ = 6.3 Hz, $^3J_{5-6a}$ = 4.1 Hz, $^3J_{5-6b}$ = 5.2 Hz, 1H); 4.31 (H_{6a}, dd, $^3J_{6a-5}$ = 4.1 Hz, $^2J_{6a-6b}$ = 12.2 Hz, 1H); 4.12 (H_{6b}, dd, $^3J_{6b-5}$ = 5.2 Hz, $^2J_{6b-6a}$ = 12.2 Hz, 1H); 2.22; 2.09; 2.08; 2.05 (-OC(O)CH3, s, 15H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 170.4; 169.6; 169.4, 169.3; 169.2 (-O<u>C</u>(O)CH_3); 162.3 (-C(O)Cl); 76.6 (C_2); 69.1, 68.6, 67.7 (C_3, C_4, C_5); 61.4 (C_6); 20.7; 20.5; 20.2; 20.1 (-OC(O)CH_3)

EI-MS (70eV): calc. for $C_{16}H_{21}ClO_{11}$ m/z: 424.7843; found m/z = 388 (2) $[M-Cl]^+$; 361 (16) $[M-C(O)Cl]^+$.

N-*n*-octylimidazole (**3**)

327 mg (8.17 mmol, 60% in oil) of sodium hydride is washed with PE for 15 min to afford, after removal of the solvent, a white powder. 503 mg (7.39 mmol) of imidazole is added and the mixture is dissolved in 15 mL of absolute THF at 0°C. After 30 min 1.33 mL (7.35 mmol) of octyl iodide is given and the reaction mixture is left to run overnight at room temperature. A yellow liquid can be recovered after a PE/DCM (40/60) purification over silica gel column chromatography, giving a 83% yield (1.10 g).



(**3**)

Yield : 83% (Rf: 0.57)

Formula : $C_{11}H_{20}N_2$

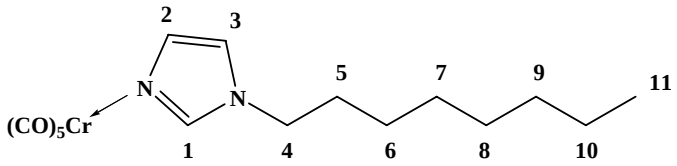
Mass : 180.3 g mol^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.39 (H_1, s, 1H); 6.97 (H_3, s, 1H); 6.82 (H_2, s, 1H); 3.83 (H_4, dt, $^3J_{H-H}$ = 7.14 Hz, $^4J_{H-H}$ = 2.48 Hz , 2H); 1.68 (H_5, t, $^3J_{H-H}$ = 6.80 Hz, 2H); 1.21 (H_6,H_7,H_8, m, 6H); 1.18 (H_9,H_{10}, s, 4H,); 0.80 (H_{11}, t, $^3J_{H-H}$ = 6.92 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 136.9 (C_1); 129.1, 118.6 (C_2, C_3); 46.8(C_4); 31.5, 30.8, 28.9, 28.8, 26.3, 22.4(C_5, C_6, C_7, C_8, C_9, C_{10}); 13.8 (C_{11}).

η^1-3-*N*-Pentacarbonyl(1-*N*-octylimidazole)chromium (**4**)

In a round flask covered with aluminium foil 126 mg (0.7 mmol) of **3** and 327 mg (0.77 mmol)of **2** are dried for 15 min under vacuum and solved in 20 mL absolute DCM. 165 mg of silveroxide is given to the reaction mixture and stirred overnight. The black solution is filtrated and concentrated. The black solid is then dissolved in THF at -78°C. 212 mg of $Cr(CO)_5$(cyclooctene) complex is solved in 20 mL THF at -78°. The yellow chromium complex solution is transferred to the silver carbene one via canula or syringe. The reaction is left to reach room temperature as the -78°C cooling bath raises its temperature, at least overnight. The product is purified over silica gel by column chromatography cooled at 0°C with a PE/DCM (7/3) eluent, affording a yellowish powder with 24% yield.



(**4**)

Yield : 24% (Rf: 0.58)

Formula : $C_{16}H_{20}CrN_2O_5$

Mass : 372.33 g mol^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.37 (s, 1H, H_1); 6.85 (s, 2H, H_2, H_3); 3.87 (t, $^3J_{4\text{-}5}$= 7.3 Hz, 2H, H_4); 1.76 (m, 2H, H_5); 1.26 (m, 12H, H_5, H_6, H_7, H_8, H_9, H_{10}); 0.87 (t, $^3J_{11\text{-}10}$= 6.1 Hz; 3H, H_{11}).

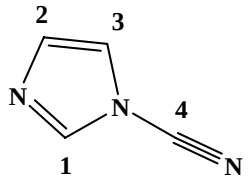
^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 220.7 (CO_{Trans}); 215.2 (CO_{Trans}); 140.3 (C_1); 134.3 (C_2); 120 (C_3); 48 (C_4); 31.6, 30.6, 29, 28.9, 26.4, 22.6, (C_5, C_6, C_7, C_8, C_9, C_{10}); 14 (C_{11}).

FAB-MS (mNBA): calc. for $C_{16}H_{20}CrN_2O_5$ m/z: 373.3365; found m/z = 372.1 (29) $[M]^+$.

FT-IR (DCM): ν CO [cm^{-1}] = 2067 (m, A_1); 1974 (sh, B_1); 1932 (vs, E).

Imidazole-1-carbonitrile (**5**)

To a solution of 680 mg (10 mmol) of imidazole in acetonitrile (30 mL) was added 1.05 g (10 mmol) of bromocyanide. The reaction mixture is protected from light with aluminium foil and is stirred at room temperature for 3h. The reaction mixture is then concentrated under low pressure using a water pump. A trap containing a one to one solution of NaOH/NaOCl in H_2O (30 mL/ 30 mL) is needed to destroy the excess of BrCN. The yellow syrup is then extracted from water with 3 aliquots of 30 mL of chloroform. After concentration under low pressure vacuum white needles are recovered with 48% (450 mg) yield. No further purification is necessary.



(**5**)

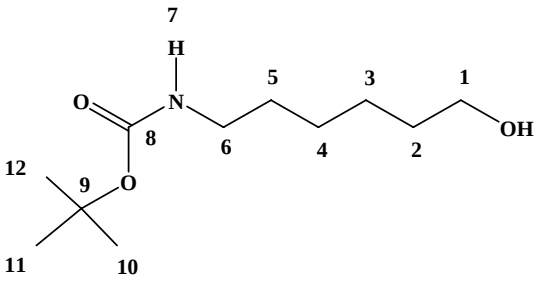
Yield : 48%
Formula : $C_9H_{13}N_3$
Mass : 163.22 g mol^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.93 (s, 1H, H_1); 7.28 (s, 1H, H_2); 7.15 (s, 1H, H_3).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 138.9 (C_1); 130.7 (C_2); 119.9 (C_3); 104.6 (C_4).

tert-Butyl 6-hydroxyhexylcarbamate (**6**)

In a Schlenk tube 2.34 g (20 mmol) of 6-aminohexan-1-ol is dried under vacuum for 15 min and then dissolved in 30 mL ^{t}BuOH. 4.36 g (20 mmol) Boc anhydride dissolved in 20 mL ^{t}BuOH is added dropwise and stirred for 16 h at room temperature. Crude product is concentrated under low pressure. The product is purified over silica gel column chromatography with DCM/MeOH (10/1). The recovered oil can be crystallised at low temperature (-24°C), affording a white solid with 98% yield (4.28 g).



(**6**)

Yield : 98% (Rf: 0.39)

Formula : $C_{11}H_{23}NO$

Mass : 217.3 g mol^{-1}

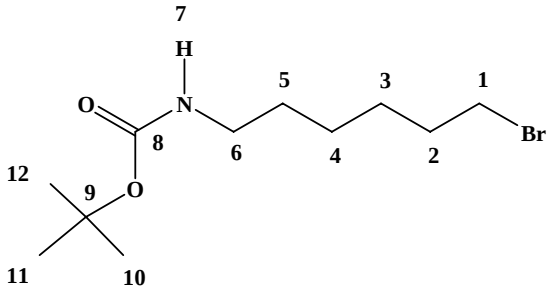
^{1}H-NMR (400 MHz, CD_3OD): δ [ppm] = 4.82 (s, 1H, H_7); 3.57 (t, $^{3}J_{6\text{-}5}$= 6.63 Hz, 2H, H_6); 3.05 (t, $^{3}J_{1\text{-}2}$= 7 Hz, 2H, H_1); 1.59 (m, 4H, H_2, H_3, H_4, H_5); 1.55 (s, 9H, H_{10},H_{11},H_{12}); 1.39 (m, 4H, H_2, H_3, H_4, H_5).

^{13}C-NMR (100 MHz, CD_3OD): δ [ppm] = 158.5 (C_8); 79.7 (C_9); 62.8 (C_1); 41.3 (C_6); 33.5, 30.9 (C_2, C_3, C_4, C_5); 28.8 (C_{10}, C_{11}, C_{12}); 27.6, 26.5 (C_2, C_3, C_4, C_5).

EI-MS (70 eV): calc. for $C_{11}H_{23}NO$ m/z: 217.3052; found m/z = 217.1 $[M]^{+}$.

tert-Butyl 6-bromohexylcarbamate (**7**)

In a round flask 9.17 g (42.2 mmol) of *tert*-butyl 6-hydroxyhexylcarbamate and 15.4 g (46.4 mmol) tetrabromocarbon is dried for 30 min under vacuum and then solved in 70 mL absolute DCM at 0°C. 14.94 g (56.97 mmol) triphenylphosphine are added over 5 min. A colorless oil is recovered after purification over silica gel chromatography (DCM/MeOH 20/1), affording 96% yield of a colourless oil (11.41 g).



(**7**)

Yield : 96% (Rf: 0.62)

Formula : $C_{11}H_{22}BrNO_2$

Mass : 280.2 g mol^{-1}

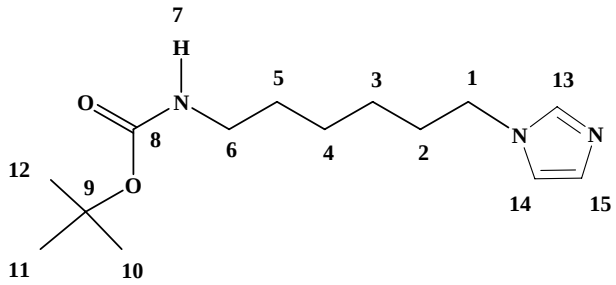
^{1}H-NMR (300 MHz, CD_3OD): δ [ppm] = 4.79 (s, 1H, H_7); 3.46 (t, $^3J_{6\text{-}5}$= 6.8Hz, 2H, H_6); 3.06 (t, $^3J_{1\text{-}2}$= 6.8 Hz, 2H, H_1); 1.90 (m, 2H, H_2); 1.51, 1.46, 1.39 (m, 15H, H_{10}, H_{11}, H_{12}, H_3, H_4, H_5)/

^{13}C-NMR (75 MHz, CD_3OD): δ [ppm] = 158.4 (C_8); 79.7 (C_9); 62.8 (C_1); 41.2 (C_6); 34.2, 33.8, 30.7 (C_2, C_3, C_4, C_5); 28.8 (C_{10}, C_{11}, C_{12}); 28.7 (C_1); 26.9 (C_2, C_3, C_4, C_5).

EI-MS (70 eV): High Resolution for [M]: calc. for $C_{11}H_{22}BrNO_2$ m/z: 279.0834; found m/z = 279.084 $[M\text{-}H]^+$.

tert-Butyl 6-(1H-imidazol-1-yl)hexylcarbamate (**8**)

0.026 g (0.04 mmol, 60% in oil) of sodium hydride is washed with PE for 15 min to afford, after removal of the solvent, a white powder. 0.040 g (0.58 mmol) of imidazole is added and dissolved in 5 mL of absolute THF at 0°C. After 30 min 0.180 g (0.64 mmol) of *tert*-butyl 6-bromohexylcarbamate is added and the reaction mixture left to run overnight at room temperature. The product can be recovered after a DCM/MeOH (20/1) purification over silica gel column, giving a 83% yield (0,130 g).



(**8**)

Yield : 83% (Rf: 0.25)

Formula : $C_{14}H_{25}N_3O_2$

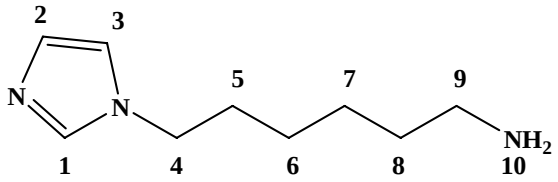
Mass : 267.4 g mol^{-1}

^{1}H-NMR (300 MHz, CD_3OD): δ [ppm] = 7.66 (s, 1H, H_{13}), 7.14 (s, 1H, H_{14}); 6.98 (s, 1H, H_{15}); 4.85 (s, 1H, H_7); 4.03 (t, $^3J_{6\text{-}5}$= 7 Hz, 2H, H_6); 3.04 (t, $^3J_{1\text{-}2}$= 6.8 Hz, 2H, H_1); 1.84 (m, 2H, H_2); 1.46, 1.34 (m, 15H, H_{10}, H_{11}, H_{12}, H_3, H_4, H_5).

^{13}C-NMR (75 MHz, CD_3OD): δ [ppm] = 158.4 (C_8); 138.3 (C_{13}); 128.9, 120.5 (C_{14}, C_{15}) 79.7 (C_9); 47.8 (C_1); 41.2 (C_6); 31.9, 30.7 (C_2, C_3, C_4, C_5); 28.8 (C_{10}, C_{11}, C_{12}); 27.2, 27.1 (C_2, C_3, C_4, C_5).

6-(1H-Imidazol-1-yl)hexyl-1-amine (**9**)

In a round flask equipped with a dropping funnel 2.52 g (9.43 mmol) **8** is dried under low pressure and then solved in DCM. A solution of TFA (7 mL; 94.3 mmol) in 40 mL of DCM is added dropwise to the reaction. The solution turns light yellow. After 20 hours the solution is biphasic. An aqueous 2M solution of Na_2CO_3 is added to neutralise the system. The aqueous phase was extracted three times with DCM. The combined organic phase are concentrated under low pressure to afford a crude oil. The oil is purified over silica gel with DCM/MeOH 5/2 ratio and a colorless oil is recovered with 17% yield.



(**9**)

Yield : 17% (Rf: 0.55)

Formula : $C_9H_{17}N_3$

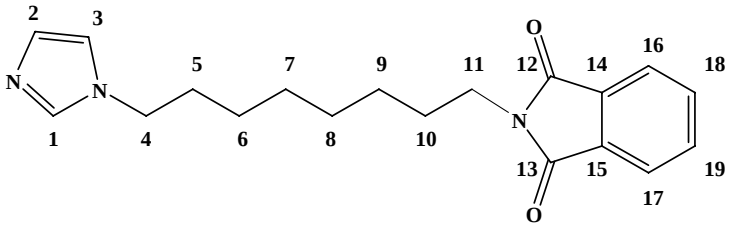
Mass : 167.25 g mol^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.33 (s, 1H, H_1); 6.89 (s, 1H, H_2); 6.77 (s, 1H, H_3); 3.78 (t, $^3J_{4\text{-}5}$ = 7.1 Hz, 2H, H_4); 2.55 (t, $^3J_{9\text{-}8}$ = 6.9 Hz, 2H, H_9); 2.05 (br s, NH_2) 1.64, 1.32, 1.19 (m, 4 × 2H, H_5, H_6, H_7, H_8).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 136.7 (C_1); 128.9 (C_2); 118.5 (C_3); 46.6 (C_4); 41.5 (C_9); 32.6, 30.6, 26, 25.9 (C_5, C_6, C_7, C_8).

2-(8-(1H-Imidazol-1-yl)octyl)isoindoline-1,3-dione (**10**)

44 mg (1.1 mmol, 60% in oil) of sodium hydride is washed with PE for 15 min to afford, after removal of the solvent, a white powder. 68 mg (1 mmol) of imidazole is added and solved in 5 mL of absolute THF at 0°C. After 30 min 338 mg (1 mmol) of 8-bromo-octylphthalimide is given and left to run eight hours at 100°C. The product can be recovered after a DCM/MeOH (20/1) purification over silica gel column, giving a 98% yield (0.320 g).



(**10**)

Yield : 98% (Rf: 0.39)

Formula : $C_{19}H_{23}N_3O_2$

Mass : 325.4 g mol^{-1}

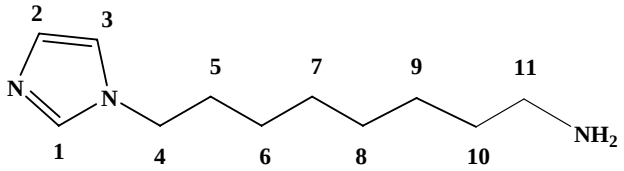
^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.77 (m, 2H, H_{16}-H_{19}); 7.65 (m, 2H, H_{16}-H_{19}); 7.40 (s, 1H, H_1); 6.98 (s, 1H, H_2); 6.84 (s, 1H, H_3); 3.85 (t, $^3J_{4\text{-}5}$= 7.15 Hz, 2H, H_4); 3.61 (t, $^3J_{11\text{-}10}$= 7.25 Hz, 2H, H_{11}); 1.70 (m, 2H, H_5); 1.61 (m, 2H, H_{10}); 1.25 (m, 8H, H_6, H_7, H_8, H_9).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 168.3 (C_{12}, C_{13}); 136.9 (C_1); 133.7 (C_{18}, C_{19}); 132 (C_{14}, C_{15}); 129.2 (C_2); 122.9 (C_{16}, C_{17}); 118.6 (C_3); 46.8 (C_4); 37.7 (C_{11}); 30.8 (C_5); 28.7 (C_{10}); 28.3, 26.5, 26.3 (C_6, C_7, C_8, C_9).

EI-MS (70 eV): High Resolution for [M]: calc. for $C_{19}H_{23}N_3O_2$ m/z: 325.1790; found m/z = 325.1773 $[M]^+$.

8-(1H-Imidazol-1-yl)hexyl-1-amine (**11**)

In a round flask equipped with a reflux condenser 320 mg ($9{,}83.10^{-4}$ mol) 2-(8-(1H-imidazol-1-yl)octyl)isoindoline-1,3-dione is dried and then solved in an excess (7,9 mL) of acetic acid. Under argon atmosphere 14 mL of hydrazine 96% is added and the mixture is heated at 165°C for 4 hours. Extract the aqueous phase three times with DCM, the combined organic phase are concentrated under low pressure and afford a crude oil. The system is purified over silica gel with DCM/MeOH (5/2 ratio) and a colorless oil is recovered with 42%.



(**11**)

Yield : 42% (Rf: 0.74)

Formula : $C_{11}H_{21}N_3$

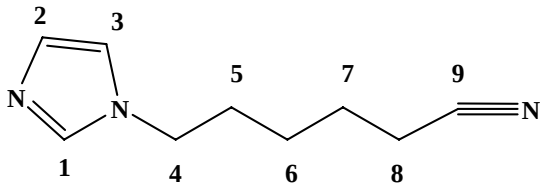
Mass : 195.30 g mol^{-1}

^{1}H-NMR (300 MHz, MeOD): δ [ppm] = 7.65 (s, 1H, H_1); 7.13 (s, 1H, H_2); 6.98 (s, 1H, H_3); 4.03 (t, $^3J_{4\text{-}5}$ = 7.1 Hz, 2H, H_4); 3.16 (t, $^3J_{9\text{-}8}$ = 7.1 Hz, 2H, H_{11}); 1.81 (m, 2H, H_5); 1.50 (m, 2H, H_{10}); 1.48 (br s, 4 × 2H, H_6, H_7, H_8, H_9).

^{13}C-NMR (75 MHz, MeOD): δ [ppm] = 138.4 (C_1); 128.9 (C_2); 120.5 (C_3); 40.4 (C_4); 32.1 (C_{11}); 30.3, 30.2, 30, 27.8, 27.5, 22.6 (C_5, C_6, C_7, C_8, C_9, C_{10}).

5-(1H-Imidazol-1-yl)hexanenitrile (**12**)

330 mg (8.25 mmol, 60% in oil) of sodium hydride is washed with PE for 15 min to afford, after removal of the solvent, a white powder. 510 mg (7.5 mmol) of imidazole and 1.24 mL (8.25 mmol) of TMEDA are added and solved in 15 mL of THF at 0°C. After 30 min 1 mL (7.5 mmol) of 1-bromhexanenitril is given and the reaction mixture left to run 4 h at room temperature. A yellow liquid can be recovered after a DCM/MeOH (9/1) purification over silica gel column, giving a 90% yield (1.10 g).



(**12**)

Yield : 90% (Rf: 0.58)

Formula : $C_9H_{13}N_3$

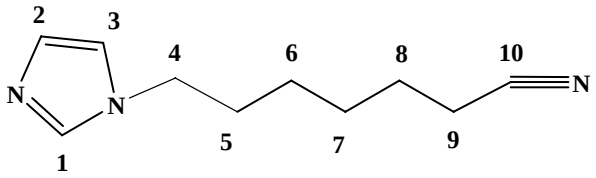
Mass : 163.22 g mol^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.37(s, 1H, H_1); 6.95 (s, 1H, H_2); 6.82 (s, 1H, H_3); 3.87 (t, $^3J_{4\text{-}5}$ = 7.1 Hz, 2H, H_4); 2.25 (t, $^3J_{8\text{-}7}$ = 7.0 Hz, 2H, H_5); 1.73, 1.58, 1.36 (m, 3 * 2H, H_5, H_6, H_7).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 136.7 (C_1); 129.2 (C_2); 119.1 (C_9); 118.6 (C_3); 46.3 (C_4); 30.1, 25.4, 24.6, 16.7 (C_5, C_6, C_7, C_8).

6-(1H-Imidazol-1-yl)heptanenitrile (**13**)

1.24 g (30.9 mmol, 60% in oil) of sodium hydride is washed with PE for 15 min to afford, after removal of the solvent, a white powder. 1.91 g (28.05 mmol) of imidazole and 1.24 mL (8.25 mmol) of TMEDA are added and solved in 15 mL of THF at 0°C. After 30 min, 4.23 mL (28.05 mmol) of 7-bromoheptanenitril is given and left to stir four hours at room temperature. The yellow liquid can be recovered after a DCM/MeOH (9/1) purification over silica gel column, giving a 85% yield (4.24 g).



(**13**)

Yield : 85% (Rf: 0.51)

Formula : $C_{10}H_{15}N_3$

Mass : 177.25 g mol^{-1}

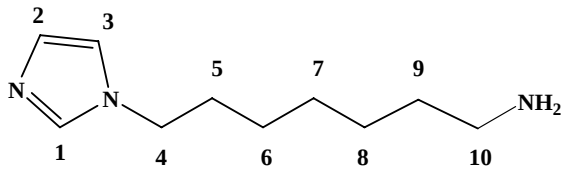
^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.38 (s, 1H, H_1); 6.96 (s, 1H, H_2); 6.83 (s, 1H, H_3); 3.85 (H_4, t, $^3J_{4\text{-}5}$ = 7.1 Hz, 2H); 2.25 (H_5, t, $^3J_{9\text{-}8}$ = 7.0 Hz, 2H); 1.72, 1.56, 1.40, 1.25 (m, 4 × 2H, H_5, H_6, H_7, H_8).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 136.8 (C_1); 129.2 (C_2); 119.3 (C_{10}); 118.5 (C_3); 46.5 (C_4); 30.5, 27.8, 25.5, 24.9, 16.8 (C_5, C_6, C_7, C_8, C_9).

EI-MS (70eV): High Resolution for [M]: calc. for $C_{10}H_{15}N_3$ m/z: 177.1266; found m/z = 177,1268 $[M]^+$.

7-(1H-Imidazol-1-yl)heptan-1-amine (**14**)

In a three neck round bottomed flask equipped with a reflux condenser and a dropping funnel 885 mg (5 mmol) of 7-(1H-imidazol-1-yl)heptanenitrile is dried for 15 min under vacuum and solved in 25 mL absolute THF. Under argon atmosphere is given dropwise a 1M solution of 380 mg (10 mmol) $LiAlH_4$ in THF to the system at 0°C. After four hours the system is quenched carefully and dropwise with H_2O at 0°C. The system is concentrated under vacuum; 3 times the residual volume of DCM is given to the white crude product and stirred with sodiumpotassiumtartrat for 30 min. The system is then extracted three times with 50 mL DCM. The organic phase is then reduced under low pressure and affords a yellowish syrup with 92 % yield (834 mg). The product is light, temperature and decomposes after some time.



(**14**)

Yield : 92%

Formula : $C_{10}H_{19}N_3$

Mass : 181.3 g mol^{-1}

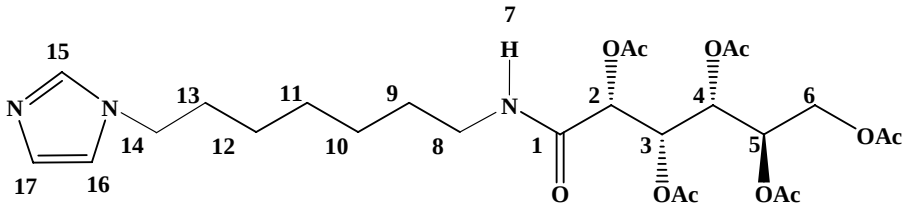
^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.39 (s, 1H, H_1); 6.97 (s, 1H, H_2); 6.83 (s, 1H, H_3); 3.86 (t, H_4, $^3J_{4\text{-}5}$ = 7.1 Hz, 2H); 1.70 (m, H_5, 2H); 1.35, 1.25 (m, 10H, H_5, H_6, H_7, H_8, H_9, H_{10}).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 136.9 (C_1); 129.2 (C_2); 118.6 (C_3); 46.5 (C_4); 41.9 (C_{10}); 33.5, 30.9, 28.8, 26.6, 26.4 (C_5, C_6, C_7, C_8, C_9).

EI-MS (70eV): High Resolution for [M]: calc. for $C_{10}H_{19}N_3$ m/z: 181.1579; found m/z = 180.1501 $[M\text{-}H]^+$.

N-(7-(1H-Imidazol-1-yl)heptyl)-2,3,4,5,6-penta-*O*-acetyl-D-gluconamide (**15**)

In a three neck round bottomed flask equipped with a dropping funnel 1.82 g (10,05 mmol) of 7-(1H-imidazol-1-yl)heptan-1-amine **14** is dried for 15 min under vacuum and solved in 20 mL absolute DCM. 1.6 mL (11.56 mmol) of triethylamine is given to the amine. Under argon atmosphere is given dropwise a solution of 4.27 g (10,05 mmol) of penta-O-acetylated gluconic acid chloride **2**. The reaction is monitored by TLC. After two hours the system is quenched carefully and dropwise with H_2O. The system is extracted through separatory funnel with 3 times 30 mL of DCM. The combined organic phases are reduced under low pressure. The product is obtained after purification over silica gel column chomatogaphy with a 9/1 DCM/MeOH eluent, affording 3.11 g of a yellowish powder with 54% yield.



(**15**)

Yield : 54% (Rf: 0.6)

Formula : $C_{26}H_{39}N_3O_{11}$

Mass : 569.6 g mol^{-1}

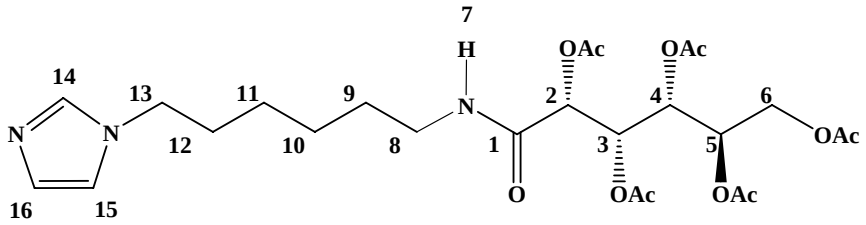
^{1}H-NMR (400 MHz, $CDCl_3$): δ[ppm] = 7.42 (s, 1H, H_{15}); 6.98 (s, 1H, H_{16}); 6.84 (s, 1H, H_{17}); 6.56 (t, $^3J_{7\text{-}8}$ = 5.9 Hz, 1H, H_7); 5.6 (dd, $^3J_{3\text{-}2}$ = 5.1 Hz, $^3J_{3\text{-}4}$ = 5.2 Hz, 2H, H_3); 5.37 (dd, $^3J_{4\text{-}3}$ = 5.0 Hz, $^3J_{4\text{-}5}$ = 6.4 Hz, 1H, H_4); 5.19 (d, $^3J_{2\text{-}3}$ = 5.3 Hz, 1H, H_2); 4.98 (ddd, $^3J_{5\text{-}4}$ = 6.4 Hz, $^3J_{5\text{-}6a}$ = 3.8 Hz, $^3J_{5\text{-}6b}$ = 5.7 Hz, 1H, H_5); 4.24 (dd, $^3J_{6a\text{-}5}$ = 3.8 Hz, $^2J_{6a\text{-}6b}$ = 12.2 Hz, 1H, H_{6a}); 4.05 (dd, $^3J_{6b\text{-}5}$ = 5.7 Hz, $^2J_{6b\text{-}6a}$ = 12.2 Hz, 1H, H_{6b}); 3.85 (t, $^3J_{14\text{-}13}$ = 7.13 Hz, 2H, H_{14}); 3.15 (m, 2H, H_8); 2.09; 2.02; 2.00; 1.98, 1.97 (m, 15H, -OC(O)CH_3); 1.69, 1.40, 1.23 (m, 10H, H_9, H_{10}, H_{11}, H_{12}, H_{13}).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 170.4, 169.7, 169.6, 169.5, 169.0 (-O<u>C</u>(O)CH_3); 165.9 (C_1); 136.9 (C_{15}), 129.1 (C_{16}); 118.7 (C_{17}); 71.7, 69.3, 68.9, 68.7 (C_2, C_3, C_4, C_5); 61.4 (C_6); 46.7 (C_{14}); 39 (C_8); 30.7, 29, 28.4, 26, 25.9 (C_{13}, C_{12}, C_{11}, C_{10}, C_9); 20.6, 20.5, 20.4, 20.3 (-OC(O)<u>C</u>H_3).

EI-MS (70eV): calc. for $C_{26}H_{39}N_3O_{11}$ m/z: 569.6014; found m/z = 569.1 $[M]^+$.

N-(6-(1H-Imidazol-1-yl)hexyl)-2,3,4,5,6-penta-*O*-acetyl-D-gluconamide (**16**)

In a two neck round flask equipped with a dropping funnel 740 mg (4.42 mmol) of 6-(1H-imidazol-1-yl)hexaneamine is dried for 15 min under vacuum and then solved in 20 mL of absolute DCM. 0.4 mL of pyridine is given to the amine. Under argon atmosphere is given dropwise a solution of 2.06 g (4.86 mmol) of Penta-O-acetylated gluconic acid chloride in DCM. The reaction is monitored by TLC. After two hours the system is quenched carefully and dropwise with H_2O. The crude reaction mixture is extracted through a separatory funnel 3 times with 30 mL of DCM. The combined organic phases are concentrated under low pressure. The product is obtained after purification over silica gel column chromatography with a DCM/MeOH (9/1) eluent, affording a yellowish powder with 41% yield.



(**16**)

Yield : 41% (Rf: 0.54)

Formula : $C_{25}H_{37}N_3O_{11}$

Mass : 555.57 g mol^{-1}

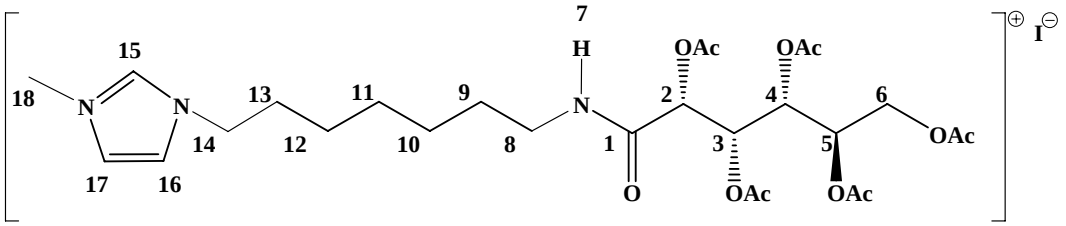
^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] = 8.15 (s, 1H, H_{14}); 7.18 (s, 1H, H_{15}); 6.96 (s, 1H, H_{16}); 6.33 (t, $^3J_{7\text{-}8}$ = 5.6 Hz, 1H, H_7); 5.66 (dd, $^3J_{3\text{-}2}$ = 5.1 Hz, $^3J_{3\text{-}4}$ = 5.2 Hz, 2H, H_3); 5.4 (dd, $^3J_{4\text{-}3}$ = 5.1 Hz, $^3J_{4\text{-}5}$ = 6.2 Hz, 1H, H_4); 5.22 (d, $^3J_{2\text{-}3}$ = 5.1 Hz, 1H, H_2); 5.01 (ddd, $^3J_{5\text{-}4}$ = 6.1 Hz, $^3J_{5\text{-}6a}$ = 3.7 Hz, $^3J_{5\text{-}6b}$ = 5.9 Hz, 1H, H_5); 4.28 (dd, $^3J_{6a\text{-}5}$ = 3.7 Hz, $^2J_{6a\text{-}6b}$ = 12.2 Hz, 1H, H_{6a}); 4.09 (dd, $^3J_{6b\text{-}5}$ = 5.8 Hz, $^2J_{6b\text{-}6a}$ = 12.2 Hz, 1H, H_{6b}); 3.99 (t, $^3J_{13\text{-}12}$ = 6.86 Hz, 2H, H_{13}); 3.18 (m, 2H, H_8); 2.15; 2.07; 2.04; 2.03, 2.01 (m, 15H, -OC(O)CH_3); 1.78, 1.43, 1.27 (m, 8H, H_9, H_{10}, H_{11}, H_{12}).

^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 170.7, 170.6, 169.8, 169.7, 169.2 (-O<u>C</u>(O)CH_3); 166.1 (C_1); 136.1 (C_{14}), 124.2 (C_{16}); 119.4 (C_{15}); 71.6, 69.3, 68.9, 68.7 (C_2, C_3, C_4, C_5); 61.5 (C_6); 47.9 (C_{13}); 39 (C_8); 30.2, 29, 25.7, 25.6 (C_{12}, C_{11}, C_{10}, C_9); 20.71; 20.69, 20.6; 20.5; 20.4 (-OC(O)<u>C</u>H_3).

EI-MS (70eV) (High resolution): calc. for $C_{25}H_{37}N_3O_{11}$ m/z: 555.5748; found m/z = 555.2419 $[M]^+$.

1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamido)heptyl]-3-*N'*-methylimidazolium iodide (**17**)

In a round bottomed flask 4.92 g (8.63 mmol) amide **15** is dried for 15 min under vacuum and solved in 20 mL absolute DCM. 10.85 mL (20 eq.) of methyl iodide is given to the reaction. The reaction is monitored by TLC and runs overnight. The product is obtained after purification over silica gel column chromatogaphy with a DCM/MeOH (85/15) eluent, affording 6.15 g of a yellowish powder with up to >99% yield.



(**17**)

Yield : >99% (Rf: 0.4)

Formula : $C_{27}H_{42}IN_3O_{11}$

Mass : 711.5 g mol^{-1}

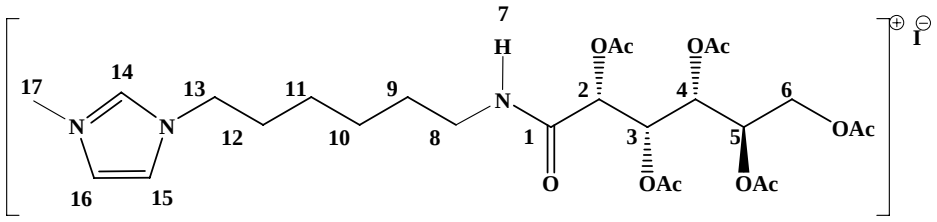
^{1}H-NMR (400 MHz, $CDCl_3$): δ[ppm] = 9.63 (s, 1H, H_{15}); 7.50 (s, 1H, H_{16}); 7.44 (s, 1H, H_{17}); 6.93 (t, $^3J_{7\text{-}8}$ = 5.9 Hz, 1H, H_7); 5.6 (dd, $^3J_{3\text{-}2}$ = 4.1 Hz, $^3J_{3\text{-}4}$ = 5.2 Hz, 2H, H_3); 5.39 (dd, $^3J_{4\text{-}3}$ = 5.3 Hz, $^3J_{4\text{-}5}$ = 5.8 Hz, 1H, H_4); 5.27 (d, $^3J_{2\text{-}3}$ = 4.1 Hz, 1H, H_2); 5.01 (ddd, $^3J_{5\text{-}4}$ = 5.9 Hz, $^3J_{5\text{-}6a}$ = 3.6 Hz, $^3J_{5\text{-}6b}$ = 6.1 Hz, 1H, H_5); 4.29 (dd, $^3J_{6a\text{-}5}$ = 3.6 Hz, $^2J_{6a\text{-}6b}$ = 12.2 Hz, 1H, H_{6a}); 4.27 (s, 3H, H_{18}); 4.05 (dd, $^3J_{6b\text{-}5}$ = 6.2 Hz, $^2J_{6b\text{-}6a}$ = 12.2 Hz, 1H, H_{6b}); 4.01 (m, 2H, H_{14}); 3.14 (m, 2H, H_8); 2.17; 2.04; 2.00; 1.97 (m, 15H, -OC(O)CH_3); 1.87, 1.44, 1.29 (m, 10H, H_9, H_{10}, H_{11}, H_{12}, H_{13}).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 170.5, 169.8, 168.7, 168.6, 168.3 (-O<u>C</u>(O)CH_3); 166.3 (C_1); 136.5 (C_{15}), 123.5 (C_{17}); 122.3 (C_{16}); 71.8, 69.6, 68.9, 68.8 (C_2, C_3, C_4, C_5); 61.5 (C_6); 49.5 (C_{14}); 38.7 (C_8); 36.8 (C_{18}) 29.4, 28.4, 25.3, 24.9 (C_{13}, C_{12}, C_{11}, C_{10}, C_9); 21; 20.7, 20.6, 20.5 (-OC(O)<u>C</u>H_3).

ESI-MS (mode: positiv) (MeOH): calc. for $C_{27}H_{42}IN_3O_{11}$ m/z: 711.5403; found m/z = 584.2834 $[M\text{-}I]^+$.

1-*N*-[6-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamido)hexyl]-3-*N'*-methylimidazolium iodide (**18**)

339 mg (0.6 mmol) of **16** is dried under vacuum for 15 min, solved in 5 mL absolute DCM, 0.37 mL (6 mmol) of iodomethane is added to the reaction and left to run 48 h. The solution turns from light yellow to orange and affords after filtration a yellow oil with 71% yield. No further purification is necessary.



(**18**)

Yield : 71% (Rf: 0.4)

Formula : $C_{26}H_{40}IN_3O_{11}$

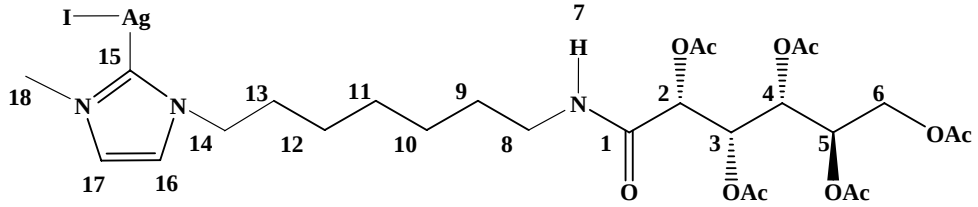
Mass : 697.51 g mol^{-1}

^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] = 9.62 (s, 1H, H_{14}); 7.46 (s, 1H, H_{15}); 7.39 (s, 1H, H_{16}); 6.94 (t, $^3J_{7\text{-}8}$ = 6 Hz, 1H, H_7); 5.59 (m, 1H, H_3); 5.38 (m, 1H, H_4); 5.28 (d, $^3J_{2\text{-}3}$ = 4.1 Hz, 1H, H_2); 4.99 (m, 1H, H_5); 4.28 (dd, $^3J_{6a\text{-}5}$ = 3.4 Hz, $^2J_{6a\text{-}6b}$ = 12.1 Hz, 1H, H_{6a}); 4.09 (dd, $^3J_{6b\text{-}5}$ = 6.6 Hz, $^2J_{6b\text{-}6a}$ = 12.1 Hz, 1H, H_{6b}); 4.05 (m, 2H, H_{13}); 3.99 (s, 3H, H_{17})3.14 (m, 2H, H_8); 2.16; 2.13; 2.10; 2.08, 2.02, 1.99, 1.96 (m, 18H, -OC(O)CH_3); 1.85, 1.43, 1.27 (m, 8H, H_9, H_{10}, H_{11}, H_{12}).

^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 170.6, 169.9, 169.8, 169.7, 169.3 (-O<u>C</u>(O)CH_3); 166.3 (C_1); 136.5 (C_{14}), 123.4 (C_{16}); 122.2 (C_{15}); 71.8, 69.5, 68.8, 68.7 (C_2, C_3, C_4, C_5); 61.5 (C_6); 49.4 (C_{13}); 38.8 (C_8); 36.6 (C_{17}); 29.4, 28.4, 25.2, 24.8 (C_{12}, C_{11}, C_{10}, C_9); 20.9; 20.7, 20.6; 20.5; 20.4 (-OC(O)<u>C</u>H_3).

[1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamido)heptyl]-3-*N'*-methyl-2,3-dihydro imidazol-2-ylidene]silver(I)iodide (**19**)

In a round flask covered with aluminium foil 1.06 g (1.5 mmol) imidazolium salt **17** is dried for 15 min under vacuum and solved in 20 mL absolute DCM. 347.6 mg silver(I)oxide (1.5 mmol) is given to the reaction. The reaction mixture turns black. The solution is filtered through celite to yield a dark brown solid. The product will not be purificated over silica gel column chomatogaphy because of its high sensitivity to light and air. The filtrate yields 770 mg of dark brown foam (63%).



(**19**)

Yield : 63%

Formula : $C_{27}H_{41}AgIN_3O_{11}$

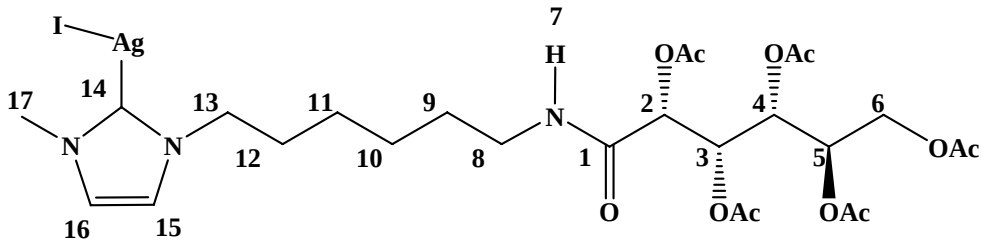
Mass : 818.4 g mol^{-1}

^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] = 6.96 (br. s., 1H, H_7); 6.95 (s, 2H, $H_{16,}$ H_{17}); 5.66 (dd, $^3J_{3\text{-}2}$ = 4.7 Hz, $^3J_{3\text{-}4}$ = 5.3 Hz, 2H, H_3); 5.44 (dd, $^3J_{4\text{-}3}$ = 5.3 Hz, $^3J_{4\text{-}5}$ = 6.1 Hz, 1H, H_4); 5.30 (d, $^3J_{2\text{-}3}$ = 4.7 Hz, 1H, H_2); 5.03 (ddd, $^3J_{5\text{-}4}$ = 5.9 Hz, $^3J_{5\text{-}6a}$ = 3.8 Hz, $^3J_{5\text{-}6b}$ = 5.9 Hz, 1H, H_5); 4.30 (dd, $^3J_{6a\text{-}5}$ = 3.9 Hz, $^2J_{6a\text{-}6b}$ = 12.2 Hz, 1H, H_{6a}); 4.12 (dd, $^3J_{6b\text{-}5}$ = 5.8 Hz, $^2J_{6b\text{-}6a}$ = 12.2 Hz, 1H, H_{6b}); 4.05 (m, 2H, H_{14}); 3.80 (m, 3H, H_{18}); 3.18 (m, 2H, H_8); 2.07; 2.06; 2.02, 2.01, 2.00 (m, 15H, -OC(O)CH_3); 1.79, 1.45, 1.28 (m, 10H, H_9, H_{10}, H_{11}, H_{12}, H_{13}).

^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 178,4 (C_{15}) 170.6, 169.9, 169.8, 169.7, 169.2 (-O<u>C</u>(O)CH_3); 166.1 (C_1); 122.1 (C_{17}); 120.9 (C_{16}); 71.7, 69.6, 69.2, 68.8 (C_2, C_3, C_4, C_5); 61.5 (C_6); 51.5 (C_{14}); 39.2 (C_8); 38.8 (C_{18}) 30.7, 28.9, 28.2, 26.2, 25,7 (C_{13}, C_{12}, C_{11}, C_{10}, C_9); 20,9; 20,8, 20.7, 20.7, 20.5 (-OC(O)<u>C</u>H_3).

[1-*N*-[6-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamido)hexyl]-3-*N'*-methyl-2,3-dihydro imidazol-2-ylidene]silver(I)iodide (**20**)

To a solution of 297 mg (0.426 mmol) of **18** in 15 mL of absolute DCM, is given 58 mg (0.25 mmol) of silver oxide and the reaction left to run overnight. The system must be covered with aluminium foil because of its light sensitivy. After filtration over celite a brown black oil is recovered in 98% yield (338 mg).



(**20**)

Yield : 98%

Formula : $C_{26}H_{39}AgIN_3O_{11}$

Mass : 803.068 g mol^{-1}

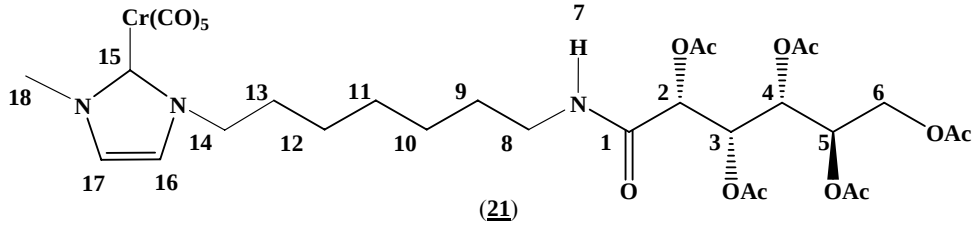
^{1}H-NMR (400 MHz, $CDCl_3$): δ[ppm] = 6.93 (s, 2H, H_{15}, H_{16}); 6.74 (t, $^3J_{7-8}$ = 5.9 Hz, 1H, H_7); 5.69 (dd, $^3J_{3-2}$ = 4.9 Hz, $^3J_{3-4}$ = 4.9 Hz, 1H, H_3); 5.46 (dd, $^3J_{4-3}$ = 5.7 Hz, $^3J_{4-5}$ = 5.7 Hz, 1H, H_4); 5.2 (d, $^3J_{2-3}$ = 4.8 Hz, 1H, H_2); 5.05 (m, 1H, H_5); 4.25 (dd, $^3J_{6a-5}$ = 4.3 Hz, $^2J_{6a-6b}$ = 12.3 Hz, 1H, H_{6a}); 4.06 (dd, $^3J_{6b-5}$ = 5.9 Hz, $^2J_{6b-6a}$ = 12.2 Hz, 1H, H_{6b}); 4.03 (m, 2H, H_{13}); 3.74 (s; 3H, H_{17}); 3.15 (m, 2H, H_8); 2.13; 2.10; 2.02, 1.99, 1.97, 1.96 (m, 18H, -OC(O)CH_3); 1.73, 1.40, 1.25 (m, 8H, H_9, H_{10}, H_{11}, H_{12}).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 178.6 (C_{14}); 170.3, 169.6, 169.5, 169.3, 169.0 (-O<u>C</u>(O)CH_3); 166.0 (C_1); 122.1 (C_{16}); 120.0 (C_{15}); 71.6, 70.1, 69.4, 68.8 (C_2, C_3, C_4, C_5); 61.5 (C_6); 51.2 (C_{13}); 38.9 (C_8); 37.8 (C_{17}); 30.6, 28.8, 25.6, 25.1 (C_{12}, C_{11}, C_{10}, C_9); 20.7, 20.6; 20.5; 20.3 (-OC(O)<u>C</u>H_3).

FAB-MS (mNBA): calc. for $C_{26}H_{39}AgIN_3O_{11}$ m/z: 804.374; found m/z = 676.2 (10) $[M-I]^+$; 1247.5 (3.5) $[2M-Ag-2I]^+$.

Pentacarbonyl[1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamido)heptyl]-3-*N'*-methyl-2,3-dihydro imidazol-2-ylidene]chromium (**21**)

In a round flask covered with aluminium foil 770 mg (0.94 mmol) of the silver carbene complex **19** is dried for 15 min under vacuum and solved in 20 mL absolute THF at -78°C. 100 mL of THF solvent can be pre-cooled in a Schlenk tube at -78°C. 284 mg (0.94 mmol) of $Cr(CO)_5$(cyclooctene) complex is solved in 20 mL THF at -78°. The yellow chromium complex solution is transferred to the silver carbene one via canula or syringe. The reaction is left to reach room temperature as the -78°C cooling bath raises its temperature, at least overnight. The product is purificated over silica gel cooled column chromatography at 0°C with a DCM/MeOH (96/4) eluent. The purification yields 550 mg of a yellow powder (69%).



(**21**)

Yield : 69% (Rf: 0.57)

Formula : $C_{32}H_{41}CrN_3O_{16}$

Mass : 775.7 g mol^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$): δ[ppm] = 6.97 (s., 1H, H_{17}); 6.95 (s, 1H, H_{16}); 6.04 (t, 1H, H_7); 5.65 (dd, $^3J_{3\text{-}2}$ = 5.2 Hz, $^3J_{3\text{-}4}$ = 5.1 Hz, 2H, H_3); 5.42 (dd, $^3J_{4\text{-}3}$ = 5.0 Hz, $^3J_{4\text{-}5}$ = 6.4 Hz, 1H, H_4); 5.26 (d, $^3J_{2\text{-}3}$ = 5.3 Hz, 1H, H_2); 5.03 (ddd, $^3J_{5\text{-}4}$ = 6.4 Hz, $^3J_{5\text{-}6a}$ = 3.9 Hz, $^3J_{5\text{-}6b}$ = 5.6 Hz, 1H, H_5); 4.30 (dd, $^3J_{6a\text{-}5}$ = 3.9 Hz, $^2J_{6a\text{-}6b}$ = 12.2 Hz, 1H, H_{6a}); 4.15 (m, 2H, H_{14}); 4.11 (dd, $^3J_{6b\text{-}5}$ = 5.6 Hz, $^2J_{6b\text{-}6a}$ = 12.2 Hz, 1H, H_{6b}); 3.80 (m, 3H, H_{18}); 3.21 (m, 2H, H_8); 2.18, 2.09, 2.07; 2.03; 2.02 (m, 15H, -OC(O)CH_3); 1.76, 1.47, 1.33 (m, 10H, H_9, H_{10}, H_{11}, H_{12}, H_{13}).

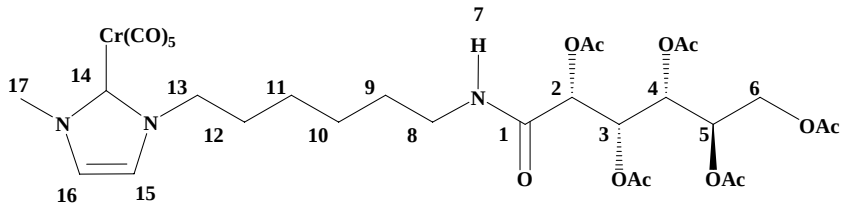
^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 221.5 (CO_{trans}); 217.9 (CO_{cis}), 190.4 (C_{15}) 170.5, 169.9, 169.8, 169.6, 169.2 (-O<u>C</u>(O)CH_3); 165.9 (C_1); 123.9 (C_{17}); 121 (C_{16}); 71.7, 69.4, 69.0, 68.8 (C_2, C_3, C_4, C_5); 61.6 (C_6); 51.4 (C_{14}); 39.3 (C_8); 39.3 (C_{18}) 31.3, 29.2, 28.7, 26.4, 26,3 (C_{13}, C_{12}, C_{11}, C_{10}, C_9); 20.7, 20.6, 20.4 (-OC(O)<u>C</u>H_3).

FAB-MS (mNBA): calc. for $C_{32}H_{41}CrN_3O_{16}$ m/z: 776.6825; found m/z = 776.1 $[M+H]^+$.

FT-IR (CH_2Cl_2): ν CO [cm^{-1}] = 2055 (m, A_1), 1920 (vs, E), 1899 (sh) 1754 (m, acetyl).

Pentacarbonyl[1-*N*-[6-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamido)hexyl]-3-*N'*-methyl-2,3-dihydro-imidazol-2-ylidene]chromium (**22**)

To a -78°C solution of 338 mg (0.42 mmol) of **20** in 10 mL of absolute THF is given 127 mg (0.42 mmol) of $Cr(CO)_5$(cyclooctene) in pre-cooled THF and left to stir overnight. The system must be covered with aluminium foil because of light sensitiveness of the silver carbene complex. The obtained yellow powder can be purified over a long silica gel column chromatography with DCM/MeOH (9/1) as eluent, affording 120 mg of a yellow solid.



(**22**)

Yield : 40% (Rf: 0.75)

Formula : $C_{30}H_{39}CrN_3O_{16}$

Mass : 762.66 g mol^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$): δ[ppm] = 6.97 (s, 2H, H_{15}, H_{16}); 6.74 (br s, 1H, H_7); 5.64 (br s, 1H, H_3); 5.43 (br s, 1H, H_4); 5.24 (br s, 1H, H_2); 5.03 (br s, 1H, H_5); 4.29 (br s, 1H, H_{6a}); 4.13 (br s, 1H, $H_{6b,}$ 2H, H_{13}); 3.80 (br s, 3H, H_{17}); 3.21 (m, 2H, H_8); 2.16; 2.07; 2.05, 2.02 (m, 18H, -OC(O)CH_3); 1.75, 1.46, 1.23 (m, 8H, H_9, H_{10}, H_{11}, H_{12}).

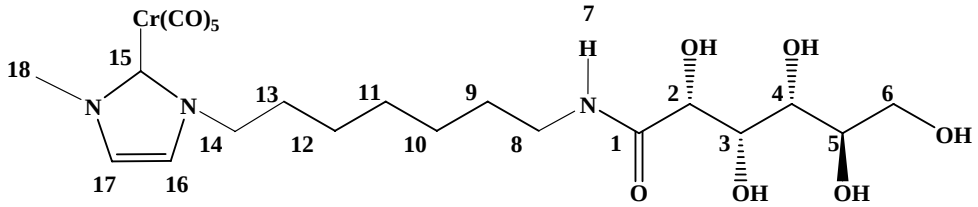
^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 221,4 (CO_{trans}); 217.8 (CO_{cis}); 190.4 (C_{14}); 170.5, 169.7, 169.6, 169.5, 169.1 (-O<u>C</u>(O)CH_3); 165.9 (C_1); 123.9 (C_{16}); 121 (C_{15}); 71.6, 69.4, 69, 68.8 (C_2, C_3, C_4, C_5); 61.5 (C_6); 51.3 (C_{13}); 39.2 (C_{17}); 39.1 (C_8); 31.3, 29.1, 26.3, 26.0 (C_{12}, C_{11}, C_{10}, C_9); 20.7, 20.6; 20.5; 20.4, 20.3 (-OC(O)<u>C</u>H_3).

FAB-MS (mNBA): calc. for $C_{30}H_{39}CrN_3O_{16}$ m/z: 761.648; found m/z = 762.3 (5) $[M+H]^+$

FT-IR (CH_2Cl_2): ν CO [cm^{-1}] = 2056 (m, A_1), 1969 (sh, B_1), 1921 (vs, E), 1751 (m, acetyl).

Pentacarbonyl[1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-hydroxy-hexanoylamido)heptyl]-3-*N'*-methyl-2,3-dihydro-imidazol-2-ylidene]chromium (**23**)

In a coolable schlenk tube 100 mg (0,13 mmol) of the chromium complex **21** is dried for 15 min under vacuum and solved in 10 mL absolute MeOH. 10 ml of NH_3 saturated MeOH solution is added and the reaction mixture is let to stir overnight. The product (Rf: 0.75) will be purificated over silica gel cooled column chromatography at 0°C with a DCM/MeOH (80/20) eluent, affording a yellowish powder with 60% yield.



(**23**)

Yield : 60% (Rf: 0.75)

Formula : $C_{22}H_{31}CrN_3O_{11}$

Mass : 565.5 g mol^{-1}

^{1}H-NMR (500 MHz, CD_3OD): δ[ppm] = 7.28 (s, 1H, H_{16}); 7.24 (s, 1H, H_{17}); 4.21 (br s, 2H, H_3, H_4); 4.09 (br s, 1H, H_2); 3.85 (br s, 1H, H_5); 3.78 (br s, 1H, H_{6a}); 3.70 (m, 2H, H_{14}); 3.61 (br s, 1H, H_{6b}); 3.30 (s, 3H, H_{18}); 3.23 (m, 2H, H_8); 1.80, 1.54, 1.42 (m, 10H, H_9, H_{10}, H_{11}, H_{12}, H_{13}).

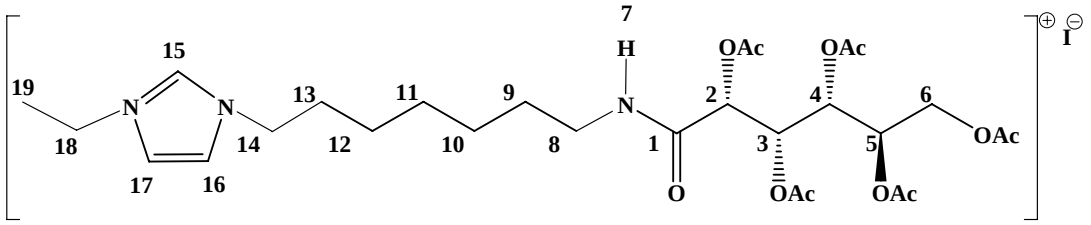
^{13}C-NMR (125 MHz, CD_3OD): δ [ppm] = 222.8 (CO_{trans}); 219.3 (CO_{cis}), 189.4 (C_{15}) 175 (C_1); 125.7 (C_{17}); 122.9 (C_{16}); 75.4, 74.3, 73, 71.9 (C_2, C_3, C_4, C_5); 64.7 (C_6); 52.6 (C_{14}); 39.7 (C_{18}); 40.6 (C_8);, 32.6, 30.4, 30, 27.7, 27,5 (C_{13}, C_{12}, C_{11}, C_{10}, C_9).

ESI-MS (mode: negativ) (MeOH): calc. for $C_{22}H_{31}CrN_3O_{11}$ m/z: 565.4911; found m/z = 564.1293 $[M-H]^+$.

FT-IR (CH_2Cl_2): ν CO [cm^{-1}] = 2054 (m, A_1), 1921 (vs, E).

1-*N*-[7-*N''*-(2R,3R,4R,5S,6-Penta-*O*-acetyl-hexanoylamido)heptyl]-3-*N'*-ethyl-imidazolium iodide (**24**)

In a round flask 0.622 g (1.09 mmol) of the amide **15** is dried for 15 min under vacuum and solved in 20 mL absolute DCM. 1.74 mL (20 eq.) of ethyliodide is given to the reaction. The reaction is monitored by TLC and left to run overnight. The product is washed three times with PE. The product can be further purified over silica gel column chromatography with a DCM/MeOH (9/1) eluent, affording a yellowish solid with up to >99% yield.



(**24**)

Yield : >99% (Rf: 0.42)

Formula : $C_{28}H_{44}IN_3O_{11}$

Mass : 725.6 g mol^{-1}

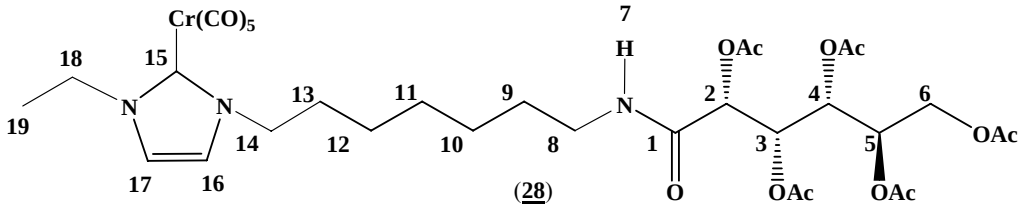
^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] =10.1 (s, 1H, H_{15}); 7.46 (s, 1H, H_{16}); 7.43 (s, 1H, H_{17}); 6.70 (t, $^3J_{7\text{-}8}$ = 6.1 Hz, 1H, H_7); 5.63 (dd, $^3J_{3\text{-}2}$ = 4.7 Hz, $^3J_{3\text{-}4}$ = 5.1 Hz, 2H, H_3); 5.42 (dd, $^3J_{4\text{-}3}$ = 5.2 Hz, $^3J_{4\text{-}5}$ = 6.0 Hz, 1H, H_4); 5.30 (d, $^3J_{2\text{-}3}$ = 4.5 Hz, 1H, H_2); 5.03 (ddd, $^3J_{5\text{-}4}$ = 6.0 Hz, $^3J_{5\text{-}6a}$ = 3.8 Hz, $^3J_{5\text{-}6b}$ = 5.9 Hz, 1H, H_5); 4.39 (m, 2H, H_{14}); 4.32 (m, 2H, H_{18}); 4.31 (dd, $^3J_{6a\text{-}5}$ = 3.9 Hz, $^2J_{6a\text{-}6b}$ = 12.1 Hz, 1H, H_{6a}); 4.09 (dd, $^3J_{6b\text{-}5}$ = 5.9 Hz, $^2J_{6b\text{-}6a}$ = 12.1 Hz, 1H, H_{6b}); 3.18 (m, 2H, H_8); 2.20, 2.06; 2.04, 2.02; 2.00 (m, 15H, -OC(O)CH_3); 1.92, 1.45, 1.33 (m, 10H, H_9, H_{10}, H_{11}, H_{12}, H_{13}); 1.33 (s, 3H, H_{19}).

^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 170.6, 169.8, 168.7, 168.6, 168.3 (-O<u>C</u>(O)CH_3); 166.2 (C_1); 136.3 (C_{15}), 122.3 (C_{17}); 121.6 (C_{16}); 71.9, 69.6, 69.0, 68.8 (C_2, C_3, C_4, C_5); 61.6 (C_6); 49.9 (C_{14}); 45.4 (C_{18}); 39 (C_8); 29.6, 28.7, 27.7, 25.8, 25.4 (C_{13}, C_{12}, C_{11}, C_{10}, C_9); 21; 20.7, 20.5 (-OC(O)<u>C</u>H_3), 15.6 (C_{19}).

FAB-MS (mNBA): calc. for $C_{28}H_{44}IN_3O_{11}$ m/z: 725.5669; found m/z = 598.2 $[M\text{-}I]^+$.

Pentacarbonyl[1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamido)heptyl]-3-*N'*-ethyl-2,3-dihydro-imidazol-2-ylidene]chromium (**28**)

In a round flask covered with aluminium foil 447 mg (0,62 mmol) of the imidazolium salt **24** is dried for 15 min under vacuum and solved in 20 mL absolute DCM. 143 mg (0,62 mmol) of silveroxide is given to the reaction mixture, and stirred overnight. The black solution is filtrated and concentrated. The black solid is then dissolved in THF at -78°C. 186 mg (0,62 mmol) of $Cr(CO)_5$(cyclooctene) complex is solved in 20 mL THF at -78°C. The yellow chromium complex solution is transferred to the silver carbene one via canula or syringe. The reaction is left to reach room temperature as the -78°C cooling bath raises its temperature, at least overnight. The product is purificated over silica gel cooled column chromatography at 0°C with a DCM/MeOH (94/6) eluent, affording a yellowish powder with 54% yield.



(**28**)

Yield : 54% (Rf: 0.74)

Formula : $C_{32}H_{43}CrN_3O_{16}$

Mass : 789,7 $g.mol^{-1}$

^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] = 7.02 (s, 2H, H_{17}, H_{16}); 6.07 (t, $^3J_{4\text{-}5}$ = 5.6 Hz, 1H, H_7); 5.65 (dd, $^3J_{3\text{-}2}$ = 5.3 Hz, $^3J_{3\text{-}4}$ = 5.0 Hz, 2H, H_3); 5.42 (dd, $^3J_{4\text{-}3}$ = 5.4 Hz, $^3J_{4\text{-}5}$ = 5.8 Hz, 1H, H_4); 5.26 (d, $^3J_{2\text{-}3}$ = 5.2 Hz, 1H, H_2); 5.02 (m, 1H, H_5); 4.28 (m, 2H, H_{14}) 4.18 (m, 1H, H_{6a}); 4.17 (m, 2H, H_{18}); 4.10 (dd, $^3J_{6b\text{-}5}$ = 5.5 Hz, $^2J_{6b\text{-}6a}$ = 12.2 Hz, 1H, H_{6b}); 3.21 (m, 2H, H_8); 2.18, 2.08; 2.06; 2.04; 2.02 (m, 15H, -OC(O)CH_3); 1.76, 1.43, 1.23 (m, 10H, H_9, H_{10}, H_{11}, H_{12}, H_{13}); 1.25 (m, 2H, H_{19}).

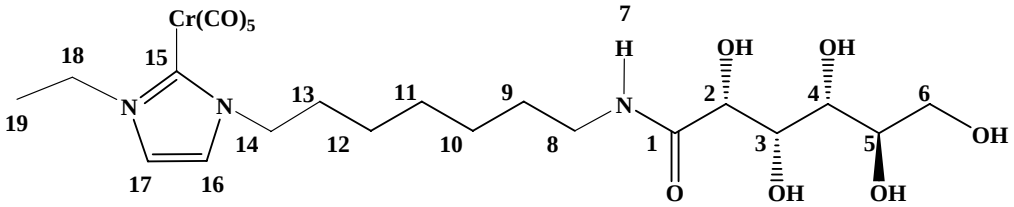
^{13}C-NMR (125MHz, $CDCl_3$): δ [ppm] = 221.6 (CO_{trans}); 217.7 (CO_{cis}), 189.3 (C_{15}) 171.1, 170.5, 169.8, 169.6, 169.2 (-OC(O)CH_3); 165.9 (C_1); 121.7 (C_{17}); 121.2 (C_{16}); 71.6, 69.3, 69.0, 68.7 (C_2, C_3, C_4, C_5); 61.5 (C_6); 51.3 (C_{14}); 46 (C_8); 39.3 (C_{18}) 31.3, 29.1, 28.7, 26.4, 26,3 (C_{13}, C_{12}, C_{11}, C_{10}, C_9); 20.7, 20.6 20.4 (-OC(O)$\underline{C}H_3$); 16.4 (C_{19}).

MALDI-MS (DCTB): calc. for $C_{32}H_{44}CrN_3O_{16}$ m/z: 789.7011; found m/z = 649 $[M\text{-}5CO]^+$; 598 $[M\text{-}Cr(CO)_5]^+$.

FT-IR (CH_2Cl_2): ~ν CO [cm^{-1}] = 2053 (m, A_1), 1920 (vs, E), 1897 (sh) 1751 (m, acetyl).

Pentacarbonyl[1-*N*-[7-*N''*-(2R,3R,4R,5S,6-pentahydroxy-hexanoylamido)heptyl]-3-*N'*-ethyl-imidazol-2-ylidene]chromium (**32**)

In a coolable schlenk tube 400 mg (0,51 mmol) of the chromium complex **28** is dried for 15 min under vacuum and dissolved in 10 mL absolute MeOH. 10 ml of NH_3 saturated MeOH solution is added and let to stir overnight. The product (Rf: 0.6) is purificated by chromatography over silica gel on a cooled column at 0°C with DCM/MeOH (80/20) as eluent, affording a yellowish powder with 17% yield.



(**32**)

Yield : 17% (Rf: 0.6)

Formula : $C_{23}H_{33}CrN_3O_{11}$

Mass : 579.5 g mol^{-1}

^{1}H-NMR (500 MHz, CD_3OD): δ[ppm] = 7.36 (s, 2H, $H_{16,}$ H_{17}); 4.36 (br s, 1H, H_3); 4.26 (br s, 2H, H_4, H_2); 4.14 (br s, 1H, H_5); 3.8 (br s, 1H, H_{6a}); 3.75 (m, 2H, H_{14}); 3.68 (br s, 1H, H_{6b}); 3.27 (m, 2H, H_8); 1.84 (m, 2H, H_{18}); 1.57, 1.46 (m, 10H, H_9, H_{10}, H_{11}, H_{12}, H_{13}); 0.93 (m, 3H, CH_3).

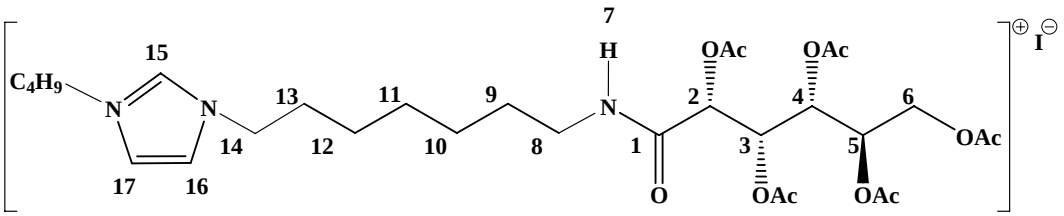
^{13}C-NMR (125 MHz, CD_3OD): δ [ppm] = 222.9 (CO_{trans}); 219.2 (CO_{cis}), 188.4 (C_{15}) 175 (C_1); 123.7 (C_{17}); 123.2 (C_{16}); 75.3, 74.3, 72.9, 71.9 (C_2, C_3, C_4, C_5); 64.7 (C_6); 52.5 (C_{14}); 47.1 (C_{18}); 40.1 (C_8); 32.6, 30.3, 30, 27.7, 27.5, 26,2 (C_{13}, C_{12}, C_{11}, C_{10}, C_9,); 17 (CH_3).

ESI-MS (mode: negativ) (MeOH): calc. for $C_{23}H_{33}CrN_3O_{11}$ m/z: 579.5177; found m/z = 578.1558 $[M-H]^-$; 614.1418 $[M+Cl]^-$.

FT-IR (CH_2Cl_2): ν CO [cm^{-1}] = 2054 (m, A_1), 1921 (vs, E).

1-N-[7-N''-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamido)heptyl]-3-N'-butyl-imidazolium iodide (**25**)

In a round flask 338 mg (0.59 mmol) amide **15** is dried for 15 min under vacuum and solved in 20 mL absolute DCM. 1.31 mL (20 eq.) of butyl iodide is given to the reaction. The reaction is monitored by TLC and left to run overnight. The product is washed three times with PE. The product is further purified over silica gel column chromatography with a DCM/MeOH (9/1) eluent, affording a yellowish solid with up to 91% yield.



(**25**)

Yield : 91% (Rf: 0.48)

Formula : $C_{30}H_{48}IN_3O_{11}$

Mass : 753.6 g mol^{-1}

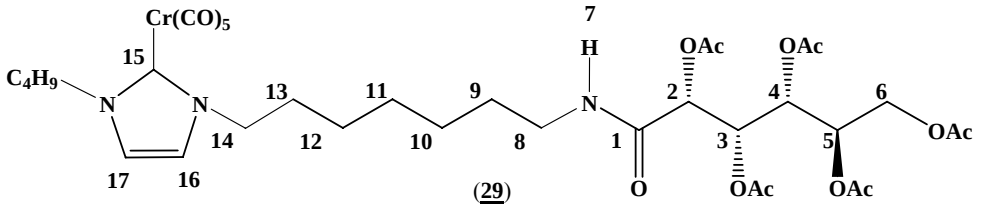
^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] =10.2 (s, 1H, H_{15}); 7.43 (s, 1H, H_{16}); 7.33 (s, 1H, H_{17}); 6.70 (t, $^3J_{7\text{-}8}$ = 6.1 Hz, 1H, H_7); 5.64 (dd, $^3J_{3\text{-}2}$ = 4.7 Hz, $^3J_{3\text{-}4}$ = 4.9 Hz, 2H, H_3); 5.42 (dd, $^3J_{4\text{-}3}$ = 5.1 Hz, $^3J_{4\text{-}5}$ = 6.1 Hz, 1H, H_4); 5.30 (d, $^3J_{2\text{-}3}$ = 4.6 Hz, 1H, H_2); 5.03 (ddd, $^3J_{5\text{-}4}$ = 6.0 Hz, $^3J_{5\text{-}6a}$ = 3.8 Hz, $^3J_{5\text{-}6b}$ = 5.8 Hz, 1H, H_5); 4.33 (m, 2H, H_{14}); 4.33 (m, 2H, C_3H_7-C<u>H</u>$_2$-N); 4.33 (m, 1H, H_{6a}); 4.09 (dd, $^3J_{6b\text{-}5}$ = 6.0 Hz, $^2J_{6b\text{-}6a}$ = 12.2 Hz, 1H, H_{6b}); 3.16 (m, 2H, H_8); 2.20, 2.07; 2.05, 2.03, 2.01 (m, 15H, -OC(O)CH_3); 1.91, 1.77, 1.45, 1.38 (m, 16H, H_9, H_{10}, H_{11}, H_{12}, H_{13}, -C_2H_4-); 0.90 (s, 3H, CH_3).

^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 170.6, 169.8, 168.7, 168.3, 168.1 (-O<u>C</u>(O)CH_3); 166.2 (C_1); 136.7 (C_{15}), 122.1 (C_{17}); 121.8 (C_{16}); 71.9, 69.6, 69.0, 68.8 (C_2, C_3, C_4, C_5); 61.6 (C_6); 49.9 (C_{14}); 39 (C_8); 35.4 (C_3H_7-<u>C</u>H_2-N), 32 (C_2H_5-<u>C</u>H_2-CH_2); 29.6, 28.7, 27.7, 25.8, 25.4 (C_{13}, C_{12}, C_{11}, C_{10}, C_9); 20.9, 20.7, 20.6, 20.5, 20.4 (-OC(O)<u>C</u>H_3); 19.4 (C_2H_5-<u>C</u>H_2-CH_2); 13.4 (CH_3).

FAB-MS (mNBA): calc. for $C_{30}H_{48}IN_3O_{11}$ m/z: 753.6201; found m/z = 626.3 $[M\text{-}I]^+$.

Pentacarbonyl[1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamido)heptyl]-3-*N'*-butyl-2,3-dihydro-imidazol-2-ylidene]chromium (**29**)

In a round flask covered with aluminium foil 405 mg (0,54 mmol) of the imidazolium salt **25** is dried for 15 min under vacuum and solved in 20 mL absolute DCM. 125 mg (0,54 mmol) of silveroxide is given to the reaction mixture, and stirred overnight. The black solution is filtrated and concentrated. The black solid is then dissolved in THF at -78°C. 162 mg (0,54 mmol) of $Cr(CO)_5$(cyclooctene) complex is solved in 20 mL THF at -78°. The yellow chromium complex solution is transferred to the silver carbene one via canula or syringe. The reaction is left to reach room temperature as the -78°C cooling bath raises its temperature, at least overnight. The product is purificated over silica gel cooled column chromatography at 0°C with a DCM/MeOH (96/4) eluent, affording a yellowish powder with 46% yield.



(**29**)

Yield : 46% (Rf: 0.55)

Formula : $C_{34}H_{43}CrN_3O_{16}$

Mass : 817.2 g mol^{-1}

^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] = 7.01 (s, 2H, $H_{16,}$ H_{17}); 6.10 (t, $^3J_{7\text{-}8}$ = 5.6 Hz, 1H, H_7); 5.65 (dd, $^3J_{3\text{-}2}$ = 5.1 Hz, $^3J_{3\text{-}4}$ = 5.0 Hz, 2H, H_3); 5.41 (dd, $^3J_{4\text{-}3}$ = 4.9 Hz, $^3J_{4\text{-}5}$ = 6.3 Hz, 1H, H_4); 5.26 (d, $^3J_{2\text{-}3}$ = 5.3 Hz, 1H, H_2); 5.02 (ddd, $^3J_{5\text{-}4}$ = 6.3 Hz, $^3J_{5\text{-}6a}$ = 4.1 Hz, $^3J_{5\text{-}6b}$ = 5.7 Hz, 1H, H_5); 4.29 (dd, $^3J_{6a\text{-}5}$ = 4.0 Hz, $^2J_{6a\text{-}6b}$ = 12.2 Hz, 1H, H_{6a}); 4.18 (m, 2H, C_3H_7-C$\underline{H_2}$-N); 4.17 (m, 2H, H_{14}); 4.10 (dd, $^3J_{6b\text{-}5}$ = 5.5 Hz, $^2J_{6b\text{-}6a}$ = 12.2 Hz, 1H, H_{6b}); 3.21 (m, 2H, H_8); 2.17 (m, 2H, C_2H_5-C$\underline{H_2}$-CH_2); 2.08, 2.07; 2.04; 2.02, 2.01 (m, 15H, -OC(O)CH_3); 1.67, 1.36 (m, 10H, H_9, H_{10}, H_{11}, H_{12}, H_{13}); 0.96 (t, 3H, $^3J_{CH_3\text{-}CH_2}$ = 7.3 Hz, CH_3).

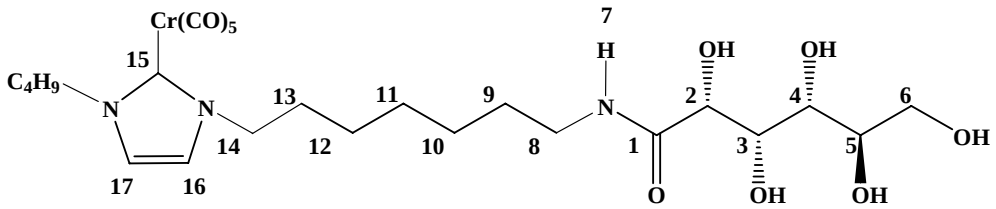
^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 221.8 (CO_{trans}); 217.3 (CO_{cis}), 187.4 (C_{15}) 170.9, 170.1, 169.8, 169.3 (-O$\underline{C}$(O)CH_3); 165.7 (C_1); 121.6 (C_{17}); 121.5 (C_{16}); 71.3, 68.9, 68.6, 68.0 (C_2, C_3, C_4, C_5); 61.1 (C_6); 50.9 (C_{14}); 39.3 (C_3H_7-$\underline{C}H_2$-N); 39.1 (C_8); 33.5, 31.4, 29.0, 28.7, 26.3, 26,2 (C_{13}, C_{12}, C_{11}, C_{10}, C_9, CH_3-$\underline{C_2}H_4$-CH_2); 20.8, 20.5, 19.7 (-OC(O)$\underline{C}H_3$); 13.9 (CH_3).

FAB-MS (mNBA): calc. for $C_{34}H_{43}CrN_3O_{16}$ m/z: 817.7543; found m/z = 818.2 $[M]^+$.

FT-IR (CH_2Cl_2): ν CO [cm^{-1}] = 2054 (m, A_1), 1921 (vs, E), 1894 (sh) 1751 (m, acetyl).

Pentacarbonyl[1-*N*-[7-*N''*-(2R,3R,4R,5S,6-pentahydroxy-hexanoylamido)heptyl]-3-*N'*-butyl-2,3-dihydro-imidazol-2-ylidene]chromium (**33**)

In a coolable schlenk tube 405 mg (0,54 mmol) of the chromium complex **29** is dried for 15 min under vacuum and dissolved in 10 mL absolute MeOH. Add 10 ml of NH_3 saturated MeOH solution and let it stir overnight. The product (Rf: 0.51) is purificated by chromatography over silica on a cooled column at 0°C with DCM/MeOH (80/20) as eluent, affording a yellowish powder with 15% yield.



(**33**)

Yield : 15% (Rf: 0.51)

Formula : $C_{25}H_{37}CrN_3O_{11}$

Mass : 607.6 g mol^{-1}

^{1}H-NMR (500 MHz, CD_3OD): δ[ppm] = 7.36 (s, 2H, H_{16}, H_{17}); 4.27 (br s, 3H, H_3, H_4, H_2); 4.14 (br s, 1H, H_5); 3.80 (br s, 1H, H_{6a}); 3.74 (m, 2H, H_{14}); 3.67 (br s, 1H, H_{6b}); 3.37 (m, 2H, N-CH_2-C_3H_{10}); 3.27 (m, 2H, H_8); 1.83, 1.56, 1.47, 1.32 (m, 14H, H_9, H_{10}, H_{11}, H_{12}, H_{13}, CH_2-C_2H_4-CH_3); 1.02 (br s, 3H, -CH_3).

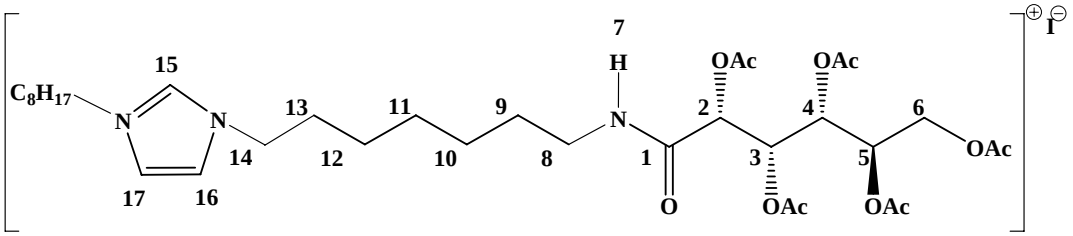
^{13}C-NMR (125 MHz, CD_3OD): δ [ppm] = 222.9 (CO_{trans}); 219.3 (CO_{cis}), 188.7 (C_{15}); 175 (C_1); 123.6 (C_{17}, C_{16}); 75.3, 74.3, 73, 71.9 (C_2, C_3, C_4, C_5); 64.7 (C_6); 52.5 (C_{14}); 52.3 (C_3H_7-CH_2-N); 40.7 (C_8); 34.7, 32.6, 30.3, 30.1, 27.7, 27.5, 20.9 (C_{13}, C_{12}, C_{11}, C_{10}, C_9, CH_3-C_2H_4-CH_2); 14.1 (CH_3).

ESI-MS (mode: negativ) (MeOH): calc. for $C_{25}H_{37}CrN_3O_{11}$ m/z: 607.5709; found m/z = 606.1719 $[M-H]^-$; 642.1476 $[M+Cl]^-$.

FT-IR (CH_2Cl_2): ν CO [cm^{-1}] = 2054 (m, A_1), 1930 (vs, E), 1890 (sh).

1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamino)heptyl]-3-*N'*-octyl-imidazolium iodide (**26**)

In a round bottomed flask 622 mg (1.09 mmol) amide **15** is dried for 15 min under vacuum and solved in 20 mL absolute DCM. 3.93 mL (20 eq.) of octyl iodide is given to the reaction. The reaction is monitored by TLC and left to run overnight. The product is washed three times with PE. The product can be further purified over silica gel column chromatography with a DCM/MeOH (9/1) eluent, affording a yellowish solid with up to 88% yield.



(**26**)

Yield : 88% (Rf: 0.44)

Formula : $C_{34}H_{56}IN_3O_{11}$

Mass : 809.7 g mol^{-1}

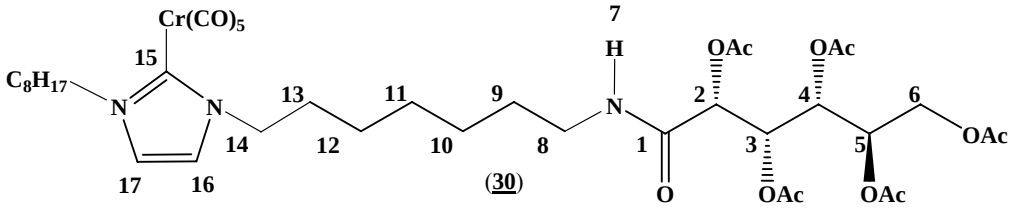
^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] = 10.3 (s, 1H, H_{15}); 7.40 (s, 1H, H_{16}); 7.28 (s, 1H, H_{17}); 6.70 (t, $^{3}J_{7\text{-}8}$ = 5.7 Hz, 1H, H_7); 5.64 (dd, $^{3}J_{3\text{-}2}$ = 4.7 Hz, $^{3}J_{3\text{-}4}$ = 4.9 Hz, 2H, H_3); 5.42 (dd, $^{3}J_{4\text{-}3}$ = 5.6 Hz, $^{3}J_{4\text{-}5}$ = 5.7 Hz, 1H, H_4); 5.31 (d, $^{3}J_{2\text{-}3}$ = 4.5 Hz, 1H, H_2); 5.03 (m, 1H, H_5); 4.32 (m, 2H, H_{14}); 4.32 (m, 1H, H_{6a}); 4.10 (m, 2H, C_7H_{15}-C$\underline{H_2}$-N) 4.10 (dd, $^{3}J_{6b\text{-}5}$ = 5.9 Hz, $^{2}J_{6b\text{-}6a}$ = 12.1 Hz, 1H, H_{6b}); 3.16 (m, 2H, H_8); 2.18 (s, 2H, C_6H_{13}-$\underline{C}H_2$-CH_2); 2.20, 2.08; 2.05, 2.03, 2.02 (m, 15H, -OC(O)CH_3); 1.90, 1.80, 1.77, 1.45, 1.34, 1.25 (m, 22H, H_9, H_{10}, H_{11}, H_{12}, H_{13}, -C_6H_{12}-); 0.83 (s, 3H, CH_3).

^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 170.5, 169.9, 169.8, 169.4, 169.3 (-O$\underline{C}$(O)CH_3); 166.3 (C_1); 136.9 (C_{15}), 122.0 (C_{17}); 121.7 (C_{16}); 71.9, 69.6, 69.1, 68.9 (C_2, C_3, C_4, C_5); 61.6 (C_6); 49.9 (C_{14}); 39.2 (C_8); 33.6 (C_7H_{15}-$\underline{C}H_2$-N); 31.7-25.5 (C_{13}, C_{12}, C_{11}, C_{10}, C_9, CH_3-$\underline{C}_6H_{12}$-CH_2); 21; 20.8, 20.7, 20.6, 20.5 (-OC(O)$\underline{C}H_3$), 14 (CH_3).

FAB-MS (mNBA): calc. for $C_{34}H_{56}IN_3O_{11}$ m/z: 809.7264; found m/z = 682.3 $[M\text{-}I]^+$.

Pentacarbonyl[1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamino)heptyl]-3-*N'*-octyl-2,3-dihydro-imidazol-2-ylidene]chromium (**30**)

In a round flask covered with aluminium foil 469 mg (0,58 mmol) of the imidazolium salt **26** is dried for 15 min under vacuum and solved in 20 mL absolute DCM. 134 mg (0,58 mmol) of silver(I)oxide is given to the reaction mixture, and stirred overnight. The black solution is filtrated and concentrated. The black solid is then dissolved in THF at -78°C. 175 mg (0,58 mmol) of $Cr(CO)_5$(cyclooctene) complex is solved in 20 mL THF at -78°. The yellow chromium complex solution is transferred to the silver carbene one via canula or syringe. The reaction is left to reach room temperature as the -78°C cooling bath raises its temperature, at least overnight. The product is purificated over silica gel cooled column chromatography at 0°C with a DCM/MeOH (94/6) eluent, affording a yellowish powder with 38% yield.



Yield : 38% (Rf : 0.38)

Formula : $C_{32}H_{41}CrN_3O_{16}$

Mass : 873.3 g mol^{-1}

^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] = 7.01 (s, 2H, H_{17}, H_{16}); 6.06 (t, $^3J_{7\text{-}8}$ = 5.0 Hz, 1H, H_7); 5.65 (dd, $^3J_{3\text{-}2}$ = 4.9 Hz, $^3J_{3\text{-}4}$ = 5.1 Hz, 1H, H_3); 5.43 (dd, $^3J_{4\text{-}3}$ = 5.2 Hz, $^3J_{4\text{-}5}$ = 5.9 Hz, 1H, H_4); 5.26 (d, $^3J_{2\text{-}3}$ = 5.3 Hz, 1H, H_2); 5.03 (ddd, $^3J_{5\text{-}4}$ = 5.8 Hz, $^3J_{5\text{-}6a}$ = 4.1 Hz, $^3J_{5\text{-}6b}$ = 5.5 Hz, 1H, H_5); 4.30 (dd, $^3J_{6a\text{-}5}$ = 4.0 Hz, $^2J_{6a\text{-}6b}$ = 12.2 Hz, 1H, H_{6a}); 4.17 (m, 4H, H_{14}, C_7H_{15}-C$\underline{H_2}$-N); 4.10 (dd, $^3J_{6b\text{-}5}$ = 5.4 Hz, $^2J_{6b\text{-}6a}$ = 12.2 Hz, 1H, H_{6b}); 3.22 (m, 2H, H_8); 2.20, 2.09, 2.07; 2.05; 2.03 (m, 15H, -OC(O)CH_3); 1.77, 1.39, 1.28 (m, 22H, H_9, H_{10}, H_{11}, H_{12}, H_{13}, -$C_6\underline{H_{12}}$-); 0.86 (s, 3H, CH_3).

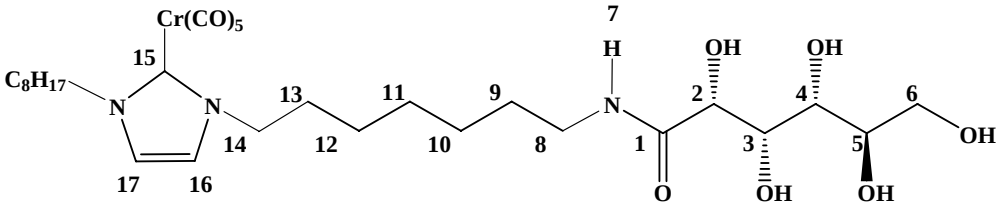
^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 221.7 (CO_{trans}); 217.7 (CO_{cis}), 189.4 (C_{15}) 170.6, 169.8, 169.6, 169.2 (-O$\underline{C}$(O)CH_3); 165.9 (C_1); 121.6 (C_{17}); 121.5 (C_{16}); 71.6, 69.4, 69.0, 68.7 (C_2, C_3, C_4, C_5); 61.5 (C_6); 51.4 (C_{14}); 39.3 (C_8); 39.3 (C_7H_{15}-$\underline{C}H_2$-N); 31.3-22,6 (C_{13}, C_{12}, C_{11}, C_{10}, C_9, CH_3-$\underline{C}_6H_{12}$-CH_2); 20.8, 20.7, 20.6 20.4 (-OC(O)$\underline{C}H_3$), 14 (CH_3).

MALDI-MS (mNBA): calc. for $C_{32}H_{41}CrN_3O_{16}$ m/z: 873.8606; found m/z = 733.1 $[M\text{-}5CO]^+$; 682.1 $[M\text{-}Cr(CO)_5]^+$.

FT-IR (CH_2Cl_2): ν CO [cm^{-1}] = 2055 (m, A_1), 1920 (vs, E), 1899 (sh) 1754 (m, acetyl).

Pentacarbonyl[1-*N*-[7-*N''*-(2R,3R,4R,5S,6-pentahydroxy-hexanoylamino)heptyl]-3-*N'*-octyl-2,3-dihydro-imidazol-2-ylidene]chromium (**34**)

In a coolable schlenk tube 990 mg (1,13 mmol) of the chromium complex **30** is dried for 15 min under vacuum and solved in 10 mL absolute MeOH. 10 ml of NH_3 saturated MeOH solution is added and let to stir overnight. The product (Rf: 0.85) is purificated by chromatography over silica on a cooled column at 0°C with DCM/MeOH (80/20) as eluent, affording a yellowish powder with 36% yield.



(**34**)

Yield : 36% (Rf: 0.85)

Formula : $C_{29}H_{45}CrN_3O_{11}$

Mass : 663.7 g mol^{-1}

^{1}H-NMR (500 MHz, CD_3OD): δ[ppm] = 7.32 (s, 1H, H_{16}); 7.31 (s, 1H, H_{17}); 4.21 (br s, 4H, H_3, H_4, C_7H_{15}-C$\underline{H_2}$-N); 4.09 (br s, 1H, H_2); 3.85 (br s, 1H, H_5); 3.76 (br s, 1H, H_{6a}); 3.69 (m, 2H, H_{14}); 3.62 (br s, 1H, H_{6b}); 3.22 (m, 2H, H_8); 1.79, 1.38, 1.30 (m, 22H, H_9, H_{10}, H_{11}, H_{12}, H_{13}, -C_6H_{12}-); 0.89 (s, 3H, CH_3).

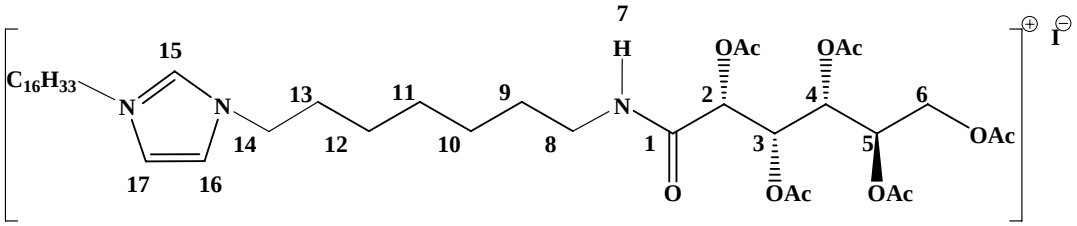
^{13}C-NMR (125 MHz, CD_3OD): δ [ppm] = 222.9 (CO_{trans}); 219.3 (CO_{cis}), 188.6 (C_{15}) 175 (C_1); 123.5 (C_{17}, C_{16}); 75.3, 74.2, 72.9, 71.8 (C_2, C_3, C_4, C_5); 64.7 (C_6); 52.5 (C_{14}); 52.5 ($C_{15}H_{31}$-$\underline{C}H_2$-N); 40.1 (C_8); 32.8- 23,6 (C_{13}, C_{12}, C_{11}, C_{10}, C_9, CH_3-$\underline{C_{14}}H_{28}$-CH_2); 14.4 (CH_3).

ESI-MS (mode: negativ) (MeOH): calc. for $C_{29}H_{45}CrN_3O_{11}$ m/z: 663.6772; found m/z = 662.2378 $[M-H]^+$.

FT-IR (CH_2Cl_2): ν CO [cm^{-1}] = 2054 (m, A_1), 1921 (vs, E)

1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamino)heptyl]-3-*N'*-hexadecyl-imidazolium iodide (**27**)

In a round flask 622 mg (1.09 mmol) amide **15** is dried for 15 min under vacuum and solved in 20 mL absolute DCM. 2.48 mL (20 eq.) of iodohexadecane is given to the reaction. The reaction is monitored by TLC and runs overnight. The product is washed three times with PE. The product can be further purified over silica gel column chromatography with a DCM/MeOH (9/1) eluent, affording a yellowish solid with up to >99% yield.



(**27**)

Yield : >99% (Rf: 0.58)

Formula : $C_{42}H_{72}IN_3O_{11}$

Mass : 921.9 g mol^{-1}

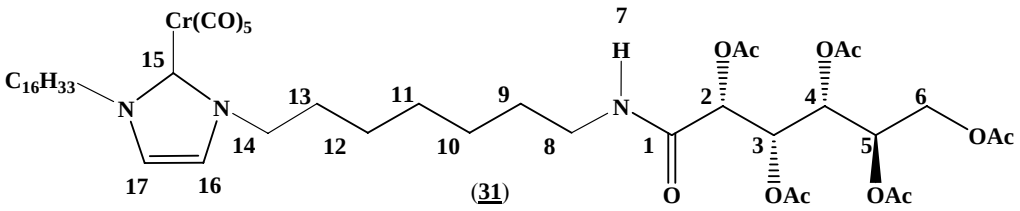
^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] = 10.25 (s, 1H, H_{15}); 7.40 (s, 1H, H_{16}); 7.27 (s, 1H, H_{17}); 6.70 (t, $^3J_{7\text{-}8}$ = 5.9 Hz, 1H, H_7); 5.64 (dd, $^3J_{3\text{-}2}$ = 4.6 Hz, $^3J_{3\text{-}4}$ = 5.0 Hz, 2H, H_3); 5.43 (dd, $^3J_{4\text{-}3}$ = 5.1 Hz, $^3J_{4\text{-}5}$ = 6.2 Hz, 1H, H_4); 5.31 (d, $^3J_{2\text{-}3}$ = 4.6 Hz, 1H, H_2); 5.03 (m, 1H, H_5); 4.31 (m, 2H, H_{14}); 4.31 (m, 1H, H_{6a}); 4.10 (m, 2H, $C_{15}H_{31}$-C$\underline{H_2}$-N); 4.10 (m, 1H, H_{6b}); 3.16 (m, 2H, H_8); 2.18 (s, 2H, $C_{14}H_{29}$-C$\underline{H_2}$-CH_2); 2.20, 2.08; 2.05, 2.03, 2.02 (m, 15H, -OC(O)CH_3); 1.90, 1.79, 1.47, 1.30, 1.22 (m, 40H, H_9, H_{10}, H_{11}, H_{12}, H_{13}, -$C_{14}H_{30}$-); 0.84 (s, 3H, CH_3).

^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 170.7, 170, 169.9, 169.8, 169.4 (-O$\underline{C}$(O)CH_3); 166.3 (C_1); 137 (C_{15}), 122.1 (C_{17}); 121.7 (C_{16}); 71.9, 69.6, 69.1, 68.9 (C_2, C_3, C_4, C_5); 61.7 (C_6); 50.2 (C_{14}); 39.1 (C_8); 33.6 ($C_{15}H_{31}$-C$\underline{H_2}$-N); 31.9-22.7 (C_{13}, C_{12}, C_{11}, C_{10}, C_9, CH_3-$\underline{C}_6H_{12}$-CH_2); 21; 20.8, 20.7, 20.6, 20.5 (-OC(O)$\underline{C}H_3$), 14.1 (CH_3).

FAB-MS (mNBA): calc. for $C_{42}H_{72}IN_3O_{11}$ m/z: 921.939; found m/z = 794.5 $[M\text{-}I]^+$.

Pentacarbonyl[1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamino)heptyl]-3-*N'*-hexadecyl-2,3-dihydro-imidazol-2-ylidene]chromium (**31**)

In a round flask covered with aluminium foil 506 mg (0,55 mmol) of the imidazolium salt **27** is dried for 15 min under vacuum and solved in 20 mL absolute DCM. 128 mg (0,55 mmol) of silveroxide is given to the reaction mixture, and stirred overnight. The black solution is filtrated and concentrated. The black solid is then dissolved in THF at -78°C. 166 mg (0,55 mmol) of $Cr(CO)_5$Cyclooctene complex is solved in 20 mL THF at -78°. The yellow chromium complex solution is transferred to the silver carbene one via canula or syringe. The reaction is left to reach room temperature as the -78°C cooling bath raises its temperature, at least overnight. The product is purificated over silica gel cooled column chromatography at 0°C with a DCM/MeOH (94/6) eluent, affording a yellowish powder with 46% yield.



(**31**)

Yield : 46% (Rf: 0.38)

Formula : $C_{47}H_{71}CrN_3O_{16}$

Mass : 985.4 g mol^{-1}

^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] = 7.00 (s., 2H, H_{17}, H_{16}); 6.06 (br s, 1H, H_7); 5.65 (br s, 1H, H_3); 5.42 (br s, 1H, H_4); 5.25 (br s, 1H, H_2); 5.02 (br s, 1H, H_5); 4.30 (br d, $^2J_{6a\text{-}6b}$ = 12.2 Hz, 1H, H_{6a}); 4.17 (m, 4H, H_{14}, $C_{15}H_{33}$-C$\underline{H_2}$-N); 4.10 (br dd, $^3J_{6b\text{-}5}$ = 5.1 Hz, $^2J_{6b\text{-}6a}$ = 12.2 Hz, 1H, H_{6b}); 3.22 (m, 2H, H_8); 2.21, 2.12, 2.09; 2.07, 2.06 (m, 15H, -OC(O)CH_3); 1.80, 1.39, 1.28 (m, 38H, H_9, H_{10}, H_{11}, H_{12}, H_{13}, -$C_{14}H_{28}$-); 0.89 (s, 3H, CH_3).

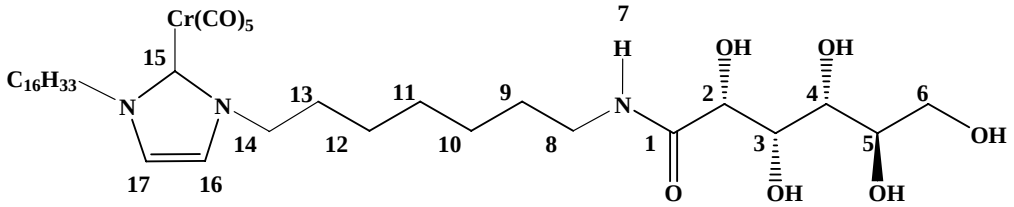
^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 221.6 (CO_{trans}); 217.7 (CO_{cis}), 189.5 (C_{15}) 171.1, 170.6, 169.8, 169.6, 169.2 (-O$\underline{C}$(O)CH_3); 165.9 (C_1); 121.6 (C_{17}); 121.5 (C_{16}); 71.7, 69.4, 69.0, 68.9, 68.7 (C_2, C_3, C_4, C_5); 61.5 (C_6); 51.4 (C_{14}); 39.3 (C_8); 39.2 ($C_{15}H_{31}$-$\underline{C}H_2$-N); 31.9-22,7 (C_{13}, C_{12}, C_{11}, C_{10}, C_9, CH_3-$\underline{C}_{14}H_{28}$-CH_2); 20.8, 20.7, 20.6, 20.5, 20.4 (-OC(O)$\underline{C}H_3$), 14.1 (CH_3).

MALDI-MS (DCTB): calc. for $C_{47}H_{71}CrN_3O_{16}$ m/z: 986.0732; found m/z = 845.2 $[M\text{-}5CO]^+$; 794.3 $[M\text{-}Cr(CO)_5]^+$.

FT-IR (CH_2Cl_2): ν CO [cm^{-1}] = 2055 (m, A_1), 1920 (vs, E), 1899 (sh) 1754 (m, acetyl).

Pentacarbonyl[1-*N*-[7-*N''*-(2R,3R,4R,5S,6-pentahydroxy-hexanoylamino)heptyl]-3-*N'*-hexadecyl-2,3-dihydro-imidazol-2-ylidene]chromium (**35**)

In a coolable schlenk tube 1.28 g (1,3 mmol) of the chromium complex salt is dried for 15 min under vacuum and solved in 10 mL absolute MeOH. 10 ml of NH_3 saturated MeOH solution is added and let to stir overnight. The product (Rf: 0.8) is purificated over silica gel cooled column chromatography at 0°C with a DCM/MeOH (80/20) eluent, affording a yellowish powder with 13% yield.



(**35**)

Yield : 13% (Rf: 0.8)

Formula : $C_{37}H_{61}CrN_3O_{11}$

Mass : 775.9 g mol^{-1}

^{1}H-NMR (500 MHz, CD_3OD): δ[ppm] = 7.28 (s, 2H, H_{16}, H_{17}); 4.26 (br s, 3H, H_3, H_4, H_2); 4.03 (br s, 1H, H_5); 3.80 (br s, 1H, H_{6a}); 3.74 (m, 2H, N-C$\underline{H_2}$-$C_{15}H_{31}$); 3.67 (br s, 1H, H_{6b}); 3.27 (m, 2H, H_8); 1.83, 1.56, 1.43, 1.32 (m, 40H, H_9, H_{10}, H_{11}, H_{12}, H_{13}, N-$C_{15}\underline{H_{30}}$-CH_3); 0.93 (br s, 3H, -C$\underline{H_3}$).

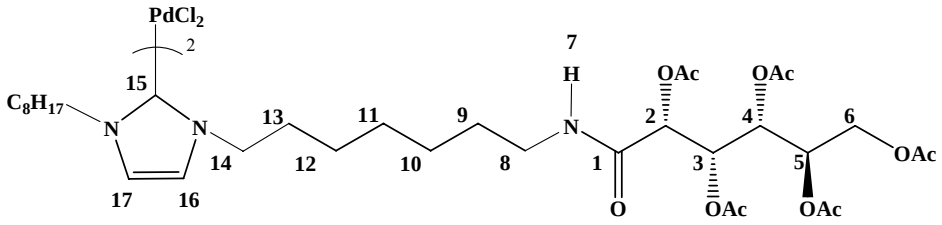
^{13}C-NMR (125 MHz, CD_3OD): δ [ppm] = 222.9 (CO_{trans}); 219.3 (CO_{cis}), 188.7 (C_{15}) 175 (C_1); 123.6 (C_{17}, C_{16}); 75.3, 74.3, 73, 71.9 (C_2, C_3, C_4, C_5); 64.7 (C_6); 52.5 (C_{14}); 40.1 ($C_{15}H_{31}$-C$\underline{H_2}$-N); 40 (C_8); 33- 23,7 (C_{13}, C_{12}, C_{11}, C_{10}, C_9, CH_3-$\underline{C_{14}}H_{28}$-CH_2); 14.4 (CH_3).

ESI-MS (mode: negativ) (MeOH): calc. for $C_{37}H_{61}CrN_3O_{11}$ m/z: 775.8898; found m/z = 774.3604 [M-H]; 810.3379 $[M+Cl]^-$.

FT-IR (CH_2Cl_2): ν CO [cm^{-1}] = 2055 (m, A_1), 1932 (vs, E), 1894 (sh).

Bis-[1-*N*-[7-*N''*-(2R,3R,4R,5S,6-penta-O-acetyl-hexanoylamino)heptyl]-3-*N'*-octyl-2,3-dihydro-imidazol-2-ylidene]palladium(II)chloride (**36**)

In a round flask covered with aluminium foil 556 mg (0,687 mmol) of the imidazolium salt **26** is dried for 15 min under vacuum and solved in 20 mL absolute DCM. 159 mg (0,687 mmol) of silver(I)oxide is given to solution and the mixture is stirred overnight. The system is covered with aluminium foil. The crude mixture is then filtered through celite. 120 mg (0.327 mmol) Palladium(II)π-allylchloride dimer is given to the solution. The system is stirred for one hour, concentrated under low pressure and then separated over column chromatography. The purification, with DCM/MeOH (94/6) as eluent, affords the dark yellow solid with 13% yield. (170 mg)



(**36**)

Yield : 13% (Rf: 0.52)

Formula : $C_{68}H_{110}Cl_2N_6O_{22}Pd$

Mass : 1538.61 g mol^{-1}

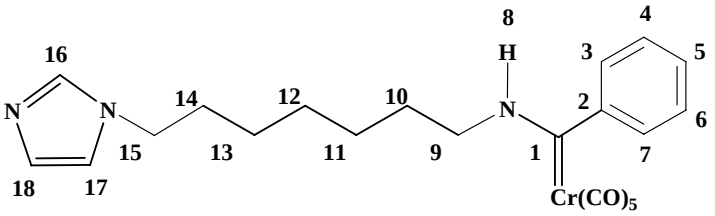
^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] = 6.85 (s, 2H, H_{16}, H_{17}); 6.53 (m, 1H, H_7); 5.47 (dd, $^3J_{3\text{-}2}$ = 4.2 Hz, $^3J_{3\text{-}4}$ = 4.7 Hz, 2H, H_3); 5.35 (dd, $^3J_{4\text{-}3}$ = 4.8 Hz, $^3J_{4\text{-}5}$ = 6.7 Hz, 1H, H_4); 5.14 (d, $^3J_{2\text{-}3}$ = 4 Hz, 1H, H_2); 4.94 (m, 1H, H_5); 4.19 (m, 2H, H_{14}); 4.19 (m, 1H, H_{6a}); 4.02 (m, 2H, C_7H_{15}-C$\underline{H_2}$-N) 4.02 (m, 1H, H_{6b}); 3.07 (m, 2H, H_8); 2.07 (s, 2H, C_6H_{13}-$\underline{C}H_2$-CH_2); 2.10 - 1.92 (m, 15H, -OC(O)CH_3); 1.72, 1.37, 1.20, 1.13 (m, 22H, H_9, H_{10}, H_{11}, H_{12}, H_{13}, -C_6H_{12}-); 1.13 (s, 3H, CH_3).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 175.1 (C_{15}); 170.3, 169.6, 169.5, 169.3, 168.9 (-O$\underline{C}$(O)CH_3); 166 (C_1); 121.9, 120.7 (C_{16}, C_{17}); 70.4, 68.9, 68.8, 68.2 (C_2, C_3, C_4, C_5); 61.1 (C_6); 52.5 (C_{14}); 38.8 (C_8); 37.7 (C_{18}) 30.4, 29.3, 29.1, 25.7, 25.4 (C_{13}, C_{12}, C_{11}, C_{10}, C_9); 20.8, 20.7, 20.6 (-OC(O)$\underline{C}H_3$), 20.1 (CH_3).

FAB-MS (mNBA): calc. for $C_{68}H_{110}Cl_2N_6O_{22}Pd$ m/z: 1538.61; found m/z = 1467.7 [M-Cl_2]$^+$; 682.4 [M-R-Pd-Cl_2]$^+$.

Pentacarbonyl[7-(1-N'-imidazole)-N-heptylamino]benzylidenechromium (**37**)

Cool down in a schlenk tube 30 mL of distillated DCM at -60°C. Use 15 mL of the -60°C DCM to dissolve 0.894 g (1,5 mmol) of phenylmethoxy carbene complex. Use another 5 mL of the -60°C DCM to dissolve 0.543 g (3 mmol) of 7-(1H-imidazol-1-yl)heptane-1-amine **14**. The amine solution is then given dropwise to the carbene solution at -60°C. The reaction is monitored by IR and TLC. The reaction color will turn from a deep red to yellow at the end of the reaction. The crude product is purified over silica gel chromatography at -20°C with DCM/MeOH (95/5) as eluent. 0.420 g (62%) of a yellow-orange solid is recovered.



(**37**)

Yield : 62% (Rf: 0.47)

Formula : $C_{22}H_{23}CrN_3O_5$

Mass : 461.4 g mol^{-1}

^{1}H-NMR (300 MHz, $CDCl_3$): δ[ppm] = 9.80 (br s, 1H, H_8); 7.30 (dd, 2H, $^3J_{4,6\text{-}5}$ = 7.7 Hz, $^3J_{4,6\text{-}3,7}$ = 7.7 Hz, H_4, H_6); 7.27 (s, 1H, H_{16}); 7.13 (t, 1H, $^3J_{5\text{-}6,4}$ = 7.4 Hz, H_5); 6.93 (s, 1H, H_{18}); 6.80 (s, 1H, H_{17}); 6.70 (d, $^3J_{3,7\text{-}4,6}$ = 7.2 Hz, 2H, H_3, H_7); 3.82 (t, $^3J_{15\text{-}14}$ = 7.2 Hz, 2H, H_{15}); 3.13 (m, 2H, H_9); 1.65, 1.51 (m, 2*2H, $H_{14,}$ H_{10}); 1.21 (m, 6H, $H_{11,}$ H_{12}, H_{13}).

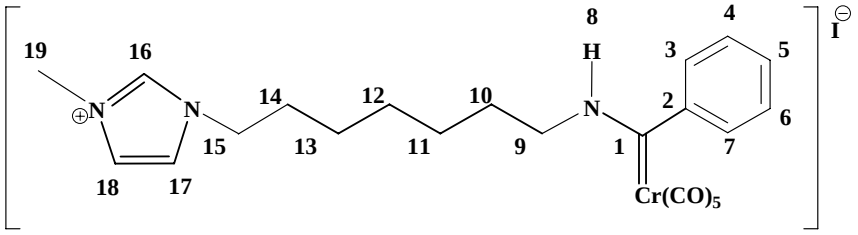
^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 279.6 (C_1); 223.5 (CO_{trans}); 217.3 (CO_{cis}), 154.9 (C_2) 136.8 (C_{16}), 129.0 (C_4), 128.4 (C_{17}); 128.1 (C_6), 126.4 (C_3); 120.9 (C_7), 119.0 (C_{18}); 118.7, (C_5); 53.5 (C_{15}); 50.5 (C_9), 46.8, 30.7, 29.2, 28.3, 26.1 (C_{10}, C_{11}, C_{12}, C_{13}, C_{14}).

FT-IR (DCM): ν CO [cm^{-1}] = 2055 (m, A_1); 1974 (sh, B_1); 1930 (vs, E).

ESI-MS (mode: positiv) (MeOH): calc. for $C_{22}H_{23}CrN_3O_5$ m/z: 461.4312; found m/z = 462.1110 $[M]^+$.

[Pentacarbonyl[7-[3-N'-(methyl)imidazolium]N-heptylamino(benzylidene)]chromium]iodide (**38**)

1.7 g (2.82 mmol) of **37** is dried under vacuum for 15 min, solved in 5 mL absolute DCM, 2.30 mL (36.7 mmol) of iodomethane is added to the reaction and left to run forty-eight hours at 10°C. The solution turns to orange and affords a dark yellow oil after filtration, a purification can be done with DCM/MeOH (80/20) (Rf: 0.6) over silica gel column chromatography and affords the product in 35% yield.



(**38**)

Yield : 35% (Rf: 0.6)

Formula : $C_{23}H_{23}ICrN_3O_5$

Mass : 603.37 g mol^{-1}

^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] = 9.99 (s, 1H, H_{16}); 9.57 (br s, 1H, H_8); 7.44 (br. s, 2H, H_4, H_6); 7.38 (br. s, 2H, H_{17}, H_{18}); 7.27 (br. s, 1H, H_5); 6.77 (br. s, 2H, H_3, H_7); 4.33 (br s, 2H, H_{15}); 4.08 (m, 3H, H_{19}); 3.24 (m, 2H, H_9); 1.92, 1.64, 1.36, 1.28 (m, 10H, H_{10}, H_{11}, H_{12}, H_{13}, H_{14}).

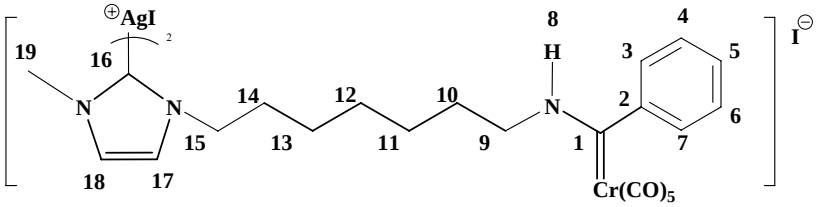
^{13}C-NMR (75 MHz, MeOD): δ [ppm] = 273.1 (C_1); 219.4 (CO_{trans}); 213 (CO_{cis}); 145.3 (C_2); 132.6 (C_{16}); 123.9 (C_{17}); 123.7 (C_4); 121.9 (C_6); 119 (C_3); 117.7 (C_7); 117 (C_5) 114.8 (C_{18}); 46.3 (C_{15}); 45.6 (C_9), 32.5 (C_{19}) 25.2, 24.5, 23.4, 21.2, 20.9 (C_{10}, C_{11}, C_{12}, C_{13}, C_{14}).

FAB-MS (mNBA): calc. for $C_{23}H_{23}ICrN_3O_5$ m/z: 603.3702; found m/z = 476.2 (97) $[M-I]^+$.

FT-IR (DCM): ν CO [cm^{-1}] = 2055 (m, A_1); 1972 (sh, B_1); 1928 (vs, E).

Bis-pentacarbonyl[7-[3-*N'*-(methyl)imidazol-2-ylidene)silver(I)iodide)*N*-heptylamino (benzylidene)]chromium (**39**)

In a schlenk tube covered with aluminium foil 0.253 g (0.43 mmol) imidazolium salt **38** is dried for 15 min under vacuum and solved in 20 mL absolute DCM. 0.199 mg silver(I)oxide (0.86 mmol) is given to the reaction. The black solution is filtered through celite to yield a dark brown solid. The product will not be purificated over silica gel column chromatography because of its high sensitivity to light and air. The filtrate yields 300 mg of crude product.



(**39**)

Yield : 54%

Formula : $C_{46}H_{50}AgCr_2I_2N_6O_{10}$

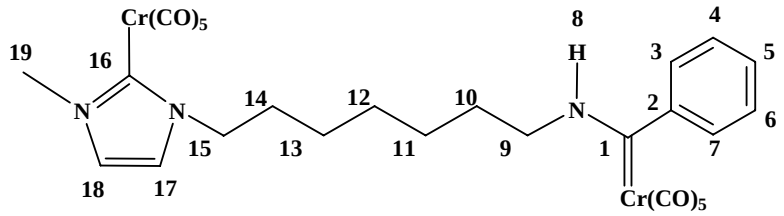
Mass : 1310.93 g mol^{-1}

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 278.9 (C_1); 221.4 (CO_{trans}); 217.1 (CO_{cis}); 182,1 (C_{16}); 149.3 (C_2); 128.4 (C_{17}), 126.4 (C_4, C_6); 123.8 (C_3, C_7); 120.9 (C_5); 118.9 (C_{18}), 51.4 (C_{15}); 50.5(C_9); 39.1 (C_{19}); 31.1, 28.4, 28.3, 26.1, 25.9 (C_{14}, C_{13}, C_{12}, C_{11}, C_{10}).

FAB-MS (mNBA): calc. for $C_{46}H_{50}AgCr_2I_2N_6O_{10}$ m/z: 1310.9539 found m/z = 1057 $[M-2I]^+$ (30).

Pentacarbonyl-7-[pentacarbonyl(1-N-(methyl)-2,3-dihydro-imidazol-2-ylidene)chromium]N-heptylamino(benzylidene)]chromium (**40**)

In a round flask covered with aluminium foil 0.67 g (1,11 mmol) of the silver carbene complex is dried for 15 min under vacuum and solved in 20 mL absolute THF at -78°C. 100 mL of THF solvent can be pre-cooled in a schlenk tube at -78°C. 336 mg (1,11 mmol) of $Cr(CO)_5$(cyclooctene) complex is solved in 20 mL THF at -78°. Transfer the yellow chromium complex solution to the silver carbene one via canula or syringe. Leave the reaction to reach room temperature as the -78°C cooling bath raises its temperature, at least overnight. The product is purificated over silica gel cooled column chromatography at 0°C with a DCM/MeOH (95/5) eluent. The separation yields 90 mg of a yellow powder (12%).



(**40**)

Yield : 12% (Rf: 0.8)

Formula : $C_{28}H_{25}Cr_2N_3O_{10}$

Mass : 667.51 g mol^{-1}

H-NMR (500 MHz, $CDCl_3$): δ[ppm] = 8.98 (br s, 1H, H_8); 7.39 (dd, 2H, $^3J_{4,6\text{-}5}$ = 7.6 Hz, $^3J_{4,6\text{-}3,7}$ = 7.4 Hz, H_4, H_6); 7.22 (t, 1H, $^3J_{5\text{-}6,4}$ = 7.4 Hz, H_5); 6.96 (s, 2H, H_{17}, H_{18}); 6.78 (d, $^3J_{3,7\text{-}4,6}$ = 7.4 Hz, 2H, H_3, H_7); 4.17 (t, $^3J_{15\text{-}14}$ = 8.2 Hz, 2H, H_{15}); 3.86 (m, 3H, H_{19}); 3.19 (m, 2H, H_9); 1.76, 1.60, 1.40 - 0.86 (m, 10H, H_{10}, $H_{11,}$ H_{12}, H_{13}, H_{14}).

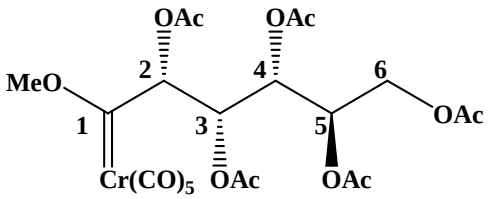
^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 281.9 (C_1); 223.3 (CO_{trans}), 221.5 (CO_{trans}); 217.8 (CO_{cis}), 217.2 (CO_{cis}); 190,3 (C_{16}); 149.5 (C_2); 128.6 (C_{17}), 126.7 (C_4, C_6); 124.0 (C_3, C_7); 120.9 (C_5); 119 (C_{18}), 51.3, (C_{15}); 51, (C_9); 39.2, (C_{19}); 31.2, 29.2, 28.5, 26.2, 26.0 (C_{14}, C_{13}, C_{12}, C_{11}, C_{10}).

FAB-MS (mNBA): calc. for $C_{28}H_{25}Cr_2N_3O_{10}$ m/z: 667.035 found m/z = 667 $[M]^+$.

FT-IR (PE): ν CO [cm-1] = 2055 (m, A_1); 1969 (sh, B_1); 1922 (vs, E).

Pentacarbonyl(methoxy)-2,3,4,5,6-penta-*O*-acetyl-hex-1-ylidene]chromium (**41**)

In a Schlenk tube are dried under vacuum at 160 °C 8 equivalents of graphite for 90 min. To this is given one equivalent of potassium metal in small pieces. The potassium should be freed from its external oxidised layer. Under hard stirring conditions the C_8K bronze colored aggregate is formed. The system is left to reach room temperature, and then cooled to -60°C where freshly distilled THF is given dropwise to obtain a 0.4 $mol.L^{-1}$ suspension. 0.5 equivalent of chromiumhexacarbonyl is added and stirred two hours. The system can be stirred another 30 min at room temperature. 0.5 equivalent of gluconic acid chloride is given dropwise at -60°C. After 30 min THF is concentrated under low pressure. The residue is solved in DCM at -25°C. At last 2 equivalents of trimethyloxoniumtetrafluoroborat are given to the reaction and left to run overnight. A red product is recovered after column chromatography with ether/PE/DCM 1:2:2 (Rf: 0.63)



(**41**)

Yield : 82% (Rf: 0.63)

Formula : $C_{22}H_{24}CrO_{16}$

Mass : 596.42 g mol^{-1}

^{1}H-NMR (300 MHz, $CDCl_3$): δ[ppm] = 5.62 (br s, 1H, H_2); 5.61 (m, 1H, H_3); 5.38 (dd, $^3J_{4\text{-}3}$ = 5Hz, $^3J_{4\text{-}5}$ = 5.6 Hz, 1H, H_4); 5.00 (ddd, $^3J_{5\text{-}4}$ = 5.6 Hz, $^3J_{5\text{-}6a}$ = 3.5 Hz, $^3J_{5\text{-}6b}$ = 5.8 Hz, 1H, H_5); 4.75 (-OCH_3, s, 3H); 4.30 (dd, $^3J_{6a\text{-}5}$ = 3.5 Hz, $^2J_{6a\text{-}6b}$ = 12.3 Hz, 1H, H_{6a}); 4.10 (dd, $^3J_{6b\text{-}5}$ = 5.8 Hz, $^2J_{6b\text{-}6a}$ = 12.3 Hz, 1H, H_{6b}); 2.28; 2.07; 2.06; 2.02; 2.01 (s, 15H, -OC(O)CH_3).

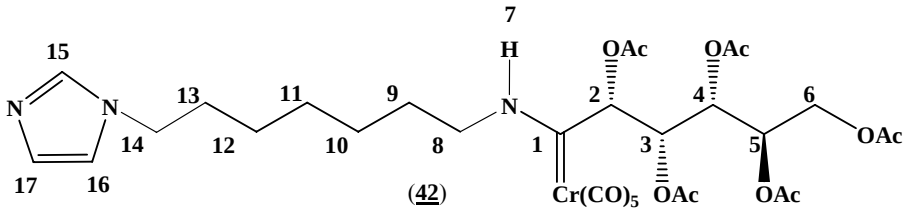
^{13}C-NMR (125 MHz, C_6D_6): δ[ppm] = 355.6 (C_1); 224.3 (CO_{trans}); 216.5 (CO_{cis}); 170.6, 170.3, 170.1, 169.9 (-O<u>C</u>(O)CH3); 86.9 (C_2); 71.2; 70.6; 70.2 (C_3, C_4, C_5); 68.2 (-O<u>C</u>H_3); 62.2 (C_6); 21.2, 20.9, 20.8, 20.7 (OC(O)<u>C</u>H_3).

EI-MS (70eV): calc. for $C_{22}H_{24}CrO_{16}$ m/z: 596.0469 found m/z = 595.9 (3) $[M]^+$.

FT-IR (PE): ν CO [cm^{-1}] = 2067 (m, A_1); 1993 (sh, B_1); 1950 (vs, E); 1756 (m, acetyl).

N-1H-Imidazol-1-yl[pentacarbonyl-[7-heptylamino(2R,3R,4R,5S,6-penta-*O*-acetyl hexylidene)]chromium] (**42**)

Cool down in a schlenk tube 30 mL of distillated DCM at -60°C. Use 15 mL of the -60°C DCM to dissolve 2.4 g (4 mmol) of **41**. Use another 5 mL of the -60°C DCM to dissolve 830 mg (4,6 mmol) of **14**. The amine solution is then given dropwise to the carbene solution at -60°C. The reaction is monitores by IR and TLC. The reaction color will turn from a deep red to yellow at the end of the reaction. The crude product is purified over silica gel chomatogaphy at -20°C with DCM/MeOH (95/5) (Rf: 0.35) as eluent. 1.09 g (37%) of a yellow-orange solid is recovered.



Yield : 37% (Rf: 0.35)

Formula : $C_{31}H_{39}CrN_3O_{15}$

Mass : 745.6 g mol^{-1}

^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] = 9.51 (br s, 1H, H_7); 7.37 (s, 1H, H_{15}); 7.08 (s, 1H, H_{16}); 6.92 (s, 1H, H_{17}); 6.05 (br s, 1H, H_2); 5.87 (br d, ^3J = 4.6 Hz, 1H, H_3); 5.45 (dd, ^3J = 5.5 Hz, ^3J = 5.2 Hz, 1H, H_4); 4.97 (m, 1H, H_5); 4.36 (dd $^2J_{6a\text{-}6b}$ = 12.0 Hz, 1H, H_{6a}); 4.17 (dd, $^3J_{6b\text{-}5}$ = 5.2 Hz, $^2J_{6b\text{-}6a}$ = 12.0 Hz, 1H, H_{6b}); 3.95 (m, 2H, H_{14}); 3.84 (m, 2H, H_8); 2.05; 2.04; 2.03; 2.02, 2.01 (m, 15H, -OC(O)CH_3); 1.76, 1.34, 1.30 (m, 10H, H_9, H_{10}, H_{11}, H_{12}, H_{13}).

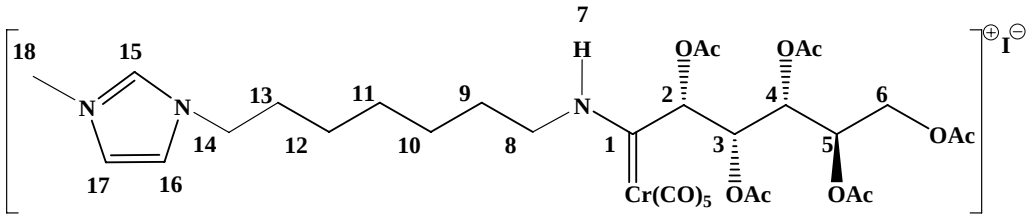
^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 268.3 (C_1); 222 (CO_{Trans}); 216.7 (CO_{Cis}); 170.6, 170.0, 169.6, 168.9, 168.4 (-O<u>C</u>(O)CH_3); 137 (C_{15}), 132.5 (C_{16}); 119.4 (C_{17}); 83.8 (C_2), 70.4, 69.2, 66.7 (C_3, C_4, C_5); 61.4 (C_6); 53.1 (C_8); 47.9 (C_{14}); 30.5, 28.9, 28.4, 26.2, 26 (C_{13}, C_{12}, C_{11}, C_{10}, C_9); 20.8; 20.7, 20.6, 20.5 (-OC(O)<u>C</u>H_3).

FT-IR (DCM): ν CO [cm^{-1}] = 2057 (m, A_1); 1974 (sh, B_1); 1930 (vs, E) 1751 (m, acetyl)

ESI-MS (mode: positiv) (MeOH): calc. for $C_{31}H_{39}CrN_3O_{15}$ m/z: 745.1786 found m/z = 746.1842 $[M+H]^+$.

[*N'*-methyl-*N*-1H-imidazolium[pentacarbonyl[7-heptylamino(2R,3R,4R,5S,6-penta-*O*-acetyl-hexylidene)]chromium]iodide (**43**)

0.350 g (0.51 mmol) of **42** is dried under vacuum for 15 min, solved in 5 mL absolute DCM, 0.64 mL (1.02 mmol) of iodomethane is added to the reaction and left to run forty-eight hours at 10°C. The solution turns to orange and affords a dark orange foam after column chromatography with (DCM/MeOH (8/2); Rf: 0.58) 86% yield.



(**43**)

Yield : 86% (Rf: 0.58)

Formula : $C_{32}H_{42}CrIN_3O_{15}$

Mass : 887.1 g mol^{-1}

^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] = 9.93 (s, 1H, H_{15}); 9.62 (s, 1H, H_7); 7.39 (br s, 2H, H_{16}, H_{17}); 6.01 (br s, 1H, H_2); 5.82 (br s, 1H, H_3); 5.43 (br s, 1H, H_4); 4.97 (m, 1H, H_5); 4.30 (m, 3H, H_{6a}, H_{14}); 4.13 (m, 1H, H_{6b}); 4.05 (m, 2H, H_{18}); 3.84 (m, 2H, H_8); 2.25; 2.06; 2.01; 1.92 (m, 15H, -OC(O)CH_3); 1.75, 1.38 (m, 10H, H_9, H_{10}, H_{11}, H_{12}, H_{13}).

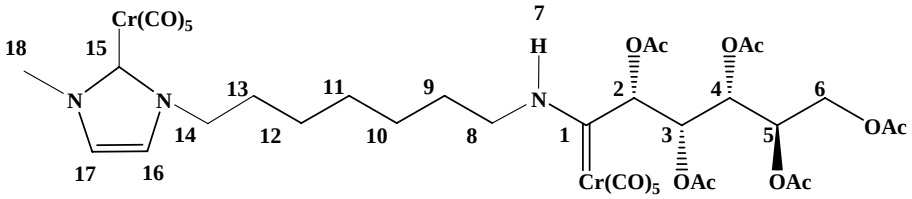
^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 265.2 (C_1); 222,1 (CO_{Trans}); 216.9 (CO_{Cis}); 170.6, 169.9, 169.6, 169.4, 169.0 (-O<u>C</u>(O)CH_3); 136.7 (C_{15}), 123.4 (C_{16}); 122.3 (C_{17}); 84 (C_2), 70.3, 68.9, 65.6 (C_3, C_4, C_5); 61.3 (C_6); 53.1 (C_8); 50 (C_{14}); 36.8 (C_{18}); 29.6, 28.5, 27.5, 25.4, 25.2 (C_{13}, C_{12}, C_{11}, C_{10}, C_9); 21.4; 20.8, 20.7, 20.64, 20.6 (-OC(O)<u>C</u>H_3).

FAB-MS (mNBA): calc. for $C_{32}H_{42}CrIN_3O_{15}$ m/z: 887.1066 found m/z = 760.3 (31) $[M-I]^+$.

FT-IR (DCM): ν CO [cm^{-1}] = 2057 (m, A_1); 1972 (sh, B_1); 1924 (vs, E) 1751 (m, acetyl).

{[Pentacarbonyl(*N'*-methyl-2,3-dihydro-*N*-imidazol-2-ylidene)chromium]pentacarbonyl[7-heptyl-amino(2R,3R,4R,5S,6-penta-*O*-acetyl-hexylidene)]chromium} (**44**)

In a round flask covered with aluminium foil 676 mg (0.36 mmol) of the silver carbene complex is dried for 15 min under vacuum and solved in 20 mL absolute THF at -78°C. 100 mL of THF solvent can be pre-cooled in a schlenk tube at -78°C. 109 mg (0.36 mmol) of $Cr(CO)_5$(cyclooctene) complex is solved in 20 mL THF at -78°. Transfer the yellow chromium complex solution to the silver carbene one via canula or syringe. Leave the reaction to reach room temperature as the -78°C cooling bath raises its temperature, at least overnight. The product is purificated over silica gel cooled column chromatography at 0°C with a DCM/MeOH (95/5) eluent. The separation yields 80 mg of a yellow powder (23%).



(**44**)

Yield : 23% (Rf: 0.85)

Formula : $C_{37}H_{41}Cr_2N_3O_{20}$

Mass : 951.2 g mol^{-1}

^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] = 8.94 (s, 1H, H_7); 6.96 (br s, 2H, H_{16}, H_{17}); 6.05 (br s, 1H, H_2); 5.78 (br s, 1H, H_3); 5.38 (br s, 1H, H_4); 5.03 (m, 1H, H_5); 4.30 (m, 1H, H_{6a}); 4.19 (m, 2H, H_{14}); 4.04 (m, 1H, H_{6b}); 3.86 (s, 3H, H_{18}); 3.22 (m, 2H, H_8); 2.29; 2.27; 2.25; 2.18 (m, 15H, -OC(O)CH_3); 1.77, 1.44, 1.24 (m, 10H, H_9, H_{10}, H_{11}, H_{12}, H_{13}).

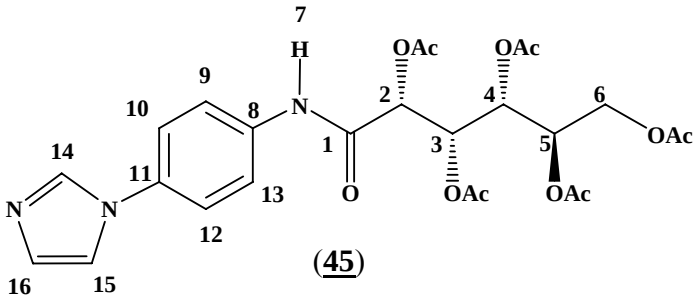
^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 266.5 (C_1); 221,8 (CO_{Trans}); 221.5 (CO_{Trans}); 217 (CO_{Cis}); 216.7 (CO_{Cis}); 190.5 (C_{15}) 170.7, 169.9, 169.8, 169.3, 169.2 (-O<u>C</u>(O)CH_3); 123.9 (C_{16}); 121 (C_{17}); 77.2 (C_2), 71.7, 69.4, 63.8 (C_3, C_4, C_5); 61.5 (C_6); 51.4 (C_8); 51.3 (C_{14}); 39.2 (C_{18}); 31.9; 31.3, 29.3; 28.7, 26.4 (C_{13}, C_{12}, C_{11}, C_{10}, C_9); 21.4; 20.8, 20.6 (-OC(O)<u>C</u>H_3).

FAB-MS (mNBA): calc. for $C_{37}H_{41}Cr_2N_3O_{20}$ m/z: 951.1094 found m/z = 951.2 $[M]^+$.

FT-IR (DCM): ν CO [cm^{-1}] = 2056 (m, A_1); 1923 (vs, E) 1751 (m, acetyl).

N-1H-[(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamido)-1,4-phenylene]imidazole (**45**)

In a two neck round flask equipped with a dropping funnel 1.08 g (6.80 mmol) of 4-(1*H*-Imidazol-1-yl)aniline is dried for 15 min under vacuum and then solved in 30 mL of absolute DCM. 3 mL of Pyridine is given to the amine. Under argon atmosphere is given dropwise a solution of 3.03 g (7.14 mmol) of Penta-O-acetylated gluconic acid chloride in DCM. The reaction is monitored by TLC. After two hours the system is quenched carefully and dropwise with H_2O. The crude reaction mixture is extracted through a separatory funnel 3 times with 30 mL of DCM. The combined organic phases are concentrated under low pressure. The product is obtained after purification over silica gel column chromatography with a DCM/MeOH (20/1) eluent, affording a yellowish powder with 64% yield.



(**45**)

Yield : 64% (Rf: 0.30)

Formula : $C_{25}H_{29}N_3O_{11}$

Mass : 547.51 g mol^{-1}

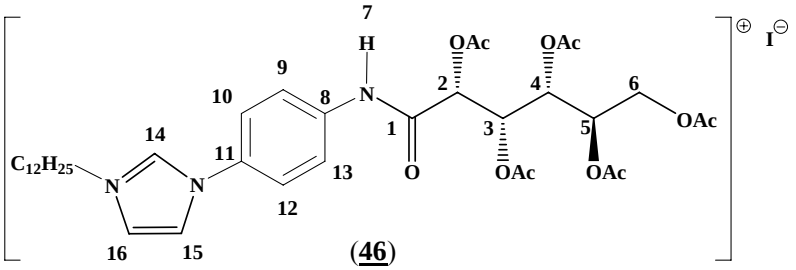
^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] = 8.93 (s, 1H, H_7); 7.82 (s, 1H, H_{14}); 7.62 (d, $^3J_{9,13\text{-}10,12}$ = 8.9 Hz, 2H, H_9, H_{13}); 7.31 (d, $^3J_{10,12\text{-}9,13}$ = 8.9 Hz, 2H, H_{10}, H_{12}); 7.22 (s, 1H, H_{15}); 7.18 (s, 1H, H_{16}); 6.96 (s, 1H, H_{16}); 5.73 (dd, $^3J_{3\text{-}2}$ = 5.4 Hz, $^3J_{3\text{-}4}$ = 4.7 Hz, 2H, H_3); 5.47 (dd, $^3J_{4\text{-}3}$ = 4.6 Hz, $^3J_{4\text{-}5}$ = 6.6 Hz, 1H, H_4); 5.35 (d, $^3J_{2\text{-}3}$ = 5.4 Hz, 1H, H_2); 5.05 (ddd, $^3J_{5\text{-}4}$ = 6.5 Hz, $^3J_{5\text{-}6a}$ = 3.4 Hz, $^3J_{5\text{-}6b}$ = 5.6 Hz, 1H, H_5); 4.29 (dd, $^3J_{6a\text{-}5}$ = 3.4 Hz, $^2J_{6a\text{-}6b}$ = 12.4 Hz, 1H, H_{6a}); 4.10 (dd, $^3J_{6b\text{-}5}$ = 5.5 Hz, $^2J_{6b\text{-}6a}$ = 12.4 Hz, 1H, H_{6b}); 2.19; 2.07; 2.04; 2.03, 2.02 (m, 15H, -OC(O)CH_3).

^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 170.7, 170.1, 169.9, 169.8, 169.4 (-O<u>C</u>(O)CH_3); 164.5 (C_1); 149.7 (C_{11}); 136.5 (C_{14}); 133.7 (C_9); 130.1 (C_{10}, C_{12}); 122.0 (C_{16}); 121.5 (C_{15}); 118.3 (C_9, C_{13}); 71.8, 69.1, 68.8, 68.7 (C_2, C_3, C_4, C_5); 61.6 (C_6); 20.7; 20.62, 20.61; 20.5; 20.4 (-OC(O)<u>C</u>H_3).

EI-MS (70 eV): High Resolution for [M]: m/z = 547.1802; found. m/z = 547.1811.

N'-dodecyl-*N*-1H-[(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamino)-1,4-phenylene]-imidazolium iodide (**46**)

In a round flask equipped with a reflux condenser 890 mg (1.6 mmol) of **45** is solved in 20 mL of absolute DCM. 8.02 mL (32.5 mmol) of 1-iododode can is given to the reaction and refluxed for twenty-four hours. The crude reaction mixture is concentrated under low pressure. The product is obtained after purification over silica gel column chromatography with a DCM/MeOH (9/1) eluent, affording a yellowish powder with 35% yield.



(**46**)

Yield : 35% (Rf. 0.38)

Formula : $C_{37}H_{54}IN_3O_{11}$

Mass : 843.74 g mol^{-1}

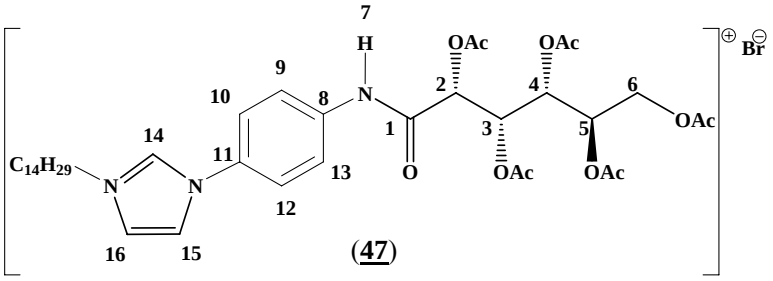
^{1}H-NMR (300 MHz, $CDCl_3$): δ[ppm] = 10 (s, 1H, H_{14}); 9.58 (s, 1H, H_7); 7.74 (s, 1H, H_{15}); 7.60 (d, $^3J_{9,13\text{-}10,12}$ = 9 Hz, 2H, H_9, H_{13}); 7.50 (s, 1H, H_{16}); 7.44 (d, $^3J_{10,12\text{-}9,13}$ = 9 Hz, 2H, H_{10}, H_{12}); 5.71 (dd, $^3J_{3\text{-}2}$ = 3.6 Hz, $^3J_{3\text{-}4}$ = 4.5 Hz, 2H, H_3); 5.54 (dd, $^3J_{4\text{-}3}$ = 4.5 Hz, $^3J_{4\text{-}5}$ = 6.2 Hz, 1H, H_4); 5.51 (d, $^3J_{2\text{-}3}$ = 3.6 Hz, 1H, H_2); 5.11 (ddd, $^3J_{5\text{-}4}$ = 6.2 Hz, $^3J_{5\text{-}6a}$ = 3 Hz, $^3J_{5\text{-}6b}$ = 6.3 Hz, 1H, H_5); 4.38 (dd, $^3J_{6a\text{-}5}$ = 3 Hz, $^2J_{6a\text{-}6b}$ = 12.2 Hz, 1H, H_{6a}); 4.37 (t, ^3J = 7.2 Hz, $C_{11}H_{23}$-C$\underline{H_2}$-N); 4.12 (dd, $^3J_{6b\text{-}5}$ = 6.3 Hz, $^2J_{6b\text{-}6a}$ = 12.3 Hz, 1H, H_{6b}); 2.22; 2.06; 2.04; 2.03 (m, 15H, -OC(O)CH_3); 1.94; 1.31; 1.21 (m, 20H, CH_3-$C_{10}\underline{H_{20}}$-CH_2-N); 0.83 (t, ^3J= 6.5 Hz, 3H, CH_3).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 170.8, 170.1, 170, 169.7, 169.6 (-O$\underline{C}$(O)CH_3); 165.1 (C_1); 139 (C_{11}); 134.1 (C_{14}); 129.6 (C_8); 122.9 (C_{15}), 121.9 (C_9, C_{13}); 121 (C_{16}); 120.9 (C_{10}, C_{12}); 72.3, 69.6, 68.9, 68.6 (C_2, C_3, C_4, C_5); 61.9 (C_6); 50.6 ($C_{11}H_{23}$-$\underline{C}H_2$-N); 31.8-22.6 (CH_3-$\underline{C_{10}}H_{20}$-CH_2-N); 20.9; 20.8, 20.7; 20.6 (-OC(O)$\underline{C}H_3$); 14 ($\underline{C}H_3$).

ESI-MS (mode: positiv) (MeOH): calc. for $C_{37}H_{54}IN_3O_{11}$ m/z: 843.7426 found m/z = 716.3757 $[M\text{-}I]^+$.

N'-tetradecyl-*N*-1H-[(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamino)-1,4-phenylene]-imidazolium bromide (**47**)

In a round flask equipped with a reflux condenser 445 mg (0.8 mmol) of **45** is solved in 20 mL of absolute DCM. 4.77 mL (16 mmol) of 1-bromotetradecan is given to the reaction and refluxed for twenty-four hours. The crude reaction mixture is concentrated under low pressure. The product is obtained after purification over silica gel column chromatography with a DCM/MeOH (9/1) eluent, affording a yellowish powder with 12% yield.



(**47**)

Yield : 12% (Rf. 0.12)

Formula : $C_{39}H_{58}BrN_3O_{11}$

Mass : 824.79 g mol^{-1}

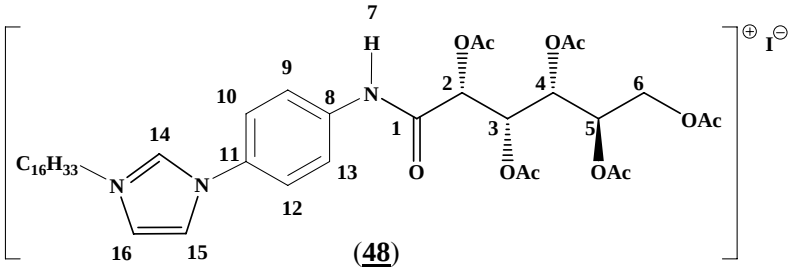
^{1}H-NMR (300 MHz, $CDCl_3$): δ[ppm] = 10.37 (s, 1H, H_7); 10.22 (s, 1H, H_{14}); 7.74 (s, 1H, H_{15}); 7.59 (d, $^3J_{9,13\text{-}10,12}$ = 9.2 Hz, 2H, H_9, H_{13}); 7.49 (s, 1H, H_{16}); 7.35 (d, $^3J_{10,12\text{-}9,13}$ = 9.1 Hz, 2H, H_{10}, H_{12}); 5.78 (dd, $^3J_{3\text{-}2}$ = 3.3 Hz, $^3J_{3\text{-}4}$ = 5.0 Hz, 2H, H_3); 5.59 (d, $^3J_{2\text{-}3}$ = 3.2 Hz, 1H, H_2); 5.57 (dd, $^3J_{4\text{-}3}$ = 5.0 Hz, $^3J_{4\text{-}5}$ = 5.8 Hz, 1H, H_4); 5.17 (ddd, $^3J_{5\text{-}4}$ = 6.1 Hz, $^3J_{5\text{-}6a}$ = 2.6 Hz, $^3J_{5\text{-}6b}$ = 6.5 Hz, 1H, H_5); 4.47 (dd, $^3J_{6a\text{-}5}$ = 2.6 Hz, $^2J_{6a\text{-}6b}$ = 12.2 Hz, 1H, H_{6a}); 4.37 (t, ^3J = 6.8 Hz, $C_{13}H_{27}$-C$\underline{H_2}$-N); 4.18 (dd, $^3J_{6b\text{-}5}$ = 6.7 Hz, $^2J_{6b\text{-}6a}$ = 12.2 Hz, 1H, H_{6b}); 2.19; 2.05; 2.03; 2.02 (m, 15H, -OC(O)CH_3); 1.92; 1.30; 1.20 (m, 24H, CH_3-$C_{12}\underline{H_{24}}$-CH_2-N); 0.81 (t, ^3J= 6.5 Hz, 3H, CH_3).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 170.8, 170.2, 169.9, 169.7, 169.6 (-O$\underline{C}$(O)CH_3); 165.1 (C_1); 139.4 (C_{11}); 134.6 (C_{14}); 129.4 (C_8); 122.7 (C_{15}), 121.6 (C_9, C_{13}); 120.8 (C_{16}); 120.7 (C_{10}, C_{12}); 72.5, 69.7, 69.1, 68.7 (C_2, C_3, C_4, C_5); 62 (C_6); 50.4 ($C_{13}H_{27}$-$\underline{C}H_2$-N); 31.8-22.6 (CH_3-$\underline{C_{10}}H_{20}$-CH_2-N); 20.8; 20.7, 20.6; 20.5 (-OC(O)$\underline{C}H_3$); 14 ($\underline{C}H_3$).

ESI-MS (mode: positiv) (MeOH): calc. for $C_{39}H_{58}BrN_3O_{11}$ m/z: 824.7953 found m/z = 744.4 $[M\text{-}Br]^+$.

N'-hexadecyl-*N*-1H-[(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamino)-1,4-phenylene]-imidazolium iodide (**48**)

In a round flask equipped with a reflux condenser 445 mg (0.8 mmol) of **45** is solved in 20 mL of absolute DCM. 5.63 g (16 mmol) of iodohexadecan is given to the reaction and refluxed for twenty-four hours. The crude reaction mixture is concentrated under low pressure. The product is obtained after purification over silica gel column chromatography with a DCM/MeOH (9/1) eluent, affording a yellowish powder with 18% yield.



(**48**)

Yield : 18% (Rf. 0.34)

Formula : $C_{41}H_{62}IN_3O_{11}$

Mass : 899.84 g mol^{-1}

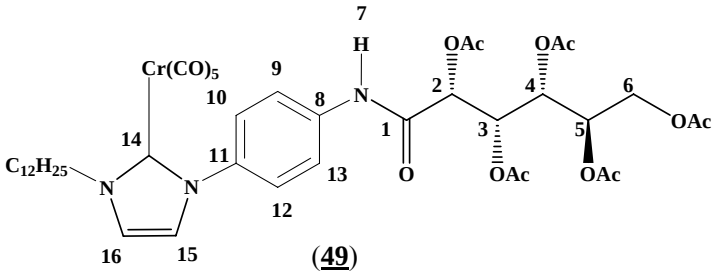
^{1}H-NMR (300 MHz, $CDCl_3$): δ[ppm] = 10.06 (s, 1H, H_{14}); 9.58 (s, 1H, H_7); 7.73 (s, 1H, H_{15}); 7.62 (d, $^3J_{9,13\text{-}10,12}$ = 9.1 Hz, 2H, H_9, H_{13}); 7.46 (d, $^3J_{10,12\text{-}9,13}$ = 9.1 Hz, 2H, H_{10}, H_{12}); 7.45 (s, 1H, H_{16}); 5.76 (dd, $^3J_{3\text{-}2}$ = 3.6 Hz, $^3J_{3\text{-}4}$ = 4.5 Hz, 2H, H_3); 5.59 (d, $^3J_{2\text{-}3}$ = 3.6 Hz, 1H, H_2); 5.59 (dd, $^3J_{4\text{-}3}$ = 4.6 Hz, $^3J_{4\text{-}5}$ = 6.3 Hz, 1H, H_4); 5.16 (ddd, $^3J_{5\text{-}4}$ = 6.2 Hz, $^3J_{5\text{-}6a}$ = 2.9 Hz, $^3J_{5\text{-}6b}$ = 6.5 Hz, 1H, H_5); 4.42 (dd, $^3J_{6a\text{-}5}$ = 2.8 Hz, $^2J_{6a\text{-}6b}$ = 12.3 Hz, 1H, H_{6a}); 4.40 (t, ^3J = 7.4 Hz, $C_{13}H_{27}$-C$\underline{H}_2$-N); 4.17 (dd, $^3J_{6b\text{-}5}$ = 6.5 Hz, $^2J_{6b\text{-}6a}$ = 12.3 Hz, 1H, H_{6b}); 2.25; 2.08; 2.07; 2.06; 2.05 (m, 15H, -OC(O)CH_3); 1.98; 1.35; 1.23 (m, 28H, CH_3-$C_{14}\underline{H}_{28}$-CH_2-N); 0.86 (t, ^3J= 6.5 Hz, 3H, CH_3).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 170.8, 170.2, 170, 169.8, 169.7 (-O$\underline{C}$(O)CH_3); 165.2 (C_1); 139.1 (C_{11}); 134.4 (C_{14}); 129.6 (C_8); 122.7 (C_{15}), 122.0 (C_9, C_{13}); 121.2 (C_{16}); 121 (C_{10}, C_{12}); 72.4, 69.7, 68.9, 68.7 (C_2, C_3, C_4, C_5); 61.9 (C_6); 50.6 ($C_{15}H_{31}$-$\underline{C}H_2$-N); 31.9-22.6 (CH_3-$\underline{C}_{14}H_{28}$-CH_2-N); 21; 20.9, 20.8; 20.7 (-OC(O)$\underline{C}H_3$); 14.1 ($\underline{C}H_3$).

ESI-MS (mode: positiv) (MeOH): calc. for $C_{41}H_{62}IN_3O_{11}$ m/z: 899.849 found m/z =772.49 $[M\text{-}I]^+$.

Pentacarbonyl{*N'*-dodecyl-*N*-[(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamino)-1,4-phenylene]-2,3-dihydro-imidazol-2-ylidene}chromium (**49**)

In a round flask covered with aluminium foil 1.05 g (1,25 mmol) of the imidazolium salt **45** is dried for 15 min under vacuum and solved in 20 mL absolute DCM. 288 mg of silveroxide is given to the reaction mixture and stirred overnight. The black solution is filtrated and concentrated. The black solid is then dissolved in THF at -78°C. 415 mg of $Cr(CO)_5$(cyclooctene) complex is solved in 20 mL THF at -78°. The yellow chromium complex solution is transferred to the silver carbene one via canula or syringe. The reaction is left to reach room temperature as the -78°C cooling bath raises its temperature, at least overnight. The product is purified over silica gel by column chromatography cooled at 0°C with a DCM/MeOH (20/1) eluent, affording a yellowish powder with 31% yield.



(**49**)

Yield : 31% (Rf: 0.8)

Formula : $C_{42}H_{53}N_3O_{16}$

Mass : 907.3 g mol^{-1}

^{1}H-NMR (500 MHz, $CDCl_3$): δ[ppm] = 8.14 (s, 1H, H_7); 7.62 (d, $^3J_{9,13\text{-}10,12}$ = 8.03 Hz, 2H, H_9, H_{13}); 7.31 (d, $^3J_{10,12\text{-}9,13}$ = 8.03 Hz, 2H, H_{10}, H_{12}); 7.07 (s, 1H, H_{15}); 6.98 (s, 1H, H_{16}); 5.72 (dd, $^3J_{3\text{-}2}$ = 5.4 Hz, $^3J_{3\text{-}4}$ = 4.1 Hz, 2H, H_3); 5.48 (dd, $^3J_{4\text{-}3}$ = 4.6 Hz, $^3J_{4\text{-}5}$ = 6.2 Hz, 1H, H_4); 5.38 (d, $^3J_{2\text{-}3}$ = 5.4 Hz, 1H, H_2); 5.07 (m, 1H, H_5); 4.33 (dd, $^3J_{6a\text{-}5}$ = 3.2 Hz, $^2J_{6a\text{-}6b}$ = 12.3 Hz, 1H, H_{6a}); 4.25 (t, ^3J = 7.9 Hz, $C_{11}H_{23}$-C$\underline{H_2}$-N); 4.13 (dd, $^3J_{6b\text{-}5}$ = 5 Hz, $^2J_{6b\text{-}6a}$ = 12.3 Hz, 1H, H_{6b}); 2.24; 2.09; 2.06; 2.05 (m, 15H, -OC(O)CH_3); 1.86; 1.44; 1.36; 1.25 (m, 20H, CH_3-$C_{10}\underline{H_{20}}$-CH_2-N); 0.86 (t, ^3J= 6.5 Hz, 3H, CH_3).

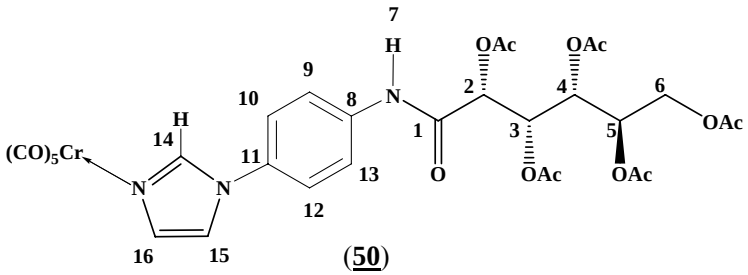
^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 221.3 (CO_{Trans}); 217.5 (CO_{Cis}); 192.5 (C_{14}); 170.7, 170.2, 169.8, 169.7, 169.3 (-O$\underline{C}$(O)CH_3); 164.5 (C_1); 137.6 (C_{11}); 129.5 (C_8, C_9, C_{13}); 124.9 (C_{15}); 121.4 (C_{16}); 120.5 (C_{10}, C_{12}); 71.6, 69, 68.8, 68.7 (C_2, C_3, C_4, C_5); 61.6 (C_6); 51.8 ($C_{11}H_{23}$-$\underline{C}H_2$-N); 31.8-22.6 (CH_3-$\underline{C_{10}}H_{20}$-CH_2-N); 20.7; 20.6, 20.3 (-OC(O)$\underline{C}H_3$); 14 ($\underline{C}H_3$).

FAB-MS (mNBA): calc. for $C_{42}H_{53}N_3O_{16}$ m/z: 907.28 found m/z = 908.3 $[M+H]^+$.

FT-IR (CH_2Cl_2): ν CO [cm^{-1}] = 2053 (m, A_1), 1924 (vs, E), 1895 (sh), 1753 (m, acetyl).

η[1]-*N'*-Pentacarbonyl-*N*-1H-[(2R,3R,4R,5S,6-penta-*O*-acetyl-hexanoylamino)-1,4-phenylene] chromium (**50**)

In a round flask covered with aluminium foil 125 mg (0,14 mmol) of the imidazolium salt **48** is dried for 15 min under vacuum and solved in 20 mL absolute DCM. 32 mg of silveroxide is given to the reaction mixture and stirred overnight. The black solution is filtrated and concentrated. The black solid is then dissolved in THF at -78°C. 46 mg of $Cr(CO)_5$(cyclooctene) complex is solved in 20 mL THF at -78°. The yellow chromium complex solution is transferred to the silver carbene one via canula or syringe. The reaction is left to reach room temperature as the -78°C cooling bath raises its temperature, at least overnight. The product is purified over silica gel by column chromatography cooled at 0°C with a DCM/MeOH (20/1) eluent, affording a yellowish powder with 10% yield.



(**50**)

Yield : 10 % (Rf: 0.8)

Formula : $C_{30}H_{29}CrN_3O_{16}$

Mass : 739,6 g.mol^{-1}

^{1}H-NMR (500 MHz, MeOD): δ[ppm] = 8.22 (s, 1H, H_{14}); 7.72 (d, $^3J_{9,13\text{-}10,12}$ = 8.82 Hz, 2H, H_9, H_{13}); 7.58 (s, 1H, H_{15}); 7.55 (d, $^3J_{10,12\text{-}9,13}$ = 8.82 Hz, 2H, H_{10}, H_{12}); 7.09 (s, 1H, H_{16}); 5.74 (dd, $^3J_{3\text{-}2}$ = 3.9 Hz, $^3J_{3\text{-}4}$ = 4.1 Hz, 2H, H_3); 5.56 (dd, $^3J_{4\text{-}3}$ = 4.3 Hz, $^3J_{4\text{-}5}$ = 6.8 Hz, 1H, H_4); 5.32 (d, $^3J_{2\text{-}3}$ = 3.8 Hz, 1H, H_2); 5.14 (ddd, $^3J_{5\text{-}4}$ = 6.7 Hz, $^3J_{5\text{-}6a}$ = 5.6 Hz, $^3J_{5\text{-}6b}$ = 3.2 Hz, 1H, H_5); 4.39 (dd, $^3J_{6a\text{-}5}$ = 3.2 Hz, $^2J_{6a\text{-}6b}$ = 12.4 Hz, 1H, H_{6a}); 4.21 (dd, $^3J_{6b\text{-}5}$ = 5.6 Hz, $^2J_{6b\text{-}6a}$ = 12.4 Hz, 1H, H_{6b}); 2.23; 2.13; 2.07; 2.06; 2.05 (m, 15H, -OC(O)CH_3).

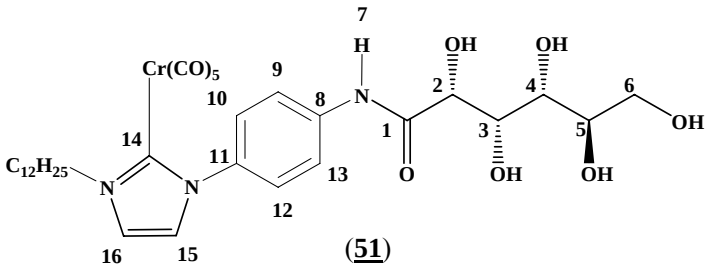
^{13}C-NMR (125 MHz, MeOD): δ [ppm] = 221.7 (CO_{Trans}); 216.2 (CO_{Cis}); 172.2, 171.5, 171.5, 171.4, 171.2 (-O<u>C</u>(O)CH_3); 167.3 (C_1); 141.1 (C_{11}); 139 (C_{14}); 135,8 (C_9, C_{13}); 133.9 (C_8); 124.9 (C_{15}); 123.1 (C_{10}, C_{12}); 121.2 (C_{16}); 74.2, 70.7, 70.1, 70.1 (C_2, C_3, C_4, C_5); 62.6 (C_6); 20.7; 20.6, 20.5, 20.4 (-OC(O)<u>C</u>H_3).

FT-IR (CH_2Cl_2): ν CO [cm^{-1}] = 2053 (m, A_1), 1926 (vs, E), 1892 (sh), 1754 (m, acetyl).

FAB-MS (mNBA): calc. for $C_{30}H_{29}CrN_3O_{16}$ m/z: 739.5579 found m/z = 739.1 $[M]^+$.

Pentacarbonyl{*N'*-dodecyl-*N*-[(2R,3R,4R,5S,6-pentahydroxy-hexanoylamino)-1,4-phenylene]-2,3-dihydro-imidazol-2-ylidene}chromium (**51**)

In a coolable schlenk tube 0.350 g (0.36 mmol) of [4-(Imidazol-2-ylidene)phenyl(2,3,4,5,6)(pentaacetetoxy)gluconamide]pentacarbonylchromium is solved in 15 mL of absolute MeOH at -5°C. 15 mL of a saturated NH_3 solution in MeOH is given, and the reaction is left to run overnight. The product is obtained after purification over silica gel column chromatography, at -5°C with a DCM/MeOH (8/2) eluent, affording a light yellow powder with 68% yield.



(**51**)

Yield : 68% (Rf: 0.81)

Formula : $C_{32}H_{42}CrN_3O_{11}$

Mass : 697.2 g mol^{-1}

^{1}H-NMR (500 MHz, MeOD): δ[ppm] = 7.86 (d, $^3J_{9,13\text{-}10,12}$ = 8.3 Hz, 2H, H_9, H_{13}); 7.46 (s, 1H, H_{15}); 7.36 (d, $^3J_{10,12\text{-}9,13}$ = 8.2 Hz, 2H, H_{10}, H_{12}); 7.28 (s, 1H, H_{16}); 4.42 (br s, 1H, H_3); 4.35 (br s, 2H, H_4, H_2); 4.26 (br s, 1H, H_5); 3.82 (br s, 2H, $C_{11}H_{23}$-C$\underline{H_2}$-N); 3.75 (br s, 1H, H_{6a}); 3.69 (br s, 1H, H_{6b}); 1.93, 1.50, 1.45, 1.43 (m, 20H, CH_3-$C_{10}\underline{H_{20}}$-CH_2-N); 0.93 (C$\underline{H_3}$).

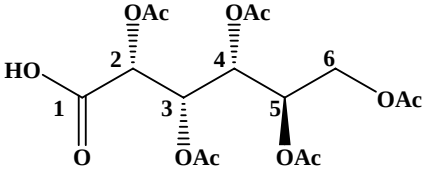
^{13}C-NMR (125 MHz, MeOD): δ [ppm] = 222.7 (CO_{Trans}); 219 (CO_{Cis}); 191.9 (C_1); 173.7 (C_1); 136.5 (C_{14}), 140.3 (C_{11}), 138.7 (C_8), 130.4 (C_{10}, C_{12}); 126.7 (C_{16}); 123.5 (C_{15}); 121.5 (C_9, C_{13}); 75.9, 74.2, 73, 72.1 (C_2, C_3, C_4, C_5); 64.5 (C_6); 52.8 ($C_{11}H_{23}$-C$\underline{H_2}$-N); 32–23 (CH_3-$\underline{C_{10}}H_{20}$-CH_2-N); 14.2 (C$\underline{H_3}$).

FT-IR (CH_2Cl_2): ν CO [cm^{-1}] = 2053 (m, A_1), 1922 (vs, E), 1891 (sh).

ESI-MS (mode: negativ) (MeOH): calc. for $C_{32}H_{42}CrN_3O_{11}$ m/z: 697.6934 found m/z = 732.2034 $[M+Cl]^-$; 696.2258 $[M-H]^-$.

Appendix

VII Appendix



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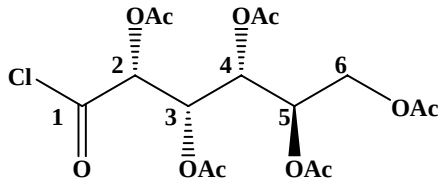

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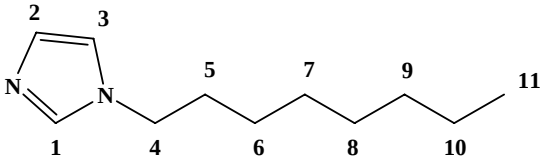

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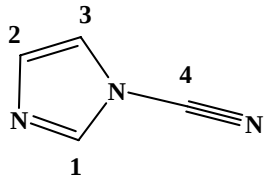

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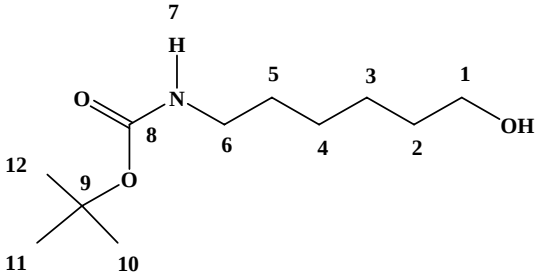

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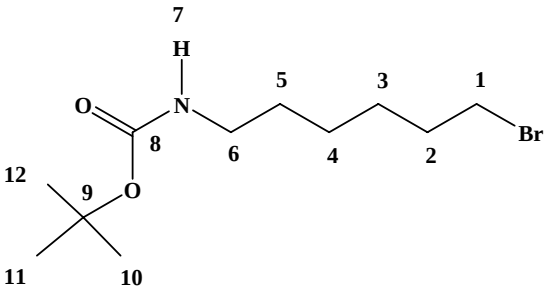

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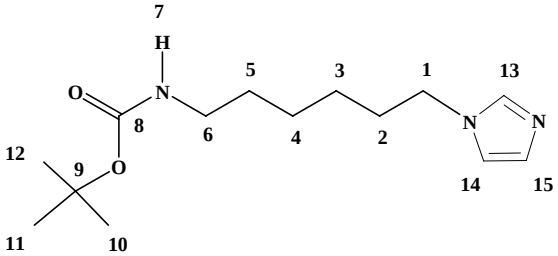

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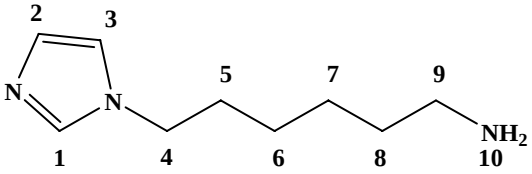

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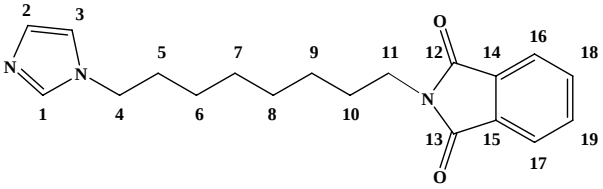

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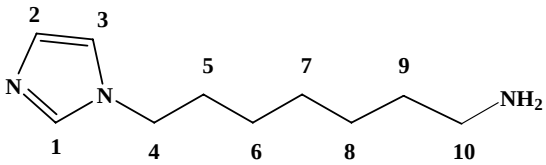

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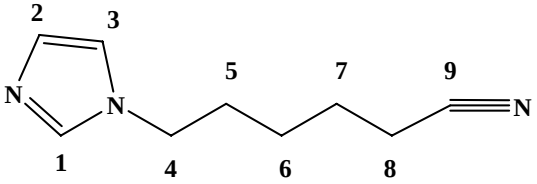

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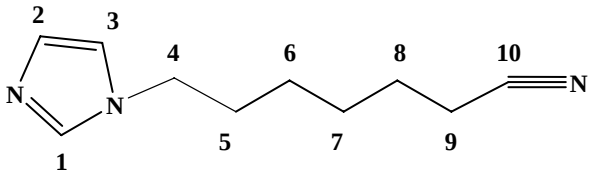

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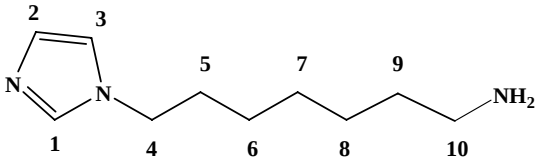

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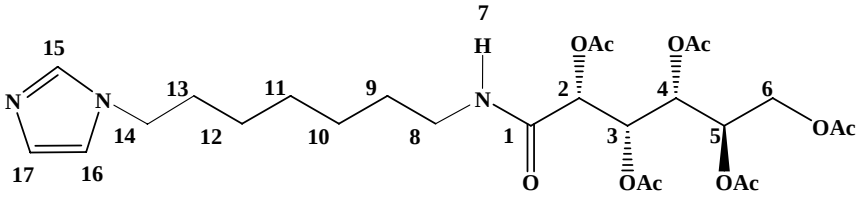

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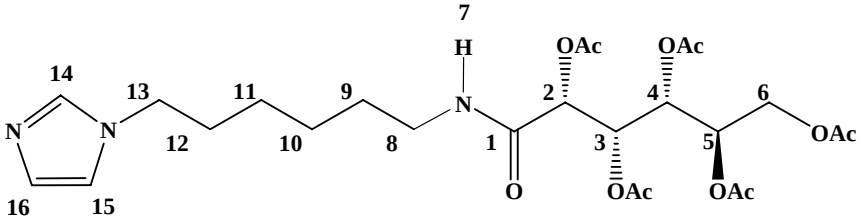

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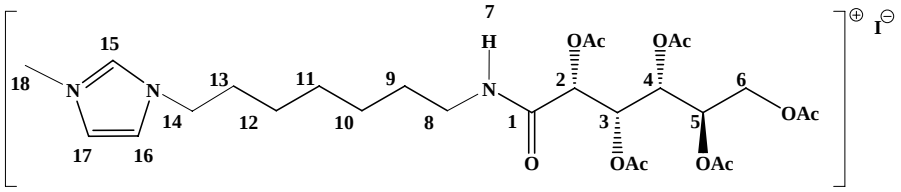

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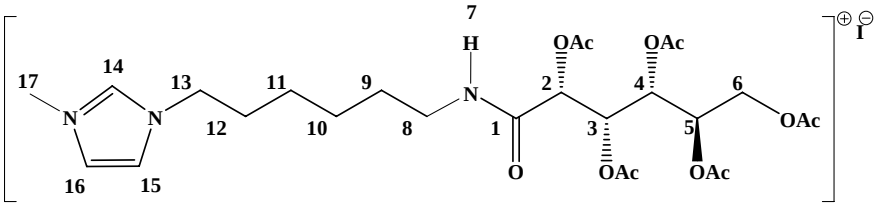

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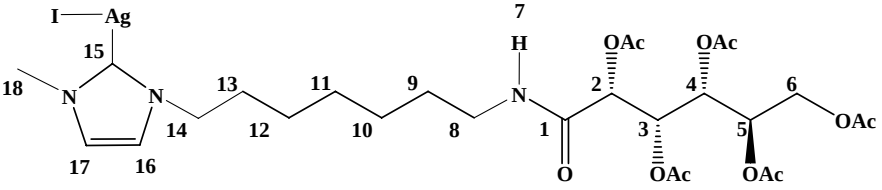

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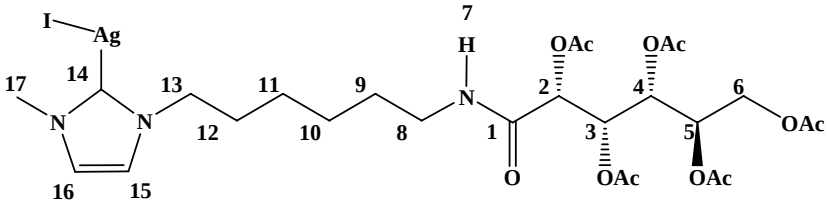

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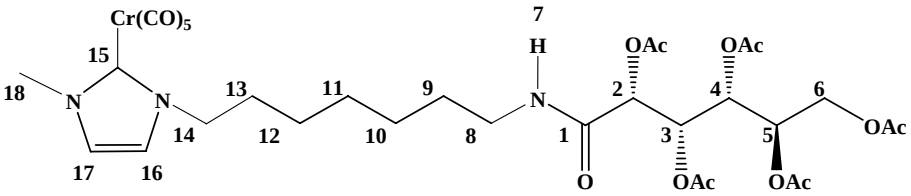

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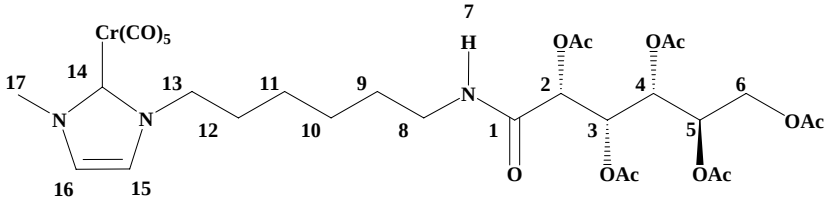

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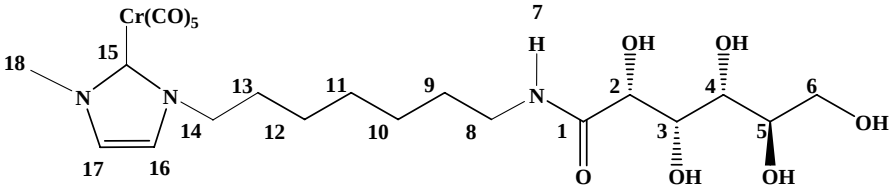

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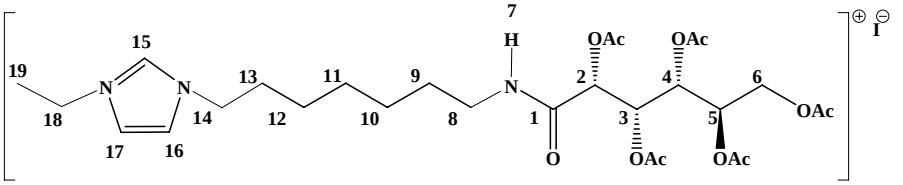

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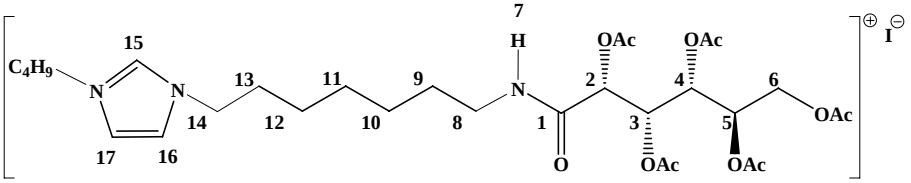

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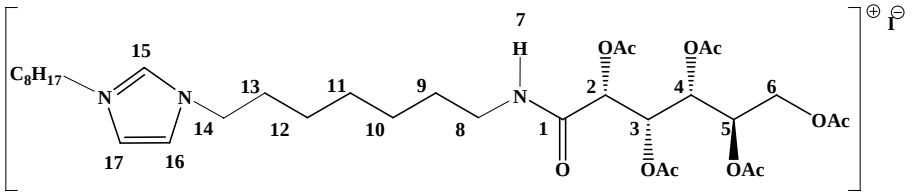

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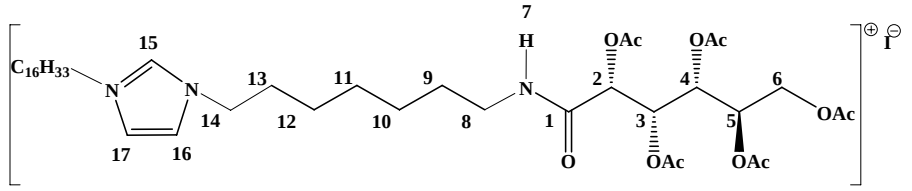

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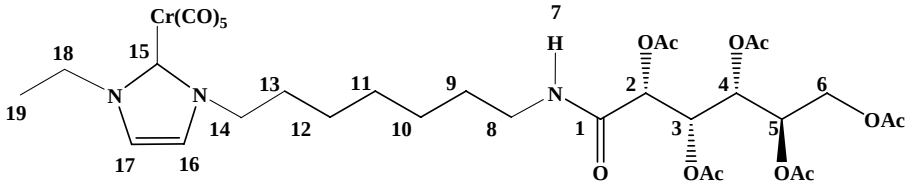

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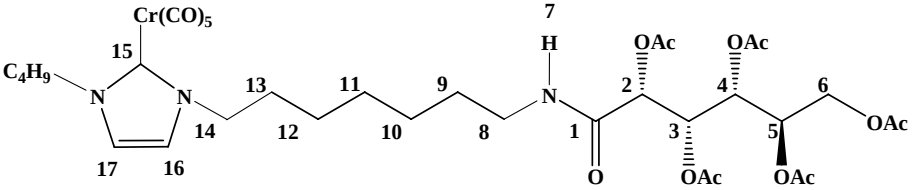

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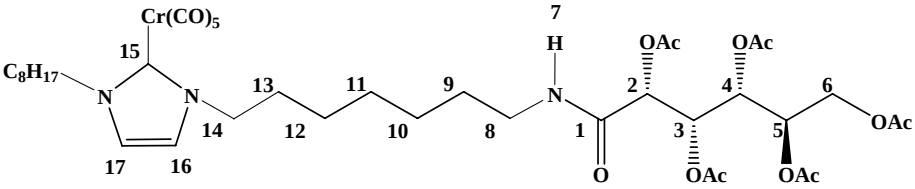

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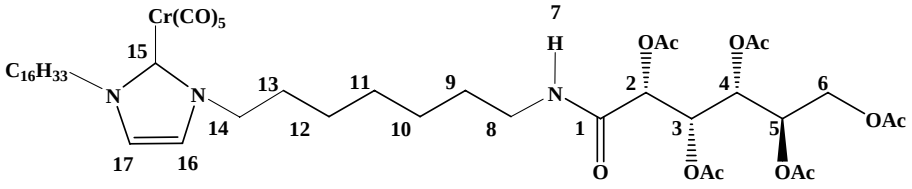

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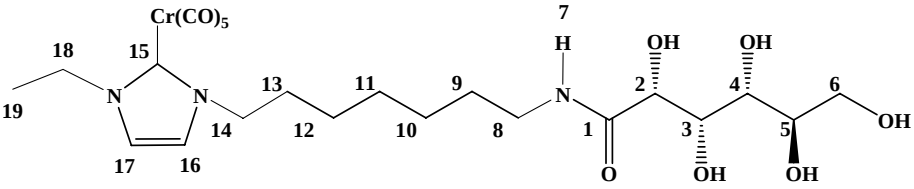

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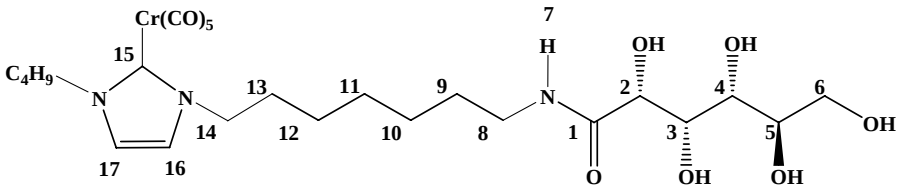

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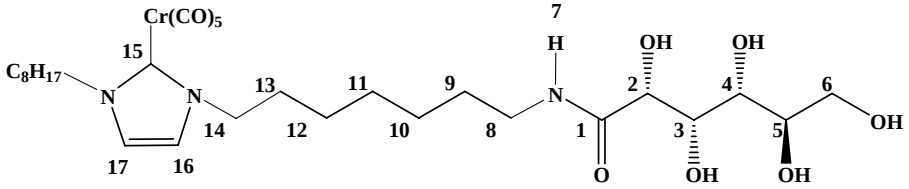

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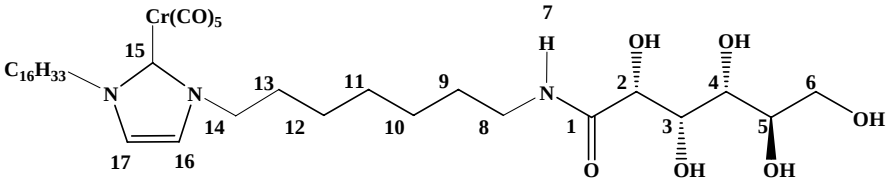

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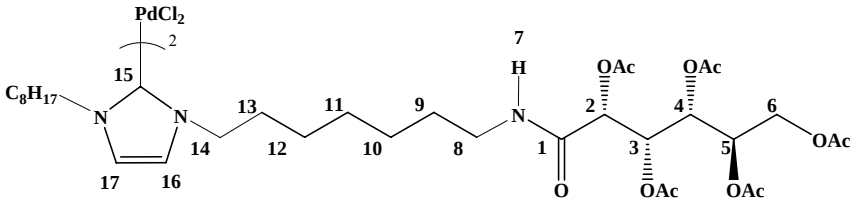

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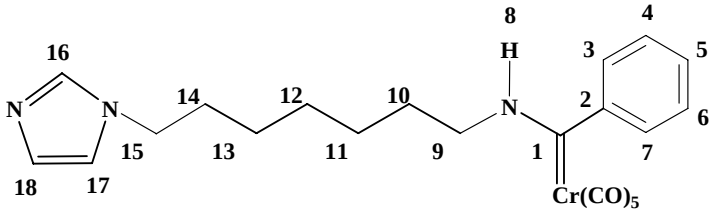

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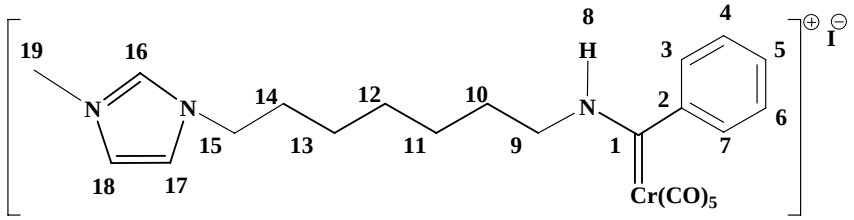

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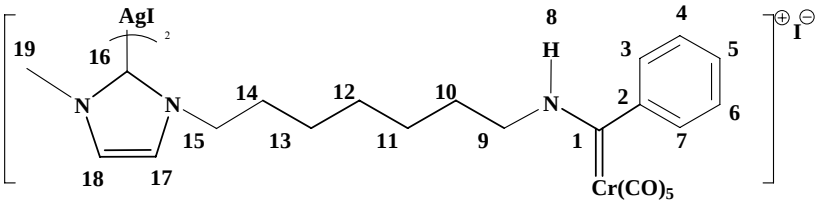

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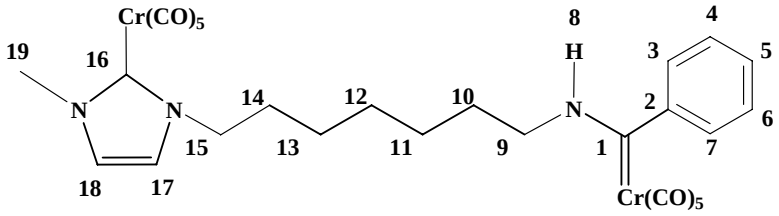

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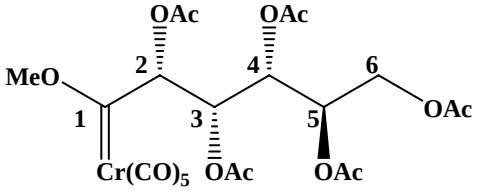

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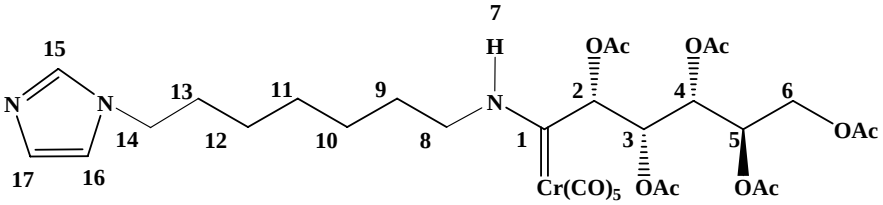

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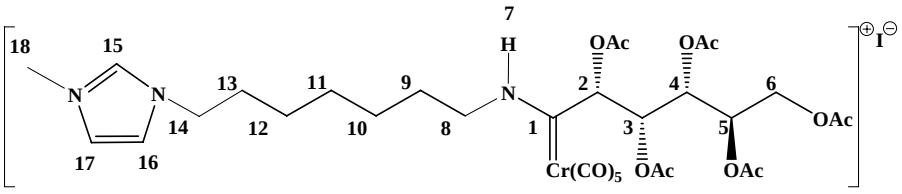

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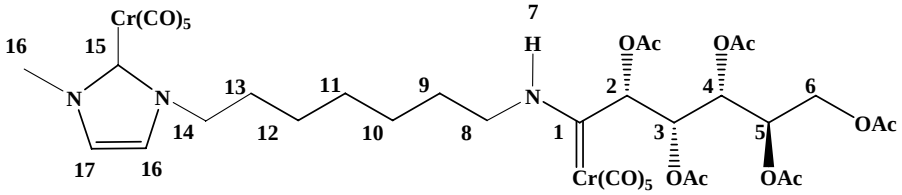

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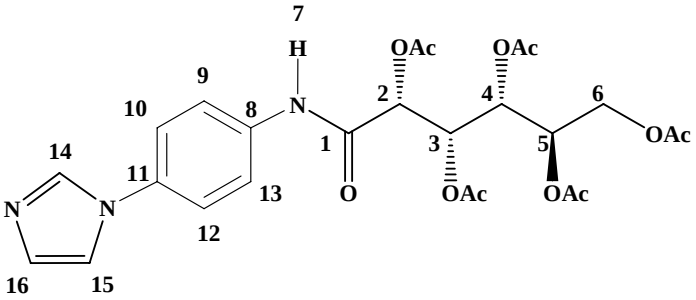

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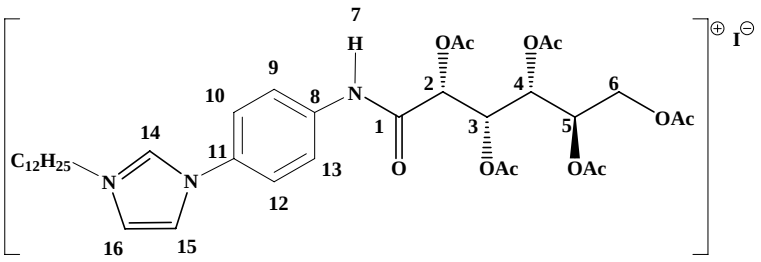

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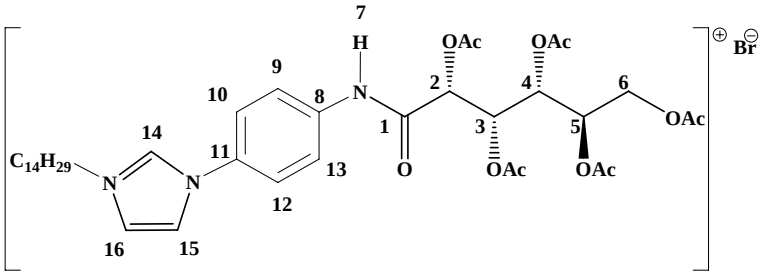

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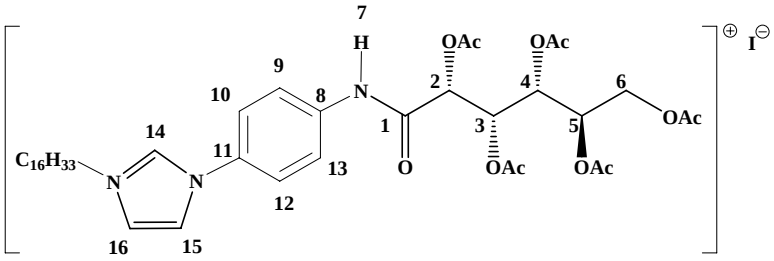

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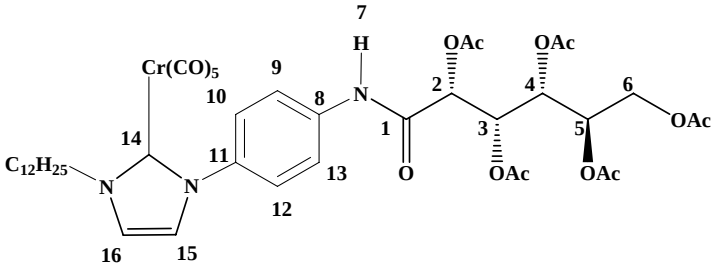
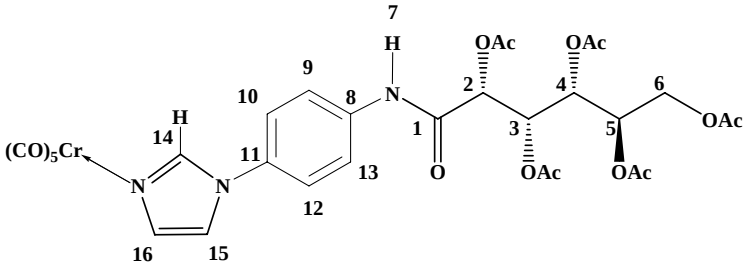
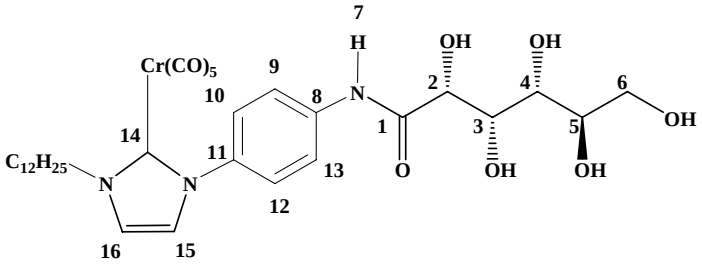


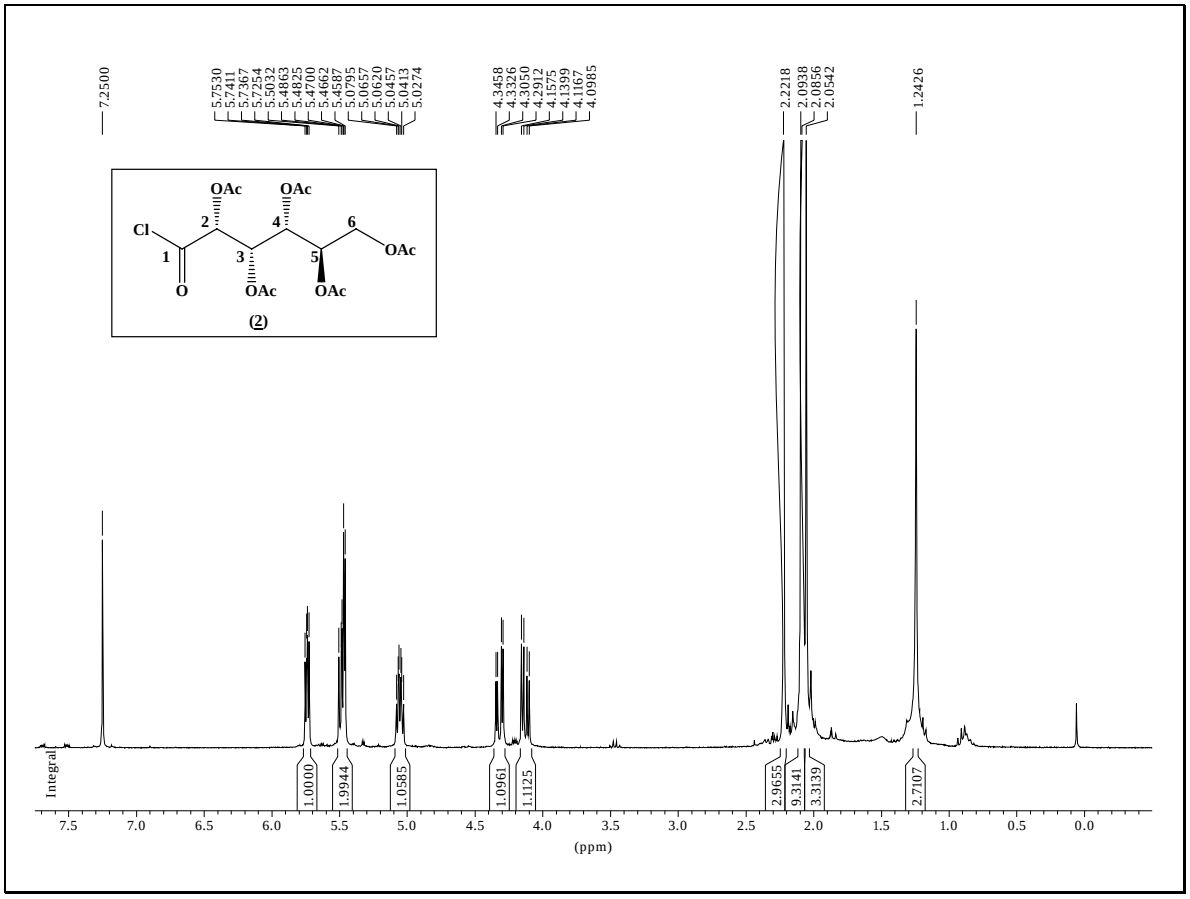
(**49**)

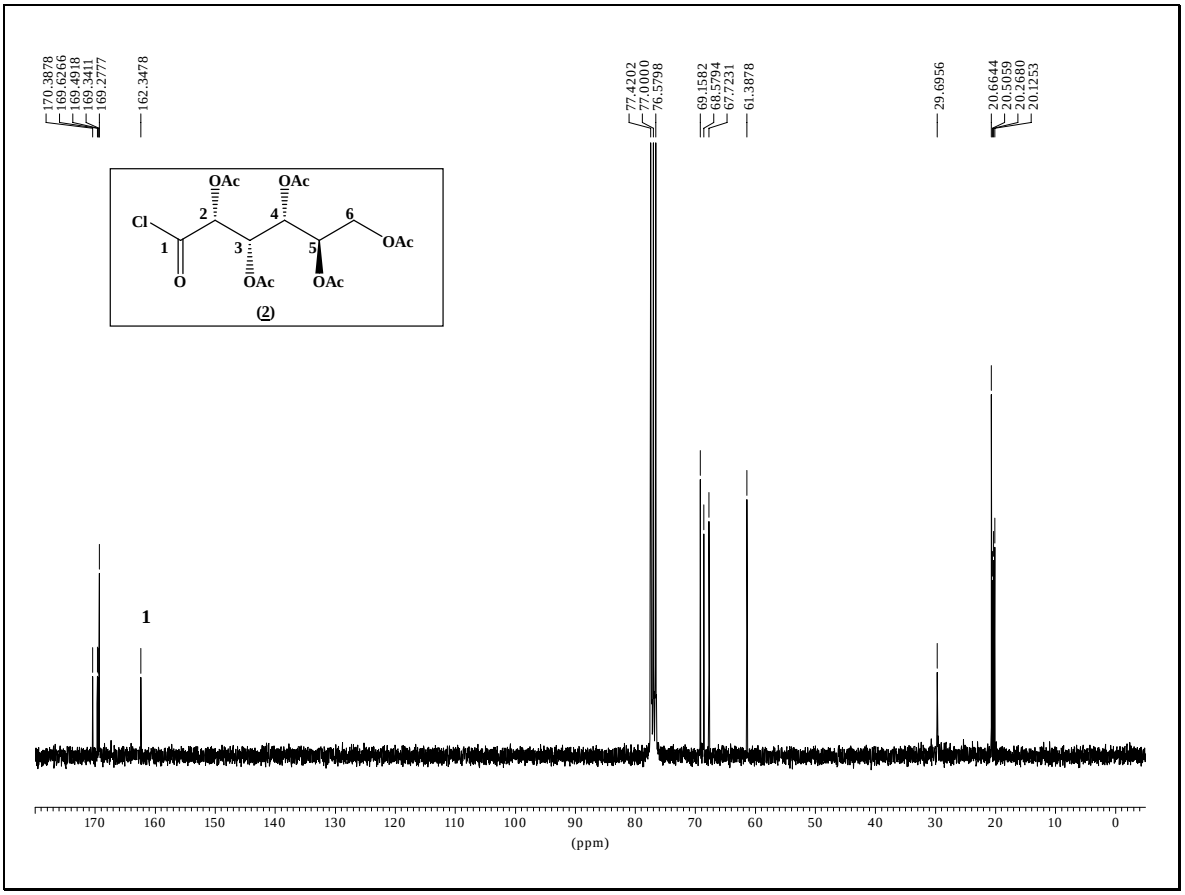

7
H
OAc
OAc
9
10
8
N
2
4
6
H
14
1
3
5
OAc
(CO)5Cr
11
13
O
OAc
OAc
N
N
12
16
15

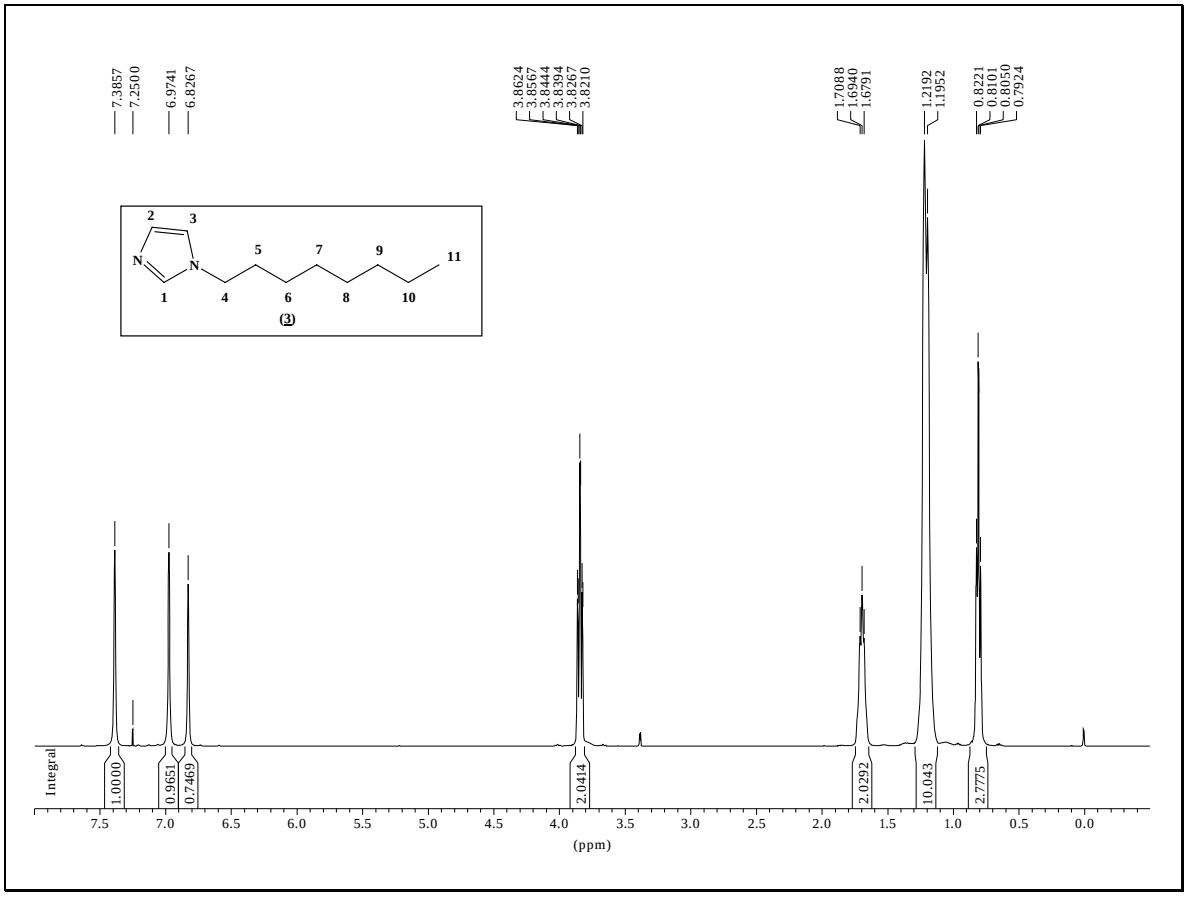
(**50**)

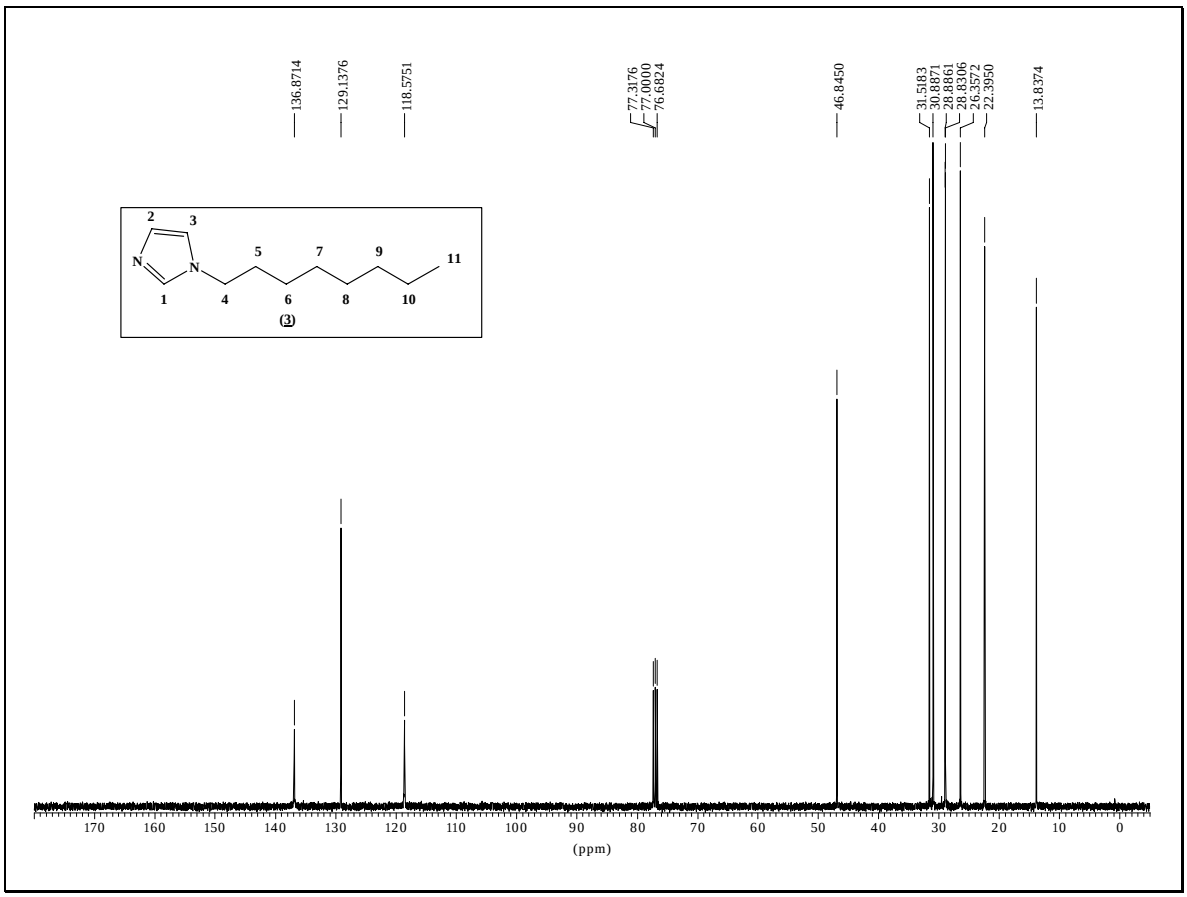

7
H
OH
OH
Cr(CO)5
9
10
8
N
2
4
6
14
1
3
5
OH
C12H25
11
13
O
OH
OH
N
N
12
16
15

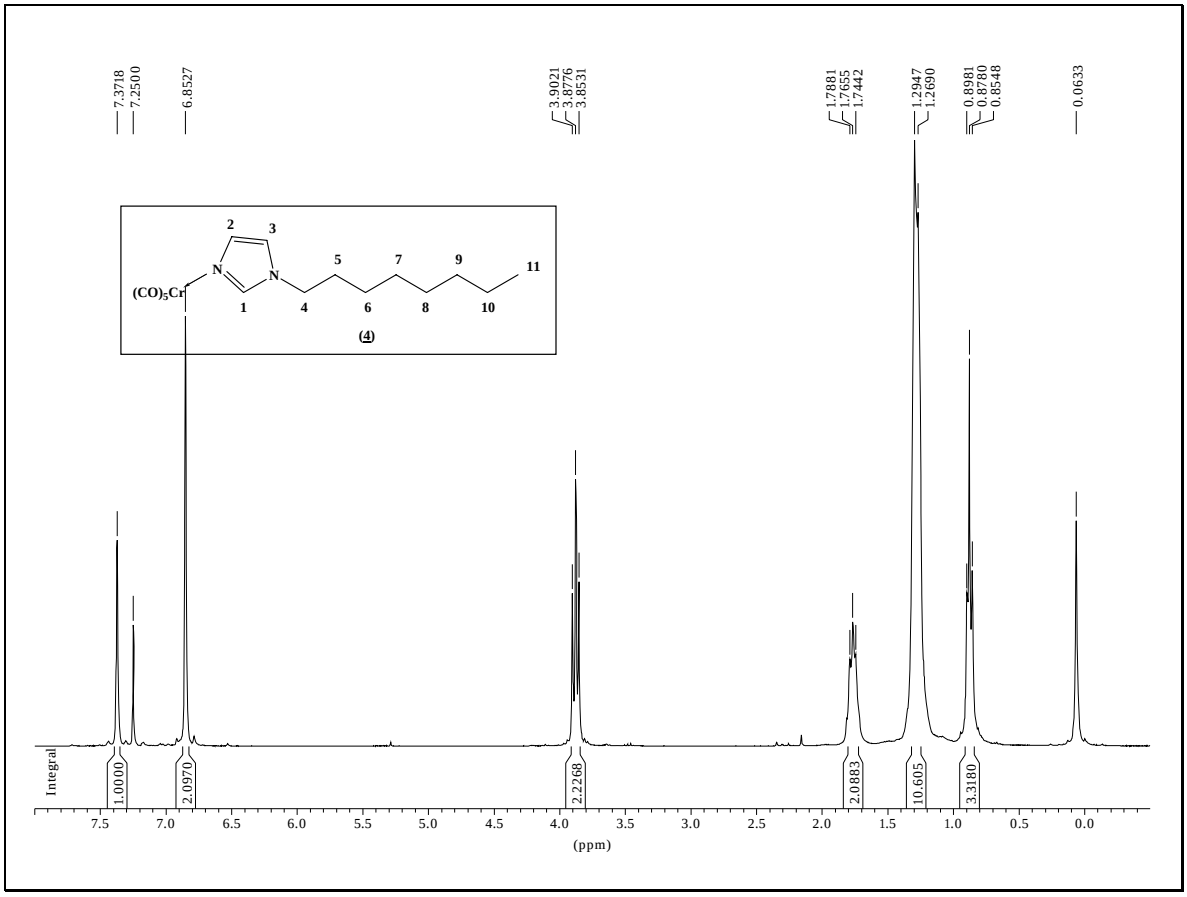
(**51**)

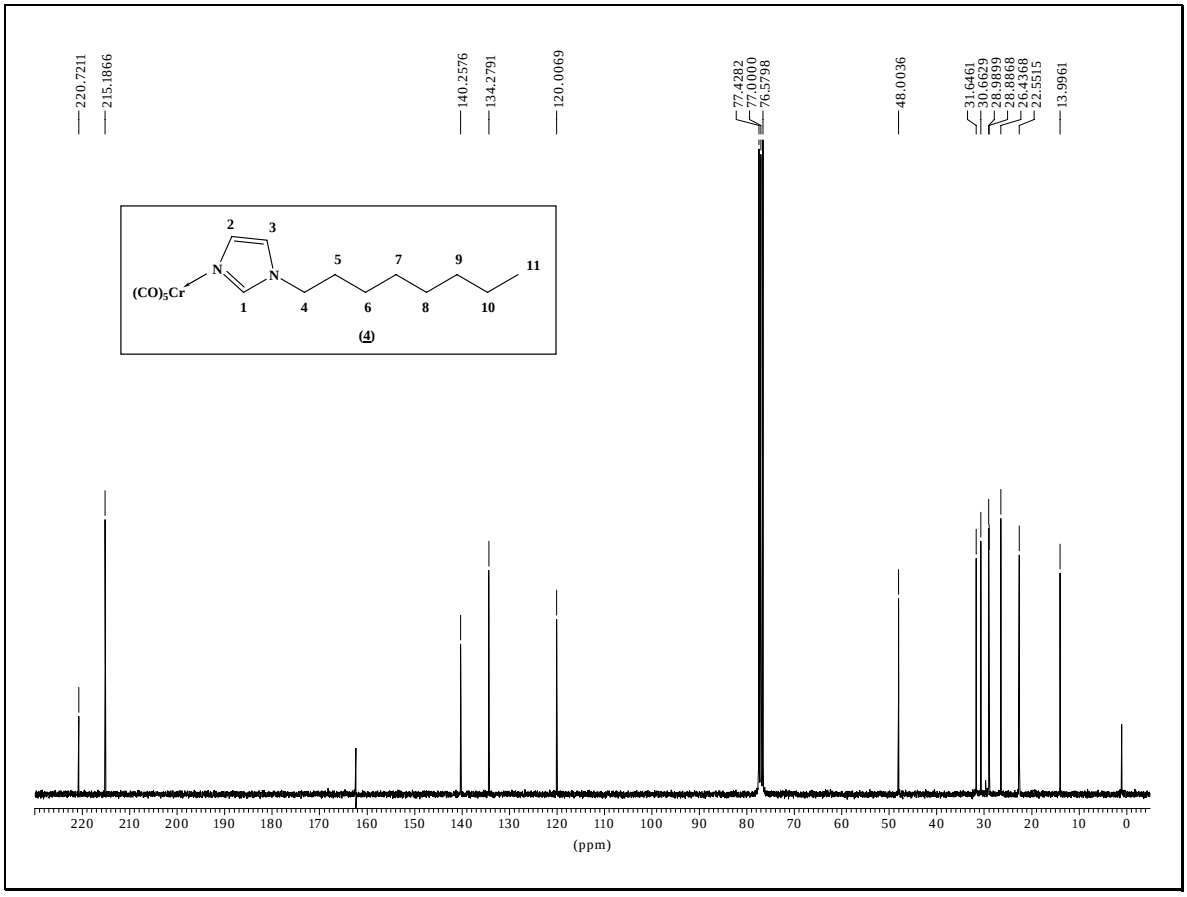

7.2500
5.7530
5.7411
5.7367
5.7254
5.5032
5.4863
5.4825
5.4700
5.4662
5.4587
5.0795
5.0657
5.0620
5.0457
5.0413
5.0274
4.3458
4.3326
4.3050
4.2912
4.1575
4.1399
4.1167
4.0985
2.2218
2.0938
2.0856
2.0542
1.2426
OAc
OAc
Cl
2
4
6
1
3
5
OAc
O
OAc
OAc
(2)
Integral
1.0000
1.9944
1.0585
1.0961
1.1125
2.9655
9.3141
3.3139
2.7107
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

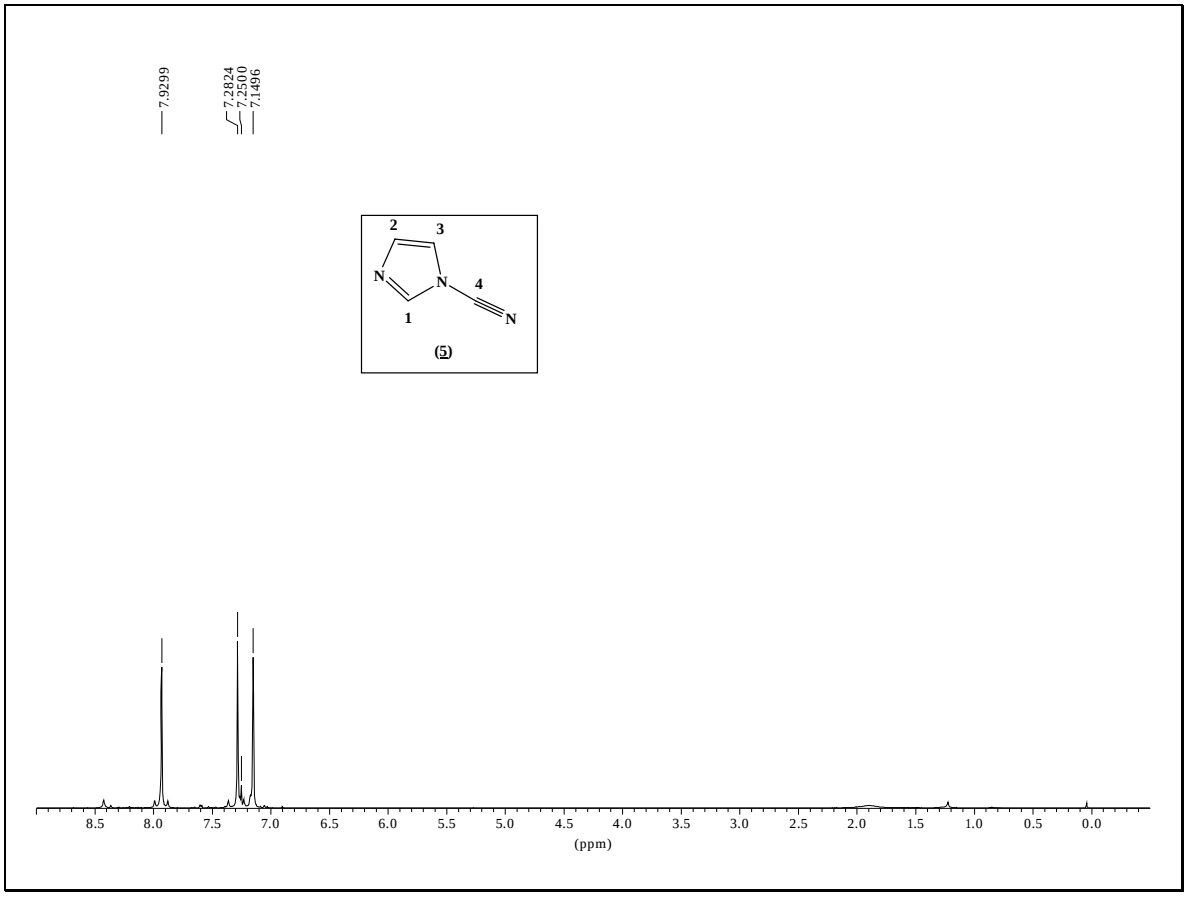

170.3878
169.6266
169.4918
169.3411
169.2777
162.3478
77.4202
77.0000
76.5798
69.1582
68.5794
67.7231
61.3878
29.6956
20.6644
20.5059
20.2680
20.1253
OAc
OAc
Cl
2
4
6
1
3
5
OAc
O
OAc
OAc
(2)
1
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

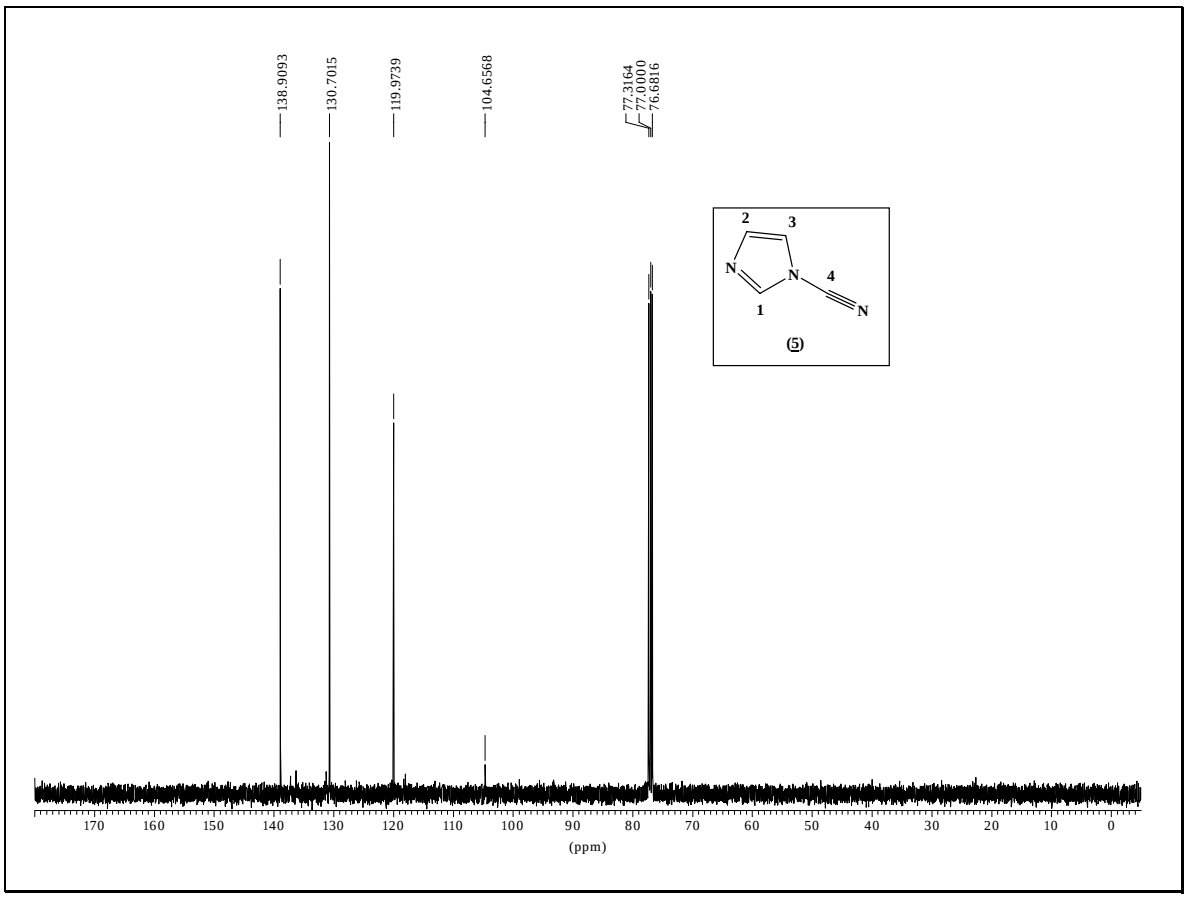

7.3857
7.2500
6.9741
6.8267
3.8624
3.8567
3.8444
3.8394
3.8267
3.8210
1.7088
1.6940
1.6791
1.2192
1.1952
0.8221
0.8101
0.8050
0.7924
2 3
N N
1 4 5 6 7 8 9 10 11
(3)
Integral
1.0000
0.9651
0.7469
2.0414
2.0292
10.043
2.7775
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

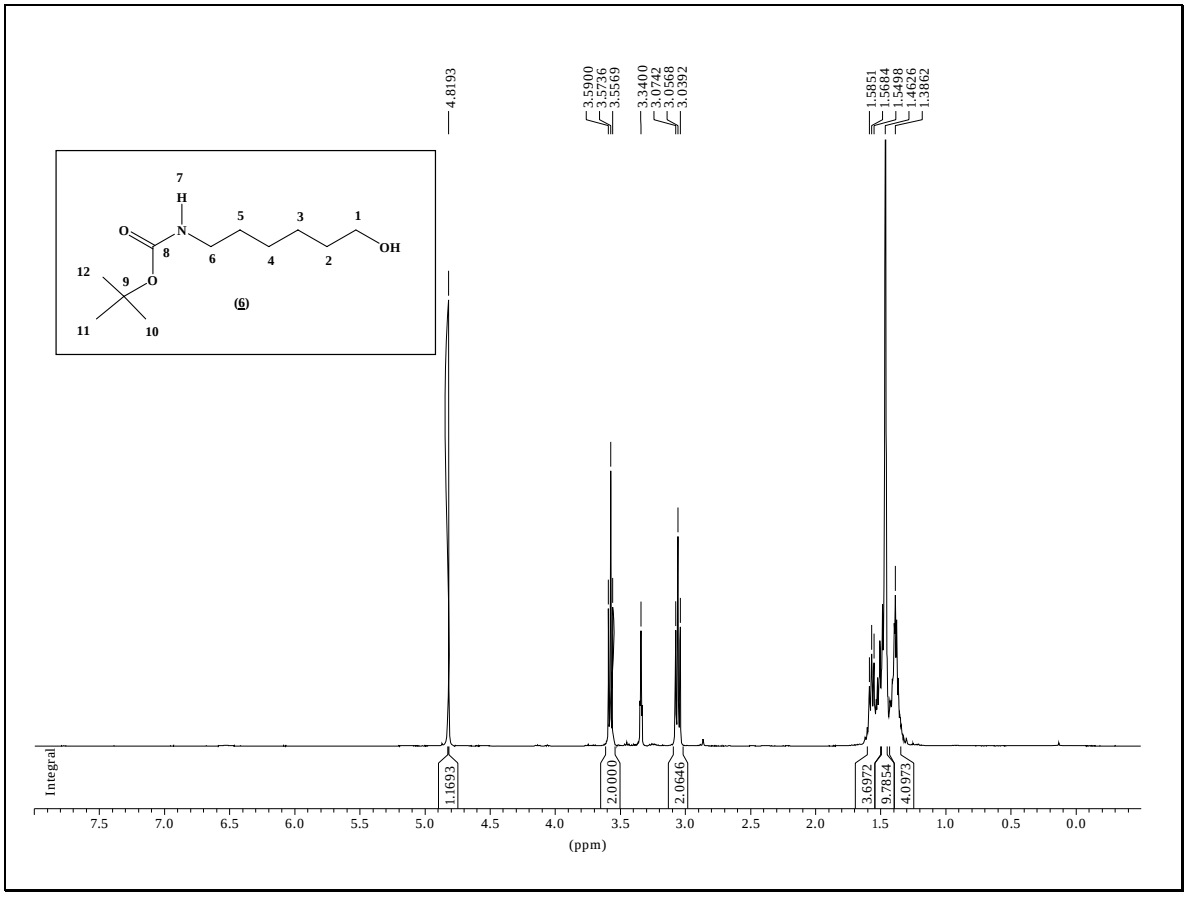

136.8714
129.1376
118.5751
77.3176
77.0000
76.6824
46.8450
31.5183
30.8871
28.8861
28.8306
26.3572
22.3950
13.8374
2 3
N N
1 4 5 6 7 8 9 10 11
(3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

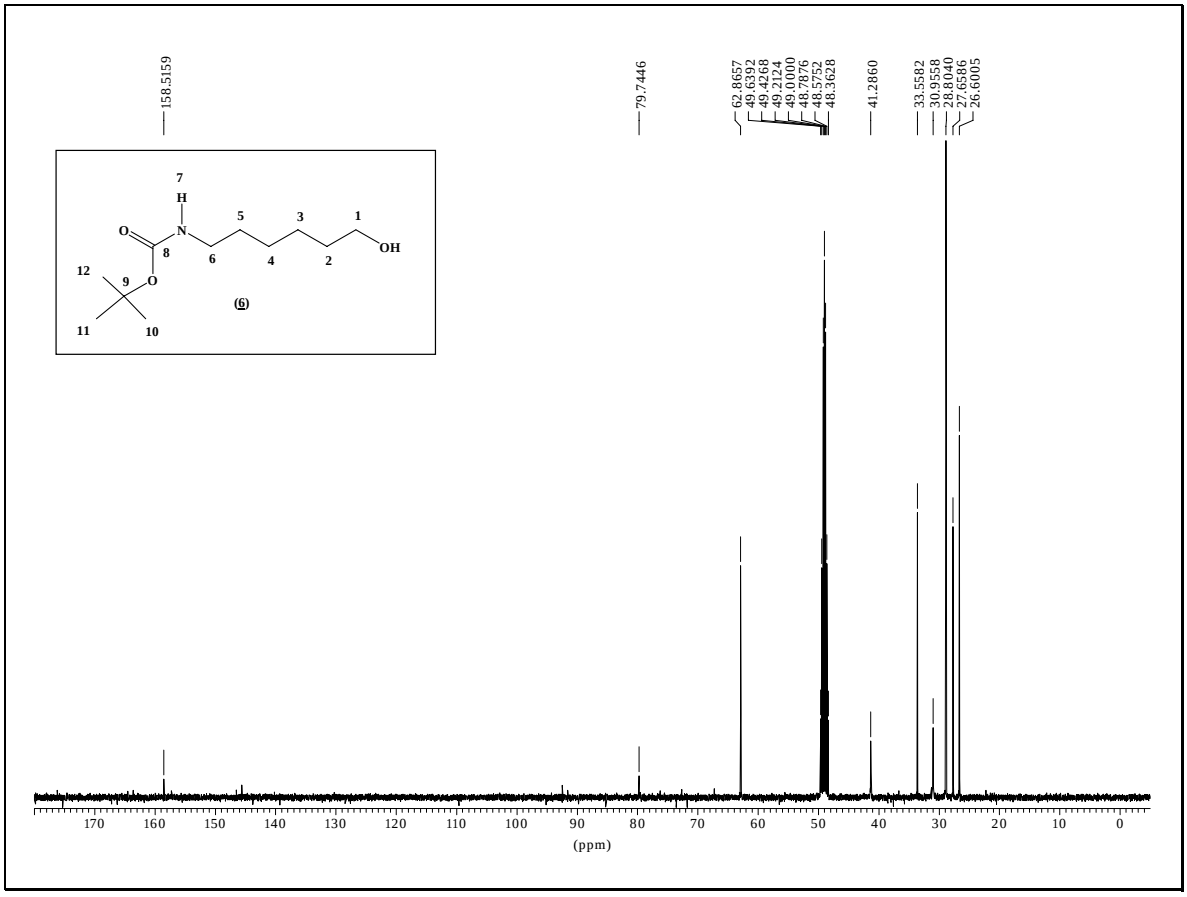

7.3718
7.2500
6.8527
3.9021
3.8776
3.8531
1.7881
1.7655
1.7442
1.2947
1.2690
0.8981
0.8780
0.8548
0.0633
(CO)5Cr
(4)
Integral
1.0000
2.0970
2.2268
2.0883
10.605
3.3180
(ppm)

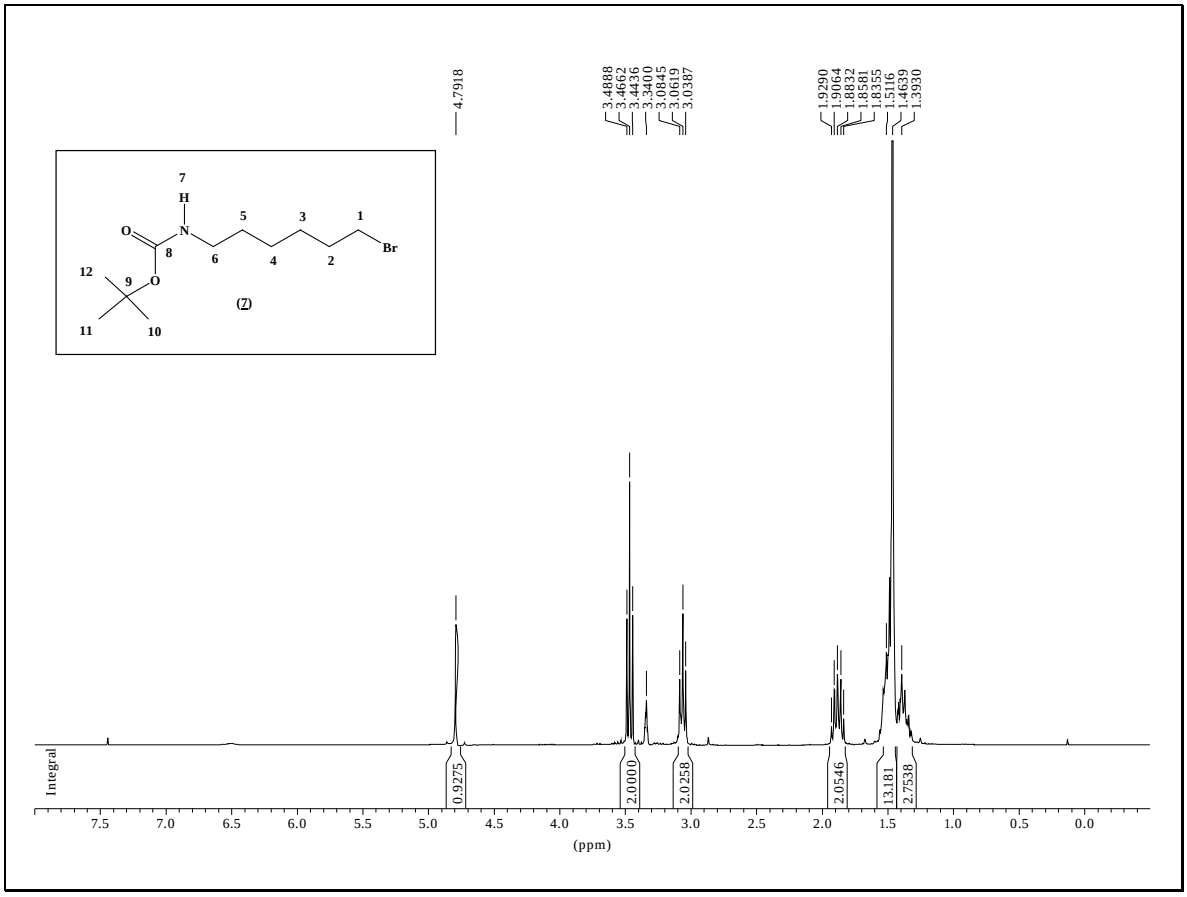

220.7211
215.1866
140.2576
134.2791
120.0069
77.4282
77.0000
76.5798
48.0036
31.6461
30.6629
28.9899
28.8868
26.4368
22.5515
13.9961
(CO)5Cr
(4)
(ppm)

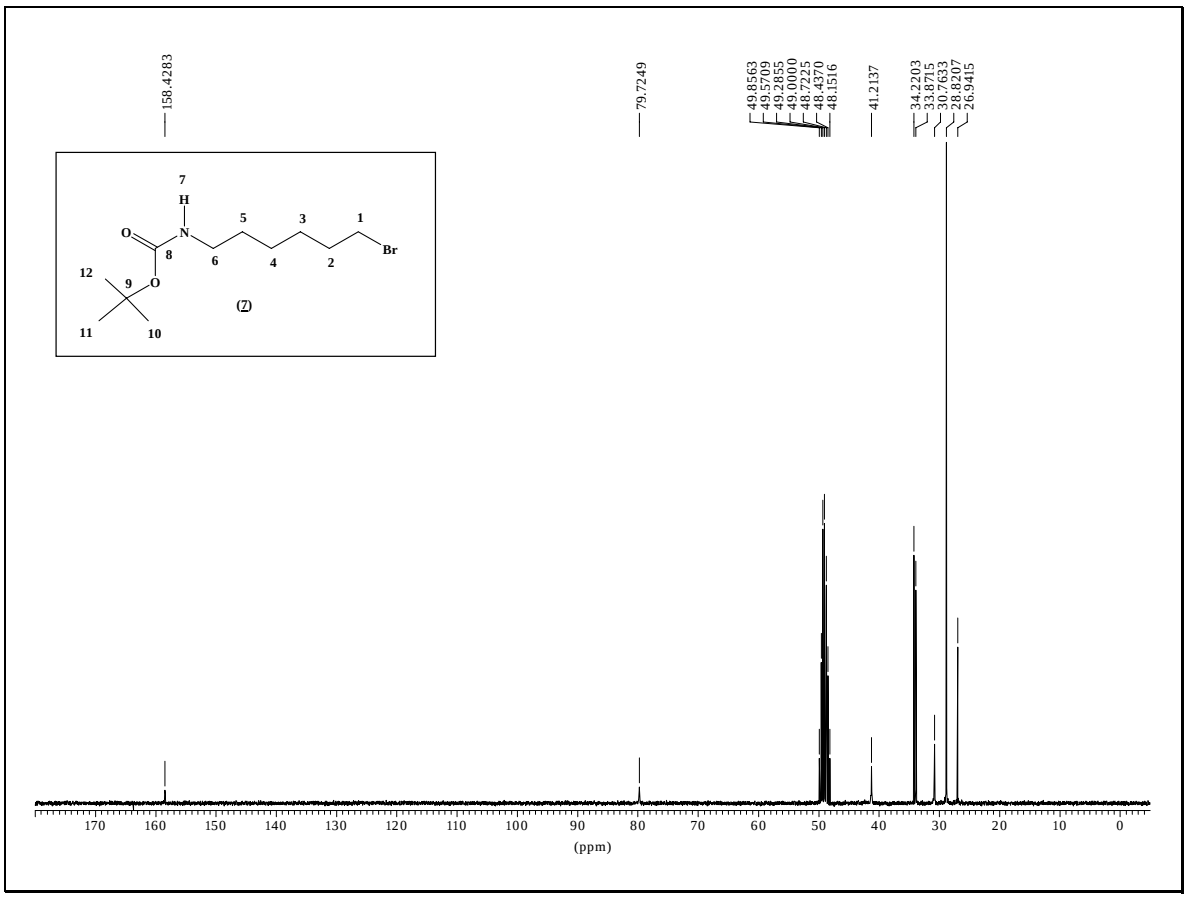

7.9299
7.2824
7.2500
7.1496
2
3
N
N
4
1
N
(5)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

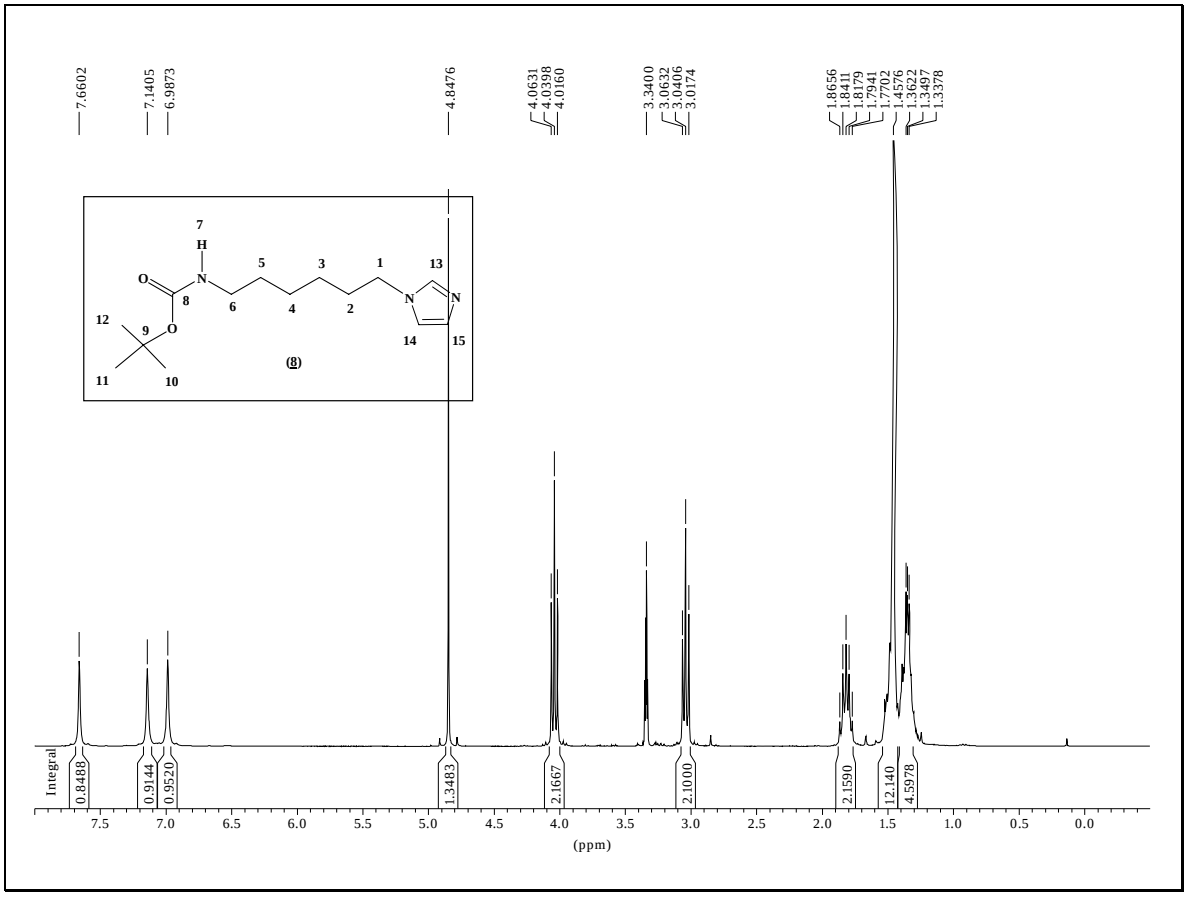

138.9093
130.7015
119.9739
104.6568
77.3164
77.0000
76.6816
2
3
N
N
4
1
N
(5)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

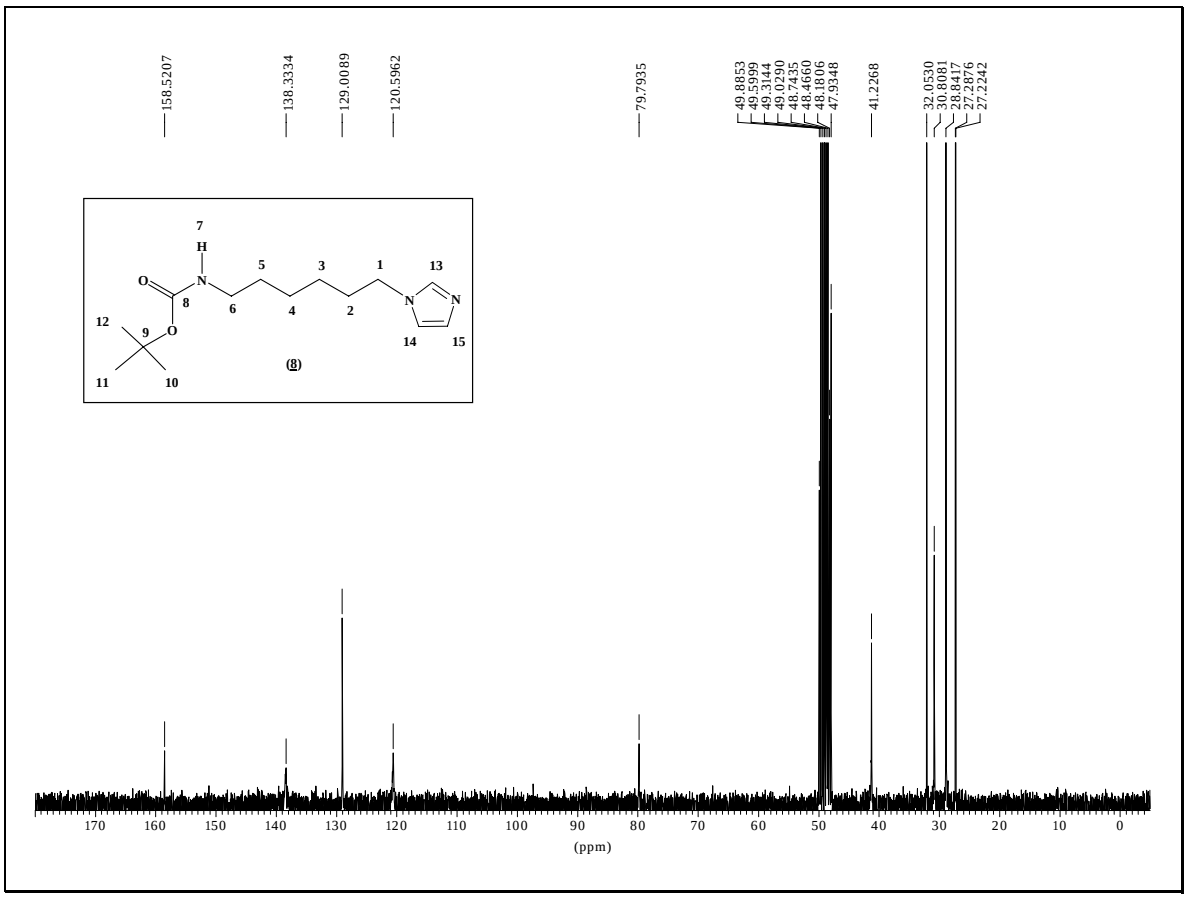

4.8193
3.5900
3.5736
3.5569
3.3400
3.0742
3.0568
3.0392
1.5851
1.5684
1.5498
1.4626
1.3862
(6)
Integral
1.1693
2.0000
2.0646
3.6972
9.7854
4.0973
(ppm)

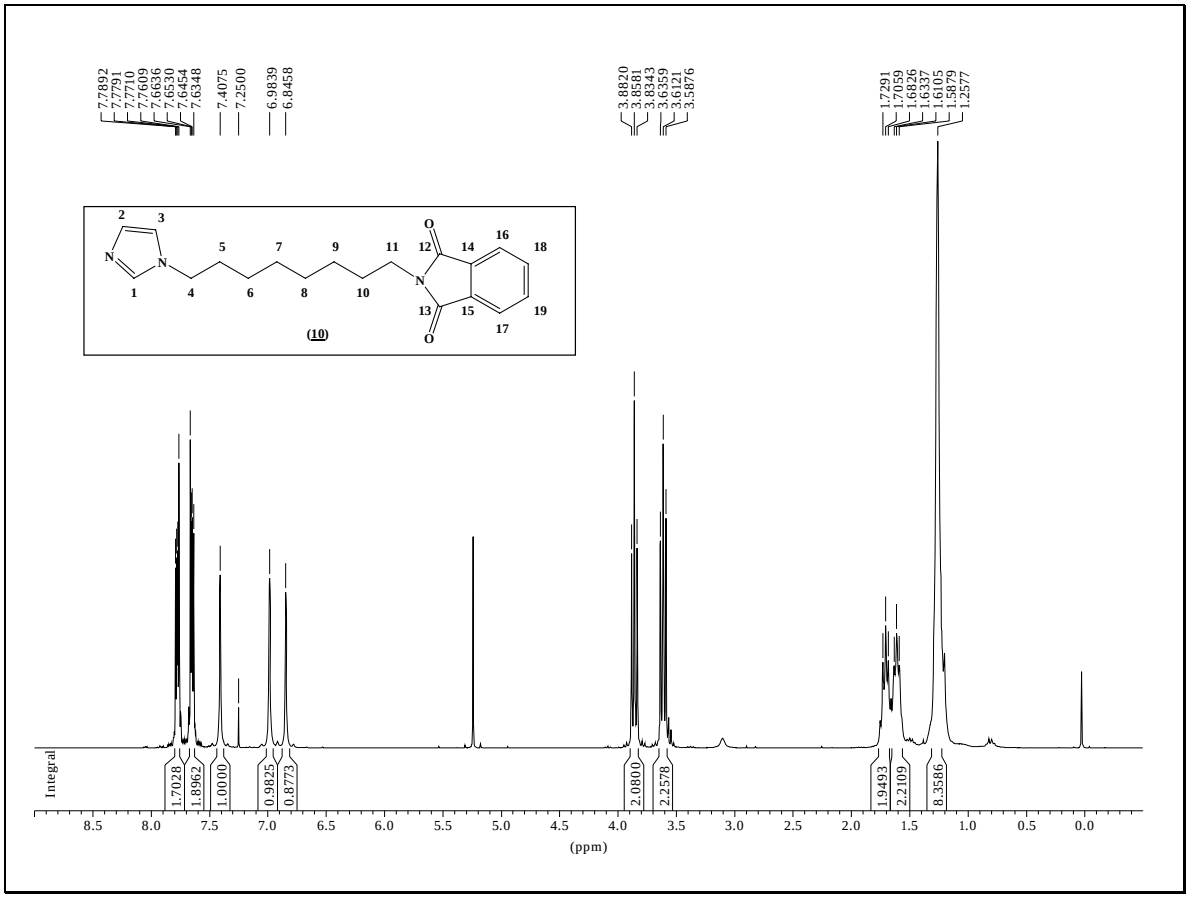

158.5159
79.7446
62.8657
49.6392
49.4268
49.2124
49.0000
48.7876
48.5752
48.3628
41.2860
33.5582
30.9558
28.8040
27.6586
26.6005
(6)
(ppm)

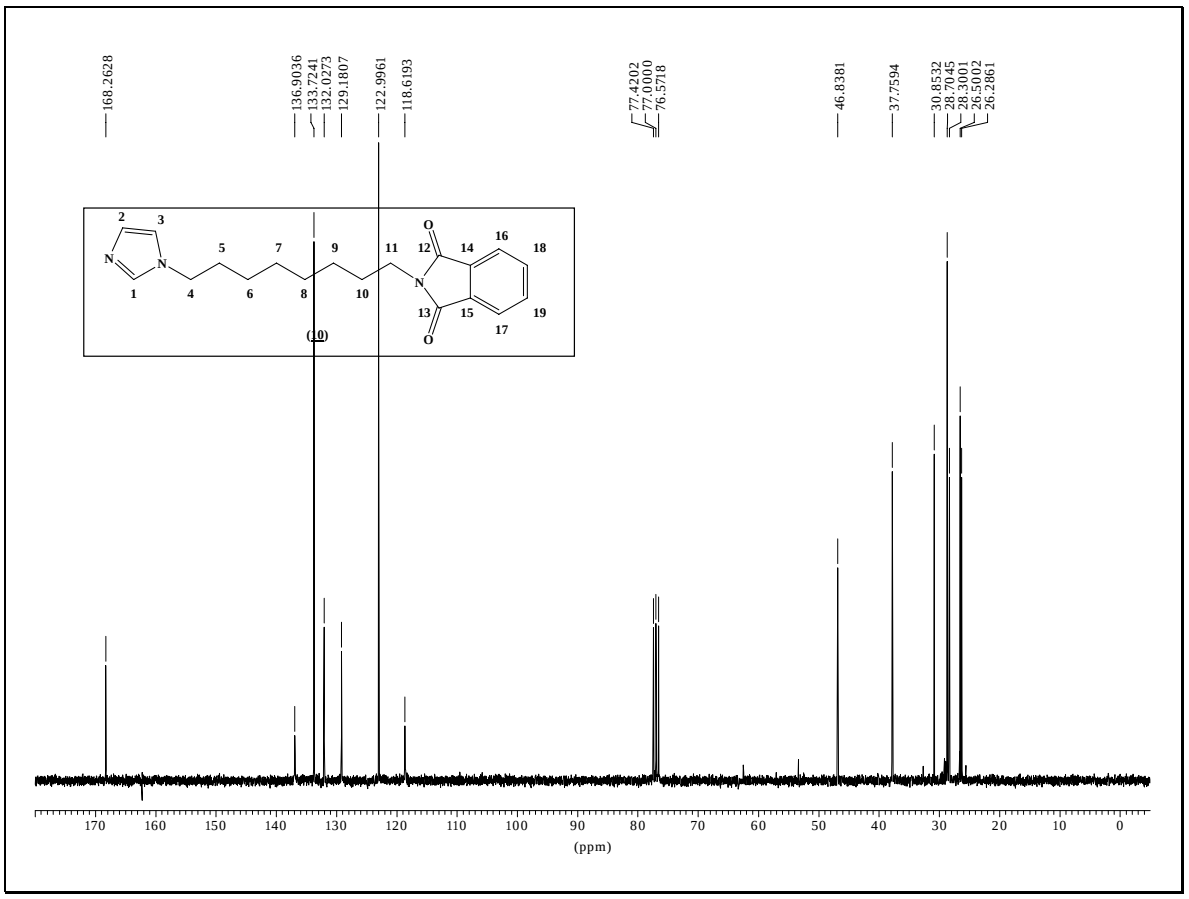

4.7918
3.4888
3.4662
3.4436
3.3400
3.0845
3.0619
3.0387
1.9290
1.9064
1.8832
1.8581
1.8351
1.5116
1.4639
1.3930
(Z)
Integral
0.9275
2.0000
2.0258
2.0546
13.181
2.7538
(ppm)

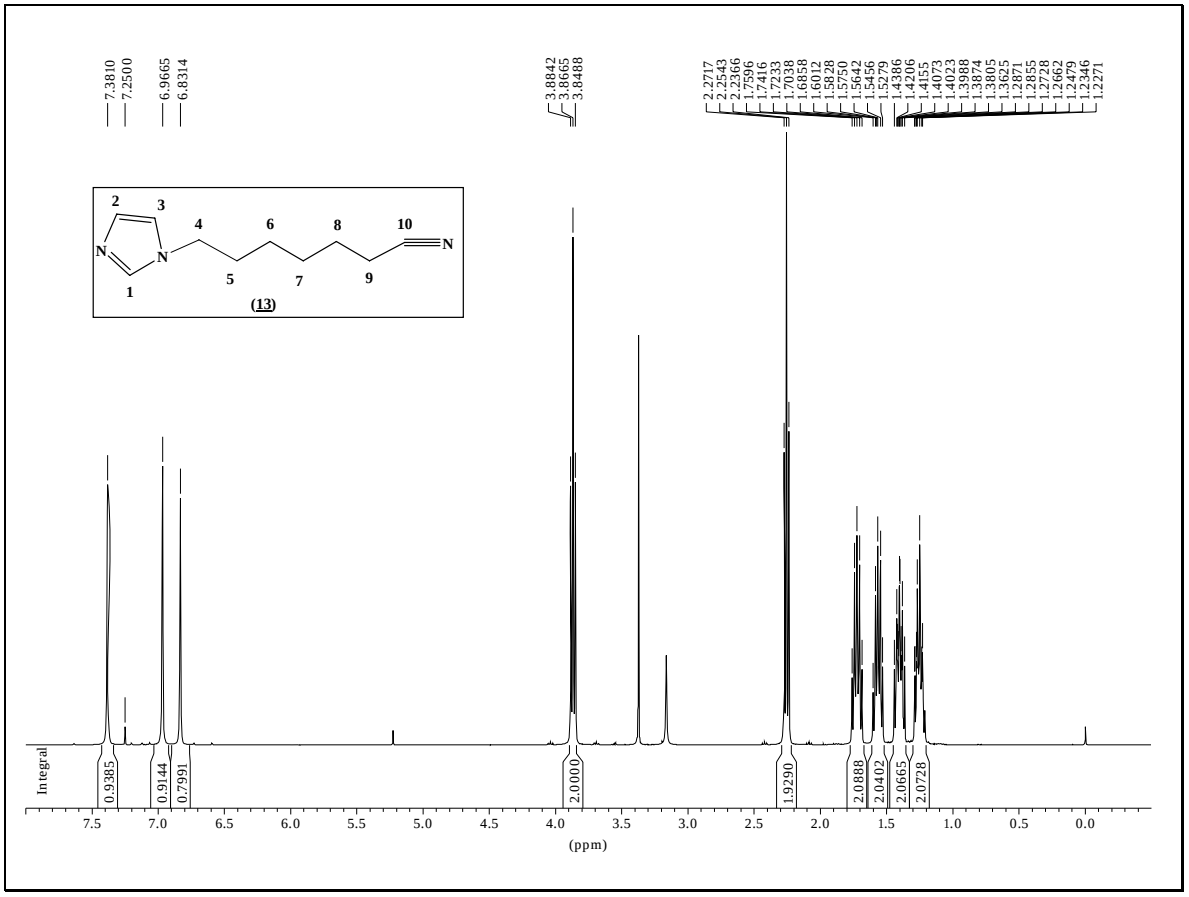

158.4283
79.7249
49.8563
49.5709
49.2855
49.0000
48.7225
48.4370
48.1516
41.2137
34.2203
33.8715
30.7633
28.8207
26.9415
(Z)
(ppm)

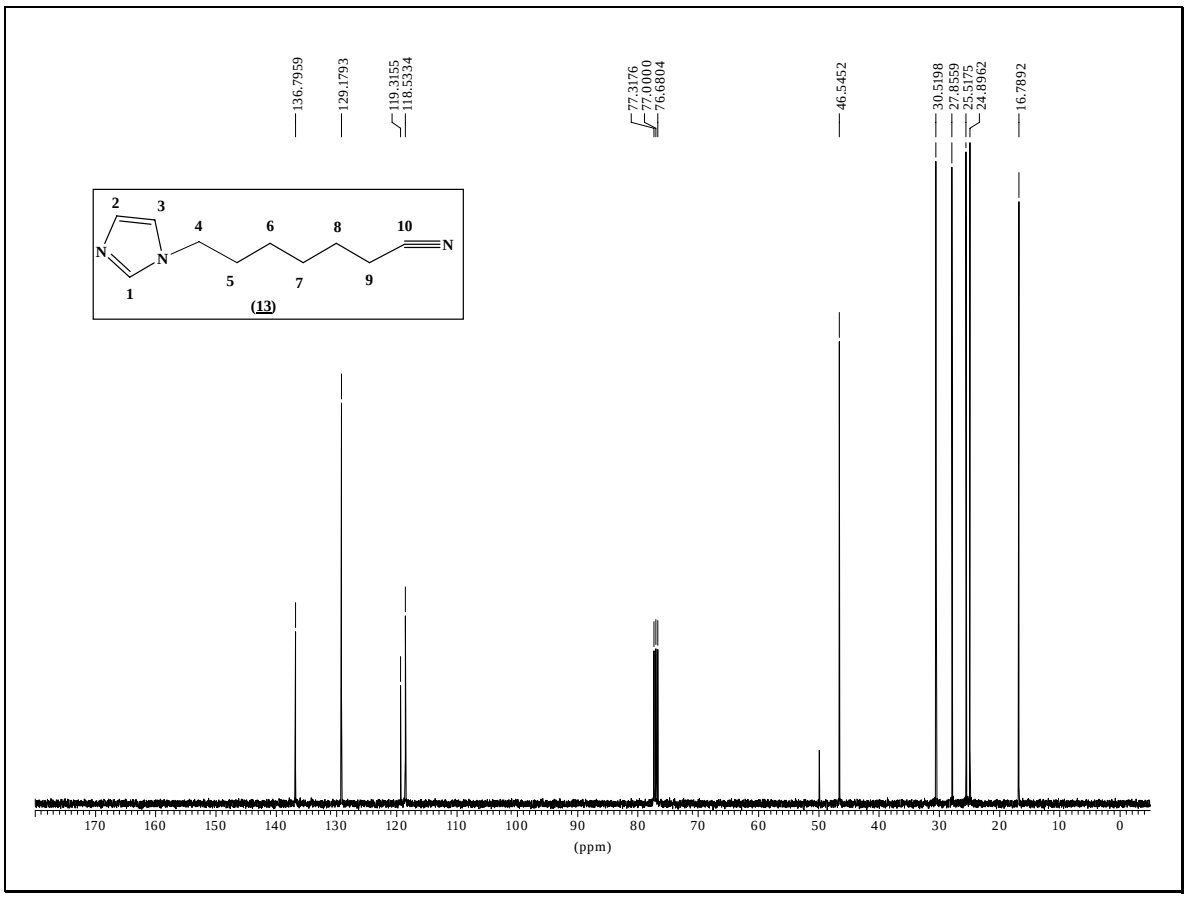

7.6602
7.1405
6.9873
4.8476
4.0631
4.0398
4.0160
3.3400
3.0632
3.0406
3.0174
1.8656
1.8411
1.8179
1.7941
1.7702
1.4576
1.3622
1.3497
1.3378
(8)
Integral
0.8488
0.9144
0.9520
1.3483
2.1667
2.1000
2.1590
12.140
4.5978
(ppm)

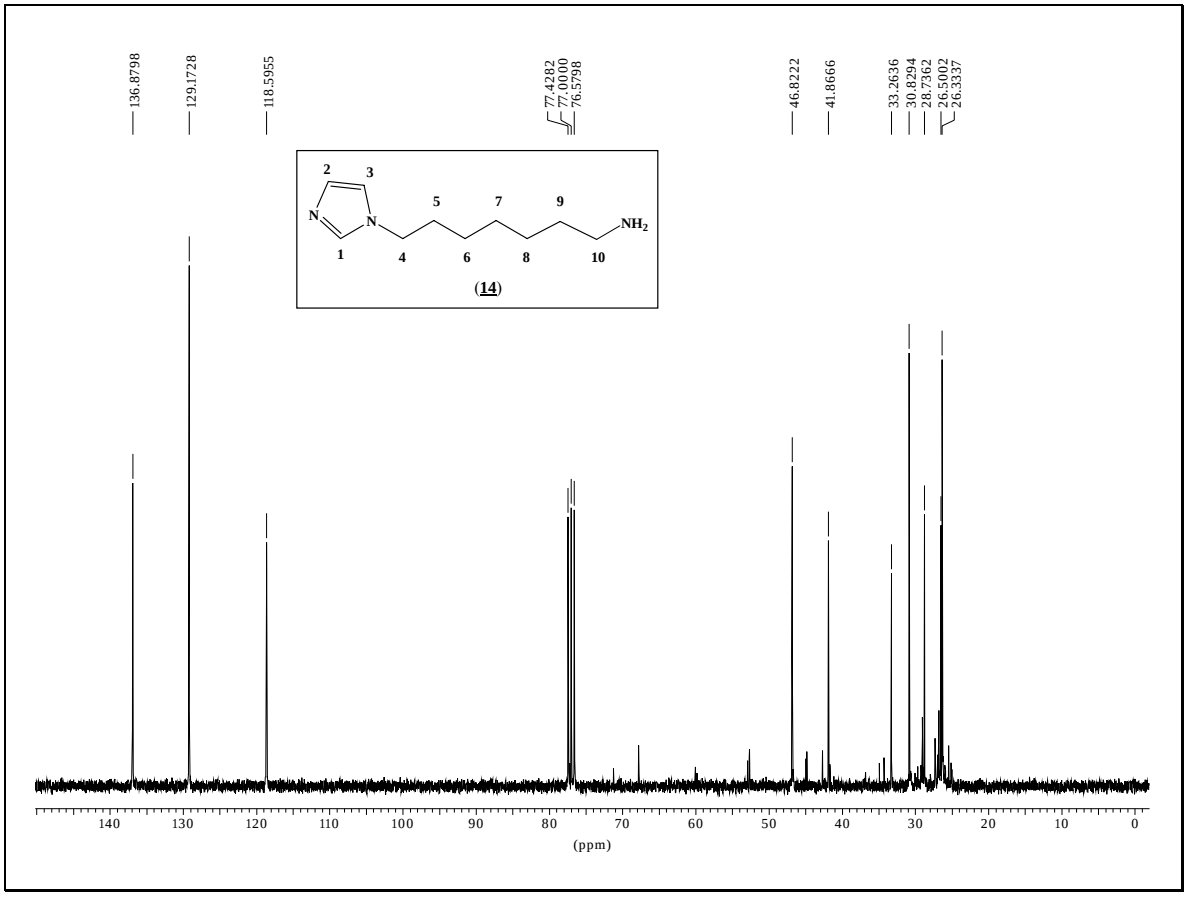

158.5207
138.3334
129.0089
120.5962
79.7935
49.8853
49.5999
49.3144
49.0290
48.7435
48.4581
48.1806
47.9348
41.2268
32.0530
30.8081
28.8417
27.2876
27.2242
(8)
(ppm)

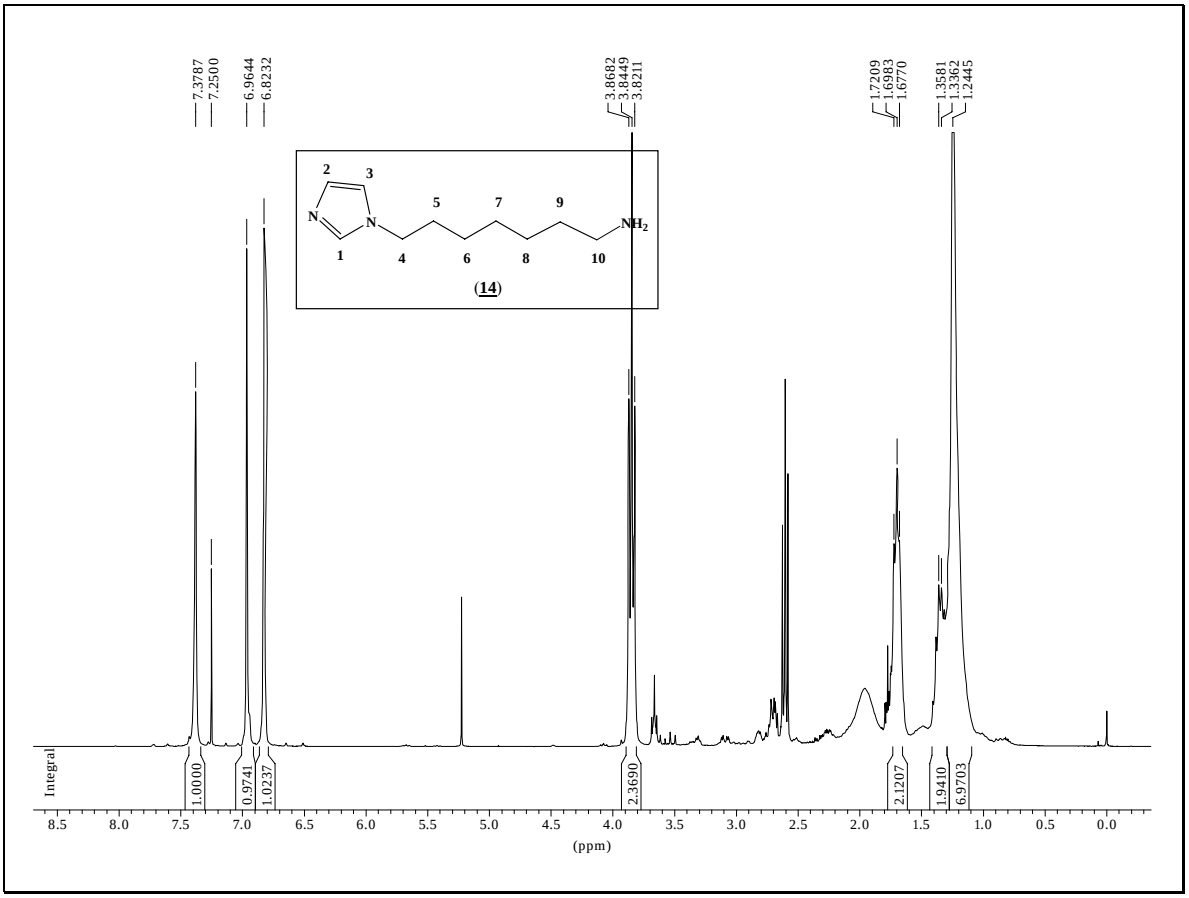

7.7892
7.7791
7.7710
7.7609
7.6636
7.6530
7.6454
7.6348
7.4075
7.2500
6.9839
6.8458
3.8820
3.8581
3.8343
3.6359
3.6121
3.5876
1.7291
1.7059
1.6826
1.6337
1.6105
1.5879
1.2577
(10)
Integral
1.7028
1.8962
1.0000
0.9825
0.8773
2.0800
2.2578
1.9493
2.2109
8.3586
(ppm)

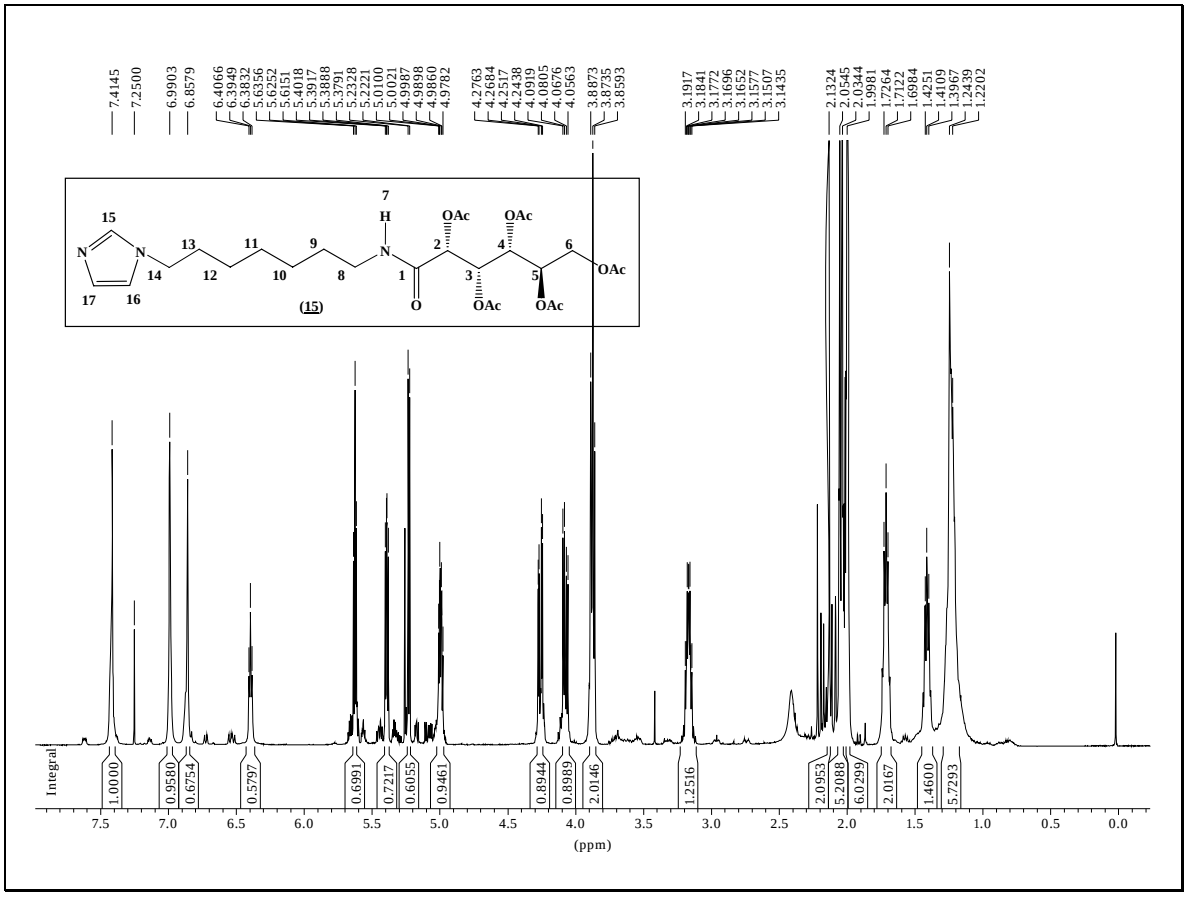

168.2628
136.9036
133.7241
132.0273
129.1807
122.9961
118.6193
77.4202
77.0000
76.5718
46.8381
37.7594
30.8532
28.7045
28.3001
26.5002
26.2861
(10)
(ppm)

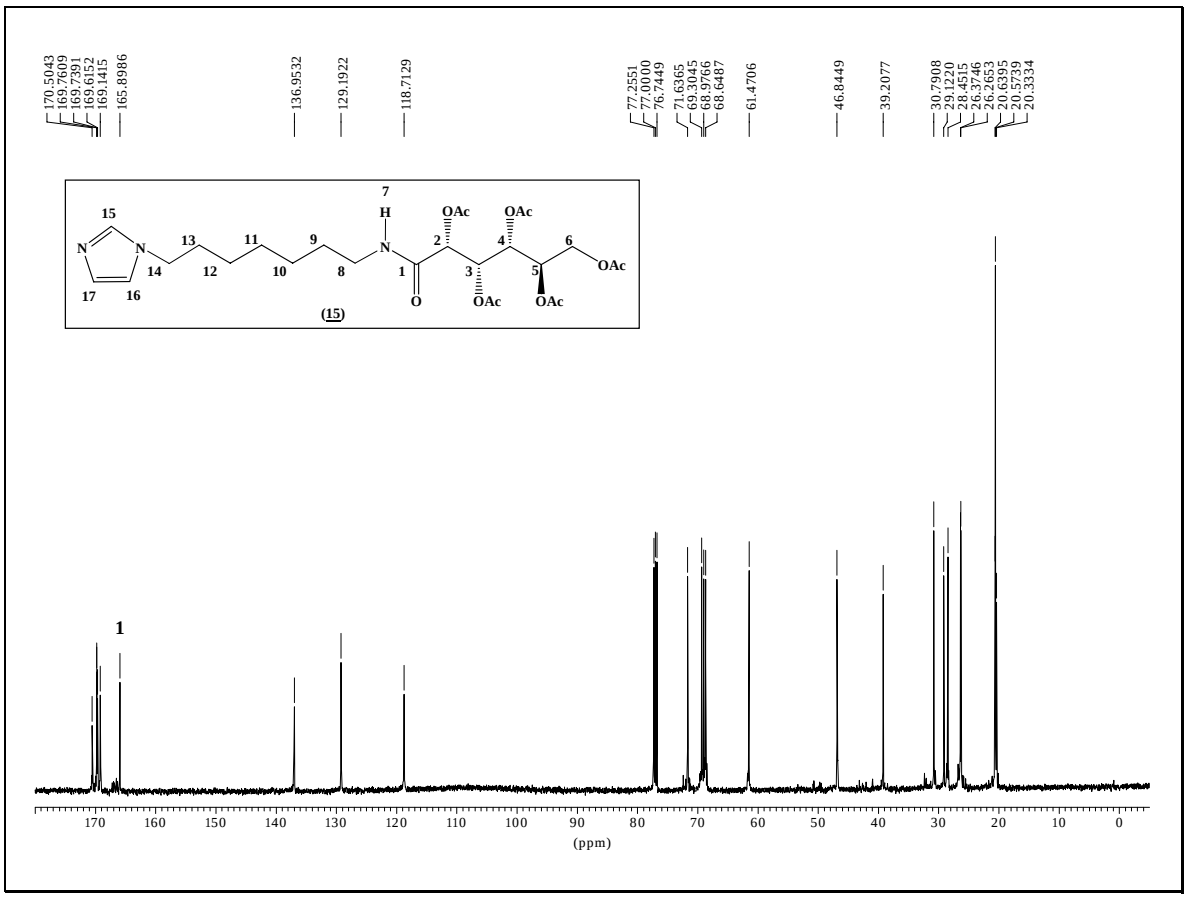

7.3810
7.2500
6.9665
6.8314
3.8842
3.8665
3.8488
2.2717
2.2543
2.2366
1.7596
1.7416
1.7233
1.7038
1.6858
1.6012
1.5828
1.5750
1.5642
1.5456
1.5279
1.4386
1.4206
1.4155
1.4073
1.4023
1.3988
1.3874
1.3805
1.3625
1.2871
1.2755
1.2728
1.2662
1.2479
1.2346
1.2271
(13)
Integral
0.9385
0.9144
0.7991
2.0000
1.9290
2.0888
2.0402
2.0665
2.0728
(ppm)

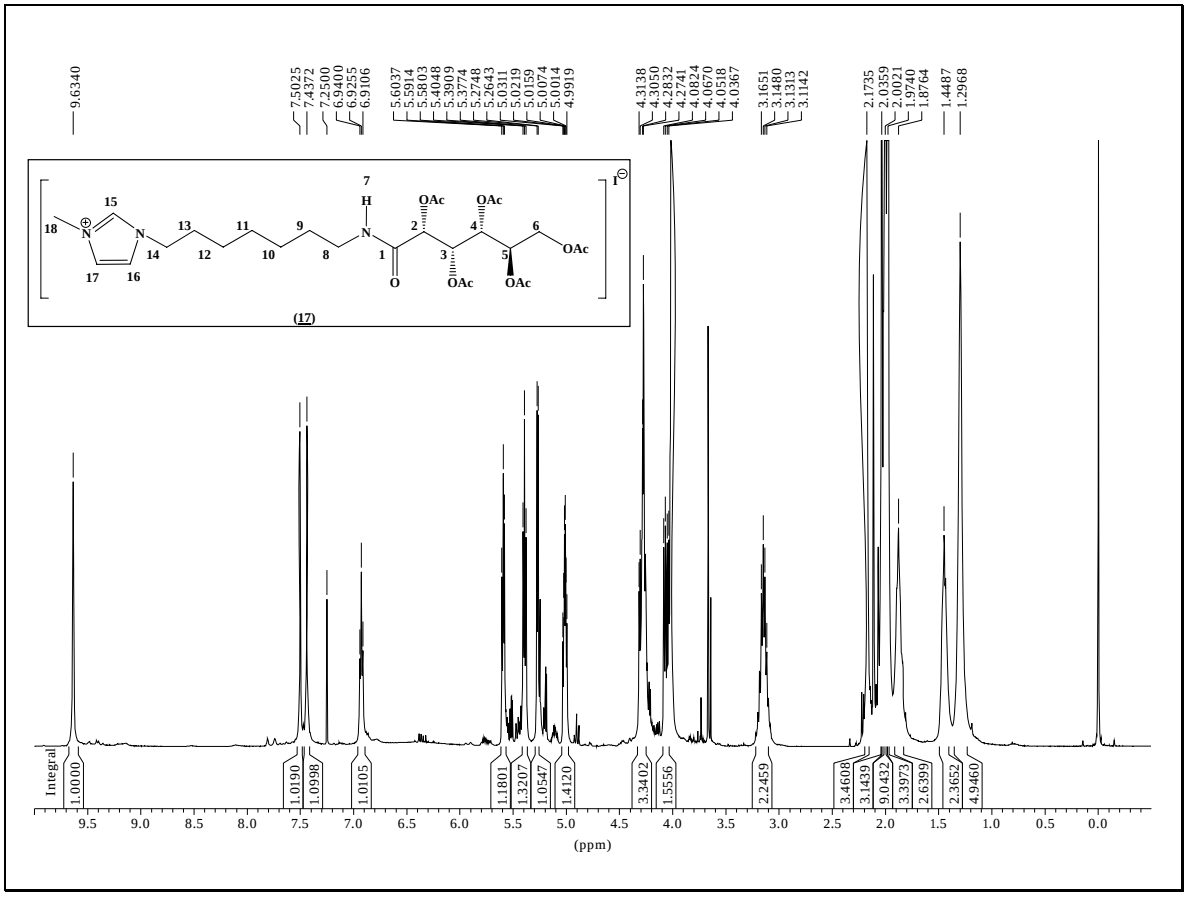

136.7959
129.1793
119.3155
118.5334
77.3176
77.0000
76.6804
46.5452
30.5198
27.8559
25.5175
24.8962
16.7892
(13)
(ppm)

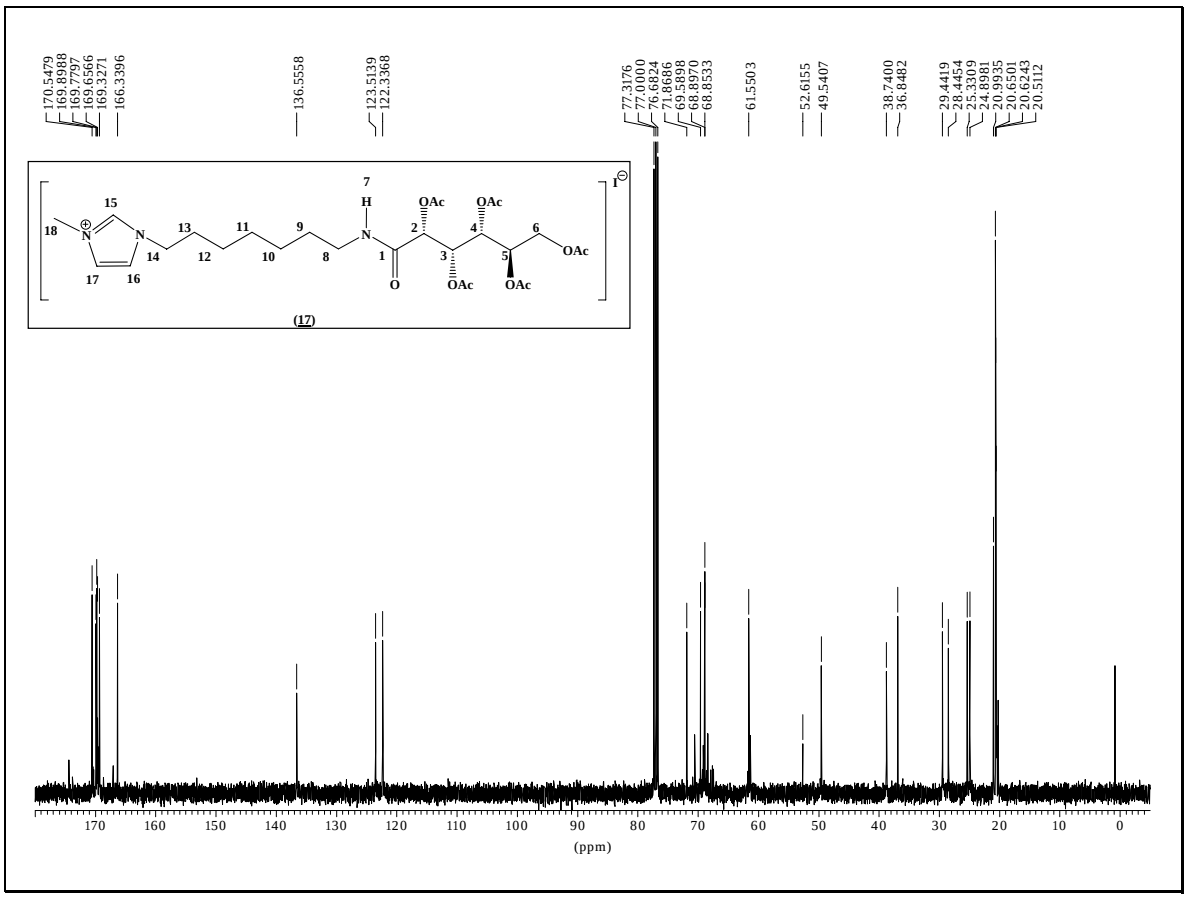

136.8798
129.1728
118.5955
77.4282
77.0000
76.5798
46.8222
41.8666
33.2636
30.8294
28.7362
26.5002
26.3337
(14)
(ppm)


7.3787
7.2500
6.9644
6.8232
3.8682
3.8449
3.8211
1.7209
1.6983
1.6770
1.3581
1.3362
1.2445
Integral
1.0000
0.9741
1.0237
2.3690
2.1207
1.9410
6.9703
(14)
(ppm)


7.4145
7.2500
6.9903
6.8579
6.4066
6.3949
6.3832
5.6356
5.6252
5.6151
5.4018
5.3917
5.3888
5.3791
5.2328
5.2221
5.0100
5.0021
4.9987
4.9898
4.9860
4.9782
4.2763
4.2684
4.2517
4.2438
4.0919
4.0805
4.0676
4.0563
3.8873
3.8735
3.8593
3.1917
3.1841
3.1772
3.1696
3.1652
3.1577
3.1507
3.1435
2.1324
2.0545
2.0344
1.9981
1.7264
1.7122
1.6984
1.4251
1.4109
1.3967
1.2439
1.2202
(15)
Integral
1.0000
0.9580
0.6754
0.5797
0.6991
0.7217
0.6055
0.9461
0.8944
0.8989
2.0146
1.2516
2.0953
5.2088
6.0299
2.0167
1.4600
5.7293
(ppm)


170.5043
169.7609
169.7391
169.6152
169.1415
165.8986
136.9532
129.1922
118.7129
77.2551
77.0000
76.7449
71.6365
69.3045
68.9766
68.6487
61.4706
46.8449
39.2077
30.7908
29.1220
28.4515
26.3746
26.2593
26.0495
20.5739
20.3334
(15)
1
(ppm)


9.6340
7.5025
7.4372
7.2500
6.9400
6.9255
6.9106
5.6037
5.5914
5.5803
5.4048
5.3909
5.3774
5.2748
5.2643
5.0311
5.0219
5.0159
5.0074
5.0014
4.9919
4.3138
4.3050
4.2832
4.2741
4.0824
4.0670
4.0518
4.0367
3.1651
3.1480
3.1313
3.1142
2.1735
2.0359
2.0021
1.9740
1.8764
1.4487
1.2968
(17)
Integral
1.0000
1.0190
1.0998
1.0105
1.1801
1.3207
1.0547
1.4120
3.3402
1.5556
2.2459
3.4608
3.1439
9.0432
3.3973
2.6399
2.3652
4.9460
(ppm)


170.5479
169.8988
169.7797
169.6566
169.3271
166.3396
136.5558
123.5139
122.3368
77.3176
77.0000
76.6824
71.6646
69.5898
68.8970
68.8533
61.5503
52.6155
49.5407
38.7400
36.8482
29.4419
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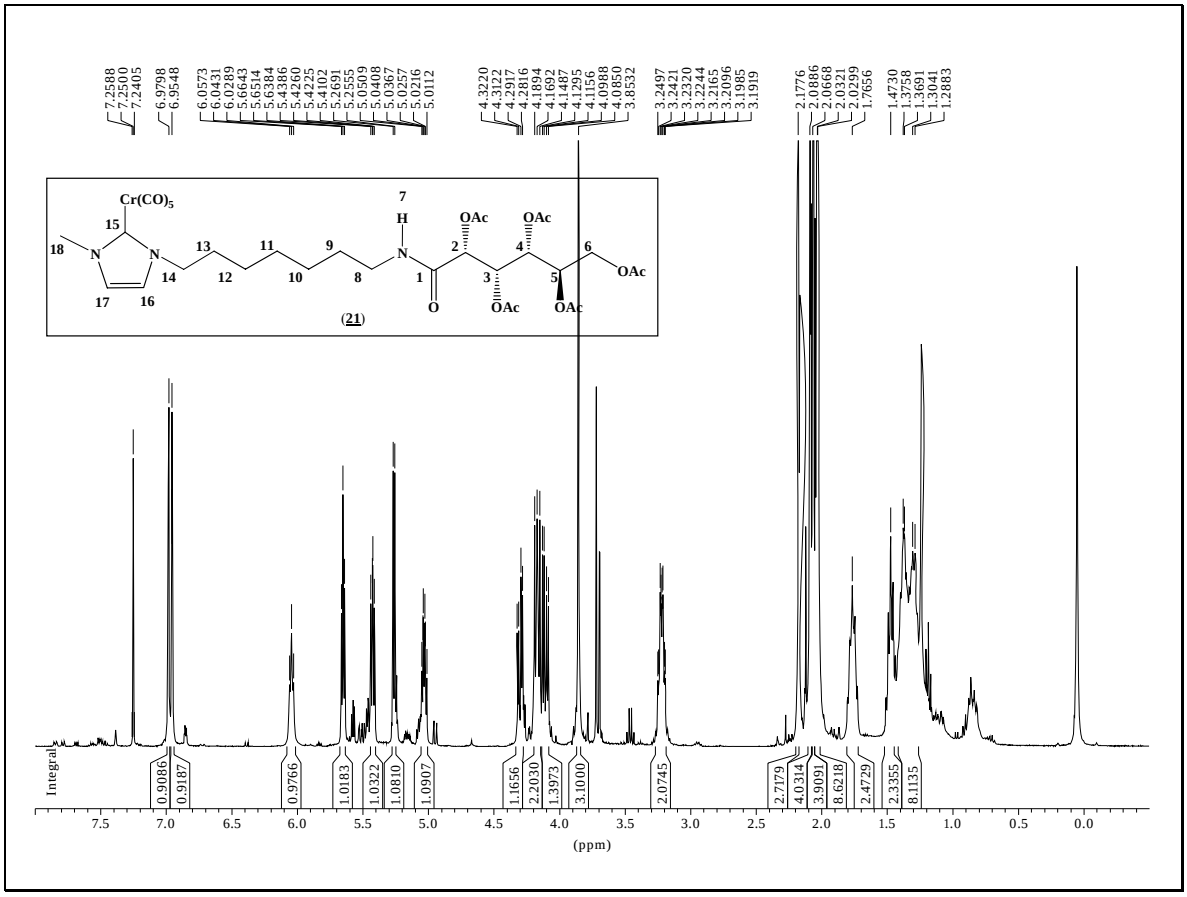
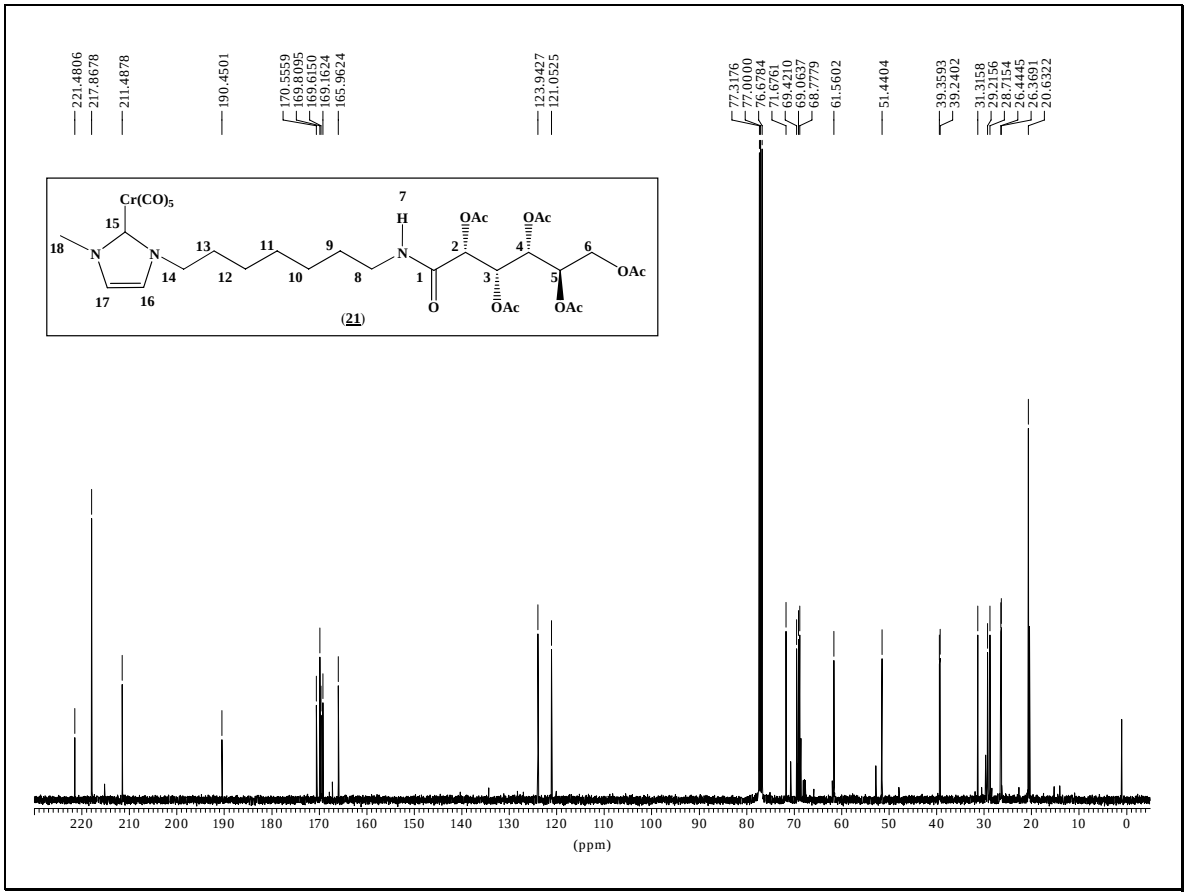
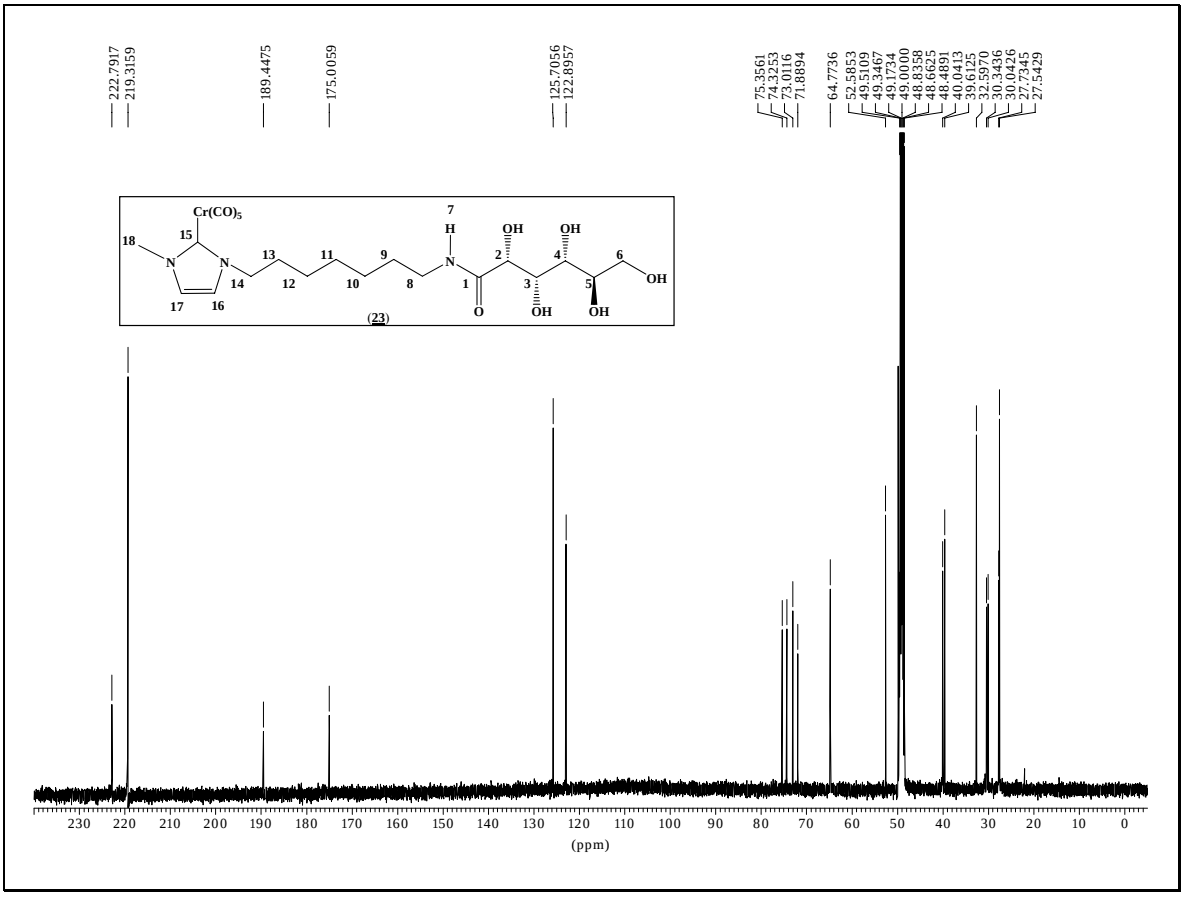
25.3309
24.8981
20.9935
20.6501
20.6243
20.5112
(17)
(ppm)


(21)
Integral
(ppm)


(21)
(ppm)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189.4475
175.0059
125.7056
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75.3561
74.3253
73.0116
71.8894
64.7736
52.5853
49.5109
49.3467
49.1734
49.0000
48.8358
48.6625
48.4891
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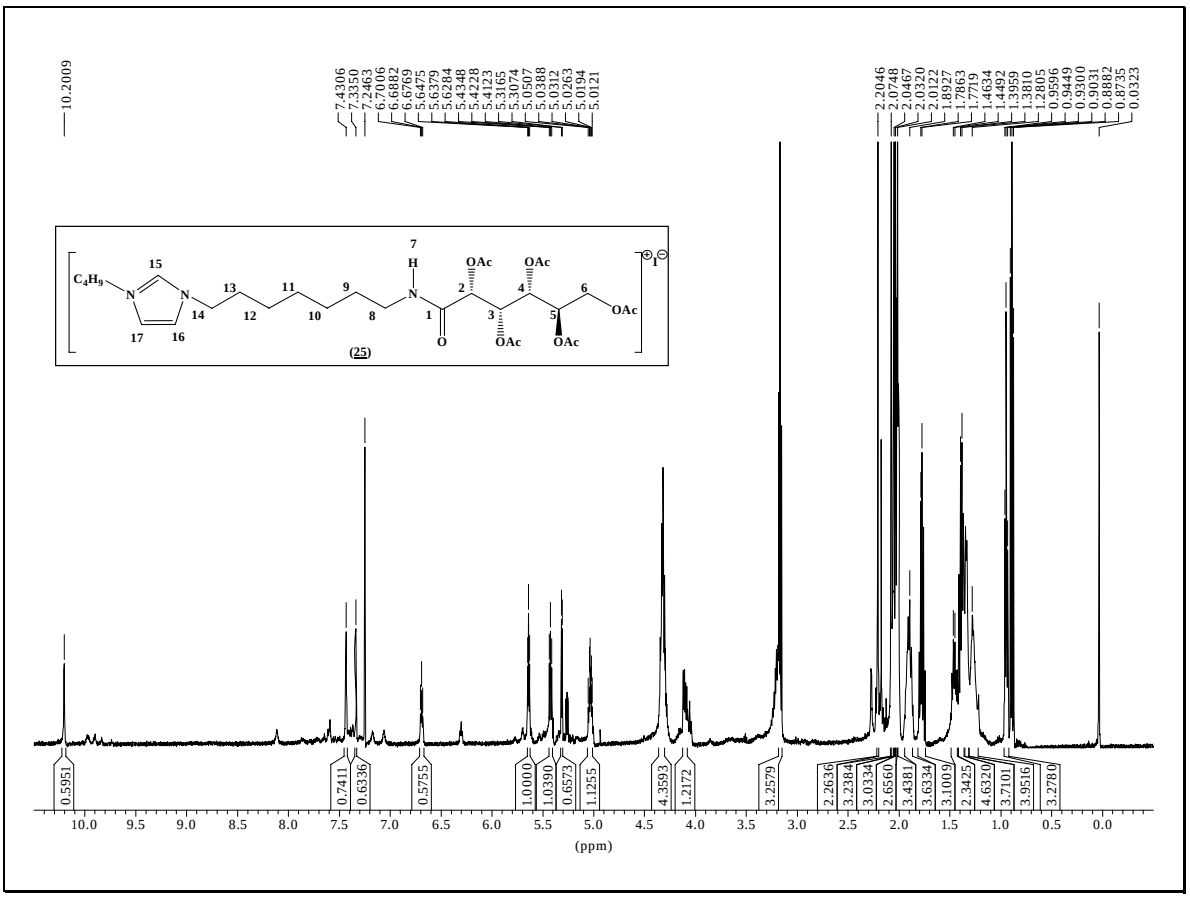
39.6125
32.5970
30.3436
30.0426
27.7345
27.5429
(23)
(ppm)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7.3350
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6.7006
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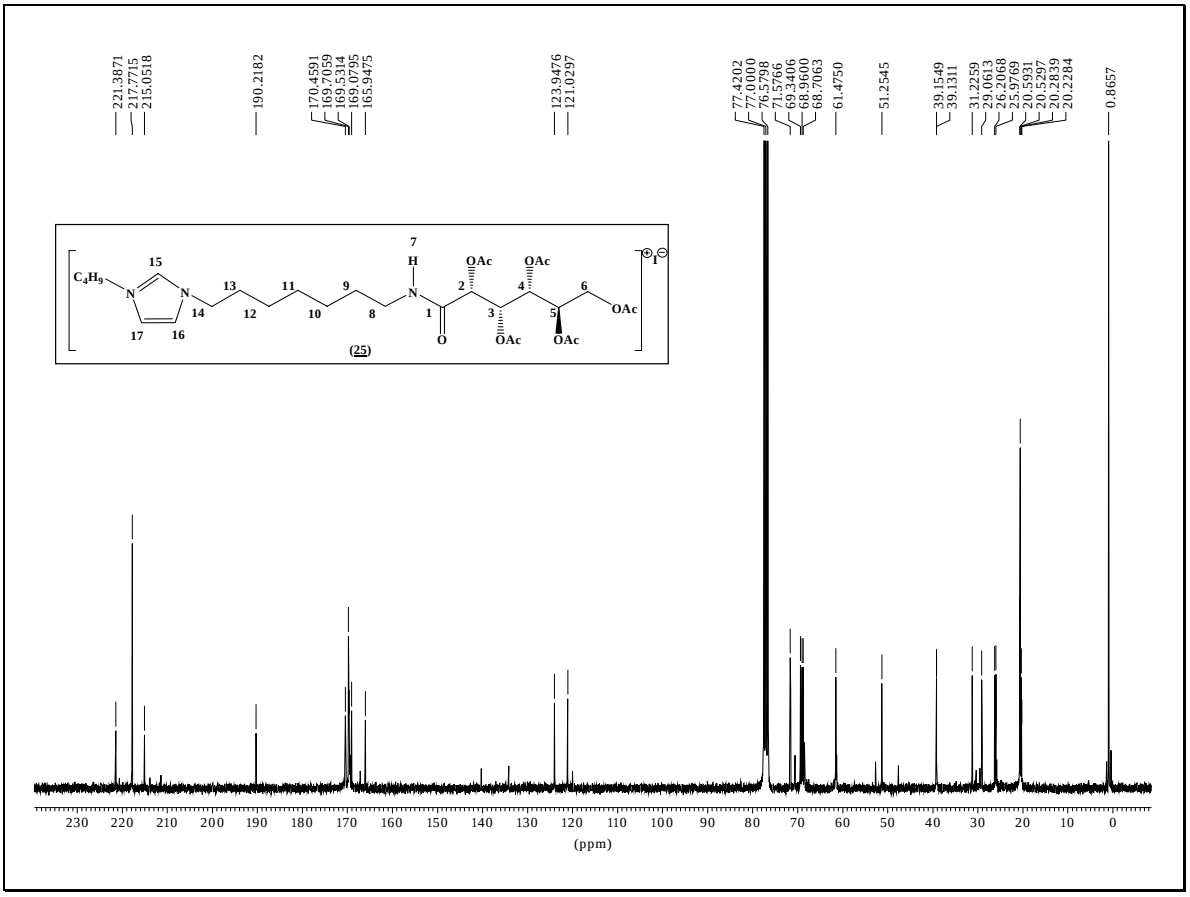
6.6769
5.6475
5.6379
5.6284
5.4348
5.4228
5.4123
5.3165
5.3074
5.0507
5.0388
5.0312
5.0263
5.0194
5.0121
2.2046
2.0748
2.0467
2.0320
2.0122
1.8927
1.7863
1.7719
1.4634
1.4492
1.3959
1.3810
1.2805
0.9596
0.9449
0.9300
0.9031
0.8882
0.8735
0.0323
(25)
0.5951
0.7411
0.6336
0.5755
1.0000
1.0390
0.6573
1.1255
4.3593
1.2172
3.2579
2.2636
3.2384
3.0334
2.6560
3.4381
3.6334
3.1009
2.3425
4.6320
3.7101
3.9516
3.2780
(ppm)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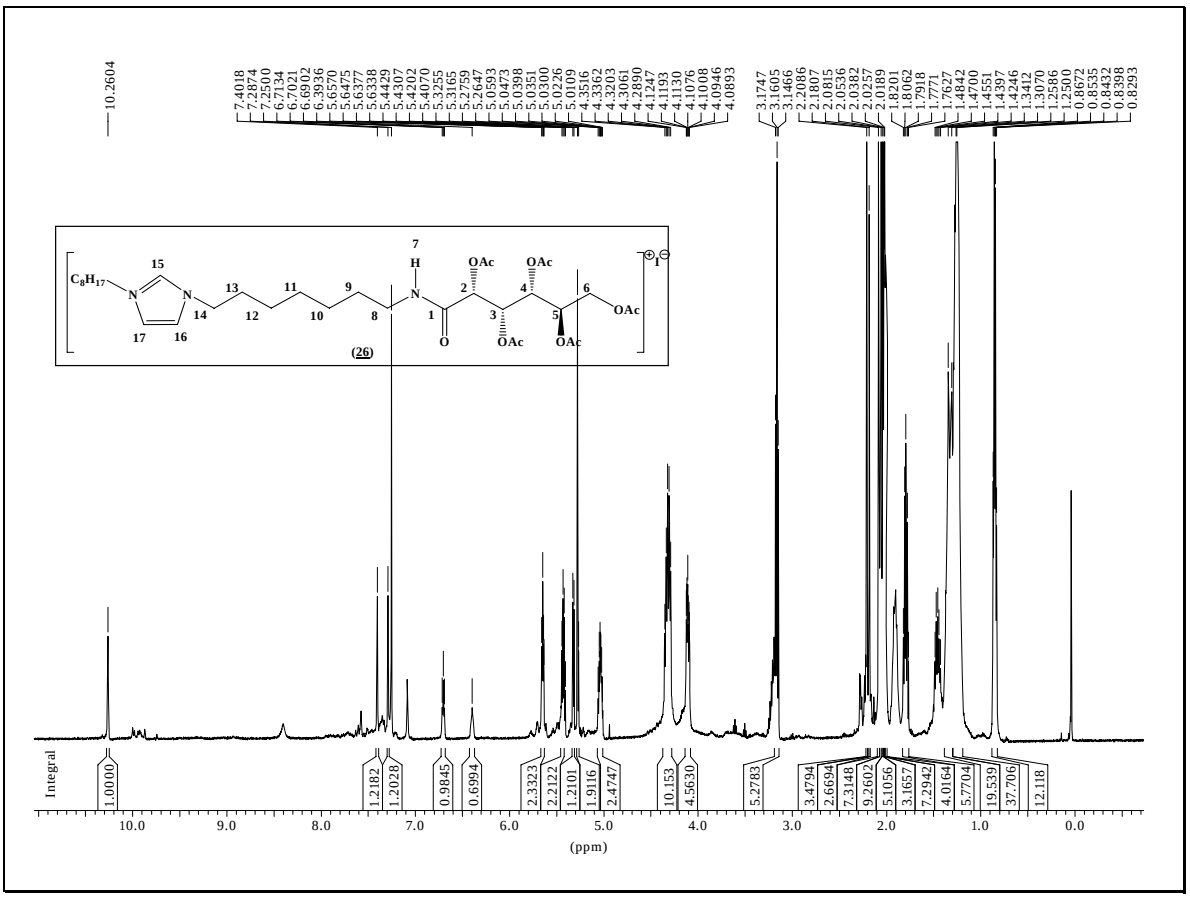
215.0518
190.2182
170.4591
169.7059
169.5314
169.0795
165.9475
123.9476
121.0297
77.4202
77.0000
76.5798
71.5766
69.3406
68.9600
68.7063
61.4750
51.2545
39.1549
39.1311
31.2259
29.0613
26.2068
25.9769
20.5931
20.5297
20.2839
20.2284
0.8657
(25)
(ppm)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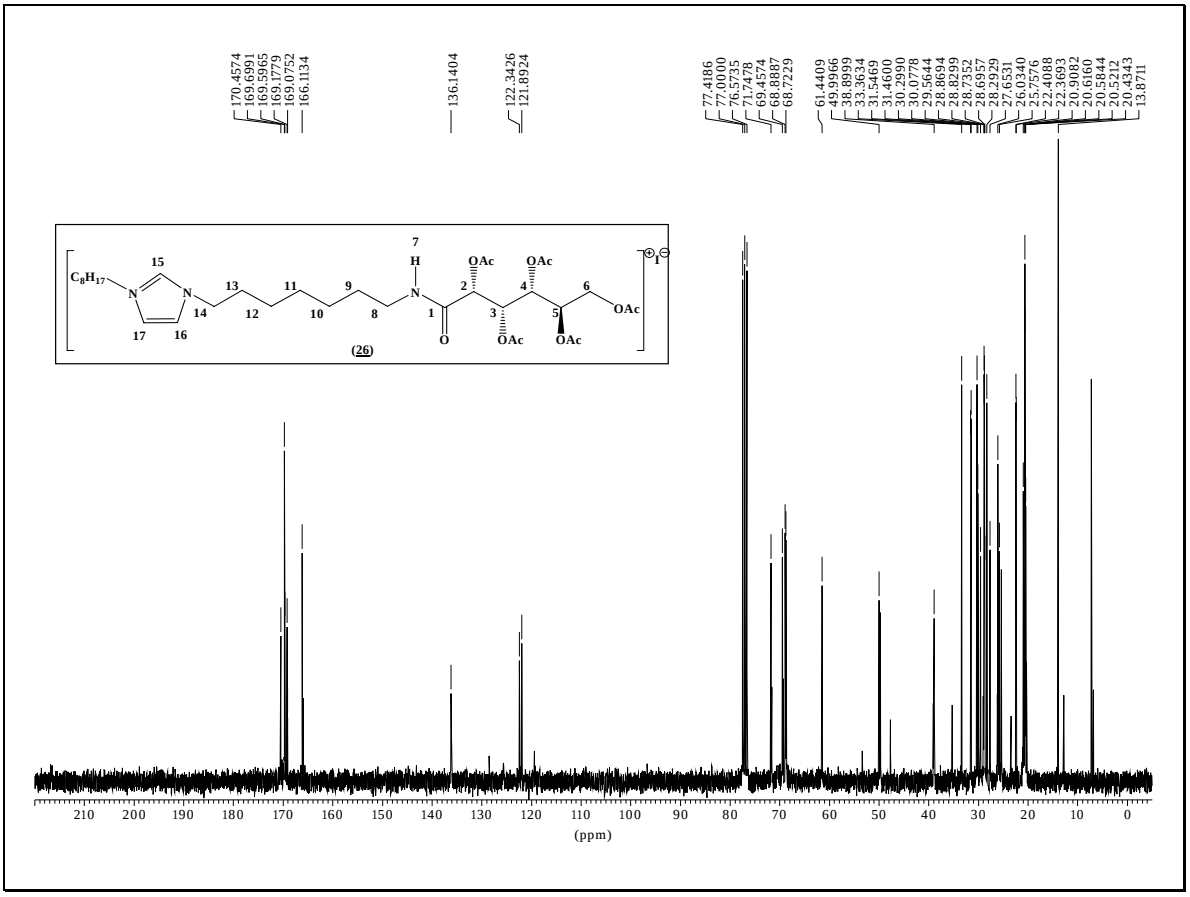
7.4018
7.2874
7.2500
6.7134
6.7021
6.6902
6.3936
6.3670
5.6575
5.6377
5.6338
5.4429
5.4307
5.4202
5.4070
5.3255
5.3165
5.2759
5.2647
5.0593
5.0473
5.0398
5.0351
5.0300
5.0226
5.0109
4.3562
4.3203
4.3061
4.2890
4.1247
4.1193
4.1130
4.1076
4.1008
4.0946
4.0893
3.1747
3.1605
3.1466
2.2086
2.1807
2.0815
2.0536
2.0382
2.0257
2.0189
1.8201
1.8062
1.7918
1.7773
1.7627
1.4842
1.4700
1.4551
1.4397
1.4246
1.3412
1.3070
1.2586
1.2500
0.8672
0.8535
0.8432
0.8398
0.8293
(26)
Integral
1.0000
1.2182
1.2028
0.9845
0.6994
2.3323
2.2122
1.2101
1.9116
2.4747
10.153
4.5630
5.2783
3.4794
2.6694
7.3148
9.2602
5.1056
3.1657
7.2942
4.0164
5.7704
19.539
37.706
12.118
(ppm)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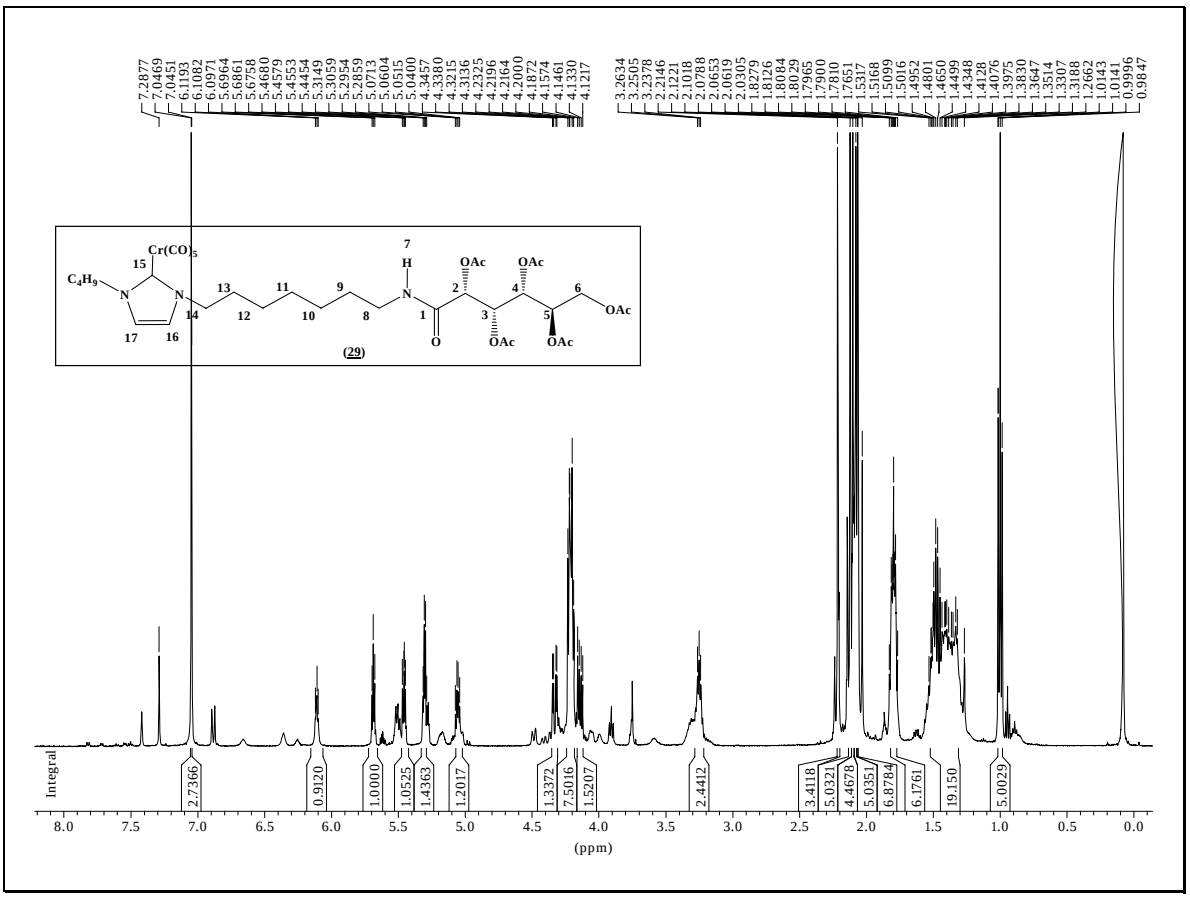
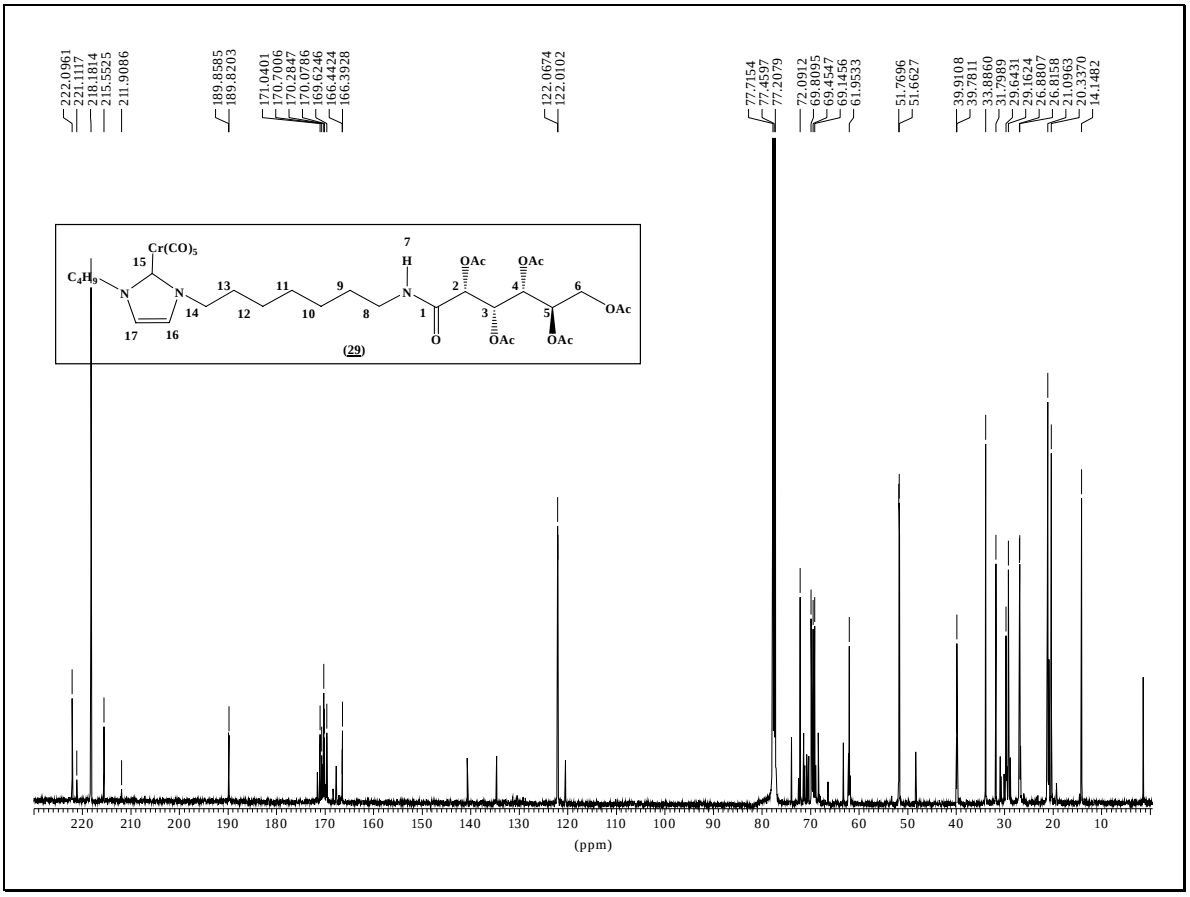
169.6991
169.5965
169.3779
169.0752
166.1134
136.1404
122.3426
121.8924
77.4186
77.0000
76.5735
71.7478
69.4574
68.8887
68.7229
61.4409
49.9966
38.8999
33.3634
31.5469
31.4600
30.2990
30.0778
29.5644
28.8694
28.8299
28.7352
28.6957
28.2929
27.6531
26.0340
25.7576
22.4088
22.3693
20.9002
20.6160
20.5844
20.5212
20.4343
13.8711
(26)
(ppm)


7.2877
7.0469
7.0451
6.1193
6.1082
6.0971
5.6964
5.6861
5.6758
5.4680
5.4579
5.4553
5.4434
5.3149
5.3059
5.2954
5.2859
5.0713
5.0604
5.0515
5.0400
4.3457
4.3380
4.3215
4.3136
4.2325
4.2196
4.2164
4.2000
4.1872
4.1574
4.1461
4.1330
4.1217
3.2634
3.2505
3.2378
2.2146
2.1221
2.1018
2.0788
2.0653
2.0619
2.0305
1.8279
1.8126
1.8094
1.8029
1.7965
1.7900
1.7810
1.7651
1.5317
1.5168
1.5099
1.5016
1.4952
1.4801
1.4650
1.4499
1.4348
1.4128
1.4076
1.3975
1.3830
1.3647
1.3514
1.3307
1.3188
1.2662
1.2463
1.0141
0.9996
0.9847
(29)
Integral
2.7366
0.9120
1.0000
1.0525
1.4363
1.2017
1.3372
7.5016
1.5207
2.4412
3.4118
5.0321
4.4678
5.0351
6.8784
6.1761
19.150
5.0029
(ppm)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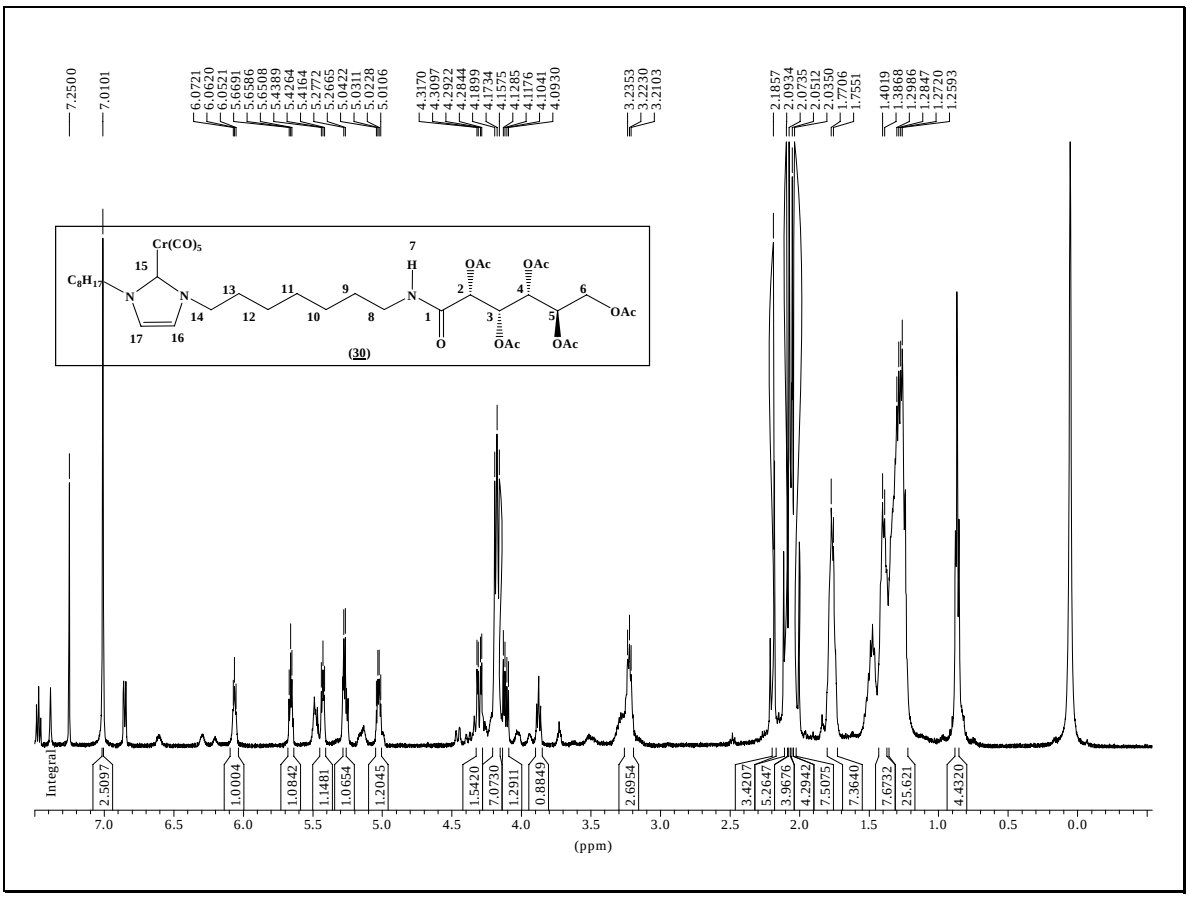
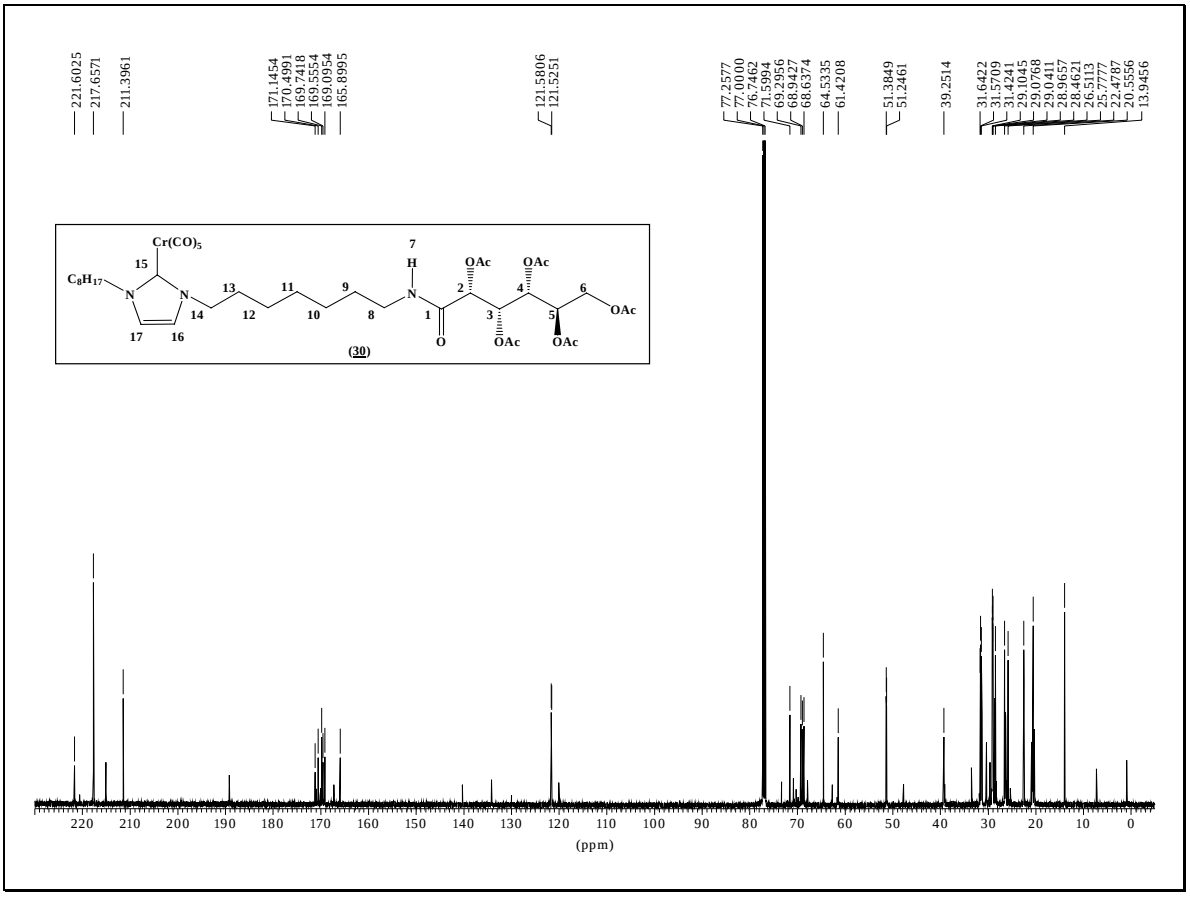
218.1814
215.5525
211.9086
189.8585
189.8203
171.0401
170.7006
170.2847
170.0786
169.4246
166.3928
122.0674
122.0102
77.7154
77.4597
77.2079
72.0912
69.8095
69.4547
69.1456
61.9533
51.7696
51.6627
39.9108
39.7811
33.8860
31.7989
29.6431
29.1624
26.8807
26.8158
21.0963
20.3370
14.1482
(29)
(ppm)


7.2500
7.0101
6.0721
6.0620
6.0521
5.6691
5.6586
5.6508
5.4389
5.4164
5.2772
5.2665
5.0422
5.0311
5.0228
5.0106
4.3170
4.3097
4.2922
4.2844
4.1899
4.1734
4.1575
4.1285
4.1176
4.1041
4.0930
3.2353
3.2230
3.2103
2.1857
2.0934
2.0735
2.0512
2.0350
1.7706
1.7551
1.4019
1.3868
1.2986
1.2847
1.2720
1.2593
Integral
2.5097
1.0004
1.0842
1.1481
1.0654
1.2045
1.5420
7.0730
1.2911
0.8849
2.6954
3.4207
5.2647
3.9676
4.2942
7.5075
7.3640
7.6732
25.621
4.4320
(30)
(ppm)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211.3961
171.1454
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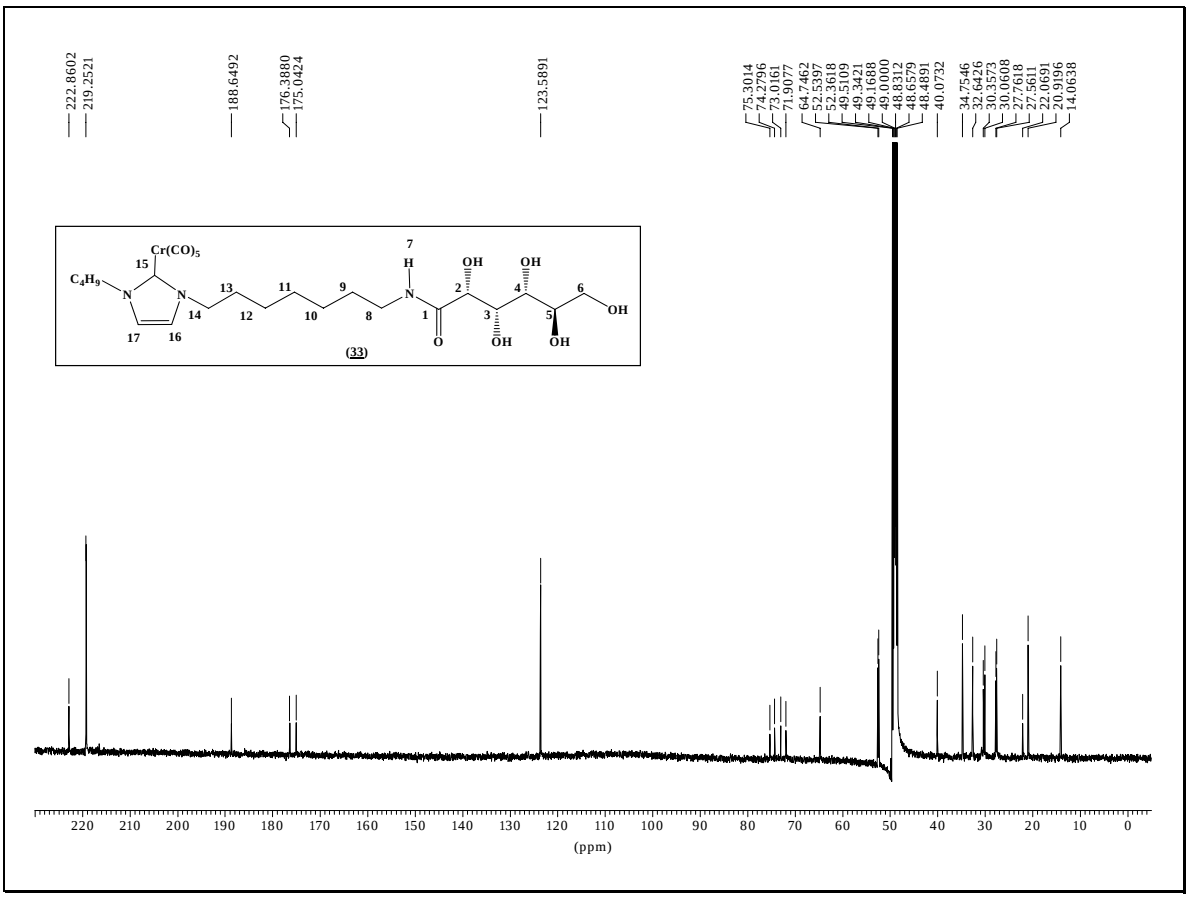
169.7418
169.5554
169.0954
165.8995
121.5806
121.5251
77.2577
77.0000
76.7462
71.5994
69.2956
68.9427
68.6374
64.5335
61.4208
51.3849
51.2461
39.2514
31.6422
31.5709
31.4241
29.1045
29.0768
29.0411
28.9657
28.4621
26.5113
25.7777
22.4787
20.5556
13.9456
Cr(CO)5
C8H17
OAc
(30)
(ppm)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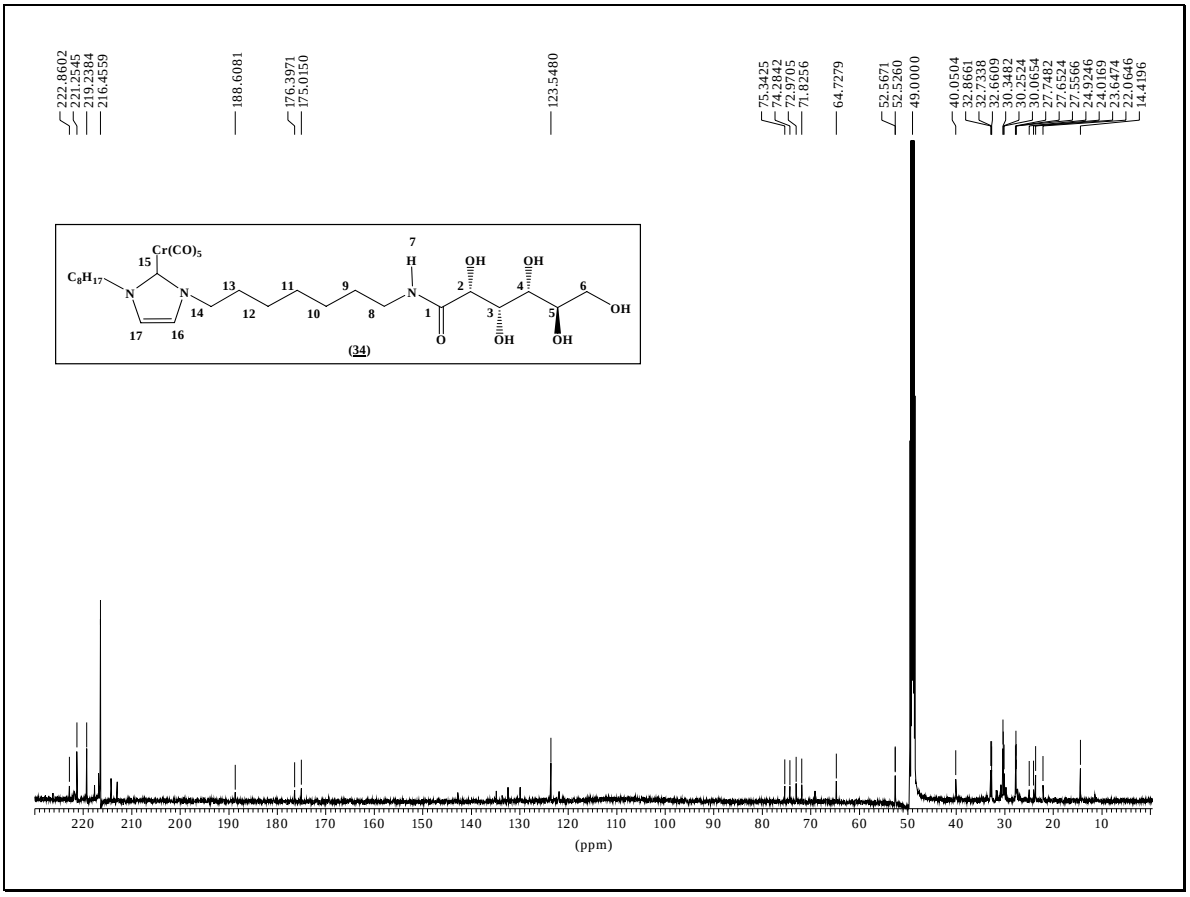
188.6492
176.3880
175.0424
123.5891
75.3014
74.2796
73.0161
71.9077
64.7462
52.5397
52.3618
49.5109
49.3421
49.1688
49.0000
48.8312
48.6579
48.4891
40.0732
34.7546
32.6426
30.3573
30.0608
27.5618
27.5611
22.0691
20.9196
14.0638
Cr(CO)5
C4H9
OH
(33)
(ppm)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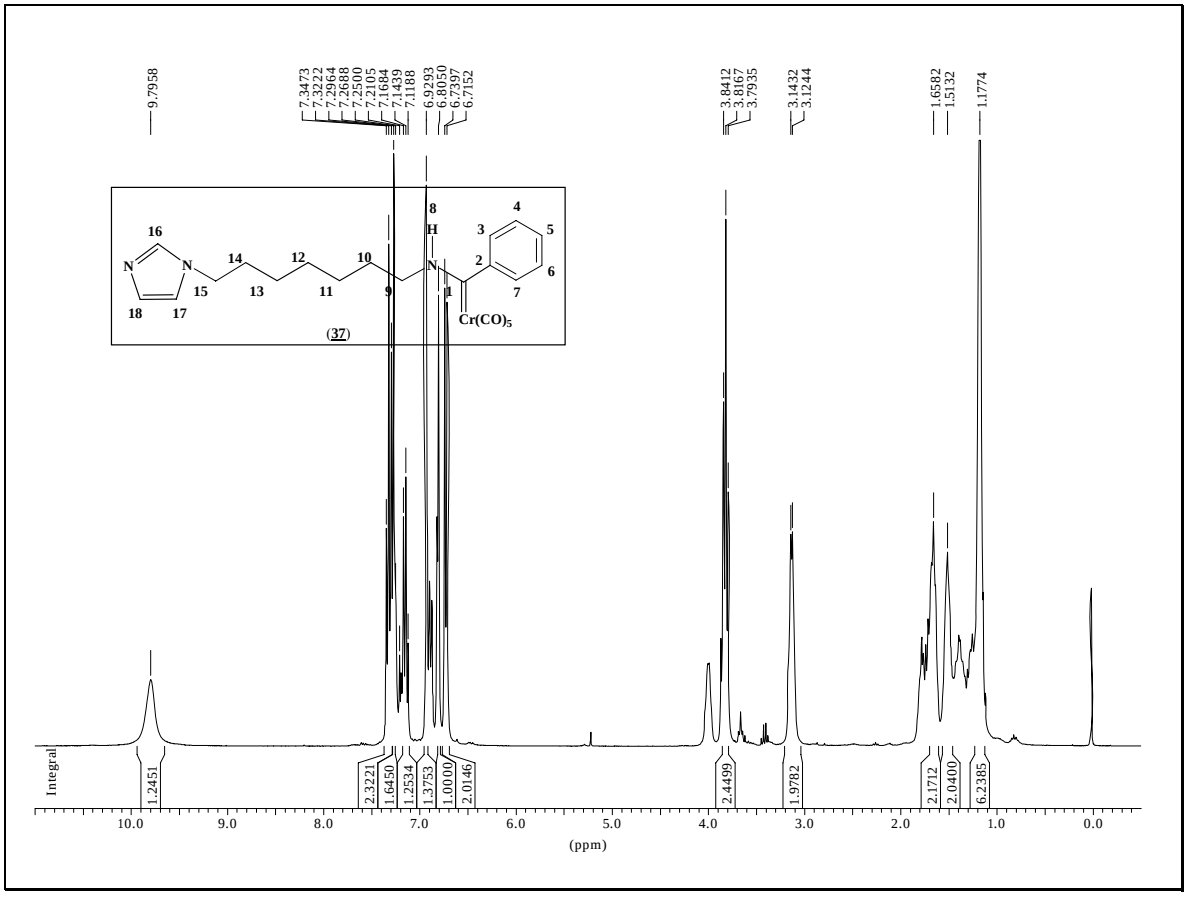
221.2545
219.2384
216.4559
188.6081
176.3971
175.0150
123.5480
75.3425
74.2842
72.9705
71.8256
64.7279
52.5671
52.5260
49.0000
40.0504
32.8661
32.7338
32.6609
30.3482
30.2524
30.0654
27.7482
27.6524
27.5566
24.1246
24.0169
23.6474
22.0646
14.4196
(34)
(ppm)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7.3064
7.2688
7.2500
7.2105
7.1684
7.1439
7.1188
6.9293
6.8050
6.7397
6.7152
3.8412
3.8167
3.7935
3.1432
3.1244
1.6582
1.5132
1.1774
(37)
Integral
1.2451
2.3221
1.6450
1.2534
1.3753
1.0000
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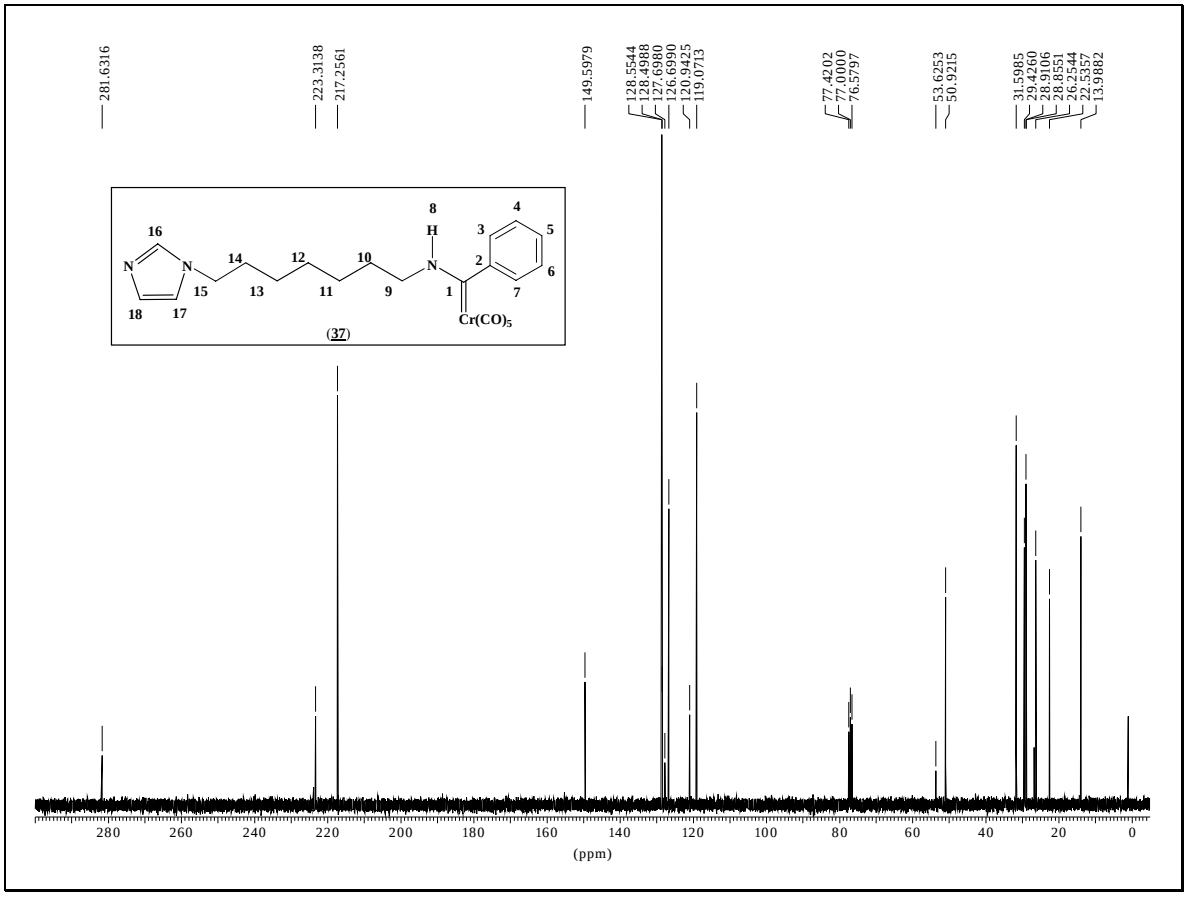
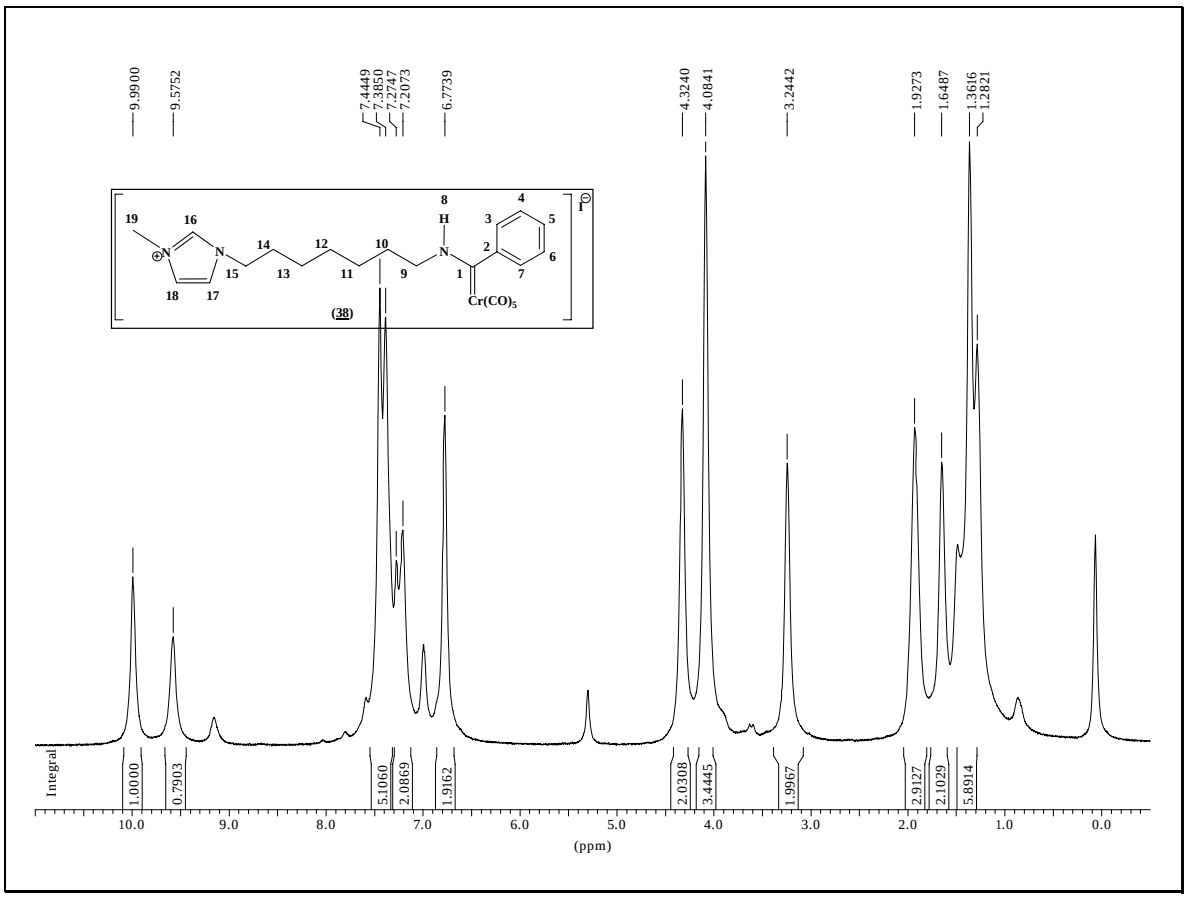
2.4499
1.9782
2.1712
2.0400
6.2385
(ppm)


281.6316
223.3138
217.2561
149.5979
128.5544
128.4988
127.6980
126.6990
120.9425
119.0713
77.4202
77.0000
76.5797
53.6253
50.9215
31.5985
29.4260
29.1006
28.8551
26.2544
22.5357
13.9882
(37)
Cr(CO)5
(ppm)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9.5752
7.4449
7.3850
7.2747
7.2073
6.7739
4.3240
4.0841
3.2442
1.9273
1.6487
1.3616
1.2821
(38)
Integral
1.0000
0.7903
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1.9162
2.0308
3.4445
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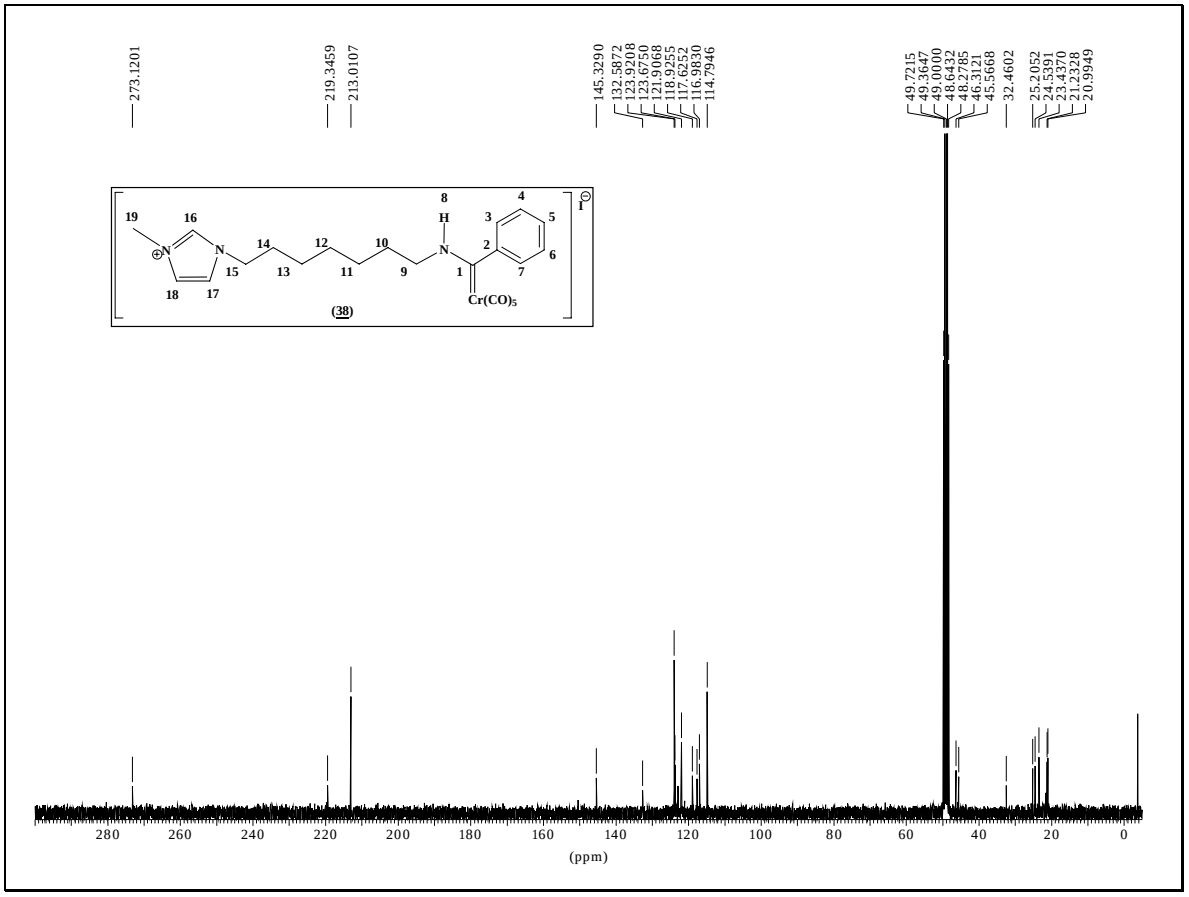
2.9127
2.1029
5.8914
(ppm)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213.0107
145.3290
132.5872
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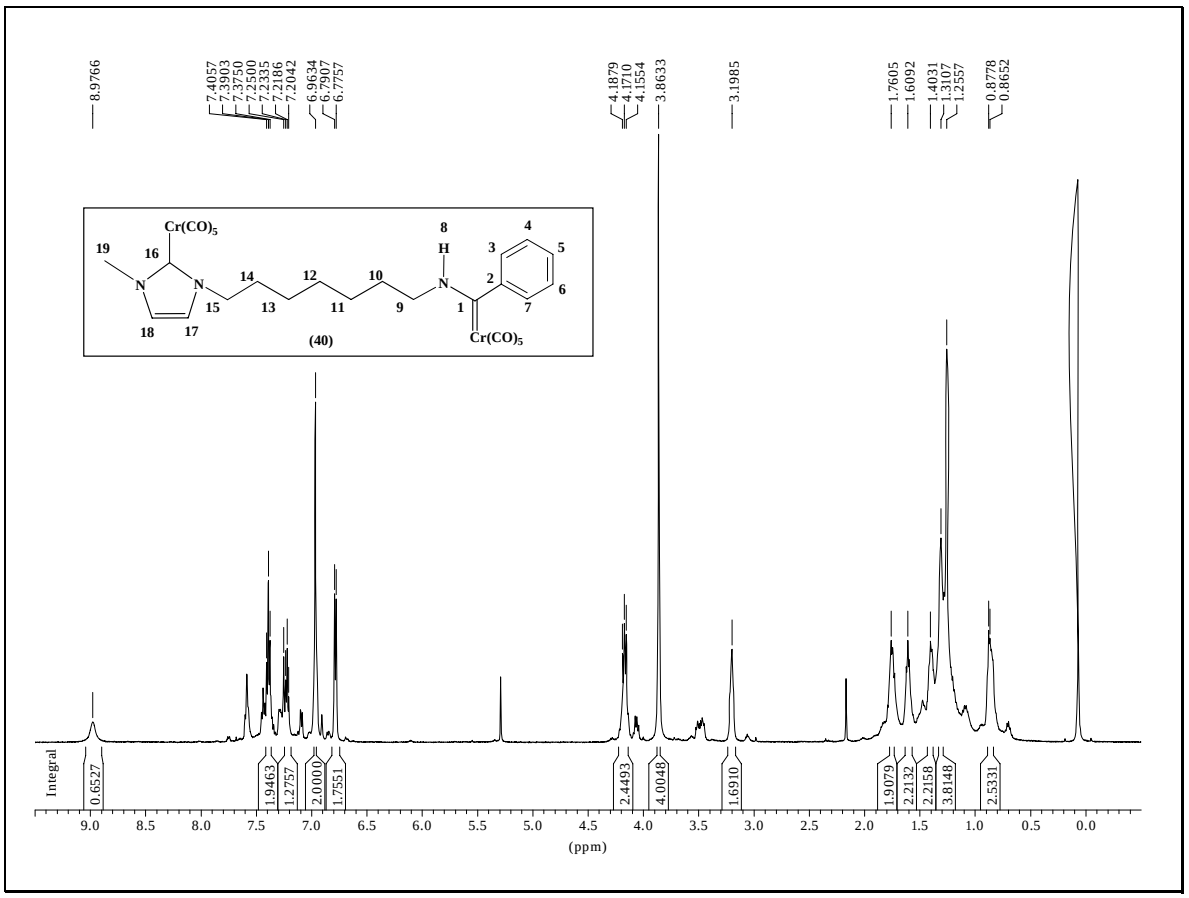
123.6750
121.9068
118.9255
117.6252
116.9830
114.7946
49.7215
49.3647
49.0000
48.6432
48.2785
46.3121
45.5668
32.4602
25.2052
24.5391
23.4370
21.2328
20.9949
(38)
(ppm)


8.9766
7.4057
7.3903
7.3750
7.2500
7.2335
7.2186
7.2042
6.9634
6.7907
6.7757
4.1879
4.1710
4.1554
3.8633
3.1985
1.7605
1.6092
1.4031
1.3107
1.2557
0.8778
0.8652
(40)
Integral
0.6527
1.9463
1.2757
2.0000
1.7551
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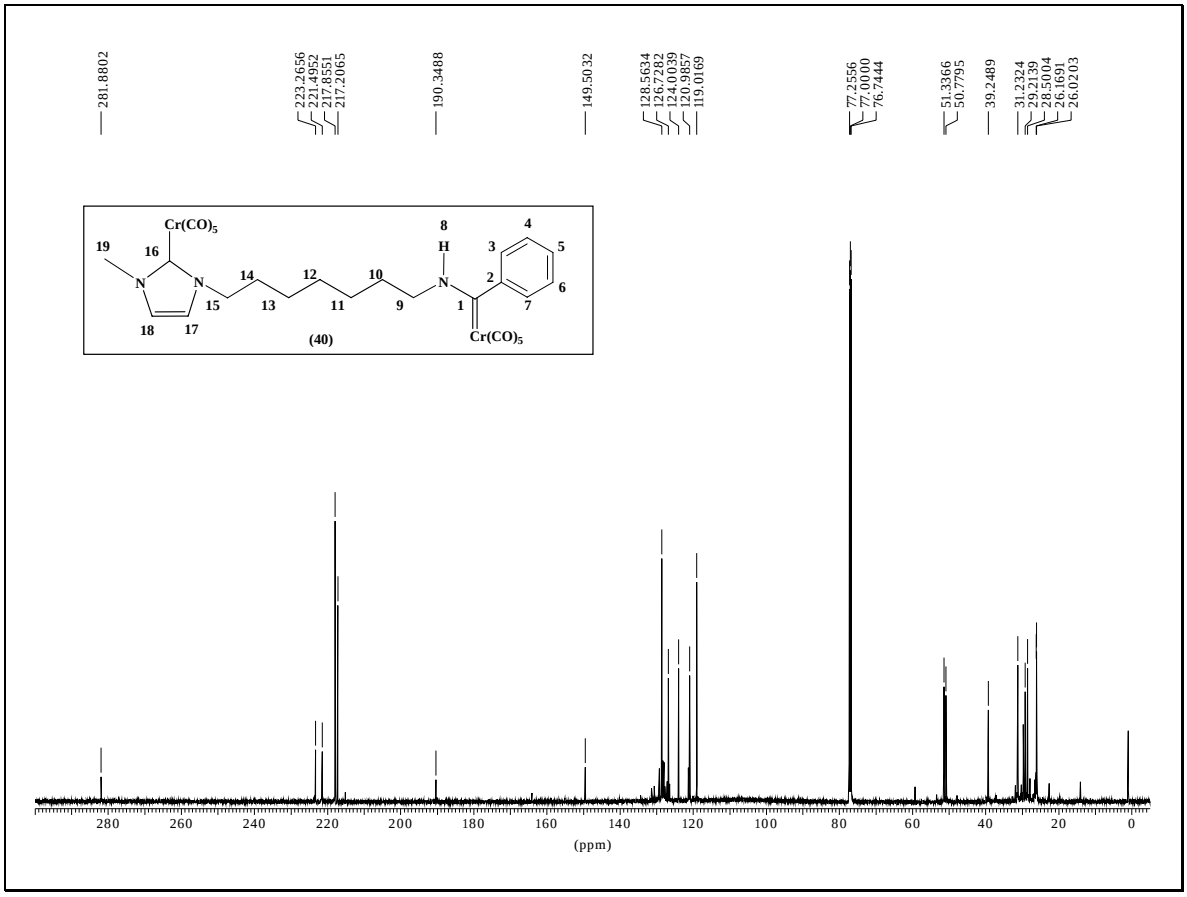
4.0048
1.6910
1.9079
2.2132
2.2158
3.8148
2.5331
(ppm)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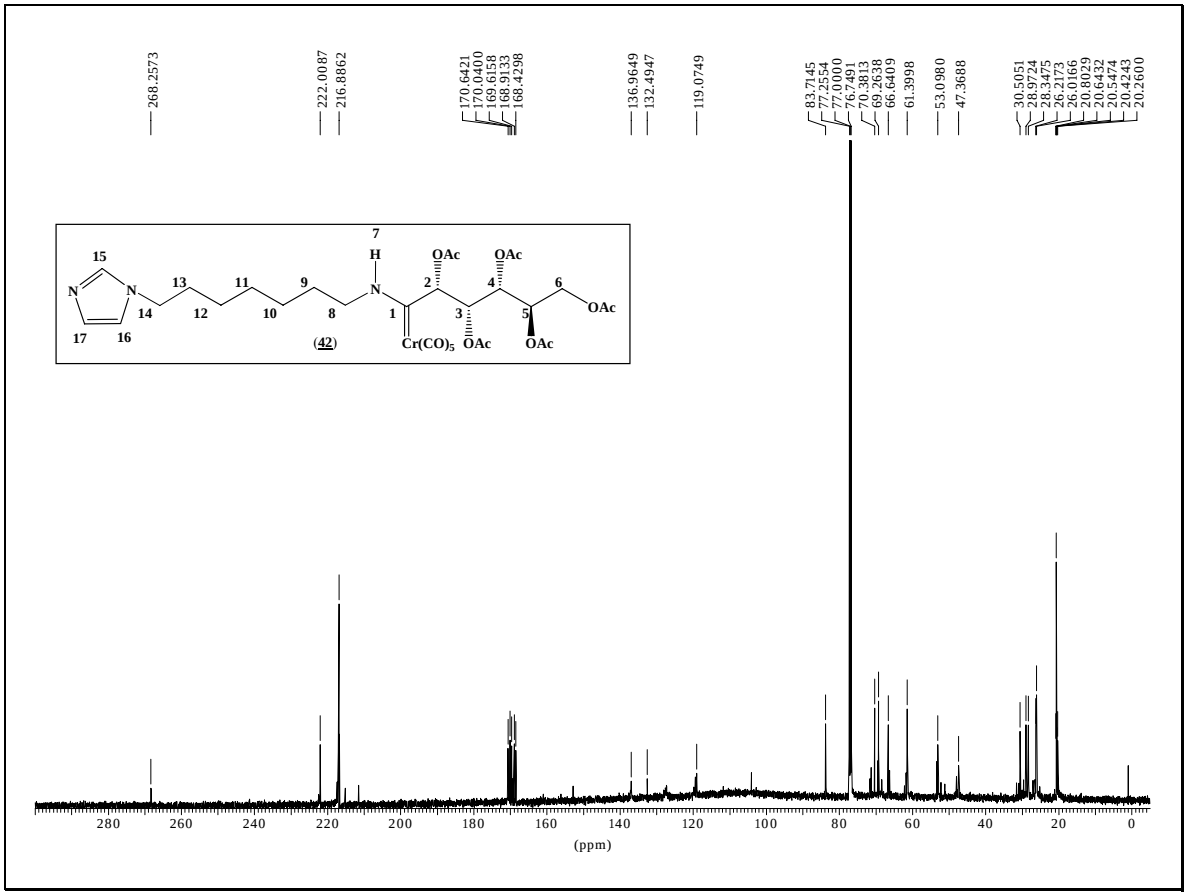
223.2656
221.4952
217.8551
217.2065
190.3488
149.5032
128.5634
126.7282
124.0039
120.9857
119.0169
77.2556
77.0000
76.7444
51.3366
50.7795
39.2489
31.2324
29.2139
28.5004
26.1691
26.0203
Cr(CO)5
(40)
(ppm)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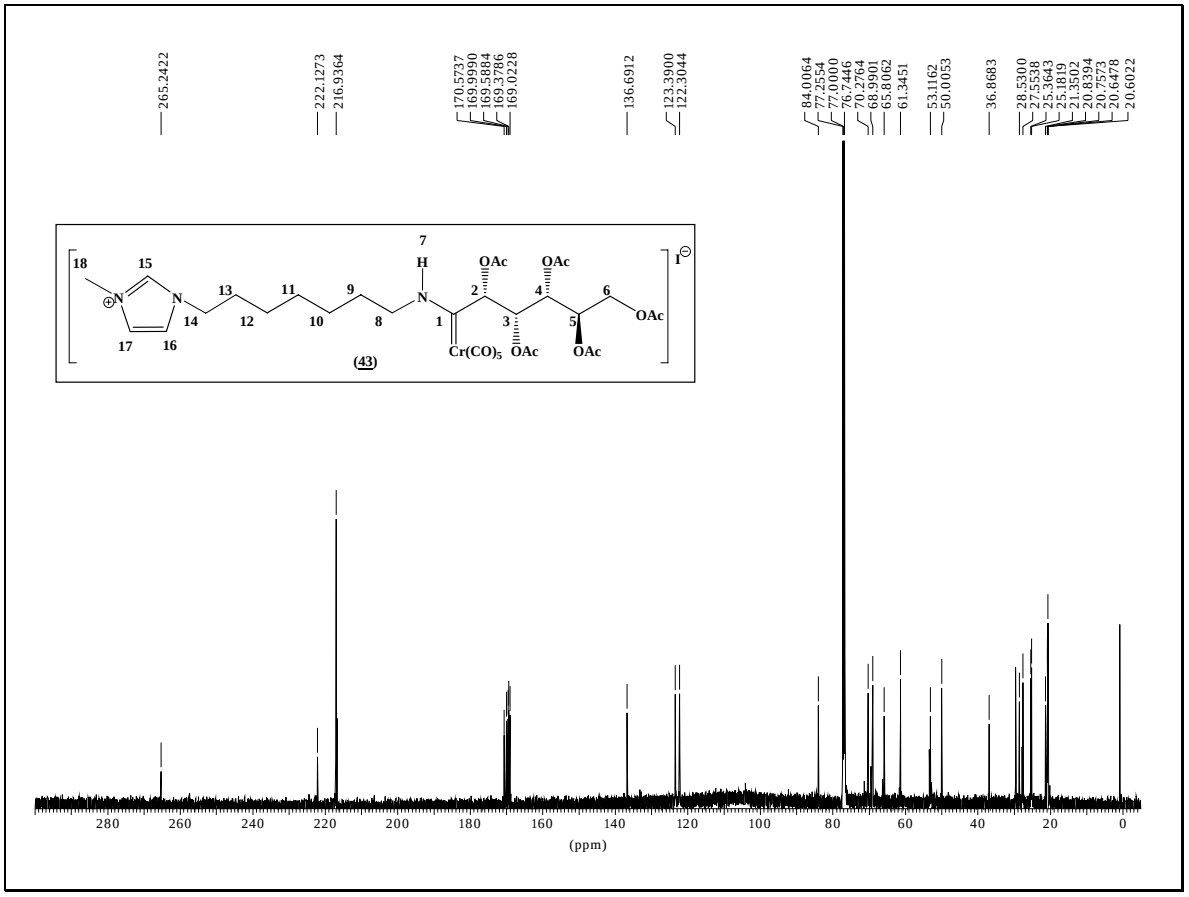
216.8862
170.6421
170.0400
169.6158
168.9133
168.4298
136.9649
132.4947
119.0749
83.7145
77.2554
77.0000
76.7491
70.3813
69.2638
66.6409
61.3998
53.0980
47.3688
30.5051
28.9724
28.3475
26.2173
26.0166
20.8029
20.6432
20.5474
20.4243
20.2600
OAc
(42)
Cr(CO)5
(ppm)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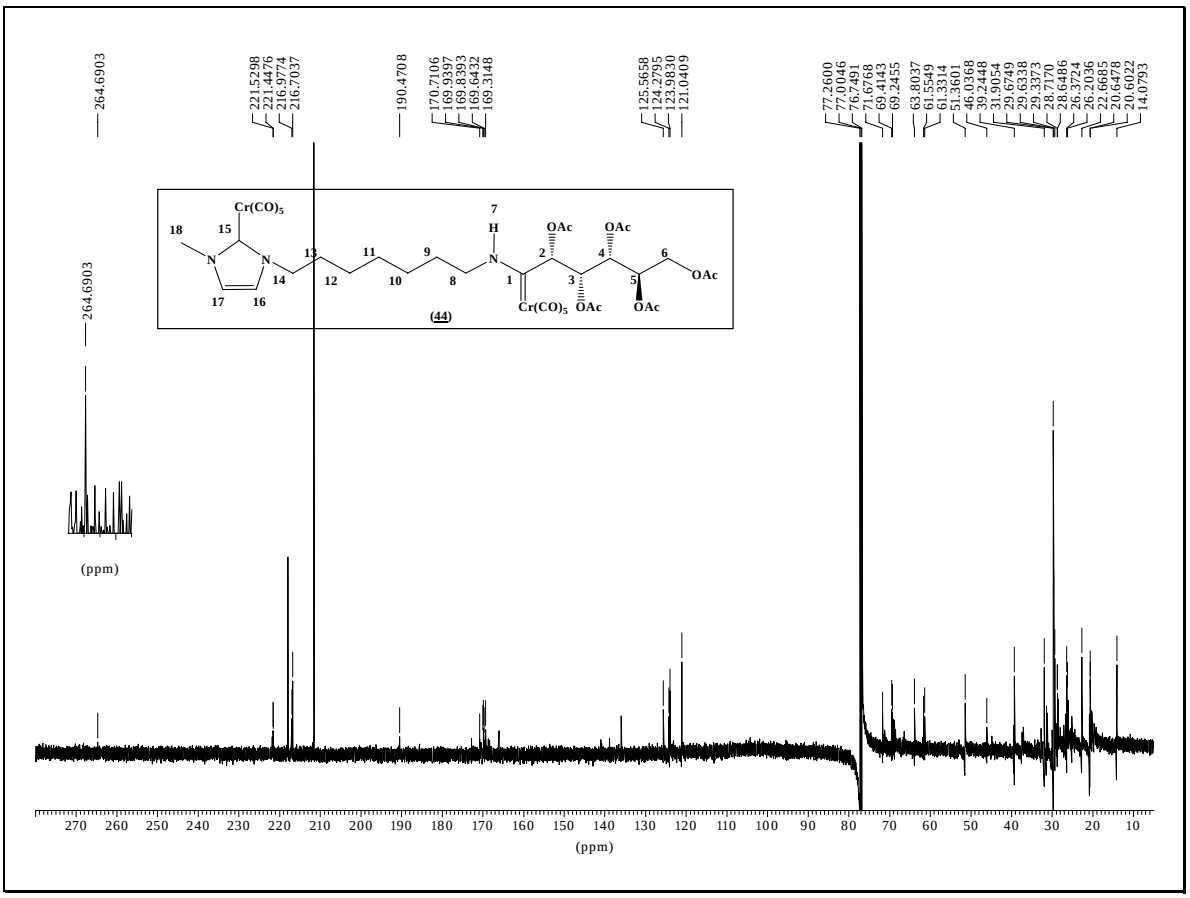
216.9364
170.5737
169.9990
169.5884
169.3796
169.0228
136.6912
123.3900
122.3044
84.0064
77.2554
77.0000
76.7446
70.2764
68.9901
65.8062
61.3451
53.1162
50.0053
36.8683
28.5300
27.5538
25.3643
25.1819
21.3502
20.8394
20.7573
20.6478
20.6022
(43)
(ppm)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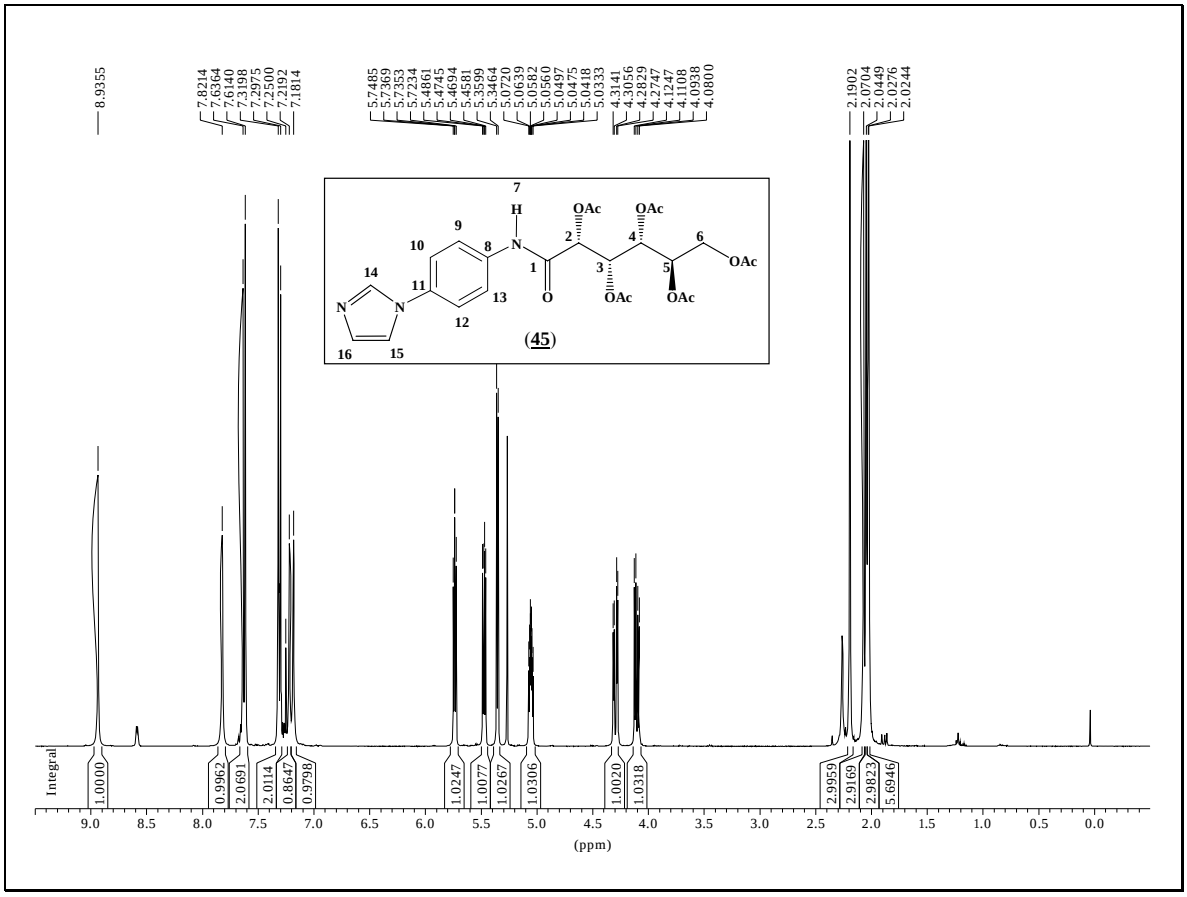
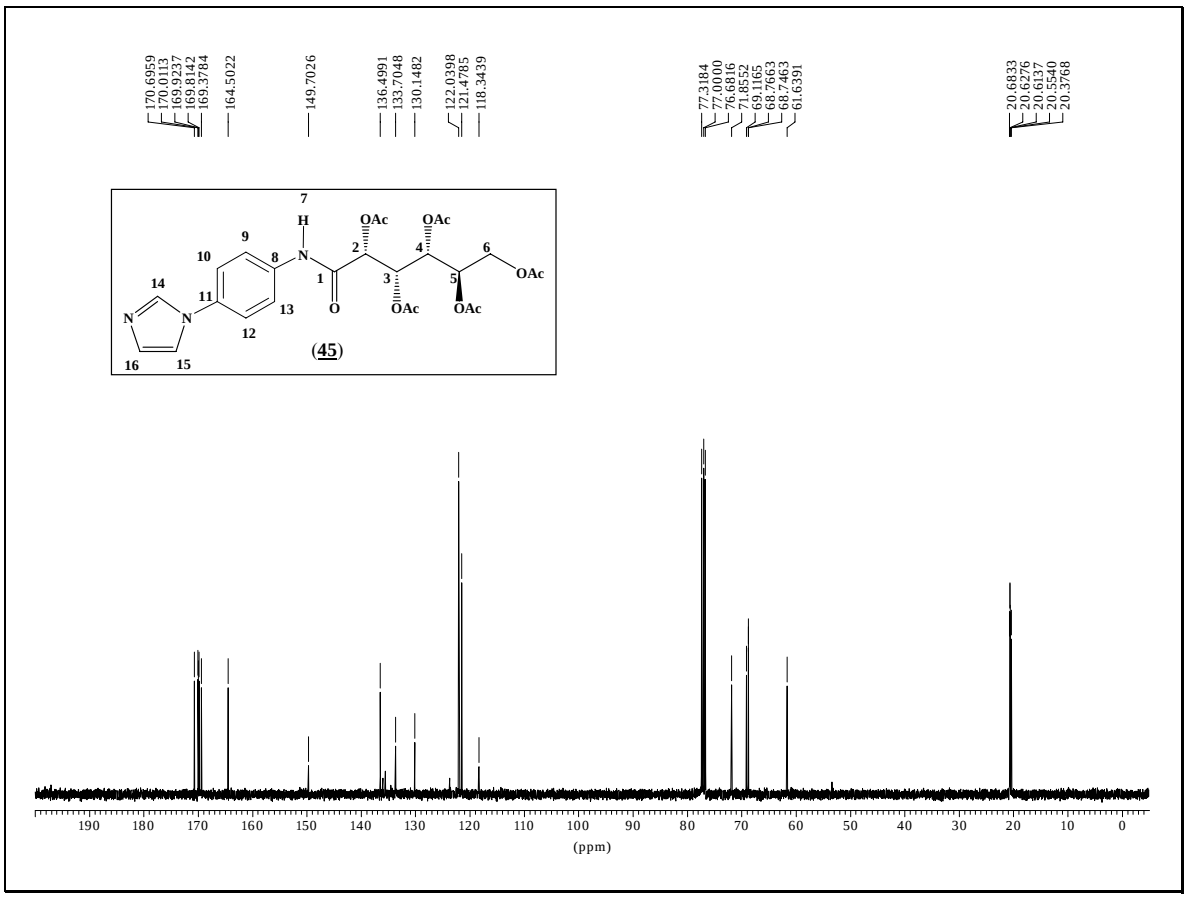
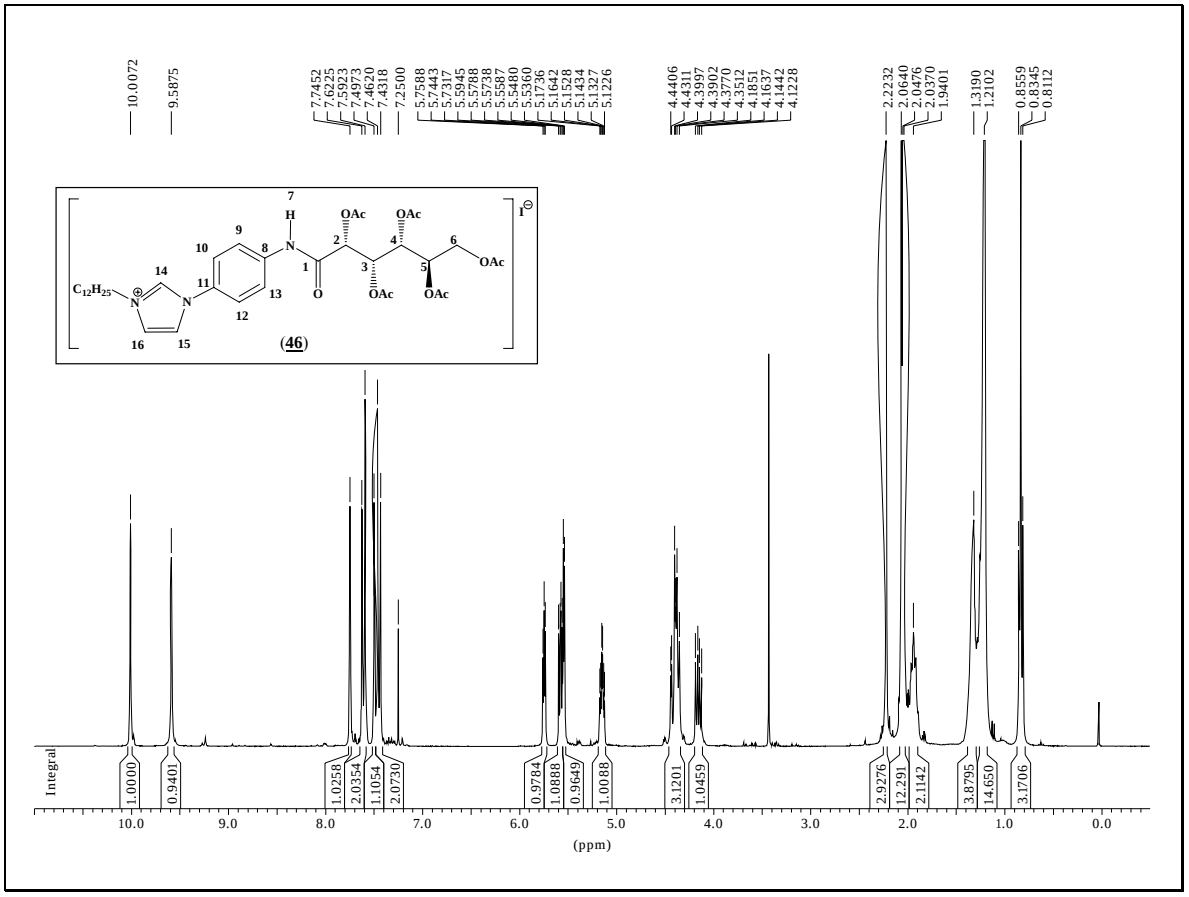
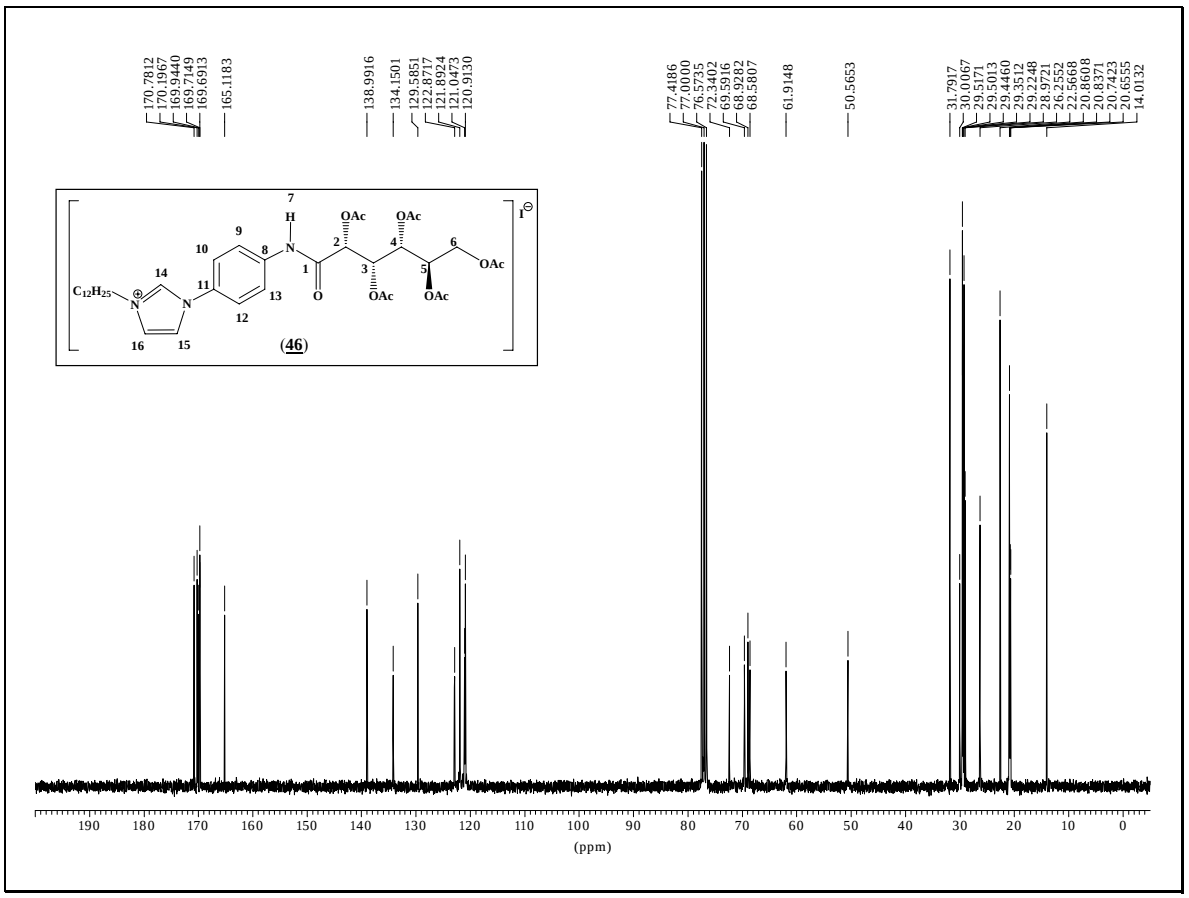
221.5298
221.4476
216.9774
216.7037
190.4708
170.7106
169.9397
169.8393
169.6432
169.3148
125.5658
124.2795
123.9830
121.0409
77.2600
77.0046
76.7491
71.6768
69.4143
69.2455
63.8037
61.5549
61.3314
51.3601
46.0368
39.2448
31.9054
29.6749
29.6338
29.3373
28.7170
28.6486
26.3724
26.2036
22.6685
20.6478
20.6022
14.0793
(44)
(ppm)


8.9355
7.8214
7.6364
7.6140
7.3198
7.2975
7.2500
7.2192
7.1814
5.7485
5.7369
5.7353
5.7234
5.4861
5.4745
5.4694
5.4581
5.3599
5.3464
5.0720
5.0639
5.0582
5.0560
5.0497
5.0475
5.0418
5.0333
4.3141
4.3056
4.2829
4.2747
4.1247
4.1108
4.0938
4.0800
2.1902
2.0704
2.0449
2.0276
2.0244
(45)
Integral
1.0000
0.9962
2.0691
2.0114
0.8647
0.9798
1.0247
1.0077
1.0267
1.0306
1.0020
1.0318
2.9959
2.9169
2.9823
5.6946
(ppm)


170.6959
170.0113
169.9237
169.8142
169.3784
164.5022
149.7026
136.4991
133.7048
130.1482
122.0398
121.4785
118.3439
77.3184
77.0000
76.6816
71.8552
69.1165
68.7663
68.7463
61.6391
20.6833
20.6276
20.6137
20.5540
20.3768
(45)
(ppm)


10.0072
9.5875
7.7452
7.6225
7.5923
7.4973
7.4620
7.4318
7.2500
5.7588
5.7443
5.7317
5.5945
5.5788
5.5738
5.5587
5.5460
5.5330
5.1736
5.1642
5.1528
5.1434
5.1327
5.1226
4.4406
4.4311
4.3997
4.3902
4.3770
4.3512
4.1851
4.1637
4.1442
4.1228
2.2232
2.0640
2.0476
2.0370
1.9401
1.3190
1.2102
0.8559
0.8345
0.8112
(46)
Integral
1.0000
0.9401
1.0258
2.0354
1.1054
2.0730
0.9784
1.0888
0.9649
1.0088
3.1201
1.0459
2.9276
12.291
2.1142
3.8795
14.650
3.1706
(ppm)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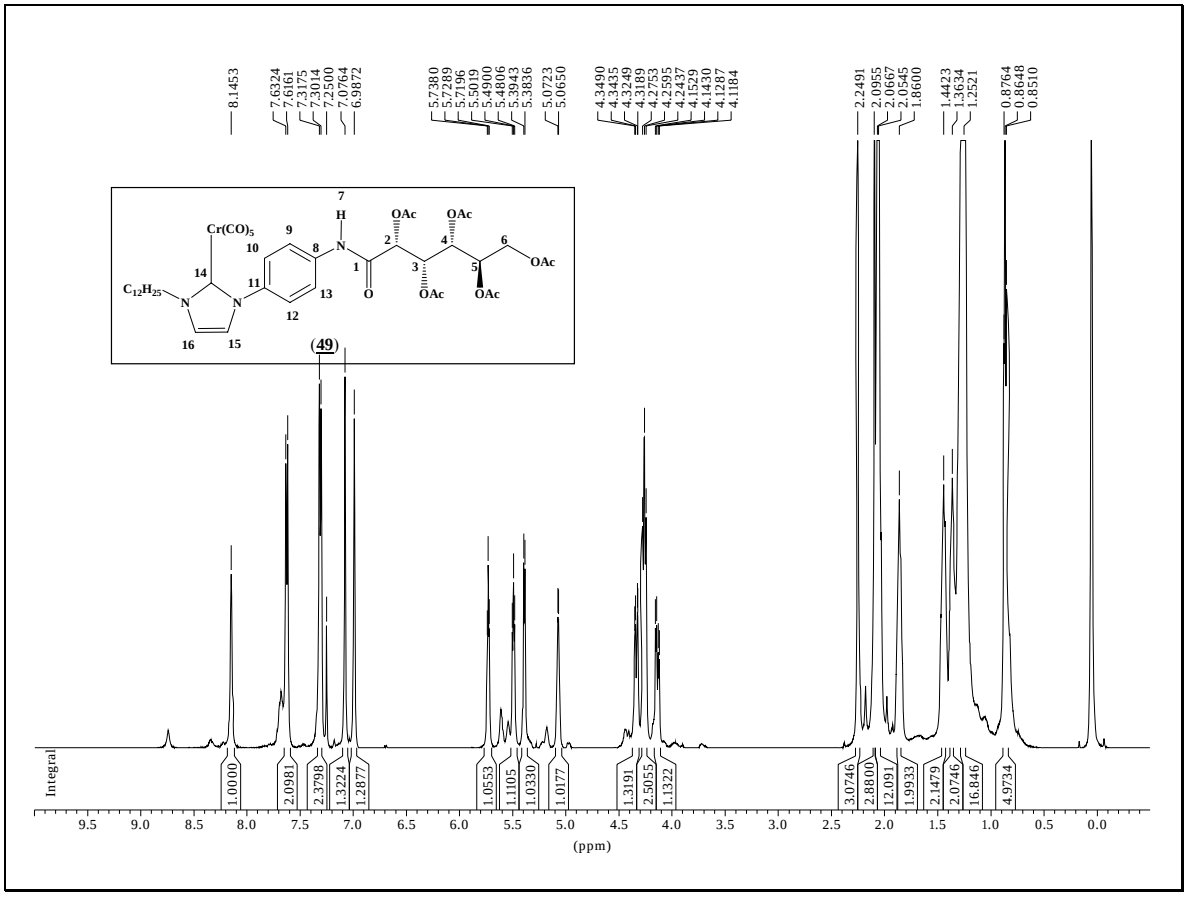
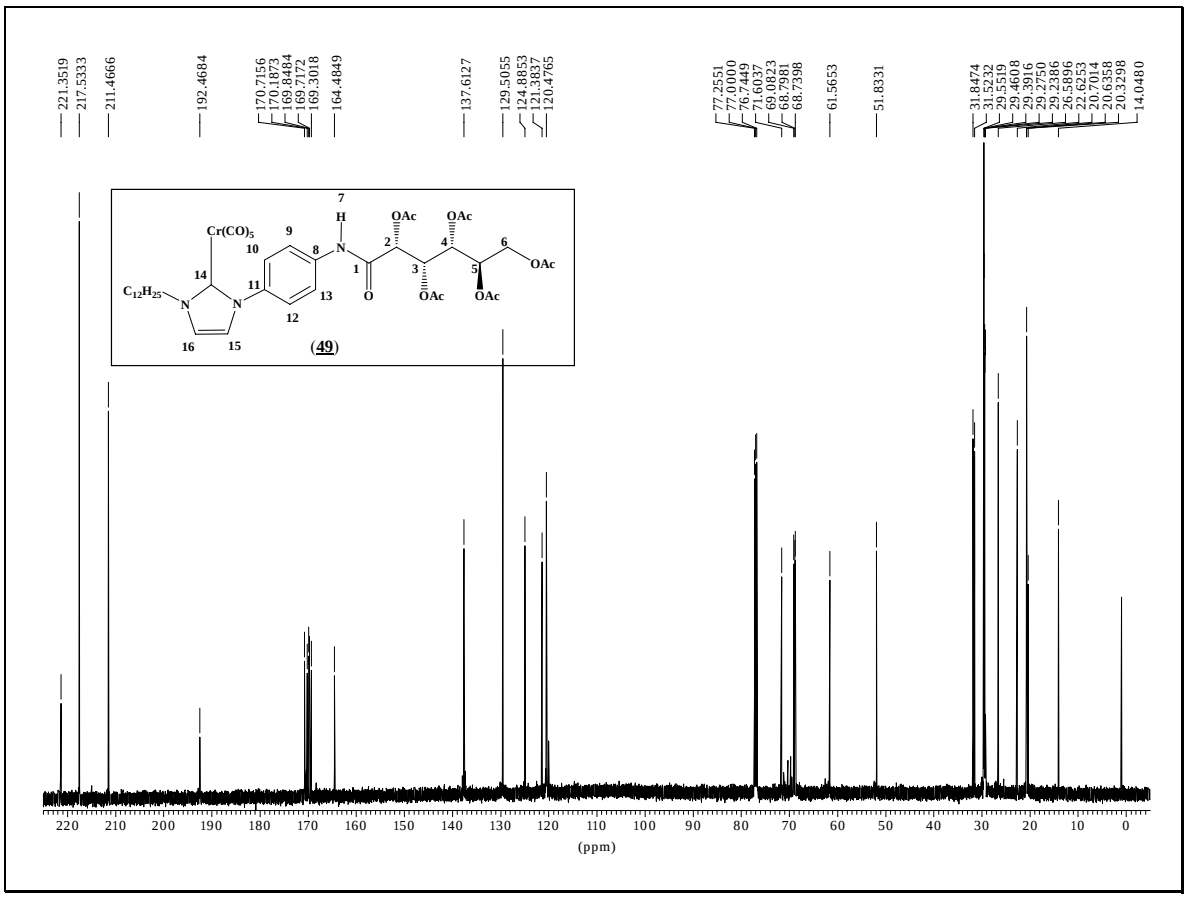
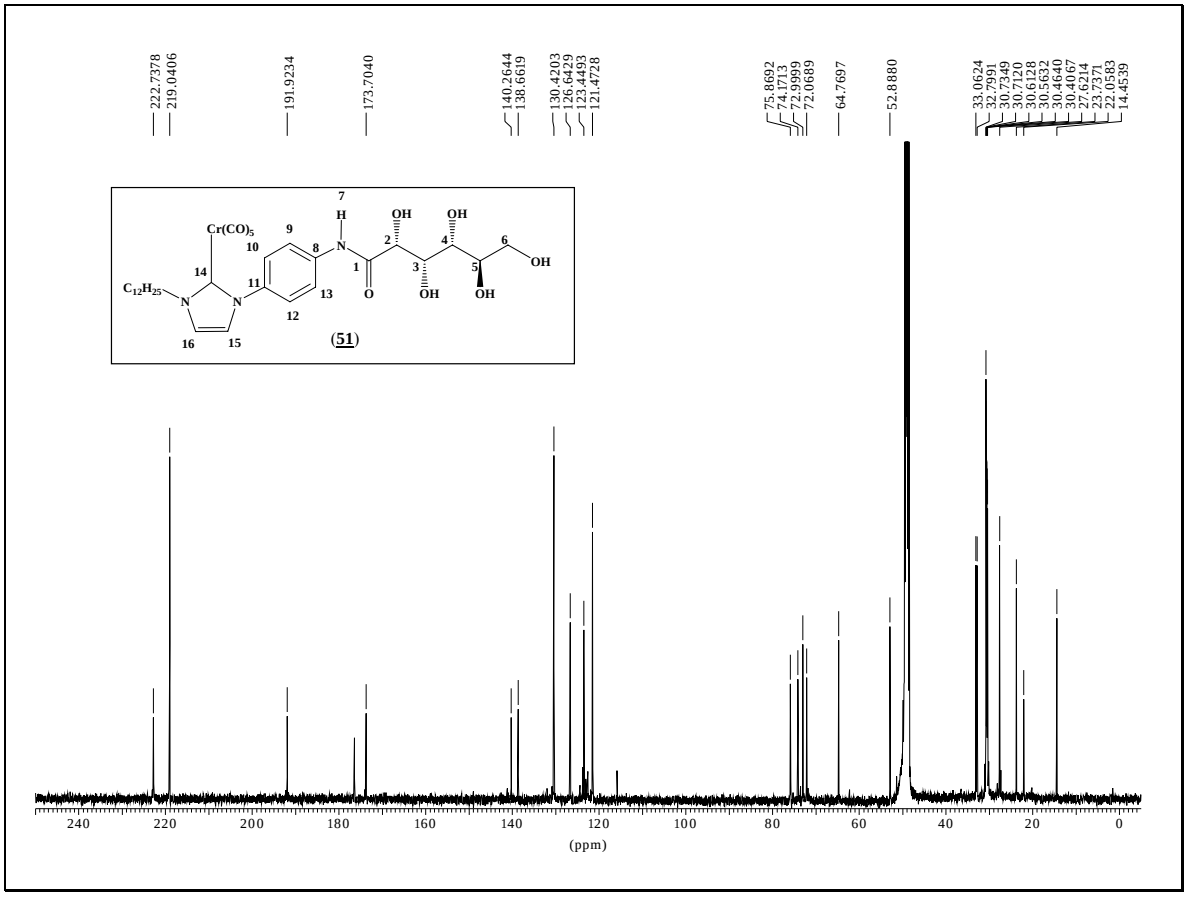
170.1967
169.9440
169.7149
169.6913
165.1183
138.9916
134.1501
129.5851
122.8717
121.8924
121.0473
120.9130
77.4186
77.0000
76.5735
72.3402
69.5916
68.9282
68.5807
61.9148
50.5653
31.7917
30.0067
29.5171
29.5013
29.4460
29.3512
29.2248
28.9721
25.5668
20.8608
20.8371
20.7423
20.6555
14.0132
(46)
(ppm)


8.1453
7.6324
7.6161
7.3175
7.3014
7.2500
7.0764
6.9872
5.7380
5.7289
5.7196
5.5019
5.4900
5.4806
5.3943
5.3836
5.0723
5.0650
4.3490
4.3435
4.3249
4.3189
4.2753
4.2595
4.2437
4.1529
4.1430
4.1287
4.1184
2.2491
2.0955
2.0667
2.0545
1.8600
1.4423
1.3634
1.2521
0.8764
0.8648
0.8510
Cr(CO)5
C12H25
OAc
(49)
Integral
1.0000
2.0981
2.3798
1.3224
1.2877
1.0553
1.1105
1.0330
1.0177
1.3191
2.5055
1.1322
3.0746
2.8800
12.091
1.9933
2.1479
2.0746
16.846
4.9734
(ppm)


221.3519
217.5333
211.4666
192.4684
170.7156
170.1873
169.8484
169.7172
169.3018
164.4849
137.6127
129.5055
124.8853
121.3837
120.4765
77.2551
77.0000
76.7449
71.6037
69.0823
68.7981
68.7398
61.5653
51.8331
31.8474
31.5232
29.5519
29.4608
29.3916
29.2750
29.2386
26.5896
22.6253
20.7014
20.6358
20.3298
14.0480
Cr(CO)5
C12H25
OAc
(49)
(ppm)


222.7378
219.0406
191.9234
173.7040
140.2644
138.6619
130.4203
126.8429
123.4493
121.4728
75.8692
74.1713
72.9999
72.0689
64.7697
52.8880
33.0624
32.7991
30.7349
30.7120
30.6728
30.6532
30.4640
30.4067
27.6214
23.7371
22.0583
14.4539
(51)
240
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

I insure that the available work has been independently written. No other aids than the indicated ones were used, as well as all marked quotations.

Ich versichere, die vorliegende Arbeit selbständig verfaßt zu haben. Es wurden keine anderen als die angegebenen Hilfsmittel verwendet, sowie alle Zitate kenntlich gemacht.

Bonn, Juli 2007 _____

Romain Germaneau

Keywords:

- Fischer Carbenes
- *N*-Heterocyclic Carbenes
- Gels
- Carbohydrates
- Amphiphiles
- Chromium

Mots-clés:

- Carbenes de Fischer
- Carbenes de type *N*-Heterocyclic (NHC)
- Gels
- Carbohydrates
- Amphiphiles
- Chrome