Polynuclear Group 13 Compounds: Synthesis, Characterization, and Reactivity

DISSERTATION
ZUR ERLANGUNG DES
DOKTORGRADES DER NATURWISSENSCHAFTEN
(DR. RER. NAT.)
DER FAKULTÄT FÜR CHEMIE UND PHARMAZIE
DER UNIVERSITÄT REGENSBURG

vorgelegt von
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aus Theuern
im Jahr 2019

Diese Arbeit wurde angeleitet von Prof. Dr. Robert Kretschmer.

Promotionsgesuch eingereicht am: 24.07.2019

Tag der mündlichen Prüfung: 13.09.2019

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This thesis was elaborated within the period from October 2016 until July 2019 in the Institute of Inorganic Chemistry at the University of Regensburg, under the supervision of Prof. Dr. Robert Kretschmer and Prof. Dr. Manfred Scheer.

Parts of this work have already been published:

- M.E. Desat, S. Gärtner, R. Kretschmer.
  ‘Dinuclear Indium and Thallium Diyls: Biscarbenoids or Metal Cluster?’
  Chem. Commun. **2017**, *53*, 1510-1513.

- M.E. Desat, R. Kretschmer.
  ‘En Route to Bis(carbene) Analogues of the Heavier Group 13 Elements: Consideration of Bridging Group and Metal(I) Source’
  Chem. Eur. J. **2018**, *24*, 12397-12404.

dedicated to my family

Preface

Some of the presented results have already been published or submitted during the preparation of this thesis (vide supra). The relevant content is reprinted with the permission of WILEY-VCH publishing and the Royal Society of Chemistry. The corresponding citations and license number are given at the beginning of the respective chapters.

Each chapter includes a list of authors. At the beginning of each chapter the individual contribution of each author is described. Additionally, if some of the presented results have already been partly discussed in other theses, it is stated at the beginning of the respective chapters.

To ensure uniform design of this work, all chapters are subdivided into ‘Introduction’, ‘Results and Discussion’, ‘Conclusion’, ‘References’, and ‘Supporting Information’. Furthermore, all chapters have the same text settings and the numeration of compounds, figures, schemes and tables begins anew. The depicted molecular structures may differ in their style. A general ‘Introduction’ and the ‘Research Objectives’ are given at the beginning of this thesis. In addition, a comprehensive ‘Conclusion’ of this work is presented at the end of this thesis.

Table of Content

1 Introduction

1.1 Catalysis – from transition metal to main group element

Catalysis is one of the most important topics in chemical industry. This fact arises from the possibility to convert fossil and alternative raw materials, like biomass or carbon dioxide, into valuable products in environmentally friendly and economical processes.[1] In 1835, Jöns Jakob Berzelius used the term ‘catalysis’ to describe reactions involving substances that accelerate the reactions but remain unchanged itself.[2] Later on, Wilhelm Ostwald defined the concept of catalysis in 1894 as a chemical process using a catalyst to reduce the activation energy without changing the position of the thermodynamic equilibrium and without consuming the catalyst in the reaction.[3]

Today, about 90%[1b] of the products in the chemical industry are produced by catalytic processes.[4] One reason for this large application is the optimization of chemical processes by using a selective and active catalyst, which requires less energy and resources, and thus leads to a positive energy efficiency. Currently, the most effective and most widely used catalyst are based on transition metals like iridium (Vaska’s complex **I**,[5] Cativa process **II**),[6] rhodium (Wilkinson’s catalyst **III**,[7] Monsanto process **IV**),[8] palladium (Lindlar catalyst **V**,[9] Hoechst-Wacker process **VI**),[10] ruthenium (Grubbs I and II catalyst **VII**, **VIII**)[11] or molybdenum (Schrock catalyst **IX**),[12] as shown in Figure 1.

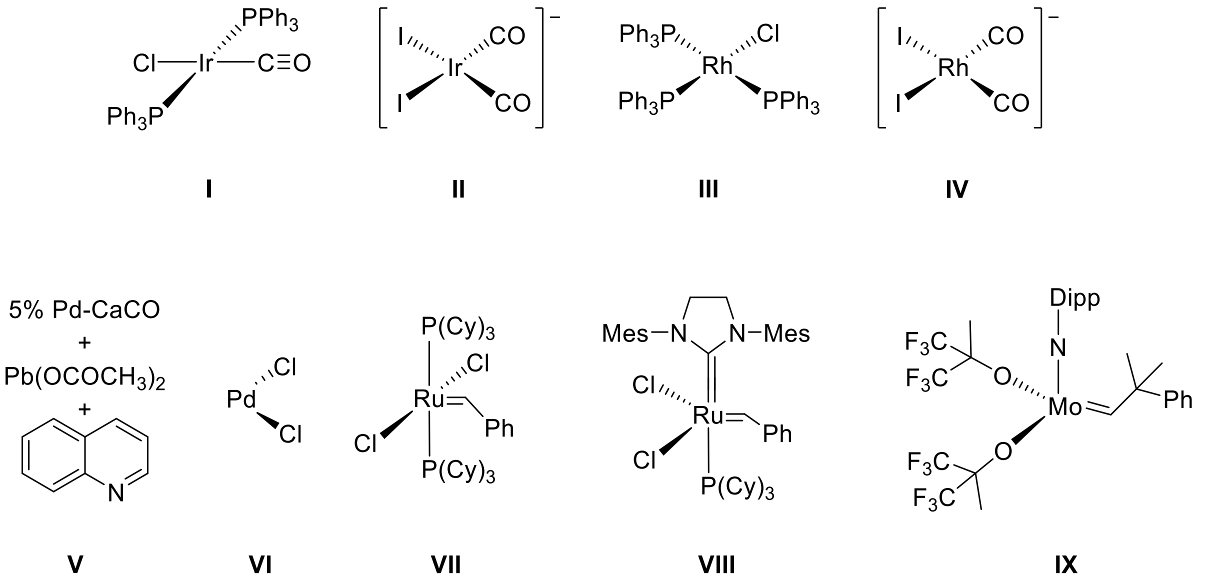
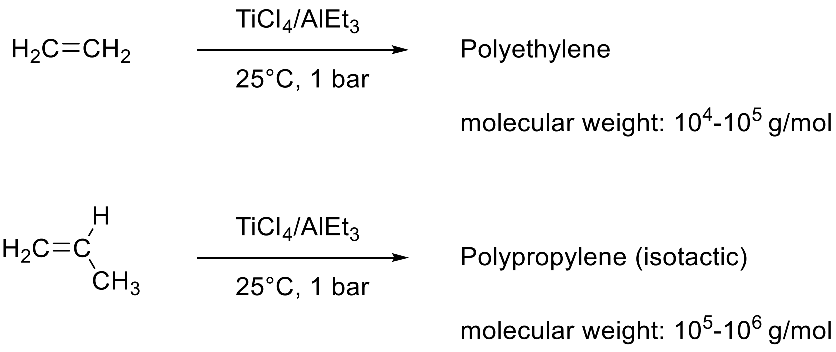


Figure 1. Selected catalysts based on transition metals. Ph = phenyl, Cy = cyclohexyl, Mes = 2,4,6-trimethylphenyl, Dipp = 2,6-diisopropylphenyl.[6-13]

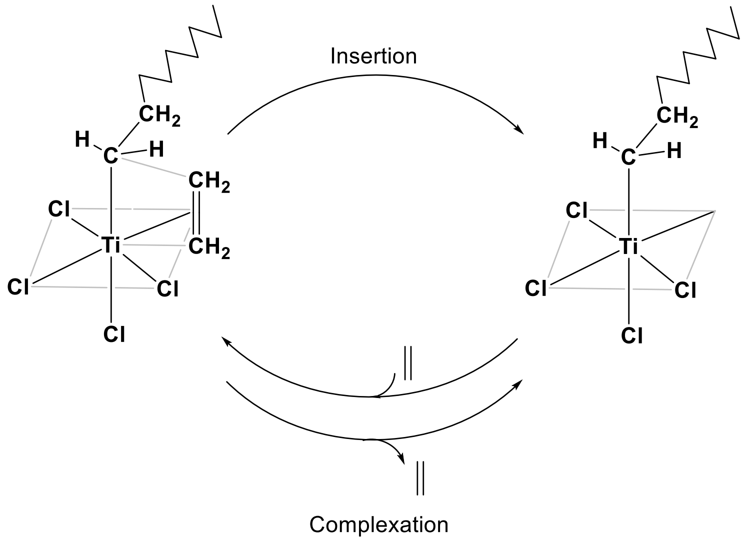
However, these catalysts have a drawback, because transition metals are available only in very limited quantities (mass-abundance in earth's crust around 0.001 to 0.005 ppm)[13] and therefore associated with high costs. Considering these disadvantages, the development of alternative catalyst is a major goal for chemical industry. Hereby main group elements, especially alkali and alkaline earth metals, triels and tetrels, are rising due to their high abundancy and their non (eco) toxic behaviour.[13,14] Particularly, aluminium is the most abundant metal element in the earth's crust with a mass-abundance of 7.57-% and an important material for many applications in the chemical industry.[13,15]

One of the most famous chemical processes involving aluminium as a co-catalyst, is the Ziegler-Natta polymerization, which was awarded with the Nobel Prize in 1963.[16] The inventor Carl Ziegler developed a method for producing polyolefins with given tacticity at atmospheric pressure and room temperature. It was possible to polymerize ethylene to linear and nearly unbranched polyethylene.[17] Due to the high degree of crystallinity and thus the higher hardness and rigidity (Young's modulus),[18] polyethylene found new applications as HDPE (high density polyethylene) in the industry in contrast to polymers prepared by free radical polymerization.[17,19] Giulio Natta transferred the catalysed process to the polymerization of propylene into isotactic polypropylene, Scheme 1.[16b,20]



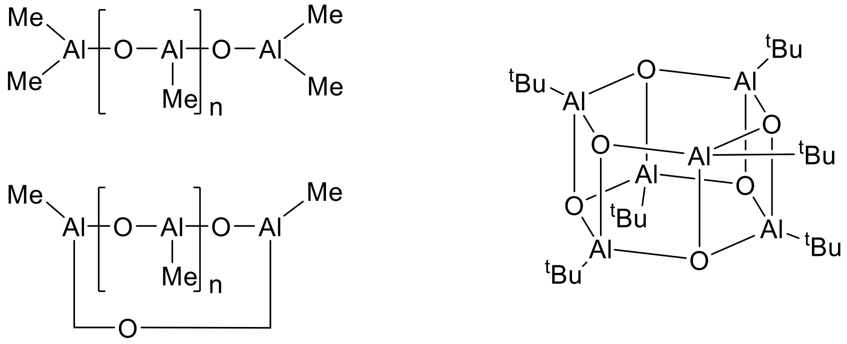
Scheme 1. Olefin polymerization of ethylene[17] and propylene[20] by the Ziegler-Natta process.

The Ziegler-Natta catalyst[21] is based on two components: A transition metal complex, like titanium(IV) chloride ($TiCl_4$), in combination with a co-catalyst consisting of organoaluminum compounds such as triethylaluminum ($AlEt_3$) or diethylaluminum chloride ($AlEt_2Cl$). Cossee and Arlman were able to describe the model, that demonstrated the polymerization at the surface of an active $TiCl_3$-center with alkyl aluminium compounds, as shown in Scheme 2.[22] The mechanism of this process is a coordinative insertion polymerization, where the monomer inserts between the metal atom and the growing chain. By coordination of the monomer to the catalyst complex, the orientation of the monomer is affected, and stereospecific polymerization is possible.[21]



Scheme 2. Catalytic cycle of the ethylene polymerization on a heterogenous $TiCl_3$-catalyst by Cossee and Arlman.[21-23]

To achieve a higher yield, the catalysts have been gradually replaced in recent years by metallocene-based catalysts, so-called Kaminsky catalyst.[24] Also, modified methyl aluminoxanes MAO (**X** and **XI**, Figure 2) were used as co-catalysts to activate the metallocene. The combination of metallocene dichloride complexes and MAO provides a highly active polymerization catalyst, that allows better control in molecular weight, polydispersity and polymer microstructures. The first step in the activation reaction is the methylation of the metallocene dichloride complex by MAO. After the formation of a metallocene dimethyl complex, one of the methyl anions is abstracted by a second MAO and a metallocene monomethyl cation is obtained with a free coordination site at the metal centre, which acts as an active species in the polymerization, Figure 2.[24b,24e,24d]



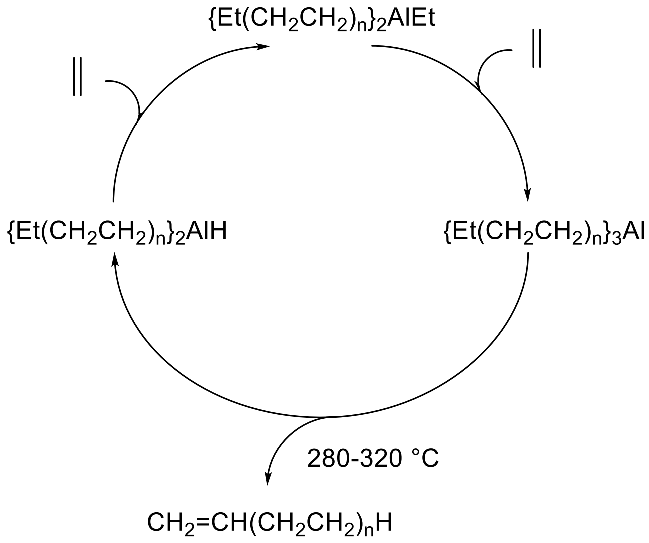
X

XI

$$Cp_2MCl_2 \xrightarrow{MAO} Cp_2MMe_2 \xrightarrow{MAO} [Cp_2MMe]^+ + [MAO\text{-}Me]^-$$

Figure 2. Formation of the active site on the metallocene by the reaction with MAO and examples of modified MAOs **X** and **XI**.[24b,24e,24d]

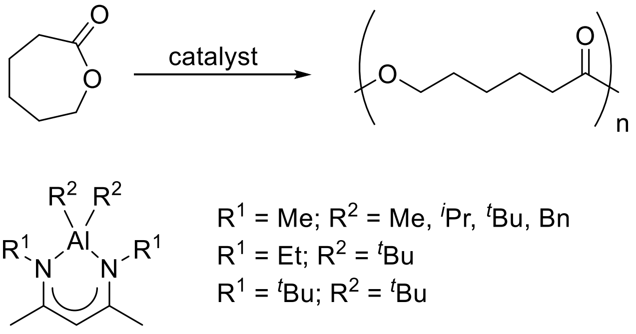
As shown above, the organoaluminum reagents serve as co-catalysts activating the transition metal for the processes. However, there are several procedures in which organoaluminum compounds act as catalyst themselves.[25] One example is the formation of long-chain terminal alkenes from ethylene, the so-called ‘Aufbau reaction’, as shown in Scheme 3. For this purpose, aluminium alkyl compounds are heated in the absence of oxygen to 280-320°C to facilitate *β*-hydride elimination and formation of terminal alkenes. The process is catalytic because the regenerated aluminium hydride is capable for further ethylene insertions.[26]



Scheme 3. Aluminium catalysed oligomerisation of ethylene.[26]

Another industrial relevant application of aluminium(III) alkyl compounds is the ring-opening polymerization (ROP) of cyclic esters (e.g. *ε*-caprolactone, lactide or glycolide).[27] ROP is a polymerization method, where a bond cleavage of a cyclic monomer forms a linear polymer with the driving force to reduce the ring strain in the monomer molecule.[28]

For example, the research group of Zhou developed organoaluminium compounds stabilized by *β*-diketiminates which initiate the ring-opening polymerization of *ε*-caprolactone, Scheme 4.[27d]



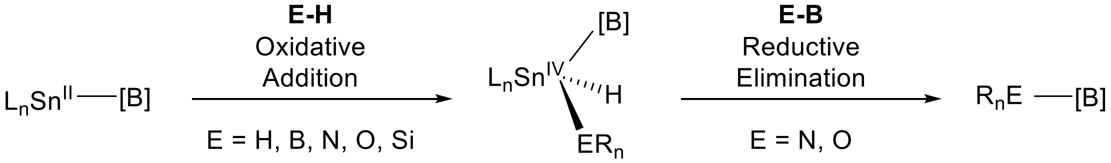
R^1 = Me; R^2 = Me, ^{i}Pr, ^{t}Bu, Bn
R^1 = Et; R^2 = ^{t}Bu
R^1 = ^{t}Bu; R^2 = ^{t}Bu

Scheme 4. Ring-opening polymerization (ROP) of *ε*-caprolactone.[27e]

Likewise, the ring-opening polymerization of cyclic esters has gained in importance because it can yield biodegradable polymers, such as polycaprolactone and poly(lactic acid)s, to replace petroleum-based polymers.[29] These polyester materials, produced by well-controlled and catalysed ROP, find many applications in packing,[30] electronics[31] and in the biomedical field.[32]

Nevertheless, the moderate number of examples shows that the concept of the classical transition-metal catalysis cannot be completely transferred to main group compounds. The sequence of oxidative addition and reductive elimination that frequently occurs in transition-metal catalysis is difficult to convey. It is also evident, that the associated $M^{n+}/M^{(n+2)+}$ redox shuttle is facile for noble metals, but not well established for main group systems, because the low oxidation states are more difficult to access.[4b,33]

The oxidative bond activation by low valent main group compounds is already known, for example the activation of small molecules (CO, H_2, NH_3, P_4) by stable 6-valence-electron carbenes.[4c,34] The problem is, that the subsequent regeneration of the reduced state via reductive elimination is typically not viable, because of the formation of thermodynamically stable M–X bonds.[35] However, remarkable examples of reductive elimination have been reported recently.[36] Aldridge and co-workers described the oxidative addition and reductive elimination at a bis(boryl)stannylene.[37] They used strongly σ-donating bis(boryl) ancillary ligands, which can achieve the oxidative addition of a range of E–H bonds from H_2, SiH_4, $PhSiH_3$, $BH_3{\cdot}NMe_3$, H_2O and NH_3. Furthermore, in the case of H_2O and NH_3 a reductive elimination was possible, shown in Scheme 5.



Scheme 5. Oxidative Addition of E–H bonds at a Sn^{II}-center followed by reductive elimination. ER_n = H, SiH_3, $PhSiH_2$, $BH_2{\cdot}NMe_3$, OH, NH_2.[37]

Besides these successful results, this concept cannot be applied to all main group elements.[36] Therefore, current efforts are also focused on the development of new models for the activation and transformation of small molecules. An interesting option provides the cooperative effect and its potential in polynuclear element compounds, because it possibly enhances the catalytic activity and selectivity compared to their mononuclear counterparts.

1.2 Cooperative effects

Models for such multimetallic systems can be found in nature, where the cooperative activation and selectivity are common features of enzyme catalysis. An example is the methane monooxygenase (MMO), which is able to oxidize the C–H bond in methane to form methanol. MMO appears in two types: the soluble sMMO[38] and the particulate pMMO.[39] In both cases, the activity is based on the interaction of two metal centres for the fixation of oxygen. sMMO contains a Fe_2-center bridged by an oxygen atom and in the case of pMMO the active site is a Cu_2-center. Additionally, the spatial proximity of the two metal centres is crucial for the binding of oxygen, Figure 3.

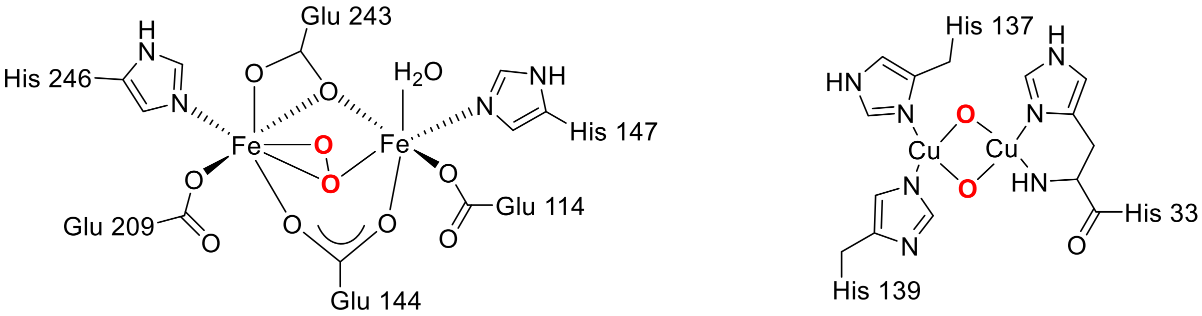
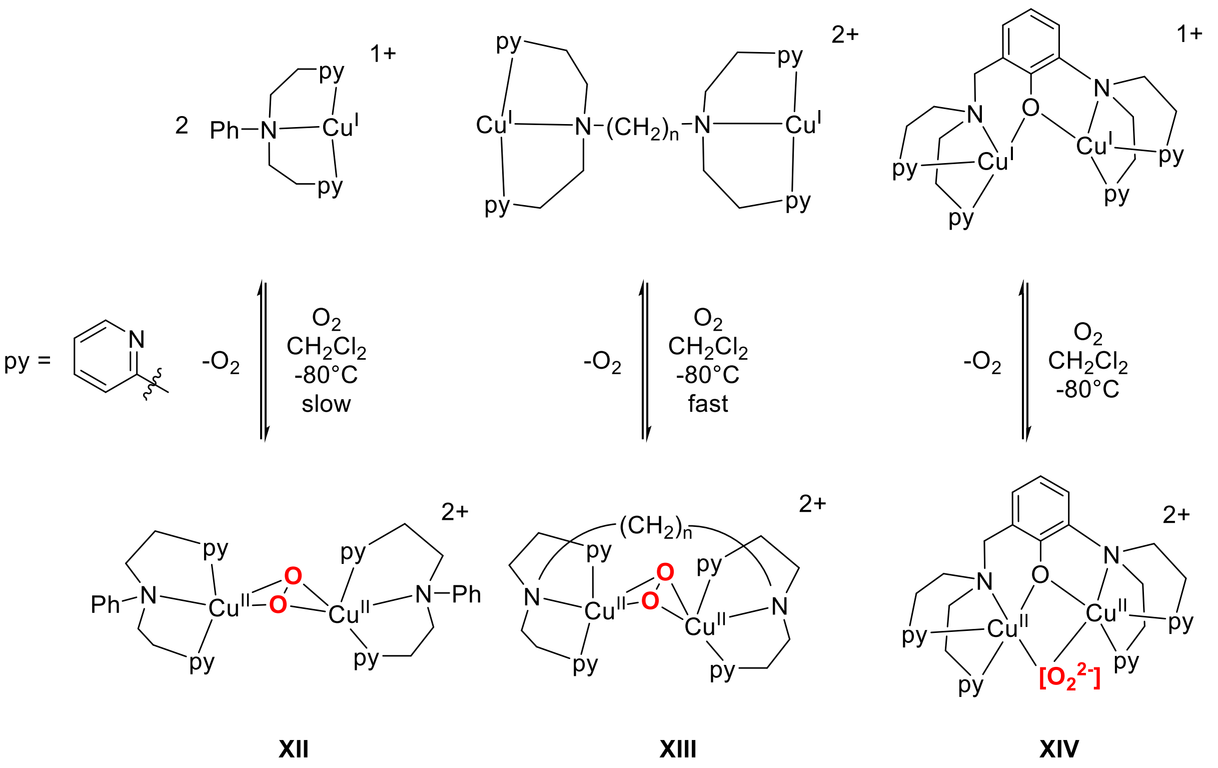


Figure 3. Fixation of O_2 (in red) by the sMMO and pMMO at the active centre.[38,39]

The research of Karlin and co-workers demonstrates further advantages of bimetallic complexes.[40] As shown in Scheme 6, the two complexes **XII** and **XIII** differ only in that **XIII** has two binding sites linked by a bridging scaffold. However, using dinuclear complexes instead of their mononuclear congener, the fixation of oxygen between the copper centre is faster. Thus, the reaction rate is influenced by the bridging ligand and the associated spatial proximity of the metal centres. Also changing the ligand design allows for new modification and other behaviours, for example decreasing the free coordination sites, shown in the example of **XIV**.



Scheme 6. Reaction of different copper(I) complexes with oxygen. [40]

Due to this finding and considering the presence of the cooperative effects between the two metal centres, more attention is paid to the design and synthesis of bimetallic complexes supported by binucleating ligands, due to their wide application in homogenous catalysis.[41]

Thus, a series of bimetallic complexes containing main-group and transition metals based on well-defined binucleating ligands has been described.[42] Compared to their mononuclear analogues, these compounds showed promising catalytic activities in the polymerization of olefins,[42g,42h,42j,42k,42l,42p] the copolymerization of epoxide with CO_2[42a,42e,42f,42m] and a series of organic transformations.[42c,42d,42n] Marks and co-workers reported, that phenylene-, siloxane-, and polymethylene linked metallocene and half-metallocene transition metal complexes (M = Ti, Zr) have shown bimetallic cooperative effects in olefin polymerization.[42h,42j,42k,42l,43] Furthermore, bimetallic aluminium(salen) compounds (salen = N,N'ethylenebis(salicylimine)) display high catalytic activity for the synthesis of cyclic carbonates from epoxides and CO_2.[41e] In addition, synergistic effects can occur by bimetallic compounds, where the structure and reactivity are inextricably linked. These allow the construction of transition state geometrics with substrates and thus react with organic substrates in special ways inaccessible to monometallic compounds.[44] Also, the combination of a Lewis base and a Lewis acid in bimetallic compounds, so called frustrated Lewis Pairs (FLPs), can lead to a variety of catalytic transformations and activation of H–X bonds (X = H, B, Si, N, P).[45]

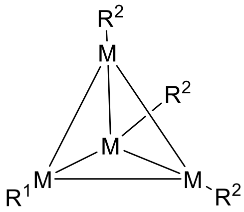
Finally, it can be summarized, that the cooperative or synergistic effect of two metal centres in close proximity influences the metal-metal interactions of binuclear compounds, thereby improving the reaction rate and product selectivity in the catalysis. Thus, the cooperativity is often recalled as ‘1+1>2’effect.[46]

1.3 Group 13 - and its reactive oxidation state +1

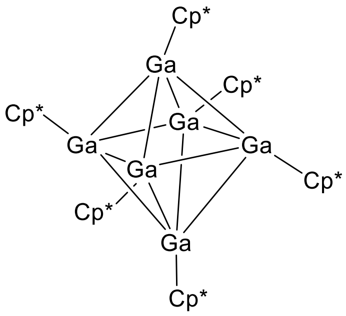
In recent decades, the chemistry of the group 13 elements – comprising boron, aluminium, gallium, indium, and thallium – has made a significant progress. The development and synthesis of low valent compounds, and their structural diversity is of great interest.[47] Characteristic features for the triels are the common valence electron configuration ns^2np^1 and their oxidation states +3 and +1. The stability of the highest oxidation state +3 decreases with increasing atomic number from boron to thallium compounds. This is known as the inert pair effect, which describes the release of the *np* electrons, remaining the ns electrons as an ‘inert pair’. The reason therefore is the decreasing willingness of the s-electron pair to participate in ionic or covalent bonds, due to the insertion of the d- and f-block elements. Therefore, compounds of the triels in the oxidation state +1 for indium can be obtained whereas it is even most stable form for thallium.[48]

As stated above, aluminium prefers the oxidation state +3, which also occurs in natural compounds.[49] The oxidation state +1, however, is rare in aluminium compounds and can only be stabilized by sterically demanding ligands.[50] In 1991, Dohmeier *et al.* synthesized the first organometallic aluminium(I) compound $[(Cp^*Al)_4]$ (**XV**) by reaction of metastable AlCl with Cp^*_2Mg ($Cp^* = C_5Me_5$).[50a] Subsequently, further Al(I) compounds could be obtained: $Al_4[Si(^tBu)_3]_4$ (**XVI**),[50b] $Al_4[C(SiMe_3)_3]_4$ (**XVII**),[50c] $[(Cp^*Al)_3AlN(SiMe_3)_2]$ (**XVIII**),[50d] and $Al_4[Si(SiMe_3)_3]_4$ (**XIX**),[50e] which are present as tetramers in the solid state. In these configurations the Al(I) compounds form a metal substituent σ-bond excluding $[(Cp^*Al)_4]$, which forms a π-bond.[51]

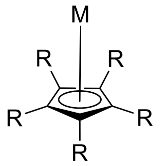
Compounds in the oxidation state +1 could also be obtained for the heavier group 13 homologues.[52] The gallium compound GaCp* (**XX**) exists as a hexamer in the solid state,[52f] whereas indium [52c,52h,52i] and thallium[52b] are monomeric species (**XXI**). In addition, for the elements indium and thallium the sterically less demanding Cp ligands are also suitable for the formation of the monomers ECp (E = In,[52a] Tl;[52d] $Cp = C_5H_5$; **XXII**). Using tris(trimethylsilyl)methyl ligands instead of Cp* for the triels Al - Tl, only tetrameric compounds of the type $M_4[C(SiMe_3)_3]_4$ (M = Al,[50c] Ga,[52e] In,[52g] Tl[52j], **XVII**) are observed.



XV: M = Al R^1 = R^2 = Cp*
XVI: M = Al R^1 = R^2 = Si(^{t}Bu)$_3$
XVII: M = Al, Ga, In, Tl R^1 = R^2 = C(SiMe$_3$)$_3$
XVIII: M = Al R^1 = N(SiMe$_3$)$_2$; R^2 = Cp*
XIX: M = Al R^1 = R^2 = Si(SiMe$_3$)$_3$



XX



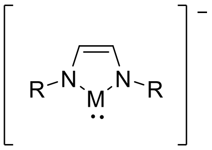
XXI: M = In, Tl R = Me
XXII: M = In, Tl R = H

Figure 4. Group 13 element compounds in the oxidation state +1.[50-52]

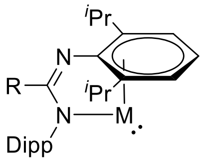
Furthermore, in all the above compounds with metal-ligand-σ-bonds, the metal has two empty orbitals and a free lone pair of electrons, which corresponds to an electron quartet configuration.[53]

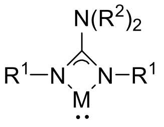
By using ligands, the unoccupied orbitals can be filled, so that an electron sextet or octet can be realized. This also applies to N-heterocyclic compounds, where the elements of the group 13 in the oxidation state +1 are integrated into the ring. Moreover, these compounds are valence isoelectronic to singlet carbenes, because the metal atom is characterized by an electron sextet, thus resulting in a bifunctionality at the element centre. The stability can be obtained by donating the electron density from the nitrogen atom into an empty orbital of the metal. Consequently, a lone pair and an unoccupied orbital remain at the metal, whereby the compound has both electrophilic and nucleophilic reactivity.

By stabilization with bulky substituents on the nitrogen atoms, low-valent group 13-metal compounds can be obtained.[54] Consequently, anionic five-membered compounds of the type $[M\{N(R)C(H)\}_2]^-$ (M = Ga, In; R = ^{t}Bu, Dipp, **XXIII**) can be isolated for gallium and indium.[10,55] The corresponding aluminium and thallium five-membered compounds could not be synthesised yet. Only Aldridge and co-workers have so far obtained an anionic aluminium(I) nucleophile, the dimethylxanthene stabilized potassium aluminyl.[56] In addition to these anionic compounds, neutral four-, five- and six-membered carbene analogues exist.[49,57] Amidinate[57j] and guanidinate[57f] ligands, collectively termed 'NCN ligands', are able to stabilize the Ga - Tl metals at the oxidation state +1. Theoretically, the amidine based carbenoids would be present as four-membered ligands, but in the case of the heavier homologs indium and thallium a five-membered 'N-Dipp chelating' compound is formed (**XXIV**). In contrast to the amidinates, the guanidinates are more electron rich ligands, because of the presence of an amino substituent in the backbone. An important consequence of the smaller bite angle is the effect on their steric properties, which allows the formation of a four-membered ring (**XXVI**).[57f,58] Only in the case of thallium, a five-membered ring is possible (**XXV**).[57f,57i] Using *β*-(diketimine)s, six membered carbenoids can be isolated for all group 13-metals (M = Al, Ga, In, Tl, **XXVII**).[49,57a-e,57h] For indium, monomeric species can be observed using 2,6-diisopropylphenyl substituents.[57c,57d] A dimeric indium diyl is obtained by the less bulky 2,6-di- and 2,4,6-trimethylphenyl derivatives.[59] In the most cases, Tl(I) β-diketiminate compounds exist as monomers in the solid state except for [:Tl{[N(3,5-dimethylphenyl)C(Me)]$_2$CH}], which forms a weakly Tl–Tl bonded trimer.[57d,57e]

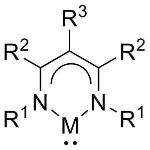

M = Ga, In
R = ^{t}Bu, Dipp

XXIII


XXIV: M = In, Tl; R = ^{t}Bu
XXV: M = Tl, R = NCy$_2$, N^{i}Pr$_2$, NC$_5$H$_8$Me$_2$-2,6


M = Ga, In
R^1 = Dipp = 2.6-^{i}Pr-C$_6$H$_3$
R^2 = Cy = C$_6$H$_{11}$

XXVI


XXVII

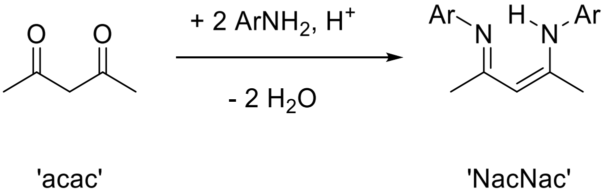
M = Al; R^1 = Dipp; R^2 = Me, ^{t}Bu; R^3 = H
M = Ga; R^1 = Dipp; R^2 = Me, R^3 = H
M = In; R^1 = Dipp; R^2 = Me, CF$_3$; R^3 = H
R^1 = C$_6$H$_3$Me$_2$-2,6; R^2 = Me; R^3 = H
R^1 = C$_6$H$_2$Me$_3$-2,4,6; R^2 = Me; R^3 = H
M = Tl; R^1 = Dipp; R^2 = Me; R^3 = H
R^1 = C$_6$H$_3$Me$_2$-2,6; R^2 = Me; R^3 = H
R^1 = SiMe$_3$; R^2 = Ph; R^3 = H
R^1 = Dipp; R^2 = H; R^3 = Ph

Figure 5. Group 13 carbene analogues.[10,49,54,55,57-59]

1.4 Bis(β-diketimine) ligands - A manifold ligand class

1.4.1 β-Diketimine ligands

β-Diketiminates are nitrogen-based monoanionic bidentate ligands having a basic structure analogue to β-diketonate ligands. The most common β-diketon is acetylaceton, in short 'acac'. Therefore, the acronym 'NacNac' has been established for the β-diketimine ligands, where the oxygen atoms are replaced by nitrogen atoms.[60]



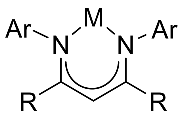
Scheme 7. Preparation of *β*-diketimine from condensation reaction of acetylacetone with primary amines.[60]

Since their first application by McGeachin, Parks and Holm in 1968, β-diketiminates have gained in importance in coordination chemistry.[61] Their popularity was obtained by a simple synthesis and the variability of the steric and electronic properties. Thus, the widely adopted NacNac ligands have been used for the stabilization of a variety of metal ions in different oxidation states and coordination numbers.[60,62]

The increased attention is due to the properties of the stereoelectronic tuneability, allowing for the isolation of coordinatively unsaturated compounds with strong metal-ligand bonds and high reactivity. The presence and the judicious selection of the substituents on the nitrogen atoms, the steric bulk and the electronic properties can be easily modified.

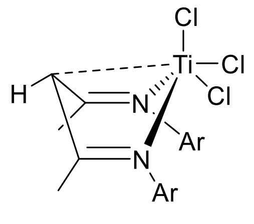
Nevertheless, numerous publications describe, that the β-diketiminates do not behave as spectators and participate in various unexpected reactivities or unwanted decompositions. This reflects in the non-innocent behaviour of the ligand in oxidation and reduction reactions and the tendency to undergo intramolecular transformations, with the consequence of the reorganization of the ligand structure. The perspective article of Camp and Arnold shows details of the reaction on the NacNac ligands, like the reductive cleavage of the C–N bond or the intramolecular cross-metathesis due to the reaction with a high-valent early transition metal fragment. By using an alkali salt, acting as a one-electron reducing agent, a NacNac radical intermediate can also be formed, which leads to dimerization by C-C radical coupling. Additionally, more models exist, leading to diverse coordination modes.[62s]

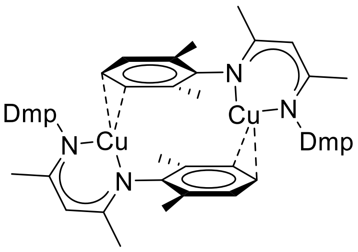
However, the most common arrangement of the deprotonated β-diketiminate ligands is in the conformation $[\{N(Ar)C(R)\}_2CH]^-$ (Ar = aryl, R = aryl, alkyl or silyl) (**XXVIII**). The negative charge leads to a η^2-coordination of the metal between the two nitrogen atoms affording a six-membered ring. In addition, the metal-ligand interaction can be modified by variation of the substituents on the nitrogen and carbon atoms of the backbone.[62r] Small substituents such as a hydrogen atom, a methyl- or silyl group on the nitrogen atoms lead to dimeric complexes and allow a higher coordination of the metal center.[60] In contrast, with sterically more bulky aryl groups on the nitrogen atoms, compounds with low coordination numbers of the metal can be formed. Thereby a variety of bonding modes can be realized, Figure 6. For example, a boat conformation can be achieved by the stabilization of a titanium complex (**XXIX**),[63] while a binuclear compound, in which the metal atoms are chelating and bridging, was found for copper (**XXX**).[64] Also, C- and N- centered metal β-diketiminates can exist with a terminal coordination by using mercury (**XXXI**)[65] or silver (**XXXII**)[66] species.

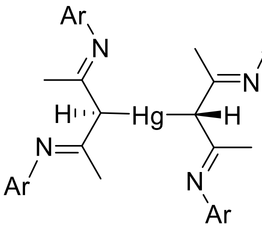


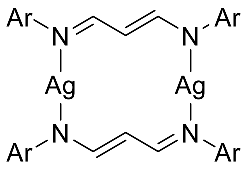
Ar = aryl
R = aryl, alkyl, silyl

XVIII









XXIX **XXX** **XXXI** **XXXII**

Figure 6. Different coordination modes of β-diketiminate compounds (Dmp = 2,6-dimetylphenyl).[60-66]

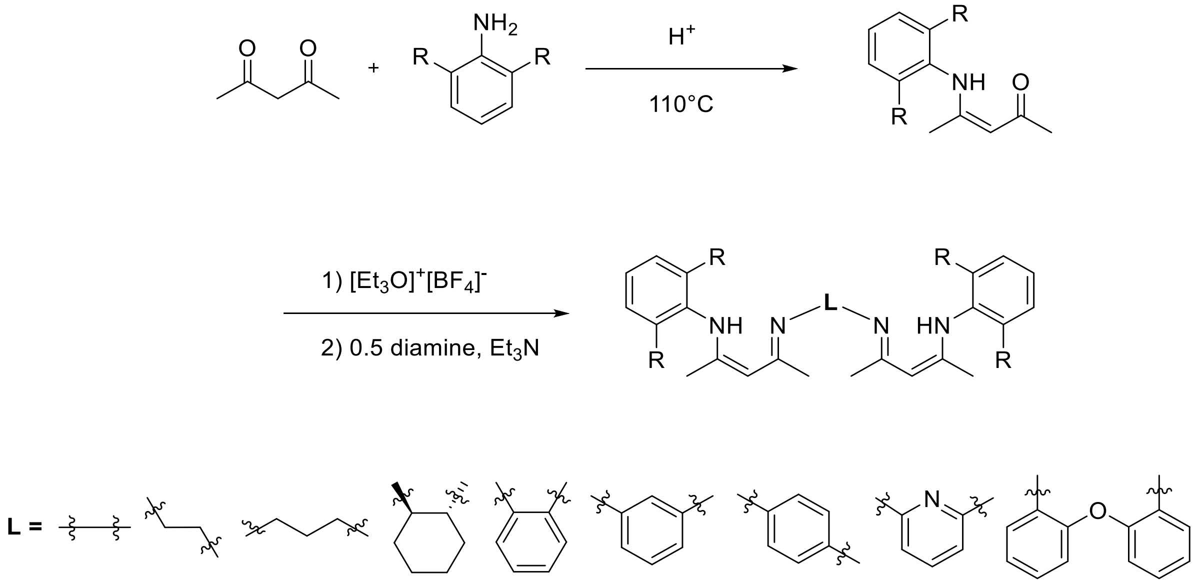
Thus, using bulky substituents on the nitrogen atoms, the low-valent group 13 compounds can be stabilized, in which the metal centre has the oxidation state +1. As shown in several articles,[49,57a,57c,57d,57e,57h] the NacNac compounds for aluminium,[49] gallium,[57a] indium,[57c,57d] and thallium[57e,57h] can be realized with 2,6-diisopropylphenyl as a substituent. All triels have η^2-coordination of the metal between the nitrogen atoms (**XVIII**).

1.4.2 Bis(β-diketimine) ligands

The connection of two or more β-diketimines by a variety of rigid, semi-rigid or flexible spacers leads to the interesting class of bis- and poly(β-diketimine) ligands.[42e,67] These offer advantages in reactivity and selectivity compared to their mononuclear compounds, as they allow for the coordination of two metals, which finally provides opportunities for cooperative and emergent effects.[67e,67f]

Alkyl-, aryl- and N-N-bridged systems have been described.[67b,67d,67e,67i,67h] By the variation of the spacer, different electronic properties and geometries can arise and the linking of the two β-diketimine units could increase the complex stability. Also, a stereoselective control can be obtained by choosing a chiral linker[67a] and a macrocyclic ligand is possible by using two connections.[42e,67c,67g]

The bis(β-diketimine) ligands are regularly prepared in a two-step condensation route, which is shown in Scheme 7. Initially, a β-enaminoketone is formed by the reaction of acetylacetone and an aniline derivate. In the second step the carbonyl function is activated using Meerweins salt and then reacted with the respective diamine to the target product.[67d,67e,67h] A variety of bridged ligands can be obtained by using different diamines, for example hydrazine, 1,2-ethylene- and 1,3-propylenediamine, (±)-trans-1,2-cyclohexanediamine, substituted phenylenediamines, 2,6-diaminopyridine or 2,2'-oxydianiline, Scheme 8.[67d,67e,67h,68]



Scheme 8. Synthesis of Bis(β-diketimine) ligands.[67,68]

In addition to the possibilities of metal-ligand interactions, the two binding sites of the bis(β-diketimine) ligands can interact with either one or two metal atoms. If both binding sites are occupied by one metal atom, it is possible to realise emergent and cooperative effects.[46c,67e,67f,69] Compared with the NacNac ligands a wide range of metal ions from the s-, p-, d- and f-block can be stabilized by bis(β-diketimine) ligands.[42r,42s,67b–i,68,70]

Bourget-Merle *et al.* synthesized an *ansa*-CH_2 bridging bis(β-diketiminate) from a β-diketiminato lithium compound and dibromomethane, which reacts with trimethylaluminium to the corresponding dinuclear aluminium compound.[67b] The working group of Patrick L. Holland reported zinc, aluminium, and lithium compounds based on macrocyclic meta- and paraxylylene bridged bis(β-diketiminate) ligands.[67g] Lee *et al.* received macrocyclic complexes with zinc and copper.[67c] In all of these compounds a η^2-coordination between the nitrogen atoms and the metal centre exits. In contrast, the bis(β-diketiminate)s of lanthanides,[67d,67e,70c] zirconium[70d] and hafnium[67h] have coordination of one metal between the four nitrogen atoms. In addition, zinc, magnesium and calcium compounds were synthesized by the working group of Harder.[67i,68a–c,70a,70b,70g,70f] Gong *et al.* isolated binuclear aluminium alkyl compounds supported by linked bis(β-diketiminate) ligands.[70j]

Some of these species can be used to catalyze the copolymerization of epoxides and CO_2,[67d,68a] the ring-opening polymerization of lactides[70h,70j] and the polymerization of ethylene[67h] and isoprene.[42s,70e]

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2 Research Objectives

In the last decades, the synthesis of a variety of group 13 compounds was possible, in which the metal has the formal oxidation state +1. The stabilization of the corresponding group 13 carbenoids - aluminium, gallium, indium and thallium - was only able by using β-diketiminate ligands. In order to be able to use these compounds as effective catalysts, a new model for the activation and transformation of small molecules should be developed, since the concept of the classical transition-metal catalysis cannot be completely transferred to main group elements. A possible approach would be the exploitation of the cooperative effect using polynuclear compounds.

In this context, the current work focused on the synthesis of polynuclear, low valent group 13 compounds and the study of their emergent and cooperative effect. The use of rigid, semi-rigid and flexible β-diketiminate ligands controls the molecular arrangement to allow or exclude a direct metaloid-metaloid interaction. Likewise, the conversion into the respective metalloid compounds provides new insights.

Therefore, the following research objectives arise:

- Synthesis and characterization of new and already known β-diketimine ligands
- Preparation of various β-diketiminate based metal(I) complexes (M = In, Tl)
- Variation of the bridging units of the β-diketimine ligands to study the metaloid-metaloid interactions
- Investigation to their reactivity towards oxygen and sulfur
- Synthesis of aluminium(III) compounds by the variation of the reactants ($AlMe_3$, $AlCl_3$, $AlBr_3$, AlI_3+I_2)
- Reduction of the aluminium(III) halide compounds to obtained aluminium in the oxidation state +1

Preface

The following chapter has already been published in Chemical Communications of the Royal Society of Chemistry
‘Dinuclear Indium and Thallium Diyls: Biscarbenoids or Metal Cluster?’
Chem. Commun. **2017**, *53*, 1510-1513.

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Author contributions

The preparation of the manuscript was done by the first author (M. E. Desat). R. Kretschmer supervised the research and revised the manuscript. Preparation and characterization (NMR, EA, X-ray) of compound **1**, **2** and **3** have been part of the first author’s master thesis. VT ^{1}H NMRs of **2** and **3** were measured at the NMR Department of the University of Regensburg, for which the first author prepared the samples. R. Kretschmer performed all DFT calculations and contributed the corresponding parts in the manuscript and the Supporting Information. S. Gärtner supported the evaluation of the single crystal X-Ray diffraction measurement of compound **2** and **3**, conducted the solvent refinement and provided the corresponding section in the Supporting Information.

Acknowledgements

The project was financially supported by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft (DFG, KR4782/2-1), and the University of Regensburg. R. Kretschmer is grateful to the Stiftung Stipendien-Fonds des Verbands der Chemischen Industrie for a Liebig fellowship and to the Rechenzentrum of the University of Regensburg for the allocation of computer time. Additionally, generous support from Professor Manfred Scheer and helpful discussions with Dr. David A. Ruiz are gratefully acknowledged.

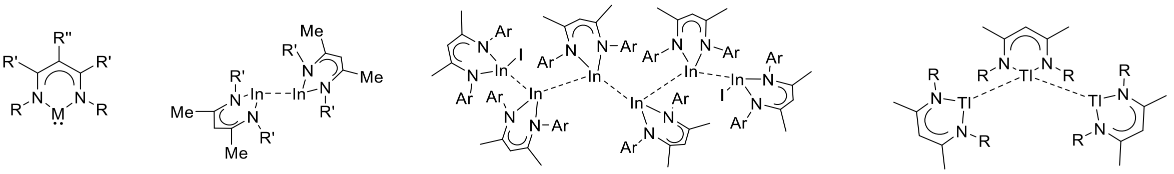
3 Dinuclear Indium and Thallium Diyls: Biscarbenoids or Metal Cluster?

Abstract: *Using Bis(β-diketiminate) ligands, we were able to synthesize unprecedented indium and thallium biscarbenoids. For indium, a novel four-membered metallacycle is derived from intra- and intermolecular In–In interactions in the solid state, while for thallium only an intramolecular Tl_2-dimer is obtained. Computational studies revealed that the solid-state structures benefit significantly from dispersion stabilization.*

3.1 Introduction

Low-valent Group 13 compounds that are isoelectronic with singlet carbenes have been a subject of remarkable interest.[1,2] Although triele species in the formal oxidation state +1 have been known for decades,[3,4] it was not until 1999 that the first Group 13 carbenoid, i.e., $[:Ga\{N(tertBu)C(H)\}_2]^-$,[5] was reported. The donation of four electrons from the bidentate nitrogen-based ligand yields a metal centre possessing an electron sextet. Consequently, the gallium atom features a vacant orbital and a lone pair of electrons as expected for a Group 13 element analogue of carbenes. In the early 2000s, this approach was extended to other icosagens and the application of chelating *N*,*N*-ligands allowed for the first preparation of Al,[6] Ga,[7] In,[8] and Tl[9,10] carbenoids.

Even though further examples have been reported in the following years,[2] the β-diketiminate (NacNac) ligand remains the only one capable of stabilizing the carbenoids of all four heavier trieles, i.e., Al, Ga, In, and Tl.[11] The structural features of these compounds do not only depend on the metal incorporated, but also on the steric bulk of the ligands. While for the aluminium[6] and gallium[7] derivatives only monomeric species have been observed, higher aggregates were identified in the solid state for indium[8, 12-15] and thallium.[10,12,16]



A (M = In, Tl) **B** **C** **D**

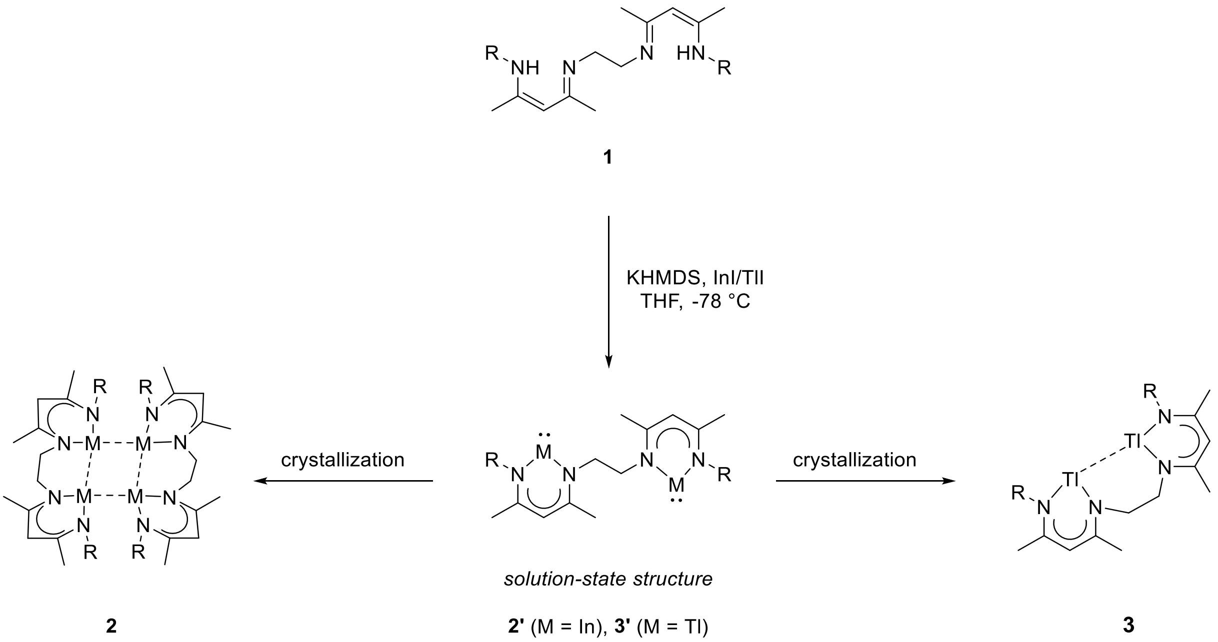
Scheme 1. Monomeric (A) and dimeric (B) diyls, linear In–In bonded hexamer (C), and Tl–Tl boned trimer (D).

Thereby, the substitution pattern of the phenyl rings attached to the NacNac ligand frame is of crucial importance, Scheme 1: While with 2,6-diisopropylphenyl substituents, monomeric species (A) are observed,[8,12] the less bulky 2,6-di- and 2,4,6-trimethylphenyl derivatives give rise to dimeric indium diyls (B).[13,15] However, these In–In contacts are very weak and it was shown by DOSY NMR studies, that they are not preserved in solution. Further modification of the steric demands by incorporating 3,5-dimethylphenyl rings, yields a linear In–In bonded hexamer (C),[14] in which only the four internal indium centres behave as In(I) atoms. For thallium, most of the Tl(I) β-diketiminate derivatives were found to be monomeric in the solid state (A), [10,12] while [:Tl{[N(3,5-dimethylphenyl)C(Me)]$_2$CH}] forms a weakly Tl–Tl bonded trimer (D).[16]

3.2 Results and Discussion

Based on our experience with polynucleating ligands, we speculated that the utilization of emergent effects[17] by incorporating bis(β-diketiminate) ligands could result in the formation of new indium and thallium species not accessible using mononucleating ligand frames. Especially, as compared to the potential dimerization of monocarbenoids, an intramolecular metal–metal bond formation is not hindered entropically when ditopic ligands are applied. In addition, Group 13 biscarbenoids possibly excel the ligand properties of their mononuclear congeners due to a beneficial chelate effect as already shown for (donor-stabilized) Group 14 biscarbenoids. [18]

The reaction of the ethylene-bridged bis(β-diketimine) **1**, [19] Scheme 2, with potassium bis(trimethylsilyl)amide (KHMDS) and indium(I) iodide in THF at -78 °C and in the absence of light, yields a brown coloured solution along with a grey precipitate indicating the formation of indium metal. After workup, **2** was isolated from a concentrated toluene solution at -20 °C in 34 % yield as yellow crystals suitable for an X-ray diffraction study. It is worthy to note that in all steps the exclusion of light is crucial as solutions of **2** are thermo- and photo-labile depositing metallic In^0, a behaviour already observed for other indium carbenoids. [8,12,13] In the solid state, however, **2** is stable and can be stored for weeks under an inert atmosphere and in the absence of light.



Scheme 2. Syntheses of the indium (**2’**) and thallium (**3’**) biscarbenoids and the respective solid-state structures **2** and **3** (R = 2,6-diisopropylphenyl).

As shown in Figure 1, the indium atoms within **2** form a four-membered ring by intramolecular and intermolecular dimerization. Within the centrosymmetric rhombus the intramolecular In1–In2 distances (3.1095(3) Å) are slightly shorter compared to the intermolecular In1–In2’ bond length (3.1342(3) Å). Both distances exceed the value for an In–In single bond according to the covalent radii approach (2.84 Å),[20] but fall in between the values of the dimeric indium diyls **B** (R = 2,4,6-trimethylphenyl: 3.1967(4) Å;[13] R = 2,6-dimethylphenyl: 3.3400(5) Å[15]) and the values of the three internal In–In bonds in the hexamer **C** (ranging from 2.8347(8) Å to 2.8535(8) Å).[14]
The diamond-shaped four-membered indacycle is planar and both ditopic ligands are oppositely arranged with respect to the ring plane. Noteworthy, cationic In_4 species, i.e., $[In_4\{Cp_2Mo_2(CO)_4P_2\}_8]^{4+}$ as well as $[In_4(bipy)_6]^{4+}$ and $[In_4(phen)_6]^{4+}$ have been reported by the groups of Scheer[21] and Krossing,[22] respectively. Although these compounds show a planar rhombic arrangement as in compound **2**, the intermetallic distances are significantly longer (shortest In–In bond: 3.482(1) Å) or shorter (2.5965(12) - 2.8083(14) Å), respectively, compared to **2**. In contrast, the neutral In_4 clusters reported so far are stabilized by Group 14 ligands and only give rise to indium(I) tetrahedrons[4,23] or to a trigonal-planar arrangement,[24] in which the indium atoms possess an average oxidation state of +1.5. Thus, the In_4 cluster **2** serves as the first example of a neutral and planar four-membered rhombic indacycle.

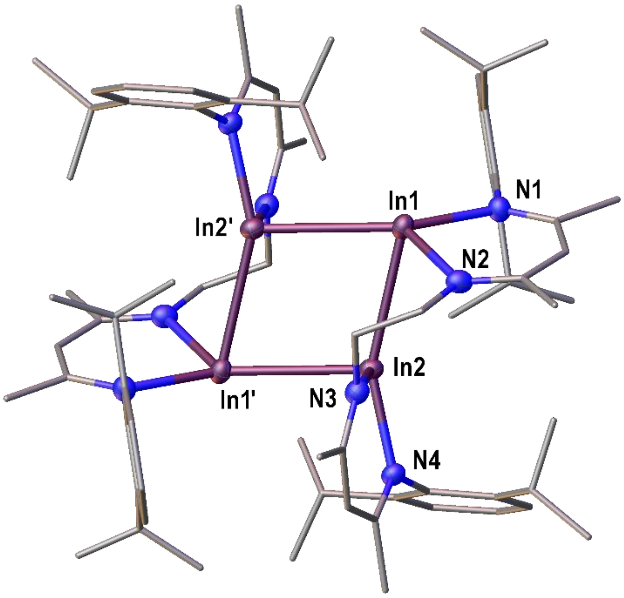


Figure 1. Solid-state structure of **2** (hydrogen atoms, solvents molecules and a co-crystallized second component are omitted for the sake of clarity). Selected bond lengths [Å] and angles [°] with calculated values (B3LYP/LANL2DZ) in square brackets: In1–In2 3.1095(3) [3.124], In1–In2' 3.1342(3) [3.120], In1–N1 2.227(2) [2.202], In1–N2 2.308(2) [2.245]; In1–In2–In1' 104.494(10) [104.27], N1–In–N2 85.58(8) [88.87].

Although **2** begins to decompose in solution of C_6D_6, immediate performed ^1H, ^{13}C and DEPT-135 NMR experiments enabled for the collection of data. The resonance pattern of the 2,6-diisopropylphenyl groups in the ^1H NMR spectrum of **2** (one isopropyl methine septet and two methyl doublets) is indicative of a symmetrical steric environment of the aryl substituents. This implies that the In_4 unit is only observed in the solid state, while in solution the structure is described best as the biscarbenoid **2'**, Scheme 2. Such different solid- and solution-state structures have previously been observed for dimeric species of type **B**.[15]

These results prompted us to synthesize and study the molecular properties of the related thallium compound. We obtained the thallium(I) species (**3**), Scheme 2, using a one-pot reaction of **1**, KHMDS and TlI, analogous to the synthesis of **2**. While the deposition of metallic Tl^0 was observed during the reaction, **3** was isolated in much better yields (79 %) as clear light-yellow crystals, which were suitable for an X-ray diffraction study. Although solutions of **3** behave less photo- and thermally sensitive than **2**, they decompose over time yielding the ligand precursor **1** along with metallic Tl^0 as observed previously for their mononuclear congeners.[12]

As shown in Figure 2, **3** does not possess a Tl_4 ring in the solid state but exhibits an intramolecular Tl–Tl bond. Similar to **2**, the Tl–Tl contacts (3.5059(3) Å) within **3** are significantly longer than predicted by using their single-bond covalent radii (2.88 Å),[20] but they are shorter compared to the weakly bound thallium triyl **D** (R = 3,5-

dimethylphenyl: 3.5794(4) - 3.7977(4) Å). In addition, they fall in between the values of unsupported (i.e., unbridged) Tl(I)–Tl(I) interactions seen in dimeric monocarbenoids, which are strongly affected by the adjacent ligand,[25-27] showing Tl–Tl distances ranging from 3.0936(8) Å[27] to 3.8636(4) Å.[26] The unusual orientation of both thallium atoms results by and large from the short ethylene linker, which also gives rise to a rather short contact of about 3 Å between Tl1 and the methine proton of the adjacent disordered *iso*-propyl group.

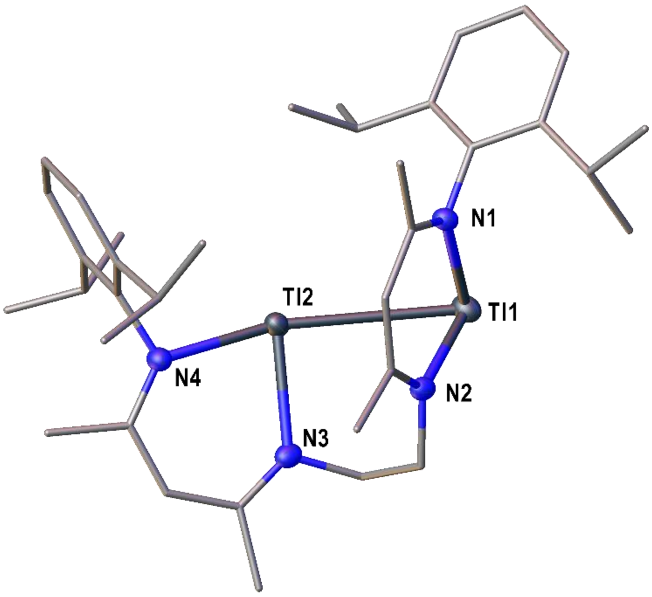
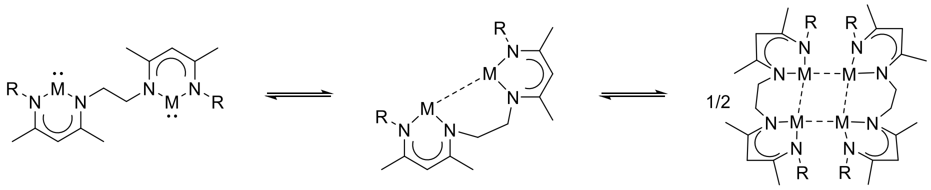


Figure 2. Solid-state structure of **3** (hydrogen atoms and a minor disorder affecting one of the isopropyl groups are omitted for the sake of clarity). Selected bond lengths [Å] and angles [°] with calculated values (B3LYP/LANL2DZ) in square bracket: Tl1–Tl2 3.5059(3) [3.506], Tl1–N1 2.418(3) [2.455], Tl1–N2 2.414(3) [2.496]; N1–In1–N2 79.64(11) [78.77], N3–Tl2–N4 79.44(12) [78.20].

Examination of a freshly prepared C_6D_6 solution of **3** allowed for the collection of ^{1}H, ^{13}C and DEPT-135 NMR data. The ^{1}H NMR spectrum of **3** gives a pattern comparable to that of **2**, i.e., two doublets and one septet for the respective methyl and methine proton resonances of the 2,6-diisopropylphenyl substituents, supporting that the Tl–Tl interaction does not remain in solution. Such a different behaviour in solution compared to the solid state is not only comparable with **2**, but has also been observed for the trimeric Tl(I) species **D**.[16]

To gain insights into the metal–metal interactions within **2** and **3** we calculated the energies of the species $\mathbf{M_2^{op}}$, $\mathbf{M_2^{dim}}$ and $\mathbf{M_4}$, Table 1, using the protocol applied by Hill.[13] The intramolecular metal–metal bond formation, i.e., $\mathbf{M_2^{op}} \rightarrow \mathbf{M_2^{dim}}$, is endergonic for both metals, as is the dimerization *en route* $\mathbf{M_2^{dim}} \rightarrow \mathbf{M_4}$. Noteworthy, the groups of Power and Schreiner recently concluded that London dispersion forces critically contribute to the thermodynamic stabilities of seemingly reactive main-group element compounds,[28] and we thus investigated the effect of the dispersion correction to our systems using the D3-corrected B3LYP functional (with the original zero-damping function).[29] Comparing the DFT and DFT-D3 energies, although not exactly equal to the dispersion stabilization, revealed a distinct attractive contribution to the intramolecular metal–metal bond formation as well as to a subsequent dimerization of two $\mathbf{M_2^{dim}}$ units, wherefore both processes become exergonic. It has been shown very recently, that large contributions to the dimerization enthalpies from London dispersion forces also arise in the case of diiminophosphinate-stabilized group 13 metal(I) species.[30] In consequence, dispersion forces account for the formation of the solid-state structures of **2** and **3**, respectively. In solution, however, dispersion forces are often effectively cancelled by competitive dispersion interactions with the solvent,[31] in agreement with the observation of different solid- and solution-state structures in this work and, before, by the groups of Hill[15] and Stasch.[30] The absence of a four-membered thallacycle $\mathbf{Tl_4}$, although thermodynamically feasible, most likely arises from packing effects.

Tabelle 1. Gibbs free energies (given in kJ mol^{-1}) for the species M_2^{op}, M_2^{dim} and M_4 as calculated on the B3LYP/LAN2DZ level of theory with (values given in parentheses) and without dispersion correction.



	M_2^{op}	M_2^{dim}	M_4
In	0.0 (0.0)	55.1 (-0.7)	152.5 (-51.1)
Tl	0.0 (0.0)	22.7 (-38.7)	144.3 (-60.8)

To provide further information on the nature of the metal–metal interactions, we calculated the Wiberg bond indices (WBIs)[32] and performed a natural bond-orbital (NBO) analysis[33] for **2** and **3**. Within **2**, the inter- and intramolecular metal–metal bonds, Figure S1a-c, can be recognized as dative bonds (WBI 0.72 and 0.67, respectively). The binding NBOs are highly polarized towards a mostly s-type orbital (79.7 % and 73.5 %, respectively), with only 25.4 % contribution from the opposite p-rich hybrid orbital (84.1 % and 92.3 % p-character, respectively). Within **3**, the metal–metal interaction is to some extent weaker (WBI 0.30) compared to **2** and results from a donor-acceptor interaction. A second-order perturbative analysis revealed that the donation occurs from the Tl2 lone pair, Figure 3e, which essentially possesses s-character (s: 97.6 %, p: 2.4%), to the empty, and basically p-type Tl1 orbital (s: 1.6 %, p: 98.4 %), Figure S1f; the donor-acceptor interaction is shown in Figure S1g.

3.3 Conclusion

In summary, dinuclear indium and thallium carbenoids are readily available in a one-pot procedure using the respective metal(I) iodide, KHMDS and the ethylene-bridged bis(β-diketimine) **1**. Both compounds are the first examples of Group 13 biscarbenoids that also adapt different solid-state structures. For thallium, an intramolecular Tl_2-dimer is obtained, while for indium intra- and intermolecular In–In interactions give rise to a novel four-membered indacycle. Dispersion stabilization has been identified as the driving force for these solid-state structures, whereby the rather weak metal–metal interactions result from donation originating from diffuse s-type orbitals to unoccupied p-type orbitals. In solution, however, NMR spectroscopy and DFT calculations indicate labile metal–metal interactions, because both species behave as unbound biscarbenoids. The reactivity of these novel polynuclear species as well as their ligand behaviour towards transition metals is under active investigation.

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3.5 Supporting Information

General Considerations

All preparations were performed under an inert atmosphere of dinitrogen by means of both standard Schlenk line or glovebox techniques (MBraun). Traces of oxygen and moisture were successively removed from the inert gas by passing it over a BASF R 3-11 ($CuO/MgSiO_3$) catalyst, through concentrated sulfuric acid, over coarsely granulated silica gel, and finally P_4O_{10}. Toluene and THF were used as p.a. grade and distilled from Na/benzophenone prior to use. C_6D_6 was dried by distillation from potassium. Indium(I) iodide was purchased from Onyxmet, while thallium(I) iodide and potassium bis(trimethylsilyl)amide (KHMDS) were purchased from Sigma Aldrich. These starting materials were used as delivered. The ligand precursor **1** was prepared according to a literature procedure.[S1]

Characterization

The NMR-spectra were recorded on a BrukerAvance 400 spectrometer (^{1}H: 400.13 MHz, ^{13}C: 101 MHz, T = 300 K) with δ (given in ppm) referenced to external trimethylsilane. ^{1}H and ^{13}C NMR spectra were calibrated using the solvent residual peak (δ ^{1}H (C_6D_5H) = 7.20) and the solvent peak (δ ^{13}C (C_6D_6) = 128.0), respectively. The coupling constants *J* are given in Hertz [Hz]. Elemental analysis were performed on a Vario micro cube (Elementar Analysensysteme GmbH).

2: THF (20 mL) was added to a mixture of InI (0.97 g, 4.00 mmol), KHMDS (0.80 g, 4.00 mmol), and **1** (1.09 g, 2.00 mmol) at -78 °C. Warming to room temperature and stirring in the absence of light for 22 h produced a dark brown suspension. The volatiles were removed, and the grey residue was extracted with toluene (20 mL). Filtration and concentration of the filtrate to about one third gave rise to **2** as clear light-yellow crystals suitable for an X-ray diffraction analysis. (371 mg, 34 %); Anal. calc. (found) for $[C_{36}H_{52}N_4In_2]_2 \cdot C_7H_8$: C 58.10 (57.99); H 6.91 (6.96); N 6.86 (6.74); ^{1}H-NMR: (400 MHz, C_6D_6): δ = 1.12 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.23 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.69 [s, 6H, C*Me*], 1.74 [s, 6H, C*Me*], 3.21 [sept, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*Me$_2$], 3.76 [s, 4H, C*H*$_2$], 4.84 [s, 2H, β-C*H*], 7.12 [s, 6H, Ar*H*]; ^{13}C{^{1}H}-NMR: (101 MHz, C_6D_6): δ = 22.4 [C*Me*], 23.9 [CH*Me*$_2$], 24.60 [C*Me*], 26.1 [CH*Me*$_2$], 28.2 [CH*Me*$_2$], 52.8 [*C*H$_2$], 99.0 [β-*C*H], 123.9 [*m*-*C*(Dipp)], 125.6 [*p*-*C*(Dipp)], 142.5 [*o*-*C*(Dipp)], 145.5 [*i*-*C*(Dipp)], 163.6 [*C*N], 165.6 [*C*N].

3 was synthesized by a procedure directly analogous to **2**, employing TlI (0.80 g, 4.00 mmol), KHMDS (1.33 g, 4.00 mmol), and **1** (1.09 g, 2.00 mmol) to yield **3** as clear light-yellow crystals suitable for an X-ray diffraction analysis. (2.98 g, 79 %); Anal. calc. (found) for [$C_{36}H_{52}N_4Tl_2\cdot0.4\ C_7H_8$: C 47.24 (47.39); H 5.64 (5.42); N 5.68 (5.96); ^{1}H-NMR: (400 MHz, C_6D_6): δ = 1.13 [d, 12H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$], 1.19 [d, 12H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$], 1.73 [s, 6H, C*Me*], 1.87 [s, 6H, C*Me*], 3.22 [br, 4H, C*H*Me$_2$], 3.78 [s, 4H, C*H*$_2$], 4.74 [s, 2H, β-C*H*], 7.06-7.10 [m, 2H, Ar*H*], 7.11-7.15 [m, 2H, Ar*H*]; ^{13}C{^{1}H}-NMR: (101 MHz, C_6D_6): δ = 21.5 [C*Me*], 23.2 [C*Me*], 23.8 [CH*Me*$_2$], 25.5 [CH*Me*$_2$], 27.8 [*C*HMe$_2$], 53.8 [*C*H$_2$], 101.6 [β-*C*H], 123.7 [*m*-*C*(Dipp)], 124.7 [*p*-*C*(Dipp)], 138.2 [*o*-*C*(Dipp)], 141.7 [*i*-*C*(Dipp)], 161.9 [*C*N], 164.4 [*C*N].

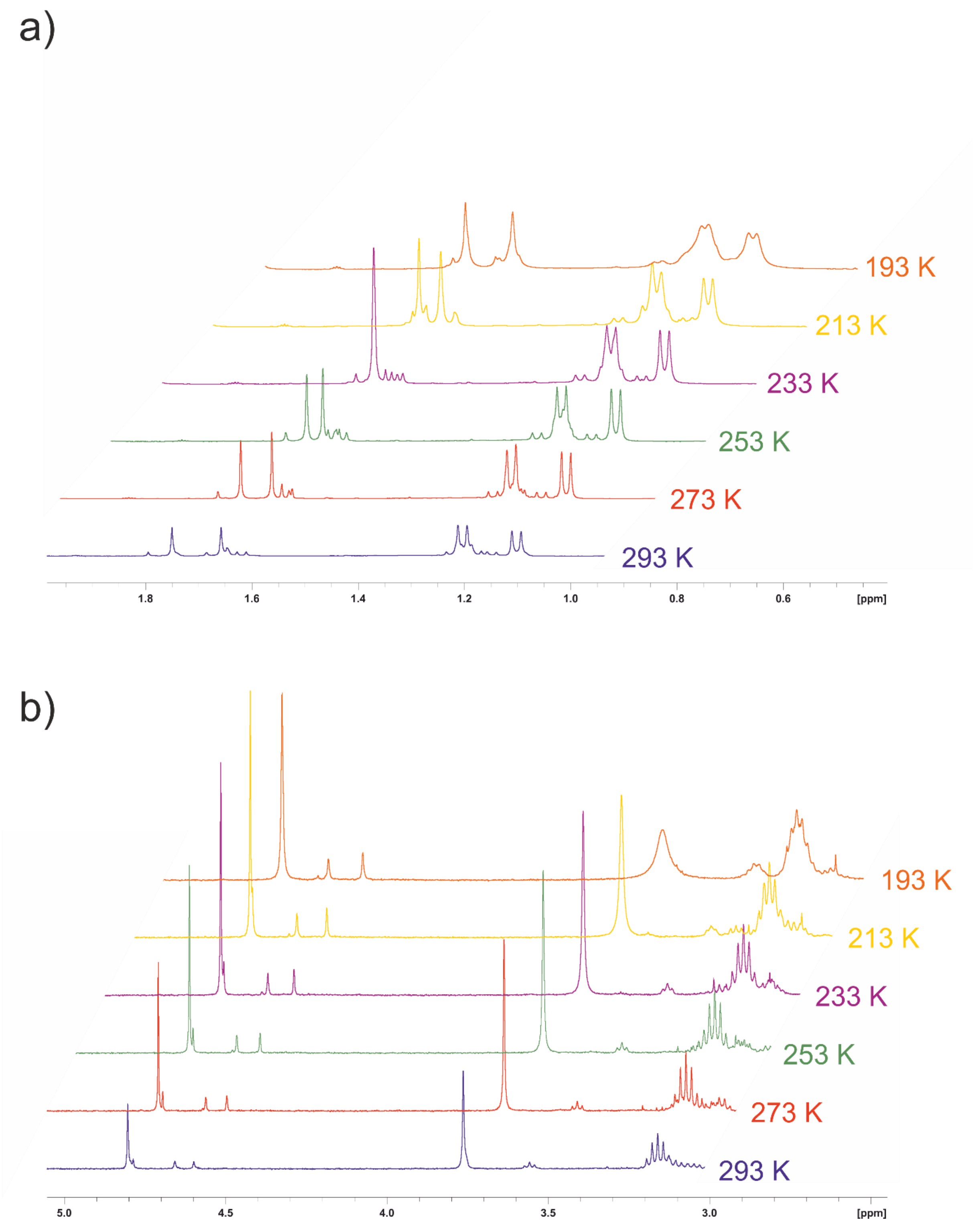

Figure S1**.** Excerpts (a) 0.9 – 1.9 ppm and b) 3.0 – 5.0 ppm) of the^{1}H NMR spectra of a solution of **2** in toluene-d_8 at different temperatures.

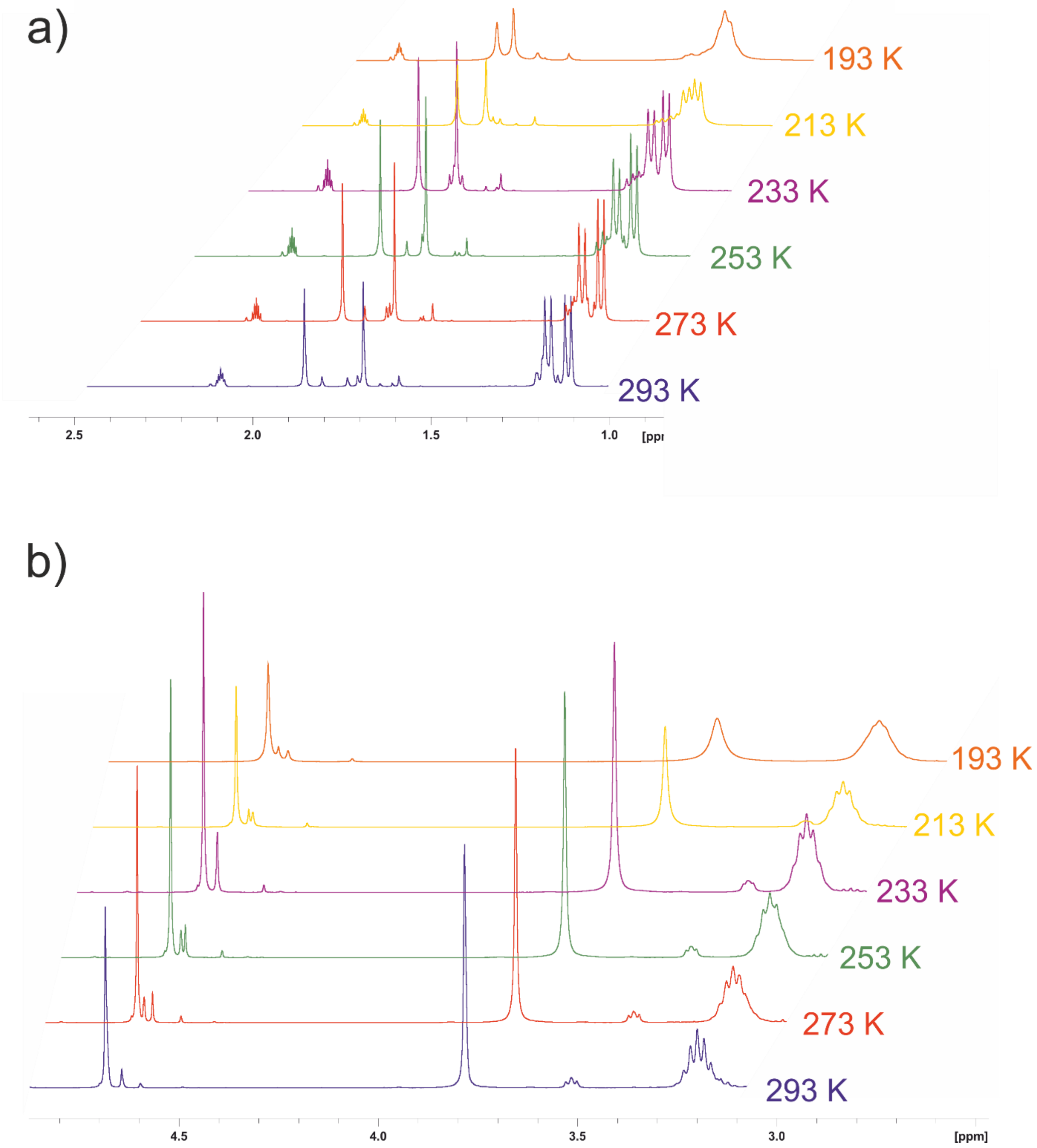

Figure S2**.** Excerpts (a) 1.0 – 2.5 ppm and b) 3.0 – 4.9 ppm) of the^{1}H NMR spectra of a solution of **3** in toluene-d$_8$ at different temperatures.

Crystallographic Details

The single crystal X-ray diffraction data were recorded on an Agilent Technologies SuperNova diffractometer with microfocus Cu K_α radiation (λ = 1.54184 Å). Empirical multi-scan[S2] and analytical absorption corrections[S3] were applied to the data. The structures were solved with SHELXT[S4] and least-square refinements on F^2 were carried out with SHELXL. [S5] Maxima in the Fourier difference maps of **2** indicated the presence of a second species, which allowed for the refinement of a second In_4 ring (0.0781(7)) including bridging oxygen atoms according to a larger distance of the corresponding Indium atoms. In this compound, also unresolved residual electron density around a centre of inversion was present, which could be assigned a disordered solvent molecule of toluene. The disorder could not be resolved completely, therefore PLATON SQUEEZE[S6] was applied and the presence of a solvent accessible void including 46 electrons was confirmed, which we assign a not fully occupied toluene molecule. In the subsequent refinement a modified reflection file without the contribution of the solvent was used.

CCDC 1504564 (**3**) and 1504565 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

	2	**3**
Empirical formula	$C_{36}H_{52}In_2N_4O_{0.08}$	$C_{36}H_{52}N_4Tl_2$
CCDC No.	1504565	1504564
Formula weight	771.73	949.55
Temperature/K	123.0(2)	123.3(6)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	11.49565(18)	11.1313(3)
b/Å	12.7946(2)	12.0117(3)
c/Å	14.8078(2)	14.7648(4)
α/°	106.4107(14)	66.579(3)
β/°	108.2254(14)	78.590(3)
γ/°	99.2006(15)	80.819(2)
Volume/Å^3	1909.34(6)	1768.50(10)
Z	2	2
ρ_{calc}g/cm^3	1.342	1.783
μ/mm^{-1}	9.845	17.502
F(000)	789.0	916.0
Crystal size/mm^3	0.118 × 0.074 × 0.025	0.14 × 0.111 × 0.054
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.722 to 150.89	6.598 to 148.144

Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 15, -18 ≤ l ≤ 18	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18
Reflections collected	89347	43841
Independent reflections	7726 [R_{int} = 0.0745, R_{sigma} = 0.0290]	7001 [R_{int} = 0.0767, R_{sigma} = 0.0364]
Data/restraints/parameters	7726/24/436	7001/12/412
Goodness-of-fit on F^2	1.058	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0291, wR_2 = 0.0722	R_1 = 0.0267, wR_2 = 0.0645
Final R indexes [all data]	R_1 = 0.0333, wR_2 = 0.0750	R_1 = 0.0314, wR_2 = 0.0673
Largest diff. peak/hole / e Å^{-3}	0.96/-0.51	1.31/-1.42

Computational Details

Calculations were performed using the Gaussian 09 program package[S7] using the B3LYP functional[S8] and LANL2DZ basis sets[S9] in conjunction with the related quasi-relativistic pseudopotentials for indium and thallium. When X-ray data were available, the geometry optimization were performed using the XYZ coordinates as initial structures and freezing the metal–metal distances. In a second optimization step, these restraints have been removed and the absence of imaginary frequencies confirmed stationary points as minima. The free energies (given in kJ mol^{-1}) were calculated for standard conditions, i.e., 298.15 K and 1 bar. To derive the contribution of London dispersion the D3 version of Grimme's dispersion with the original zero-damping function was used. [S10]

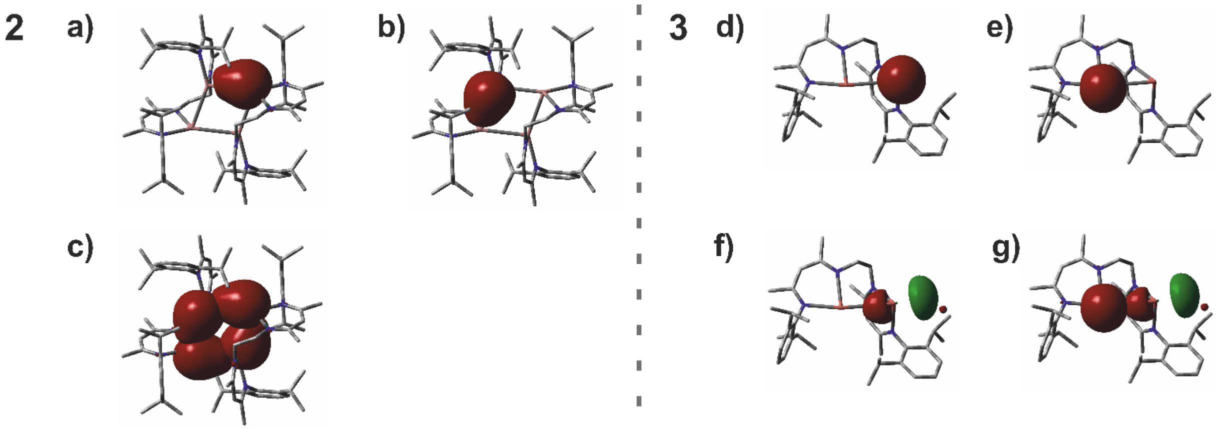

Figure S3. Calculated (B3LYP/LANL2DZ) natural bond orbitals: a) and b) show the NBOs of the respective inter- and intramolecular In–In bond and c) a combination of all four NBOs within **2**. The mostly s-type donor NBOs of **3** are shown in d) and e), while the acceptor NBO and the donor-acceptor interaction are shown in f) and g), respectively.

The coordinates of the optimized structures are given in the following:

B3LYP-LANL2DZ

	In_2^{op}				In_2^{dim}		
In	3.21545200	-0.31310900	-1.06392000	**In**	-1.23165100	0.47229700	-0.62802900
In	-3.21595200	0.31537000	1.06424700	**In**	2.10389900	1.11439200	-1.31959000
C	-5.67265200	0.17574100	-2.87113000	**C**	3.03855900	-1.02632100	2.70106200
H	-6.47516200	0.87312500	-2.60520300	**H**	4.12168400	-0.90815000	2.83047400
H	-6.10375400	-0.83183800	-2.82917500	**H**	2.87120700	-2.05148300	2.35356700
H	-5.36108500	0.37616000	-3.89960100	**H**	2.56108700	-0.90165800	3.67679700
C	0.34251100	-0.69724600	0.04341100	**C**	-0.53520800	3.43043200	-1.21167300
H	-0.29315800	-1.36599200	0.63758400	**H**	-0.87416300	4.39178700	-1.61895800
H	0.38759900	-1.12064400	-0.96962700	**H**	-0.16022500	2.84721800	-2.06353600
C	-6.18737500	-3.65087900	-1.35587900	**C**	1.56526200	-3.98030900	0.23238400
H	-7.06662600	-4.14760300	-0.92545800	**H**	2.09575600	-4.87265200	-0.12606600
H	-5.47922800	-4.43318400	-1.66033600	**H**	0.48797900	-4.18973000	0.19120900
H	-6.51396300	-3.11793800	-2.25812800	**H**	1.84206600	-3.82744300	1.28367000
C	5.05666400	3.47338700	-0.91561600	**C**	-1.33000500	-1.97471800	2.88519600
H	5.90896100	3.93175400	-1.43455300	**H**	-1.43908400	-3.04497000	3.10573100
H	4.36137600	4.27572700	-0.63296900	**H**	-0.78430000	-1.50987200	3.71733700
H	4.54863600	2.81279300	-1.63038800	**H**	-0.71864700	-1.87707200	1.97986700
C	6.44062300	1.52332600	-0.05013700	**C**	-3.44722500	-1.88084900	1.48345700
C	-3.23478400	0.57806100	-2.49497600	**C**	1.67227400	1.01251900	2.23088300
H	-3.24900300	0.69153200	-3.57299000	**H**	1.48182700	0.92770000	3.29496400
C	5.52363400	2.68902800	0.34056400	**C**	-2.71450400	-1.29877100	2.69840800
H	4.62974600	2.27430400	0.81926600	**H**	-2.53741700	-0.23342200	2.51345900
C	-8.57541400	-0.77232700	0.98896600	**C**	5.72438000	-2.99047400	-0.93216400
H	-9.55173600	-1.00679900	1.40658700	**H**	6.45544500	-3.71272600	-1.28824100
N	-4.70166800	0.14477500	-0.57816200	**N**	2.85212800	-0.11072700	0.39530600
C	6.38505100	-3.02840000	-1.59578500	**C**	-3.84769800	-1.46699600	-3.28327300
H	5.65845300	-2.49406700	-2.22122200	**H**	-2.77143600	-1.43596500	-3.07014300
H	6.05754600	-4.07296600	-1.50344200	**H**	-4.03580900	-0.87285300	-4.18788200
H	7.34811600	-3.02194300	-2.12302800	**H**	-4.11477800	-2.50933100	-3.50194700
C	-7.70938500	-1.80409400	0.59652300	**C**	4.35467200	-3.28463000	-0.99022900
H	-8.02340500	-2.83857400	0.71644400	**H**	4.02950000	-4.24050900	-1.39487600
C	7.71160600	1.80163100	-0.59501300	**C**	-3.83783200	-3.23650700	1.50637200
H	8.02695200	2.83584700	-0.71371100	**H**	-3.63005400	-3.83608100	2.38983600
N	-1.72885100	0.60687100	-0.56684100	**N**	1.22695600	2.44550600	0.29969300
N	4.70177100	-0.14490400	0.57817900	**N**	-3.27656000	0.27494200	0.23565700
C	-6.43857300	-1.52480800	0.05172800	**C**	3.38645800	-2.36244400	-0.53777100
C	-4.49285800	0.30235400	-1.90931200	**C**	2.50028000	-0.00785700	1.69652800
C	6.19285400	3.64920100	1.35854100	**C**	-3.55152400	-1.41501500	3.99965100
H	7.07173700	4.14578000	0.92719200	**H**	-3.73484000	-2.46390500	4.26659900
H	6.52045800	3.11562700	2.26005000	**H**	-4.52710500	-0.92228500	3.89931100
H	5.48551700	4.43169200	1.66440600	**H**	-3.01866900	-0.94603800	4.83778500
N	1.72856900	-0.60512200	0.56724000	**N**	-1.63620900	2.65663400	-0.58367600
C	-8.17152000	0.56322600	0.84521900	**C**	6.14553100	-1.75410500	-0.41891400
H	-8.84324200	1.36050000	1.15574000	**H**	7.20828900	-1.52511500	-0.38406000
C	-6.38869300	3.02873600	1.59135200	**C**	6.28978900	1.41038000	-0.59317500
H	-7.35155600	3.02140300	2.11895700	**H**	7.15023100	0.92115200	-1.06913800
H	-6.06277200	4.07368600	1.49775100	**H**	6.61855300	2.39108900	-0.22231300
H	-5.66107700	2.49616800	2.21711600	**H**	5.52835800	1.57283600	-1.36689400
C	8.57614600	0.76923600	-0.98911100	**C**	-4.48518100	-3.82662400	0.41087600
H	9.55264100	1.00298300	-1.40673200	**H**	-4.77781200	-4.87336900	0.44672300
C	6.90804600	-0.89455500	-0.30910700	**C**	-4.37647400	-1.69969700	-0.80407800
C	-6.04072800	-0.16340200	-0.09526800	**C**	3.82585600	-1.11449100	-0.00916800
C	-1.95403000	0.71436400	-1.89454600	**C**	1.14024800	2.18151000	1.61888800
C	6.04103500	0.16225400	0.09520300	**C**	-3.72724900	-1.10786500	0.31936000
C	1.95392100	-0.71306200	1.89487800	**C**	-2.69640900	3.30127100	-0.05326300
C	5.67307600	-0.17742100	2.87102200	**C**	-5.46614100	0.91204400	1.23814100
H	6.47659000	-0.87272900	2.60280400	**H**	-6.08469900	0.37730500	0.50725500
H	5.36217100	-0.38117900	3.89903900	**H**	-6.00155700	1.81195200	1.55220700
H	6.10254800	0.83098700	2.83181200	**H**	-5.35691200	0.24857300	2.10327300
C	0.80659300	-1.02610100	2.85861700	**C**	-2.77382100	4.83082000	-0.08571400
H	-0.02416900	-0.31726800	2.76284300	**H**	-1.86510200	5.29705900	0.31350300

H	1.15753900	-0.99597500	3.89306000
H	0.40111700	-2.03012600	2.67140400
C	4.49306800	-0.30290700	1.90930300
C	8.17051400	-0.56596500	-0.84705100
H	8.84105700	-1.36372100	-1.15887800
C	3.23487200	-0.57777000	2.49510500
C	-6.90931800	0.89279200	0.30726200
C	-0.34284800	0.69922100	-0.04288700
H	-0.38810200	1.12257500	0.97016500
H	0.29282000	1.36803300	-0.63698600
C	6.50969900	-2.37150800	-0.19449000
H	5.52469400	-2.42407200	0.28265200
C	7.49863300	-3.17421300	0.69195200
H	7.15634400	-4.21215800	0.80023000
H	7.58552600	-2.73867800	1.69564600
H	8.50359000	-3.19842300	0.25082300
C	-6.51291800	2.37012400	0.19081800
H	-5.52811500	2.42343500	-0.28665800
C	-0.80672900	1.02787300	-2.85816200
H	0.02430500	0.31935800	-2.76235200
H	-0.40164100	2.03203400	-2.67084700
H	-1.15756700	0.99766100	-3.89263900
C	-5.52005700	-2.68981500	-0.33746000
H	-4.62604800	-2.27442000	-0.81535700
C	-5.05373400	-3.47340700	0.91942400
H	-5.90613300	-3.93243200	1.43760900
H	-4.54702600	-2.81217600	1.63453900
H	-4.35744700	-4.27520100	0.63768300
C	-7.50316400	3.17059600	-0.69617400
H	-8.50793100	3.19430300	-0.25459000
H	-7.59010600	2.73366600	-1.69926000
H	-7.16205600	4.20877100	-0.80594700
H	3.24920700	-0.69153400	3.57308700
H	-3.62326300	5.18174300	0.50556100
H	-2.90845700	5.19585300	-1.11315400
C	-4.10612700	1.26785700	0.64046700
C	-4.74571600	-3.05951300	-0.73432200
H	-5.24014600	-3.52223100	-1.58545300
C	-3.81285900	2.64877400	0.53505700
C	5.21676700	-0.80160600	0.04897900
C	0.66549200	3.69973100	-0.25687000
H	1.44439600	4.19484600	-0.85707800
H	0.36240600	4.40895700	0.52096100
C	-4.67089700	-0.91443300	-2.08864200
H	-4.36332200	0.12547500	-1.93304300
C	-6.18386500	-0.90422900	-2.43214200
H	-6.36824100	-0.28437300	-3.31981900
H	-6.78141800	-0.49999400	-1.60487200
H	-6.55434000	-1.91478800	-2.64835200
C	5.72945900	0.54731900	0.56986100
H	4.88357800	1.09369400	1.00056700
C	0.44726500	3.15741300	2.57686100
H	-0.58120300	3.37222600	2.26205100
H	0.98889500	4.11156100	2.63321300
H	0.41215000	2.73685200	3.58478600
C	1.90263500	-2.73680200	-0.63364000
H	1.30834800	-1.89820200	-0.25293700
C	1.47374300	-2.97371500	-2.10579200
H	2.02770800	-3.80940100	-2.55418600
H	1.65534900	-2.08110700	-2.71717700
H	0.40286200	-3.20999300	-2.15783800
C	6.79472200	0.38441100	1.68517400
H	7.70392600	-0.10208200	1.30866300
H	6.41471700	-0.21985000	2.51923200
H	7.08394800	1.36769200	2.08015800
H	-4.57956600	3.30976300	0.92302900

In_4

In	-1.24052200	1.41283400	-0.30969400
In	1.24532200	-1.42036300	0.31233300
In	1.62939400	1.62511300	0.89501900
In	-1.63291800	-1.61689700	-0.89758700
N	-0.52610100	1.75372300	-2.35409000
C	-1.24132400	5.77444800	2.80077800
H	-1.39800700	6.46918400	1.96641400
H	-0.20331400	5.88468500	3.14291700
H	-1.90158200	6.08443300	3.62188600
C	-0.38078800	2.94911800	-2.95033800
C	6.09501500	2.71188500	1.11380700
H	6.04393400	3.69281900	0.63237800
H	6.59424600	2.03598700	0.40910600
H	6.71830200	2.78922400	2.00874800
C	-0.86774200	4.17110100	-2.40395100
H	-0.60935700	5.05876100	-2.97019000
C	-3.67509000	-4.34148100	0.80739800
N	-2.25134200	-0.83882800	-2.90946100
C	0.07897600	-0.51605800	3.02761600
H	-0.71898600	-0.70953300	3.75501200
H	-0.35782800	0.14346800	2.26750000
C	6.24925600	0.43880400	-2.07688100
H	6.51846400	0.73422500	-3.10001300
H	6.44995300	-0.63554500	-1.97326400
H	6.91372200	0.97904100	-1.39143800
C	-1.20454300	-0.23603500	-3.78215300
H	-0.72399000	-1.03666400	-4.37052100
H	-1.64428200	0.47070200	-4.49530400
C	-3.17259100	-5.16983200	-0.38218000
H	-2.99482100	-4.48842200	-1.22122200
N	-2.12882300	3.44679300	-0.42067400
H	5.99229900	-4.03465000	3.13050300
C	-4.71083700	-2.17452800	-1.46915900
N	0.52977700	-1.75865200	2.35614700
C	-1.82859900	-5.87338700	-0.06328200
H	-1.07501700	-5.14690300	0.26105300
H	-1.45175200	-6.39298200	-0.95499500
H	-1.94508300	-6.62038800	0.73393400
C	3.88683700	4.99352800	-2.04599100
H	3.68125700	6.05807400	-2.13249400
C	-4.43524100	-2.22110300	1.83635100
C	1.82599000	5.87868900	0.06046000
H	1.94133200	6.62508800	-0.73749300
H	1.44923100	6.39870600	0.95198100
H	1.07292400	5.15123100	-0.26289500
C	-5.61190900	3.86214900	0.96183600
H	-6.64242700	3.76573300	0.62646700
C	5.35203400	-4.23081400	-2.29307600
H	6.17254800	-4.41187300	-2.98364200
C	2.94131000	-4.13036300	-1.84590400
C	3.95415800	2.95131100	-0.70739500
C	3.47820100	1.01573900	3.42762000
C	3.21566400	-3.75994500	-0.49702000
C	-4.62875300	-2.91324600	3.05182600
H	-5.00021900	-2.37006300	3.91822500
C	0.38596500	-2.95303100	2.95483300
C	-4.56335700	3.62614600	0.04826000
C	-6.09912000	-2.70651500	-1.11532400
H	-6.04799300	-3.68668000	-0.63235200
H	-6.72232900	-2.78530000	-2.01020000
H	-6.59848700	-2.02954900	-0.41170900
C	2.23815600	5.83570800	1.14425200

N	-3.71148800	-2.26338700	-0.55856800
C	-3.78784300	-0.55233200	-4.86119600
H	-3.73156700	0.54143400	-4.94921200
H	-4.79520700	-0.85917300	-5.15156800
H	-3.08128200	-0.97851700	-5.58440100
C	-3.95718500	-2.94535200	0.70518400
C	-3.21356400	3.75307900	0.49946500
C	5.61917400	-1.85863000	1.44420400
H	6.55726400	-1.86468900	0.87240700
H	5.85697300	-1.58508500	2.48099900
H	4.97333400	-1.07491300	1.03377300
C	-1.72224100	4.39844500	-1.29909200
C	-3.87122200	0.08068200	2.77486900
H	-4.07126900	-0.21115600	3.81537700
H	-4.07336500	1.15472900	2.67798300
H	-2.80903200	-0.08378300	2.56648600
C	4.56610800	-3.63303000	-0.04779100
C	4.58223800	1.61829600	2.75898400
H	5.49379400	1.64967400	3.34443000
C	4.92183600	-3.24261400	1.39305400
H	3.99317900	-3.15954600	1.96640000
C	0.35201900	3.07268400	-4.28876100
H	1.40897400	2.79309100	-4.18361400
H	0.31457000	4.10395900	-4.64785000
H	-0.09137900	2.43021800	-5.06000400
C	-2.23154200	5.83016700	-1.13628000
H	-1.69860800	6.50802500	-1.80850700
H	-2.10292600	6.18066700	-0.10695100
H	-3.30236200	5.89454100	-1.36308000
C	-4.02507600	4.35477700	2.72374300
H	-3.82444200	4.64367800	3.75315200
C	-1.51538800	4.30486500	2.38199300
H	-0.81039300	4.04794100	1.58359400
C	4.36148200	4.29063000	-3.16327800
H	4.52522000	4.80710100	-4.10656300
C	-2.94130100	4.12479700	1.84841900
C	-3.48231000	-1.01290700	-3.43096200
N	3.70733700	2.26985300	0.55645800
C	-4.75432600	-0.72220900	1.78556600
H	-4.52717300	-0.35697200	0.77846600
C	1.22829100	-3.36247700	-3.57171900
H	1.42221700	-2.31771700	-3.30117800
H	0.17756000	-3.45042700	-3.87942400
H	1.85702400	-3.60845600	-4.43822500
C	4.62702200	2.91785400	-3.05357000
H	4.99875500	2.37419000	-3.91955000
C	5.61330600	-3.86871500	-0.96297700
H	6.64432300	-3.77234100	-0.62914100
C	-5.79999600	4.30964700	-2.08543400
H	-6.77644200	4.40507200	-1.59236000
H	-5.98190900	4.03247700	-3.13269900
H	-5.32429200	5.29849100	-2.07456800
C	-5.35264500	4.22489700	2.29214600
H	-6.17418700	4.40615400	2.98143400
N	2.24686400	0.84310500	2.90647900
N	2.13232100	-3.45370700	0.42470900
C	-3.88814700	-4.98809300	2.04299200
H	-3.68193900	-6.05255600	2.12895600
C	4.43268300	2.22629600	-1.83789300
C	4.70670400	2.17965100	1.46705100
C	5.80934100	-4.31253500	2.08361000
H	6.78521500	-4.40508600	1.58885400
H	5.33662700	-5.30284000	2.07368900
H	2.11336600	-6.18641300	0.11453700
H	1.70325200	-6.51368900	1.81481300
H	3.30823200	-5.89951200	1.37492500
C	-4.91707800	3.23683100	-1.39339200
H	-3.98739400	3.15128600	-1.96469700
C	-4.58643600	-1.61456200	-2.76183400
C	-0.34751600	-3.07489700	4.29302200
H	0.09278300	-2.42838900	5.06264500
H	-0.30679300	-4.10488100	4.65547500
H	-1.40536500	-2.79939000	4.18585300
C	1.72773500	-4.40420200	1.30526600
C	-0.07951900	0.51197800	-3.02997600
H	0.71833700	0.70538900	-3.75747800
H	0.35581700	-0.15162900	-2.27251800
C	4.02382400	-4.36005600	-2.72288600
H	3.82169300	-4.64808800	-3.75224300
C	0.87458400	-4.17551500	2.41091600
C	3.67305000	4.34755600	-0.81019000
C	1.20065600	0.23822500	3.77873500
H	0.71652400	1.03856300	4.36442800
H	1.64185700	-0.46511800	4.49418800
C	1.51457600	-4.30944600	-2.37763600
H	0.81068200	-4.05039400	-1.57897000
C	-4.36271800	-4.28597100	3.16079800
H	-4.52591200	-4.80297700	4.10388700
C	1.23854800	-5.77949700	-2.79347900
H	0.20033800	-5.88909400	-3.13518200
H	1.39448400	-6.47268600	-1.95767800
H	1.89830800	-6.09190800	-3.61407300
C	3.17086200	5.17664700	0.37899800
H	2.99440300	4.49591800	1.21887800
C	3.78495200	0.55253200	4.85680100
H	3.72875500	-0.54137700	4.94292600
H	3.07927500	0.97756200	5.58152900
H	4.79265800	0.85872000	5.14665300
C	4.75160200	0.72735800	-1.78606300
H	4.52400800	0.36272400	-0.77882700
C	-5.61846900	1.85505600	-1.44676700
H	-6.55746900	1.86329200	-0.87649200
H	-4.97561000	1.06902600	-1.03621100
H	-5.85541500	1.58313000	-2.48416300
C	3.86887500	-0.07614500	-2.77520600
H	4.06899200	0.21536100	-3.81579700
H	2.80664300	0.08793500	-2.56696500
H	4.07130900	-1.15011800	-2.67787800
C	-1.22949800	3.35632300	3.57493200
H	-0.17929100	3.44501100	3.88423800
H	-1.42205700	2.31176100	3.30270800
H	-1.85972000	3.60034300	4.44090700
C	4.22755300	6.21862900	0.83662700
H	4.44726800	6.93876200	0.03694300
H	5.17148200	5.73971100	1.12498400
H	3.85591500	6.78188300	1.70342200
C	-6.25189400	-0.43398900	2.07707500
H	-6.52077400	-0.73033800	3.10002600
H	-6.91643100	-0.97377500	1.39134400
H	-6.45274200	0.64041800	1.97442800
C	-4.22977800	-6.21055100	-0.84158500
H	-4.45086000	-6.93102600	-0.04257600
H	-3.85781200	-6.77352500	-1.70842400
H	-5.17299300	-5.73060400	-1.13052700
H	0.61779100	-5.06234800	2.97919400
H	-5.49790200	-1.64676700	-3.34739900

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C	5.61390900	-0.06748700	3.08184400
H	6.40741000	0.67796100	2.94729600
H	6.08246900	-1.05239200	2.96441800
H	5.22990600	0.01458000	4.10205400
C	-0.34179700	-0.69278600	-0.10761700
H	0.31252200	-1.30855700	-0.74076800
H	-0.39008000	-1.19979200	0.86768900
C	6.18560700	-3.81169800	1.26335500
H	7.06692500	-4.29293000	0.81924000
H	5.45351400	-4.59913500	1.48823000
H	6.49703500	-3.35560000	2.21180500
C	-5.11498600	3.43000100	1.01661400
H	-5.96934100	3.85771100	1.55778800
H	-4.40150200	4.24079700	0.81515400
H	-4.63059500	2.70498900	1.68529100
C	-6.52186200	1.58915900	-0.03794400
C	3.20562600	0.38309000	2.58699200
H	3.17777200	0.42479400	3.67060800
C	-5.56750500	2.75847300	-0.30791200
H	-4.67198800	2.35710700	-0.79422600
C	8.69579800	-0.80463100	-0.78096400
H	9.67595500	-1.02215600	-1.19885800
N	4.79801100	0.05452400	0.73952400
C	-6.52982300	-3.07451000	1.05473000
H	-5.77920700	-2.60965200	1.70856900
H	-6.22188600	-4.11157100	0.86325700
H	-7.47840700	-3.09939500	1.60732400
C	7.79829700	-1.84736000	-0.50313100
H	8.09318200	-2.87415300	-0.70964300
C	-7.79842400	1.84719100	0.50321600
H	-8.09340800	2.87398400	0.70958500
N	1.71860600	0.56030500	0.63534300
N	-4.79808000	-0.05453100	-0.73953000
C	6.52168900	-1.58926800	0.03789400
C	4.49578200	0.13070000	2.05360300
C	-6.18626300	3.81138200	-1.26390500
H	-7.06757200	4.29259200	-0.81974800
H	-6.49778300	3.35504300	-2.21220900
H	-5.45430800	4.59886700	-1.48906200
N	-1.71864600	-0.56018400	-0.63560700
C	8.31800000	0.52105100	-0.51722400
H	9.01507800	1.32769300	-0.73412800
C	6.53054200	3.07470400	-1.05383400
H	7.47926100	3.09959800	-1.60619600
H	6.22270800	4.11175800	-0.86216100
H	5.78001700	2.61012700	-1.70797500
C	-8.69575300	0.80440000	0.78137100
H	-9.67587300	1.02187600	1.19937900
C	-7.05224500	-0.82808700	-0.02428700
C	6.14402200	-0.23791100	0.30190400
C	1.93741700	0.57207000	1.96343400
C	-6.14407400	0.23780500	-0.30179000
C	-1.93756700	-0.57195700	-1.96368000
C	-5.61417400	0.06745900	-3.08178700
H	-6.40763100	-0.67802900	-2.94720900
H	-5.23024300	-0.01455600	-4.10202900
H	-6.08277100	1.05233800	-2.96429300
C	-0.77751200	-0.82383000	-2.93950100
H	0.03808000	-0.10273300	-2.80215100
H	-1.12202800	-0.74647800	-3.97351900
H	-0.35689000	-1.82949400	-2.80023600
C	-4.49596300	-0.13071300	-2.05363500
C	-8.31782700	-0.52128300	0.51781500
H	-9.01476300	-1.32797500	0.73499200
C	-3.20583700	-0.38303500	-2.58713200
C	7.05236600	0.82791600	0.02472600
C	0.34179900	0.69291300	0.10724600

Tl$_2^{dim}$

Tl	-1.14787500	-0.33002100	-0.56017000
Tl	2.19990600	-1.16013300	-1.18781800
N	2.76006000	0.37822600	0.64119500
N	1.06508800	-2.26474800	0.74132600
N	-3.47030100	-0.20926200	0.28682700
C	1.34860000	-0.51745400	2.44901900
N	-1.71560400	-2.71250600	-0.30593100
C	2.25503100	0.42396000	1.89041300
C	-3.98832600	-2.59411400	0.61708500
H	-4.78971500	-3.23612700	0.96705600
C	-3.91180700	1.16656000	0.32007100
C	-4.30072300	-1.20960700	0.64964700
C	-4.45992200	1.75947700	-0.85828700
C	-2.82689700	-3.29401600	0.17838600
C	5.59702000	-0.27524600	1.10806800
H	4.70569900	-0.77113400	1.50652300
C	-4.58350000	3.91697500	0.30126800
H	-4.84129900	4.97351100	0.29428900
C	-4.04417500	3.32774900	1.45505300
H	-3.88731200	3.93795200	2.34217700
C	1.92159700	2.87600700	-0.72439000
H	1.29814200	2.12087800	-0.23254000
C	6.54343700	0.01680100	2.30145400
H	6.79009000	-0.91407000	2.82989000
H	6.07913500	0.70366600	3.02066800
H	7.48619000	0.47046400	1.96829500
C	3.76838100	1.32144600	0.21133000
C	4.40178300	3.35611100	-0.98560200
H	4.12152900	4.26159600	-1.51968300
C	-5.71256200	-0.86238100	1.13366500
H	-5.67856500	-0.18507900	1.99501500
H	-6.26287900	-1.76274500	1.41956800
H	-6.27727600	-0.34574900	0.34760200
C	6.26905400	-1.26020300	0.11367200
H	7.18099300	-0.82723500	-0.31841800
H	5.59479300	-1.50734600	-0.71768800
H	6.54454000	-2.19480200	0.62123900
C	0.85683300	-1.77273700	1.97657100
C	5.14925800	1.00619100	0.39444500
C	0.55751000	-3.60477100	0.36601200
H	0.18061800	-4.17766700	1.22175500
H	1.39104100	-4.18524100	-0.06238500
C	3.39080600	2.50713900	-0.48782500
C	-3.70330000	1.95933800	1.48895500
C	-0.55877400	-3.53386100	-0.71917300
H	-0.12383700	-3.08239400	-1.62480000
H	-0.82629000	-4.56405800	-0.99399800
C	5.76031000	3.05570000	-0.80535400
H	6.52571400	3.72215900	-1.19608300
C	-2.92631600	-4.82498900	0.27368200
H	-2.92534700	-5.28534000	-0.72411700
H	-3.85279000	-5.11743300	0.77391200
H	-2.08768000	-5.25491600	0.83655500
C	-4.78570000	3.13178800	-0.84414100
H	-5.20261600	3.59047900	-1.73845100
C	2.69243900	1.55454100	2.82684600
H	3.74875100	1.43815700	3.10250700
H	2.09766500	1.55699800	3.74412300
H	2.59688000	2.53239100	2.34186300
C	-3.78995900	1.45143900	-3.29765000
H	-4.02290600	2.49214100	-3.55906600
H	-3.93514400	0.83632000	-4.19632200
H	-2.72776200	1.40967900	-3.02157800
C	6.12377700	1.88525500	-0.12133100
H	7.17781300	1.65109700	0.01232900
C	-1.71341700	1.98447400	3.07565700
H	-1.01022900	1.80461500	2.25282600

H	0.39014500	1.19989600	-0.86806800
H	-0.31255500	1.30870400	0.74034400
C	-6.67813200	-2.29308200	-0.27886000
H	-5.70427600	-2.31112500	-0.78018300
C	-7.69556100	-3.00472200	-1.20860600
H	-7.36267500	-4.02865700	-1.42611900
H	-7.80644800	-2.47270400	-2.16210300
H	-8.68886800	-3.06870400	-0.74542400
C	6.67842200	2.29290400	0.27958700
H	5.70445400	2.31096400	0.78069500
C	0.77728400	0.82396200	2.93915800
H	-0.03832000	0.10289600	2.80172200
H	0.35670900	1.82964300	2.79987400
H	1.12170700	0.74658000	3.97320500
C	5.56713800	-2.75851100	0.30748200
H	4.67159600	-2.35712600	0.79373400
C	5.11473500	-3.42971200	-1.01725000
H	5.96911700	-3.85743200	-1.55837400
H	4.63055000	-2.70450000	-1.68585800
H	4.40110800	-4.24045000	-0.81606400
C	7.69573900	3.00414100	1.20976000
H	8.68916800	3.06808400	0.74683400
H	7.80631000	2.47185700	2.16314600
H	7.36296400	4.02807300	1.42745700
H	-3.17807300	-0.42474400	-3.67075000
Tl	-3.34225700	-0.39545000	1.20637400
Tl	3.34237300	0.39555300	-1.20650300

H	-1.28663900	1.54064000	3.98557900
H	-1.78515500	3.06951400	3.22965600
C	-4.69233900	0.94838700	-2.13915100
H	-4.41924400	-0.09255800	-1.93488800
C	0.04227300	-2.56401200	3.01107800
H	-0.94978500	-2.82471900	2.62328900
H	-0.09211000	-1.97395400	3.92093700
H	0.55207300	-3.49571700	3.29228900
C	-3.10568300	1.36999100	2.77217300
H	-2.96418200	0.29462600	2.61790800
C	1.55821800	4.25264200	-0.10756200
H	1.77978800	4.28208300	0.96685000
H	0.48764800	4.45890100	-0.23989400
H	2.11832100	5.06682200	-0.58606100
C	1.57220800	2.85745100	-2.23661200
H	2.15673400	3.60548900	-2.78841800
H	0.50748100	3.08058200	-2.38846900
H	1.78389200	1.87668000	-2.68329700
C	-4.04903900	1.55034300	3.99081100
H	-4.19259200	2.61126800	4.23438500
H	-3.62559300	1.05887400	4.87732300
H	-5.03881500	1.11598100	3.80120200
C	-6.18165800	0.96333300	-2.57410000
H	-6.83565100	0.59486400	-1.77356800
H	-6.32882700	0.32426900	-3.45536700
H	-6.51352500	1.97661600	-2.83636100
H	1.04240100	-0.27872800	3.46184000

Tl$_4$

Tl	-0.67421700	-2.07075500	0.16802500
Tl	0.65915000	1.99928600	-0.23817300
Tl	2.56749300	-0.93211900	-0.54955900
Tl	-2.58057800	0.85748900	0.48332400
N	-0.02604800	-2.03030400	2.49819400
C	2.90974300	-6.40212300	-1.47755100
H	2.66518500	-7.09379000	-0.66235600
H	3.93745800	-6.05146200	-1.32602100
H	2.88426400	-6.97155700	-2.41621900
C	0.48092100	-3.01739300	3.25410000
C	6.85497700	1.41343300	-0.60880800
H	7.56693300	0.59806200	-0.78724100
H	6.93446600	1.67764900	0.45089100
H	7.16576500	2.27109200	-1.21137900
C	0.58137700	-4.38059600	2.85012500
H	0.97212100	-5.03852600	3.61888300
C	-6.62084300	1.63267400	-0.00447000
N	-2.67689900	-0.59171900	2.51120700
C	0.26777300	0.49931700	-3.09292800
H	-0.42924100	0.25399700	-3.90786500
H	0.00429700	-0.17718500	-2.26544400
C	5.17708700	2.66290900	2.83373300
H	5.71180300	2.48743000	3.77665400
H	4.52246200	3.53402100	2.96988600
H	5.92049400	2.91597100	2.06811600
C	-1.60951800	-0.30310500	3.49908700
H	-1.61268400	0.78045900	3.69847700
H	-1.78972900	-0.79567000	4.46227600
C	-6.69534000	1.88391500	1.50725800
H	-6.12515300	1.10057000	2.01678900
N	-0.19814600	-4.47296000	0.50446100
N	-4.86367800	-0.10459000	0.29473600
C	-3.30888100	-2.57477300	3.91435000
H	-2.28821600	-2.97197900	3.93051000
H	-4.00175700	-3.41726000	3.84802200
H	-3.49680100	-2.07019800	4.87238400
C	-5.70775700	0.68832800	-0.56652400

H	4.16385600	6.76415800	-2.19563500
C	-5.35750900	-1.17906700	0.94174500
N	0.12135600	1.88741300	-2.60950500
C	-6.02066500	3.23847400	1.85823900
H	-4.98699400	3.27095200	1.48931500
H	-6.00415300	3.39305700	2.94587000
H	-6.56272000	4.07837100	1.40342000
C	6.88831100	-2.10230900	2.06348300
H	7.52550100	-2.98157600	1.99271700
C	-5.56234800	0.58740900	-1.98381400
C	5.90068000	-3.76264900	-0.36571100
H	6.44829300	-4.38962600	0.35052100
H	5.96108800	-4.24746200	-1.34986100
H	4.85015400	-3.74138300	-0.05069100
C	-2.21140300	-6.47392200	-1.97140500
H	-3.24165100	-6.79203000	-2.11437400
C	1.50331700	6.82932300	2.59227200
H	1.81400000	7.43447700	3.44075900
C	-0.20327000	5.47217400	1.46843300
C	5.45553600	-0.43069700	0.99578600
C	3.73337300	1.29997600	-2.92739200
C	0.68898800	5.25468500	0.37847200
C	-6.37021900	1.39621500	-2.81037200
H	-6.27899500	1.31695700	-3.89091100
C	-0.32254700	2.85689900	-3.42616500
C	-1.87958900	-5.70225900	-0.83810900
C	-6.76959500	-1.67396100	0.60863700
H	-7.52326100	-1.04854700	1.10449300
H	-6.91134300	-2.70172500	0.95558400
H	-6.97272300	-1.62874100	-0.46604400
C	-0.44545200	6.44075000	-1.92070900
H	-1.01176600	6.77933000	-1.04591800
H	-1.00150200	6.70670500	-2.82370000
H	0.49822800	6.99900500	-1.92193300
C	-2.99144800	-5.33298100	0.15087100
H	-2.56262800	-4.69347600	0.93166400
C	-4.68333400	-1.91141800	1.95378500

C	-0.52678800	-5.29697200	-0.64329600
C	4.23912800	4.80692500	-0.21557200
H	4.79760800	5.36567600	0.54781600
H	4.92121800	4.58070200	-1.04444000
H	3.92803600	3.85281500	0.22586800
C	0.22400000	-5.05421500	1.65053200
C	-3.74007800	0.21395300	-3.75005000
H	-4.36261200	0.58107400	-4.57590200
H	-3.05284500	-0.53636400	-4.16516600
H	-3.14846300	1.05716800	-3.37296100
C	1.99936900	5.83456800	0.40458400
C	4.91340800	1.54546500	-2.16552600
H	5.56842300	2.28812800	-2.60824200
C	3.01865700	5.61977400	-0.72099800
H	2.54080400	5.03414900	-1.51240900
C	1.00051300	-2.72071300	4.66846500
H	1.90254000	-2.09427400	4.62849700
H	1.26194400	-3.64814900	5.18386600
H	0.25610400	-2.19247800	5.27781800
C	0.35546100	-6.58107300	1.70286600
H	0.69820000	-6.91107400	2.68691400
H	1.05972600	-6.94752200	0.94757500
H	-0.60809000	-7.06000500	1.49250300
C	0.08249700	-6.42158400	-2.73488300
H	0.83300900	-6.69667100	-3.47327800
C	1.92635900	-5.20277700	-1.51702600
H	2.04538500	-4.63878400	-0.58620700
C	6.68544400	-1.49927000	3.31363900
H	7.16945300	-1.90005700	4.20121900
C	0.46582900	-5.65524800	-1.61370900
C	-3.52086700	-1.62071200	2.72807200
N	4.79088600	0.09799000	-0.17579200
C	-4.58862800	-0.41432200	-2.61815500
H	-3.89800100	-0.74844600	-1.83423000
C	-1.81005000	3.91714900	2.68438700
H	-1.03778700	3.13641700	2.69001600
H	-2.79582300	3.43399300	2.64114400
H	-1.74445700	4.45151700	3.64122100
C	5.85189400	-0.37477600	3.40786500
H	5.68653300	0.08655500	4.37923300
C	2.37862800	6.61393100	1.51753000
H	3.37145800	7.05840300	1.54210200
C	-3.58211900	-6.58727200	0.84998200
H	-4.06453800	-7.25566600	0.12439800
H	-4.33900000	-6.29114300	1.58903300
H	-2.80665500	-7.16287700	1.37037000
C	-1.24290200	-6.84025400	-2.91600100
H	-1.51757800	-7.43729500	-3.78244500
N	2.78405300	0.39611000	-2.62846200
N	0.29406800	4.39217100	-0.71661500
C	-7.39955200	2.42563600	-0.87206300
H	-8.09085200	3.15360700	-0.45337600
C	5.22784300	0.17386500	2.26767000
C	5.43394000	0.97215600	-0.97648600
C	3.49763600	6.95810500	-1.34395500
H	4.05649400	7.56086000	-0.61566100
H	2.65727200	7.56535500	-1.70242200
C	-0.69702300	2.53554600	-4.88126300
H	0.11369500	2.01100400	-5.40237700
H	-0.91209000	3.45393100	-5.43313700
H	-1.58894300	1.89747200	-4.93159600
C	-0.18738900	4.93071300	-1.86151700
C	-0.16800700	-0.65677800	3.01885900
H	0.51237900	-0.43197100	3.85159300
H	0.10542400	0.04307600	2.21385700
C	0.22349500	6.25625500	2.56097200
H	-0.45721300	6.42555900	3.39273600
C	-0.48959600	4.22272000	-3.05459600
C	6.28387300	-1.59159700	0.89574500
C	1.69498100	0.12638800	-3.59568900
H	1.67861000	-0.95769200	-3.79832200
H	1.86125400	0.61657200	-4.56177000
C	-1.61974000	4.88720600	1.48855100
H	-1.76573900	4.32090300	0.56125200
C	-7.29138700	2.30378300	-2.26598000
H	-7.91280700	2.91183800	-2.91928700
C	-2.70263200	5.99887800	1.52426700
H	-3.70796100	5.55651700	1.50976700
H	-2.61560000	6.66838000	0.65930200
H	-2.61687600	6.61165300	2.43123800
C	6.49791900	-2.33244100	-0.42953900
H	5.96372400	-1.78756100	-1.21541300
C	3.62663700	2.15262900	-4.20269000
H	2.66160700	2.67059800	-4.25511900
H	3.73544600	1.54181400	-5.10954900
H	4.41579800	2.90811000	-4.21827700
C	4.34512900	1.41741500	2.42660400
H	3.88467600	1.62631100	1.45399400
C	-4.12148100	-4.53312100	-0.54792100
H	-4.62454100	-5.13841600	-1.31327200
H	-3.72718300	-3.63401500	-1.03720200
H	-4.87159400	-4.21249300	0.18529700
C	3.20353900	1.18235600	3.44810500
H	3.59436700	1.06712200	4.46792400
H	2.63638600	0.27760700	3.19996300
H	2.51120500	2.03512500	3.44957700
C	2.28075900	-4.25673200	-2.69549100
H	3.31695700	-3.90209400	-2.61472800
H	1.61379300	-3.38441700	-2.71426600
H	2.17545400	-4.77049200	-3.66005100
C	7.99361600	-2.40365700	-0.83536600
H	8.57884700	-2.97336700	-0.10145600
H	8.44106600	-1.40560400	-0.91527100
H	8.10209300	-2.90259600	-1.80803300
C	-5.33789600	-1.67087600	-3.13957400
H	-6.07723800	-1.39328900	-3.90301300
H	-5.86724000	-2.18445600	-2.32888200
H	-4.63319300	-2.38457000	-3.58752800
C	-8.14330100	1.84766700	2.05762200
H	-8.76387300	2.64102000	1.62111700
H	-8.13984200	1.99273700	3.14643400
H	-8.63071700	0.88777100	1.84451000
H	-0.88656800	4.84921500	-3.84618900
H	-5.21584200	-2.79928000	2.27875000

B3LYP-D3/LANL2DZ

		In$_2^{op}$				In$_2^{dim}$	
In	3.19436800	-0.36452300	-1.10563000	In	-1.16859200	0.60519700	-0.83594200
In	-3.19434300	0.36539700	1.10533800	In	2.18285100	1.36417800	-1.29201000
C	-5.64006800	0.16886900	-2.84451100	C	2.68702600	-1.07569300	2.63836100
H	-6.44314600	0.86343400	-2.57267900	H	3.78133400	-1.12572700	2.66595000
H	-6.06155700	-0.84135500	-2.77594100	H	2.33277200	-2.05990600	2.31194700
H	-5.34790200	0.35587900	-3.88112400	H	2.31852500	-0.89034500	3.65026200
C	0.31802200	-0.70864200	0.03400500	C	-0.64461200	3.62552100	-1.12483200
H	-0.33722400	-1.36191400	0.62387500	H	-1.03312500	4.60467400	-1.43349400
H	0.34013800	-1.12574200	-0.98198400	H	-0.27089700	3.13924500	-2.03584200
C	-5.99854500	-3.67426200	-1.35148300	C	0.91460400	-3.79608900	0.18396300
H	-6.84714400	-4.20996900	-0.90694600	H	1.28303700	-4.71927400	-0.28227000
H	-5.25656700	-4.42219900	-1.66092900	H	-0.18257800	-3.83677100	0.19898500
H	-6.36148700	-3.15909400	-2.25008100	H	1.26813000	-3.78057000	1.22275400
C	4.86375100	3.42285600	-0.91475000	C	-0.72142600	-1.80996800	2.78389700
H	5.69667900	3.90630000	-1.44220100	H	-0.71465500	-2.88878700	2.98610900
H	4.13651200	4.19928300	-0.64079600	H	-0.20938200	-1.30286400	3.61067200
H	4.38321300	2.72937300	-1.61753800	H	-0.14452100	-1.63126400	1.87206900
C	6.33836000	1.55643800	-0.03886900	C	-2.87706400	-1.94814300	1.45650900
C	-3.19958900	0.60371900	-2.48947100	C	1.39476100	1.02530500	2.21221600
H	-3.21330200	0.71120300	-3.56812800	H	1.13120900	0.88660500	3.25444900
C	5.36924600	2.67700200	0.34820200	C	-2.16656300	-1.27640300	2.63449500
H	4.49817800	2.22487400	0.83497400	H	-2.10082900	-0.20115600	2.43280700
C	-8.50488700	-0.87705300	0.95807200	C	5.15507700	-3.22213300	-0.94817900
H	-9.47541300	-1.14381200	1.36974000	H	5.79922000	-4.02260300	-1.30475400
N	-4.65408700	0.16392600	-0.56635400	N	2.62696700	-0.04637500	0.38384500
C	6.39338700	-2.97696400	-1.55640900	C	-3.68254100	-1.50161300	-3.24510700
H	5.63842800	-2.45634000	-2.15969900	H	-2.60851200	-1.32783100	-3.10068000
H	6.09743400	-4.03078600	-1.46469000	H	-4.01331200	-0.91845100	-4.11502300
H	7.34443200	-2.93640800	-2.10369100	H	-3.82098200	-2.56595800	-3.47621100
C	-7.60156900	-1.88099500	0.57467700	C	3.75996000	-3.37290500	-0.97802800
H	-7.87992000	-2.92568900	0.69326800	H	3.32795500	-4.29484900	-1.36054400
C	7.60242800	1.88056800	-0.57281200	C	-3.06995000	-3.34527600	1.47390400
H	7.88117700	2.92524800	-0.69057600	H	-2.71726400	-3.92153900	2.32615000
N	-1.70773000	0.65217800	-0.55130800	N	1.13125000	2.58375900	0.34403600
N	4.65402000	-0.16413400	0.56624700	N	-3.06019500	0.21373200	0.24009400
C	-6.33772700	-1.55680800	0.04022900	C	2.90480900	-2.34736700	-0.52424300
C	-4.45138100	0.31921200	-1.89895400	C	2.22631300	0.01404300	1.67277200
C	5.99963000	3.67344300	1.35372300	C	-2.95019900	-1.46488100	3.95946200
H	6.84827600	4.20924700	0.90939300	H	-3.00573500	-2.52551400	4.23764600
H	6.36254600	3.15784700	2.25208800	H	-3.97698500	-1.08673500	3.88125500
H	5.25776100	4.42134200	1.66351900	H	-2.45044600	-0.92881600	4.77742200
N	1.70753000	-0.65188300	0.55069700	N	-1.68713700	2.74478700	-0.54275600
C	-8.14823200	0.47241400	0.81133900	C	5.71458700	-2.03051700	-0.46144500
H	-8.84949200	1.24754300	1.11206300	H	6.79587800	-1.91381700	-0.44362500
C	-6.39378300	2.97765800	1.55435100	C	6.28219600	1.05427600	-0.61969600
H	-7.34455800	2.93708800	2.10210200	H	7.09828800	0.44300500	-1.02736700
H	-6.09831000	4.03153800	1.46175800	H	6.71313800	1.99498900	-0.25049900
H	-5.63833700	2.45776700	2.15766500	H	5.59364200	1.28780200	-1.44144800
C	8.50547000	0.87658200	-0.95675600	C	-3.70320400	-4.00444300	0.40935500
H	9.47618900	1.14329600	-1.36799700	H	-3.83857500	-5.08299000	0.43741300
C	6.89381200	-0.84184400	-0.28240800	C	-3.98811500	-1.86583900	-0.75185500
C	-5.98741300	-0.18507100	-0.10035200	C	3.48511800	-1.14576100	-0.02990800
C	-1.92222800	0.73936600	-1.88260000	C	0.89488000	2.21747500	1.62163300
C	5.98752200	0.18472600	0.10063400	C	-3.33962500	-1.20996100	0.33203200
C	1.92182500	-0.73930300	1.88200400	C	-2.74012500	3.27598800	0.11017200
C	5.63970400	-0.17017200	2.84455000	C	-5.22827000	0.58030500	1.38697100
H	6.44298400	-0.86425400	2.57210200	H	-5.82045600	0.01980500	0.65318600
H	5.34750600	-0.35824700	3.88096000	H	-5.83974800	1.39738300	1.77881900
H	6.06092800	0.84023500	2.77698400	H	-5.00119300	-0.11390700	2.20294800
C	0.76070500	-1.02214400	2.83898600	C	-2.88034600	4.79469500	0.24201600
H	-0.05333100	-0.29546900	2.73185700	H	-1.97592100	5.24590500	0.66839500
H	1.10116700	-0.99427700	3.87701000	H	-3.72375200	5.05080700	0.88797300
H	0.33483400	-2.01739300	2.65141200	H	-3.05246200	5.26058200	-0.73754600
C	4.45110300	-0.31986400	1.89877500	C	-3.94837700	1.10372900	0.74287900

C	8.14828200	-0.47285800	-0.81112700	**C**	-4.15646700	-3.26474900	-0.69370400
H	8.84932000	-1.24802000	-1.11228500	**H**	-4.64344500	-3.77850400	-1.51929200
C	3.19914600	-0.60412700	2.48906300	**C**	-3.77994500	2.50769800	0.70068500
C	-6.89401500	0.84146300	0.28207500	**C**	4.89771000	-0.98003800	0.00549900
C	-0.31814900	0.70904500	-0.03480700	**C**	0.57234000	3.85543000	-0.17495100
H	-0.34017100	1.12617500	0.98117100	**H**	1.35100100	4.35717200	-0.76848300
H	0.33701300	1.36231500	-0.62477600	**H**	0.28635500	4.54843100	0.62382900
C	6.53458500	-2.32478500	-0.15576000	**C**	-4.48688000	-1.10025100	-1.98072700
H	5.56307000	-2.40156400	0.34495500	**H**	-4.32422200	-0.03020200	-1.80996400
C	7.56509000	-3.10008200	0.70437100	**C**	-6.00535800	-1.30849100	-2.21218800
H	7.24696300	-4.14342000	0.83115900	**H**	-6.34877300	-0.69948400	-3.05892900
H	7.67388000	-2.65168700	1.70021600	**H**	-6.58774600	-1.02402700	-1.32632900
H	8.55558500	-3.10771300	0.23137300	**H**	-6.23422700	-2.35758500	-2.43994500
C	-6.53536200	2.32444000	0.15422300	**C**	5.54798900	0.30604600	0.52366800
H	-5.56408500	2.40121600	-0.34695300	**H**	4.75634700	0.96578700	0.89598400
C	-0.76132100	1.02243400	-2.83977400	**C**	0.04199100	3.09038000	2.54819200
H	0.05275900	0.29575900	-2.73294400	**H**	-0.96090800	3.23786500	2.13172300
H	-0.33543100	2.01765100	-2.65209700	**H**	0.49656200	4.07769600	2.70425500
H	-1.10199800	0.99474500	-3.87773200	**H**	-0.06556100	2.61597900	3.52668900
C	-5.36833600	-2.67729800	-0.34635100	**C**	1.38865700	-2.54392300	-0.59661100
H	-4.49739300	-2.22514700	-0.83332700	**H**	0.90859800	-1.66875000	-0.14623000
C	-4.86262600	-3.42256700	0.91684900	**C**	0.91036900	-2.61234300	-2.06914300
H	-5.69541200	-3.90594900	1.44457900	**H**	1.35249900	-3.47474700	-2.58626800
H	-4.38213400	-2.72872800	1.61931900	**H**	1.19294700	-1.70378000	-2.61482400
H	-4.13529000	-4.19898300	0.64312500	**H**	-0.18312400	-2.70559000	-2.11066400
C	-7.56652800	3.09877700	-0.70598100	**C**	6.51752500	0.02804200	1.70137800
H	-8.55676200	3.10655100	-0.23243900	**H**	7.36491900	-0.59248100	1.38194700
H	-7.67577600	2.64954700	-1.70139900	**H**	6.01111700	-0.49514100	2.52260700
H	-7.24873400	4.14209200	-0.83379000	**H**	6.92153100	0.97110400	2.09336700
H	3.21269200	-0.71184500	3.56769800	**H**	-4.57165300	3.08154800	1.16905600

In$_4$

In	-1.33279000	1.33090800	-0.34046000	**H**	6.20880100	-3.71477300	2.84048700
In	1.27368300	-1.38496900	0.31042200	**C**	-4.64108000	-2.31522900	-1.35488100
In	1.49376000	1.66823200	0.93611200	**N**	0.48534200	-1.79913700	2.31091600
In	-1.56182900	-1.70691000	-0.97138300	**C**	-1.55196500	-5.62693200	0.12129700
N	-0.48452200	1.66514300	-2.34906500	**H**	-0.87447400	-4.76903800	0.17738200
C	-1.30729200	5.72355100	2.85325500	**H**	-1.24538200	-6.26059700	-0.72249800
H	-1.51970600	6.49446000	2.10194300	**H**	-1.43062800	-6.20499900	1.04741100
H	-0.26612600	5.84437600	3.18127400	**C**	3.70548600	4.94551500	-1.98294200
H	-1.95642700	5.91293200	3.71826200	**H**	3.49996800	6.00987900	-2.07251400
C	-0.12384000	2.86877800	-2.82857900	**C**	-4.09974400	-1.97707500	1.91167000
C	5.94483700	2.66357000	1.15055500	**C**	1.65181900	5.73796900	0.22633100
H	5.88434700	3.73371500	0.92136300	**H**	1.66731400	6.46637500	-0.59623900
H	6.32903400	2.17057500	0.25140100	**H**	1.29647400	6.25315900	1.12922800
H	6.66091200	2.51788300	1.96332600	**H**	0.93581900	4.95315000	-0.03534300
C	-0.55534800	4.10509900	-2.26816000	**C**	-5.56868900	3.65181900	0.79274700
H	-0.15294000	4.99329500	-2.74120100	**H**	-6.58243600	3.47605800	0.43939500
C	-3.43845100	-4.21475700	1.07425800	**C**	5.21601400	-3.87281800	-2.52315600
N	-2.32682300	-0.88284200	-2.90109600	**H**	6.00454600	-3.96100900	-3.26688700
C	-0.05188300	-0.58570900	2.96843300	**C**	2.83806200	-3.96912800	-1.93725800
H	-0.86728900	-0.81537100	3.66476500	**C**	3.79766800	2.91495200	-0.63646800
H	-0.49304100	0.05116100	2.19319800	**C**	3.33486700	0.90392800	3.43877000
C	5.98501900	0.32463800	-2.02044400	**C**	3.17056900	-3.62651400	-0.59830200
H	6.25168200	0.62240200	-3.04351900	**C**	-4.19175600	-2.51931500	3.21053400
H	6.13764600	-0.75816100	-1.93166900	**H**	-4.48294800	-1.87588800	4.03669400
H	6.67826900	0.82786000	-1.33489000	**C**	0.39468900	-2.99792600	2.90935400
C	-1.34691400	-0.21324000	-3.80370000	**C**	-4.48468800	3.45380500	-0.08680500
H	-0.95017700	-0.96338900	-4.50942800	**C**	-5.92573200	-3.03571300	-0.95196300
H	-1.81980900	0.57859100	-4.39777000	**H**	-5.80920400	-4.11215000	-1.13584500
C	-3.02046600	-5.16169400	-0.05553400	**H**	-6.77681600	-2.68086900	-1.54027800
H	-3.07889500	-4.61313700	-1.00235100	**H**	-6.14994100	-2.91536500	0.11067300
N	-2.05023300	3.37639600	-0.47628000	**C**	2.38899700	-5.76246100	1.05320200
N	-3.60022500	-2.29154500	-0.49420200	**H**	2.22913400	-6.10894500	0.02638700
C	-3.98745700	-0.53323200	-4.72682600	**H**	1.94544000	-6.48442500	1.74409500
H	-3.96710300	0.56567600	-4.72898400	**H**	3.47378300	-5.74377900	1.21808000

H	-5.00104700	-0.85044900	-4.98279200
H	-3.31014100	-0.87806300	-5.51805500
C	-3.73703700	-2.84353000	0.83984200
C	-3.16473600	3.67829800	0.39591700
C	5.29072200	-1.54681700	1.31386700
H	6.12208900	-1.30998300	0.63637500
H	5.59251100	-1.28311300	2.33543200
H	4.44262900	-0.90714200	1.04949700
C	-1.51780500	4.34109900	-1.26194800
C	-3.83319200	0.43424200	2.74900800
H	-4.32749600	0.30198700	3.72136000
H	-3.96815800	1.47896100	2.44927300
H	-2.76156000	0.25373900	2.87888200
C	4.52724300	-3.41750200	-0.21587600
C	4.45128000	1.51107000	2.79133500
H	5.36963800	1.49226800	3.36605400
C	4.90571300	-3.04406800	1.22032900
H	4.02713600	-3.18696300	1.85741500
C	0.79206900	2.98244300	-4.04809100
H	1.75340800	2.49053400	-3.85688900
H	1.00135300	4.03089200	-4.27171900
H	0.34142500	2.52680300	-4.93972100
C	-1.98725500	5.77915300	-1.07243400
H	-1.46938700	6.45615400	-1.75675600
H	-1.80773800	6.11239000	-0.04424200
H	-3.06726600	5.85747200	-1.24973000
C	-4.05245200	4.29961200	2.57624000
H	-3.89346100	4.62086600	3.60314700
C	-1.52415900	4.29924100	2.28504300
H	-0.81007500	4.14743200	1.46881500
C	4.15080400	4.23026900	-3.10492200
H	4.29033600	4.73761900	-4.05690800
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C	-3.58156700	-1.07573700	-3.35396100
N	3.56305200	2.23753700	0.62642100
C	-4.42161500	-0.49973700	1.66806100
H	-3.96356600	-0.21203700	0.71641700
C	0.99219000	-3.21953100	-3.51292800
H	1.20236100	-2.18359400	-3.22552600
H	-0.08144300	-3.30409200	-3.72734100
H	1.54629100	-3.43426400	-4.43692100
C	4.41027500	2.85547600	-2.99413500
H	4.75306800	2.30161800	-3.86539000
C	5.53207000	-3.53253400	-1.19760400
H	6.57010800	-3.35990800	-0.92281200
C	-5.65081400	4.00817500	-2.28067500
H	-6.65192900	4.05633900	-1.83237900
H	-5.76821500	3.70394000	-3.32963800
H	-5.22582800	5.02032200	-2.26251900
C	-5.35952600	4.07686800	2.11490100
H	-6.20631200	4.22502500	2.78092400
N	2.09338800	0.81114600	2.92577700
N	2.12662700	-3.39332700	0.37938000
C	-3.52846400	-4.70832000	2.39274000
H	-3.29936800	-5.75346900	2.58719900
C	4.23379200	2.17442500	-1.77135300
C	4.57140300	2.11252100	1.51970500
C	6.03742200	-3.94122700	1.77960300
H	6.98464500	-3.77690600	1.24965400
H	5.78447700	-5.00604200	1.69156300
C	-4.74112700	3.00442500	-1.52828700
H	-3.77903100	2.97475100	-2.05005900
C	-4.61735800	-1.75869900	-2.65385900
C	-0.35343100	-3.14623200	4.23417800
H	0.04808200	-2.47565900	5.00454700
H	-0.27931000	-4.17147700	4.60548300
H	-1.41739400	-2.91448600	4.10110400
C	1.79413400	-4.37233500	1.25542800
C	-0.13816200	0.42714000	-3.08377300
H	0.63526700	0.59105000	-3.84164100
H	0.28700300	-0.29151200	-2.37322000
C	3.87827400	-4.09489900	-2.88253300
H	3.63523200	-4.36162800	-3.90860000
C	0.95554000	-4.19467800	2.37725300
C	3.52609000	4.30981700	-0.73697200
C	1.01483800	0.20928100	3.76007600
H	0.49066700	1.01864100	4.29443400
H	1.42135500	-0.47091600	4.51602600
C	1.38996900	-4.19437700	-2.37615400
H	0.73417300	-3.98430000	-1.52487600
C	-3.91293200	-3.87477800	3.45362600
H	-3.98930500	-4.27514200	4.46221900
C	1.14064700	-5.66082500	-2.80961000
H	0.08618200	-5.80072600	-3.08394100
H	1.37583300	-6.36261100	-1.99983200
H	1.75734200	-5.92986900	-3.67767500
C	3.05963600	5.13614800	0.46619300
H	2.98931100	4.47003300	1.33297000
C	3.64521600	0.32831100	4.82489200
H	3.51709900	-0.76286400	4.83339000
H	2.98718400	0.74811600	5.59604900
H	4.67796200	0.54563700	5.10727000
C	4.50720700	0.66962400	-1.70481500
H	4.29146500	0.32926700	-0.68910200
C	-5.33441700	1.57475100	-1.57780700
H	-6.28764100	1.52014300	-1.03604900
H	-4.64970900	0.84485800	-1.13376600
H	-5.51460800	1.26640600	-2.61586200
C	3.57003800	-0.11445600	-2.65592000
H	3.74766100	0.15633500	-3.70649900
H	2.52517400	0.09298300	-2.41086500
H	3.73508300	-1.19324900	-2.54887900
C	-1.20446000	3.23533100	3.36581400
H	-0.16313200	3.33611700	3.70031300
H	-1.33675800	2.22524600	2.96385200
H	-1.86537100	3.34464600	4.23677600
C	4.07637500	6.25319600	0.81778100
H	4.17231700	6.97434700	-0.00455800
H	5.07333000	5.84159100	1.02007500
H	3.74586500	6.80227800	1.70979900
C	-5.95073200	-0.26415900	1.54749300
H	-6.46904100	-0.61042700	2.45240200
H	-6.37362500	-0.79091900	0.68541800
H	-6.15146200	0.80690700	1.42182000
C	-3.96957100	-6.38267000	-0.16108700
H	-3.90391100	-7.01588000	0.73334200
H	-3.69997400	-7.00084900	-1.02795000
H	-5.01578100	-6.07049300	-0.27107900
H	0.75121900	-5.09395000	2.94692100
H	-5.55074700	-1.84703500	-3.19810500

Tl_2^{op}

C	5.56484600	-0.05690800	3.07213900
H	6.36193800	0.67855800	2.90767800
H	6.01825800	-1.04737000	2.94072600
H	5.21277000	0.03273600	4.10321400
C	-0.30924200	-0.70478800	-0.11684800
H	0.37696300	-1.28615800	-0.74884700
H	-0.34079700	-1.22525500	0.85159700
C	6.01051600	-3.80047400	1.27820300
H	6.87779100	-4.30043300	0.82743500
H	5.26273500	-4.57068800	1.51023300
H	6.33895800	-3.34625900	2.22174100
C	-4.93761500	3.39213500	0.99785700
H	-5.78120100	3.84063500	1.53898500
H	-4.20185700	4.18274400	0.79739000
H	-4.47490500	2.65135100	1.66472100
C	-6.39454800	1.59635500	-0.04764500
C	3.14321200	0.40022400	2.61688900
H	3.11555300	0.43259000	3.70091100
C	-5.41123200	2.73590200	-0.32544200
H	-4.52940800	2.31014300	-0.81592500
C	8.57394800	-0.84819700	-0.78539400
H	9.54752900	-1.08166800	-1.20992000
N	4.70813800	0.07088400	0.75387000
C	-6.44020500	-3.04410000	1.05314800
H	-5.68473100	-2.57376500	1.69728200
H	-6.13666500	-4.08357900	0.86909000
H	-7.38611700	-3.05828400	1.61066000
C	7.66199500	-1.87786200	-0.50142100
H	7.93721100	-2.90957800	-0.71007900
C	-7.66198900	1.87788000	0.50141200
H	-7.93720300	2.90960200	0.71004700
N	1.68282600	0.60730000	0.65385900
N	-4.70814500	-0.07089100	-0.75387000
C	6.39454700	-1.59634900	0.04762400
C	4.42566700	0.14944500	2.07150900
C	-6.01054100	3.80044500	-1.27829400
H	-6.87781100	4.30041500	-0.82752700
H	-6.33899500	3.34620200	-2.22181300
H	-5.26276500	4.57065500	-1.51035700
N	-1.68283500	-0.60732100	-0.65388200
C	8.22015900	0.48494900	-0.52110400
H	8.92692100	1.28113500	-0.74487000
C	6.44025600	3.04414900	-1.05303200
H	7.38618600	3.05835000	-1.61051300
H	6.13671400	4.08362200	-0.86894600
H	5.68480100	2.57384000	-1.69720800
C	-8.57393400	0.84822200	0.78542700
H	-9.54750900	1.08170200	1.20996200
C	-6.96333600	-0.80977400	-0.02894000
C	6.04469400	-0.24099500	0.31061000
C	1.88001400	0.58714200	1.98436600
C	-6.04469600	0.24099600	-0.31060100
C	-1.88003400	-0.58716900	-1.98438700
C	-5.56487300	0.05688000	-3.07213400
H	-6.36196400	-0.67858500	-2.90766400
H	-5.21280400	-0.03277000	-4.10321100
H	-6.01828400	1.04734200	-2.94072300
C	-0.69825600	-0.79218500	-2.94492300
H	0.09796200	-0.05633400	-2.77430300
H	-1.02290300	-0.69861100	-3.98411900
H	-0.25738600	-1.79065800	-2.81814200
C	-4.42568700	-0.14946800	-2.07151100
C	-8.22014600	-0.48493100	0.52116800
H	-8.92690300	-1.28111300	0.74496800
C	-3.14323700	-0.40025500	-2.61690100
C	6.96334100	0.80978000	0.02899200
C	0.30923800	0.70476800	0.11681600

Tl_2^{dim}

Tl	-1.00285200	-0.42805800	-0.67642600
Tl	2.35318400	-1.35621800	-1.08410800
N	2.45981300	0.40146100	0.63032300
N	1.08819600	-2.41350600	0.84475100
N	-3.25019200	-0.19423200	0.34530300
C	1.14072700	-0.56583500	2.46768100
N	-1.66557000	-2.80930100	-0.17779400
C	1.96041600	0.43144500	1.88347900
C	-3.83955500	-2.50946600	0.92438900
H	-4.63252000	-3.08091100	1.39561900
C	-3.61841600	1.19709100	0.27820200
C	-4.09292100	-1.11601900	0.85152400
C	-4.21764500	1.70666600	-0.91123600
C	-2.74222500	-3.29457700	0.46057700
C	5.37279600	0.17427100	0.91875000
H	4.58479800	-0.48914700	1.29222600
C	-4.12856100	3.96654700	0.03250200
H	-4.32691400	5.03177700	-0.06016200
C	-3.52808300	3.45775400	1.19507800
H	-3.26044000	4.13868700	2.00032600
C	1.17359000	2.75374100	-0.60292500
H	0.71720000	1.91961100	-0.06067200
C	6.23698900	0.59971600	2.13380500
H	6.66982100	-0.28226900	2.62469300
H	5.63829300	1.14433000	2.87454800
H	7.06291400	1.25333300	1.82437900
C	3.28710100	1.48920400	0.16047700
C	3.52753700	3.62841300	-0.98960200
H	3.07999400	4.49640200	-1.46899500
C	-5.44674300	-0.64332100	1.38752700
H	-5.31376000	0.11735400	2.16544800
H	-6.02638400	-1.47261600	1.80184000
H	-6.03098900	-0.17469900	0.58551200
C	6.22669100	-0.62816600	-0.09734500
H	7.05681900	-0.02098700	-0.48157000
H	5.62506400	-0.94675600	-0.95938700
H	6.65215500	-1.52331000	0.37628500
C	0.73569900	-1.86071900	2.02000300
C	4.70471200	1.37964800	0.25163900
C	0.59004900	-3.75977000	0.48071200
H	0.24709700	-4.33947500	1.34608700
H	1.42060200	-4.32555800	0.02967300
C	2.69116800	2.62291900	-0.46423400
C	-3.26228200	2.08018000	1.33751100
C	-0.56008100	-3.70482500	-0.57561400
H	-0.13670100	-3.32133600	-1.51706900
H	-0.87414400	-4.73825900	-0.78501100
C	4.92566900	3.52901200	-0.90450700
H	5.55606000	4.31443100	-1.31477400
C	-2.86343800	-4.80159800	0.73618100
H	-2.93063300	-5.37051100	-0.20124300
H	-3.75829100	-5.01844000	1.32481700
H	-1.99392000	-5.17890800	1.29019000
C	-4.46384900	3.09096400	-1.01280500
H	-4.92029700	3.48720000	-1.91743100
C	2.28875000	1.63679100	2.76729900
H	3.37470200	1.74861100	2.86903900
H	1.85246400	1.53240300	3.76330600
H	1.91584000	2.56411900	2.31826600
C	-3.72568100	1.13219200	-3.33665500
H	-3.94005900	2.14995000	-3.68858100
H	-3.94722700	0.43523600	-4.15627000
H	-2.65030900	1.07742600	-3.11998000
C	5.50422100	2.40816100	-0.28850900
H	6.58764400	2.33247800	-0.22337300
C	-1.16999800	2.20441300	2.76181600
H	-0.54048300	1.97852500	1.89502100

H	0.34079700	1.22523300	-0.85162900
H	-0.37697100	1.28613900	0.74881200
C	-6.59684400	-2.27340500	-0.28416700
H	-5.62786200	-2.29656900	-0.79439400
C	-7.62792900	-2.98101000	-1.19921900
H	-7.30327400	-4.00677700	-1.41962800
H	-7.74747800	-2.44717200	-2.15054000
H	-8.61489700	-3.03777100	-0.72187300
C	6.59684900	2.27340400	0.28426000
H	5.62785100	2.29655500	0.79445800
C	0.69822700	0.79214800	2.94489200
H	-0.09798900	0.05629700	2.77425700
H	0.25735800	1.79062200	2.81811500
H	1.02286400	0.69856500	3.98409100
C	5.41122400	-2.73590100	0.32537400
H	4.52939300	-2.31015400	0.81585600
C	4.93762500	-3.39209500	-0.99795100
H	5.78121800	-3.84058000	-1.53908000
H	4.47492600	-2.65129000	-1.66480100
H	4.20186200	-4.18270700	-0.79751800
C	7.62790800	2.98097000	1.19937100
H	8.61489200	3.03774200	0.72205900
H	7.74742300	2.44709600	2.15067600
H	7.30325200	4.00673100	1.41980600
H	-3.11558800	-0.43263100	-3.70092300
Tl	-3.29175900	-0.38584900	1.21481200
Tl	3.29176800	0.38585800	-1.21482300
H	-0.66626300	1.80867500	3.65232300
H	-1.23428400	3.29599000	2.86086300
C	-4.57084400	0.78657800	-2.08227200
H	-4.32901700	-0.24136100	-1.79160500
C	-0.16449000	-2.61600400	3.00815400
H	-1.12870700	-2.85908300	2.54829600
H	-0.35805000	-2.00547600	3.89353000
H	0.30222000	-3.55203700	3.34313300
C	-2.57432800	1.57165800	2.60622100
H	-2.44031800	0.48821700	2.51112700
C	0.62016000	4.06376000	0.01132200
H	0.92749000	4.17600400	1.05840100
H	-0.47749500	4.06158200	-0.02268500
H	0.97582500	4.94437500	-0.53940600
C	0.74532800	2.63288200	-2.08766000
H	1.17166100	3.44967200	-2.68467100
H	-0.34878400	2.67557300	-2.17785100
H	1.08859100	1.68447700	-2.52206800
C	-3.43032400	1.83804100	3.87083200
H	-3.56758700	2.91501300	4.03605200
H	-2.93954800	1.42087400	4.76062900
H	-4.42527800	1.38404900	3.78513700
C	-6.08267900	0.83753600	-2.41995900
H	-6.69359100	0.58533500	-1.54413700
H	-6.32141200	0.12512500	-3.22108000
H	-6.38135700	1.83817000	-2.75940100
H	0.78808500	-0.31416300	3.46174400

Tl$_4$

Tl	-1.97272500	0.78070900	-0.34974200
Tl	1.97291200	-0.78332700	0.35057000
Tl	0.83190000	2.49511600	0.88102700
Tl	-0.83255600	-2.49394700	-0.88370300
N	-0.59853100	1.70814400	-2.20733000
C	-2.58848800	5.48693300	2.86689600
H	-2.98205900	6.24179100	2.17552600
H	-1.58137500	5.79531000	3.17899400
H	-3.22700600	5.48869700	3.75981100
C	-0.41629000	2.99153300	-2.55998100
C	5.77461800	2.81717800	1.34275100
H	5.90785800	3.38198900	0.41807600
H	6.51199300	2.00686500	1.36921300
H	5.99069400	3.48405200	2.18774800
C	-1.17224600	4.08554300	-2.04075100
H	-0.87285900	5.05542900	-2.42497900
C	-3.35343600	-4.66067200	0.77799400
N	-1.77500900	-0.98484700	-2.89772700
C	-0.18072600	-0.62939800	2.83657700
H	-0.99574000	-0.98197200	3.48130200
H	-0.66370200	-0.04312300	2.03946000
C	6.29773700	0.98675300	-1.71782700
H	6.62863900	1.30235700	-2.71628400
H	6.59930900	-0.05787000	-1.57396400
H	6.81981700	1.60636300	-0.98104500
C	-0.69593900	-0.33674000	-3.67852900
H	-0.02854300	-1.12750400	-4.05497900
H	-1.05815400	0.21718500	-4.55239500
C	-2.82512600	-5.49545900	-0.39176100
H	-2.62569700	-4.81856800	-1.23152600
N	-2.85373200	3.06683900	-0.56604200
N	-3.39429500	-2.61227900	-0.61576800
C	-3.43307500	0.21416200	-4.34611000
H	-3.00968400	1.20398400	-4.13104600
H	-4.51815900	0.32128900	-4.41937500
H	-3.05857700	-0.10892700	-5.32631600
H	5.56105900	-2.90509500	3.67575400
C	-4.34974600	-2.26293000	-1.49650200
N	0.59843900	-1.70968700	2.20725900
C	-1.51241100	-6.24418600	-0.04860300
H	-0.74905900	-5.56066300	0.34490600
H	-1.11062000	-6.73885200	-0.94388100
H	-1.68287200	-7.02025700	0.70929900
C	3.56478500	5.28428900	-2.02653000
H	3.29709300	6.33096900	-2.15176900
C	-4.30088700	-2.57150000	1.70417700
C	1.51075500	6.24615600	0.04461100
H	1.68177500	7.02155600	-0.71384800
H	1.10874600	6.74165500	0.93933300
H	0.74732200	5.56260800	-0.34869300
C	-6.37555800	2.72330200	0.66449100
H	-7.33572000	2.35470800	0.31738600
C	6.27338100	-3.22065100	-1.97125900
H	7.14627700	-3.23754800	-2.61942000
C	3.89081000	-3.66186300	-1.61661100
C	3.71029700	3.28885500	-0.61563200
C	3.06144700	0.78012100	3.22969200
C	4.01023100	-3.18708500	-0.27821000
C	-4.49867400	-3.24056000	2.92985000
H	-4.94913800	-2.70172600	3.76058700
C	0.41604100	-2.99305000	2.55991700
C	-5.26092100	2.68819200	-0.19688600
C	-5.77638400	-2.81350500	-1.34282300
H	-5.90953400	-3.37924900	-0.41869200
H	-5.99354300	-3.47921300	-2.18845300
H	-6.51301500	-2.00248600	-1.36787500
C	2.89811000	-5.52388100	0.95100800
H	2.48058500	-5.96305400	0.03589500
H	2.66487200	-6.19521300	1.78238100
H	3.98434300	-5.47951900	0.82314000
C	-5.38406500	2.14738200	-1.62528000
H	-4.46476300	1.59277100	-1.85485000

C	-3.71165200	-3.28773000	0.61467200
C	-4.00833600	3.18627500	0.28085500
C	6.56531500	-1.17122200	1.81843800
H	7.53334600	-1.68493100	1.74720400
H	6.50901200	-0.71296400	2.81293500
H	6.54087100	-0.36795300	1.07269100
C	-2.30216800	4.12937700	-1.18243000
C	-4.07099500	-0.19831200	2.62774100
H	-4.37313500	-0.46564300	3.64922300
H	-4.35022500	0.84837000	2.45664000
H	-2.98111500	-0.28118300	2.56872200
C	5.26235200	-2.68802200	0.19977800
C	4.18617600	1.41023100	2.61771100
H	5.12468800	1.20582300	3.12428600
C	5.38449700	-2.14661300	1.62802900
H	4.46446400	-1.59301700	1.85712900
C	0.67816700	3.37811100	-3.56135300
H	1.67160300	3.08807300	-3.19746100
H	0.69415000	4.45853100	-3.72103100
H	0.52116800	2.89408800	-4.53457600
C	-2.89684500	5.52257500	-0.94911900
H	-2.66403600	6.19390300	-1.78061100
H	-2.47870300	5.96166000	-0.03424600
H	-3.98299500	5.47834700	-0.82057100
C	-5.03103100	3.67443400	2.44540600
H	-4.94632400	4.03410100	3.46836000
C	-2.54057400	4.08719700	2.20636100
H	-1.80929800	4.13035500	1.39286600
C	4.13144700	4.58408700	-3.10174000
H	4.28976800	5.07836400	-4.05716400
C	-3.88836600	3.66111500	1.61918700
C	-3.06224900	-0.77808800	-3.23006900
N	3.39287200	2.61426700	0.61522900
C	-4.75762700	-1.11307800	1.58353100
H	-4.48414800	-0.74308100	0.59019300
C	2.04523600	-3.03067000	-3.22431700
H	1.96186700	-2.03991500	-2.76174700
H	1.06194200	-3.31117800	-3.62711500
H	2.74528900	-2.94179800	-4.06506700
C	4.49799000	3.24008100	-2.93056500
H	4.94885500	2.70068300	-3.76071800
C	6.37723200	-2.72254400	-0.66127800
H	7.33703100	-2.35314600	-0.31402000
C	-5.47563700	3.30671700	-2.65304600
H	-6.35869400	3.92862100	-2.45266500
H	-5.56082300	2.90660500	-3.67268800
H	-4.58640900	3.94288300	-2.61561700
C	-6.27102900	3.22103900	1.97454600
H	-7.14371500	3.23832600	2.62297900
N	1.77408800	0.98478700	2.89643400
N	2.85537900	-3.06809900	0.56831300
C	-3.56628700	-5.28430700	2.02394200
H	-3.29885500	-6.33116300	2.14826100
C	4.30012000	2.57197800	-1.70438900
C	4.34834800	2.26562300	1.49625200
C	5.47703300	-3.30555500	2.65615300
H	6.36103000	-3.92634300	2.45645700
H	4.58868200	-3.94293300	2.61830100
C	-4.18736400	-1.40697300	-2.61759900
C	-0.67902700	-3.37946100	3.56068200
H	-0.52211400	-2.89587100	4.53413500
H	-0.69559500	-4.45993500	3.71994400
H	-1.67217300	-3.08874600	3.19655800
C	2.30313800	-4.13073200	1.18391700
C	0.18062900	0.62810500	-2.83722200
H	0.99554700	0.98094500	-3.48190600
H	0.66378100	0.04162100	-2.04036700
C	5.03376900	-3.67472500	-2.44245500
H	4.94955400	-4.03449700	-3.46541300
C	1.17241600	-4.08701900	2.04124300
C	3.35179800	4.66161300	-0.78012700
C	0.69570400	0.33584200	3.67755300
H	0.02804400	1.12614600	4.05442700
H	1.05852000	-0.21807900	4.55115800
C	2.54326100	-4.08798800	-2.20437900
H	1.81150800	-4.13088300	-1.39129300
C	-4.13251100	-4.58481900	3.09984100
H	-4.29075300	-5.07980700	4.05491000
C	2.59148000	-5.48788300	-2.86457000
H	1.58456500	-5.79625000	-3.17728900
H	2.98452100	-6.24261200	-2.17275800
H	3.23060500	-5.48989700	-3.75704800
C	2.82309600	5.49727000	0.38885800
H	2.62310000	4.82096700	1.22896300
C	3.43311800	-0.21099100	4.34654700
H	3.01120300	-1.20155100	4.13198200
H	3.05776700	0.11220800	5.32639100
H	4.51830900	-0.31659100	4.42036200
C	4.75722400	1.11381900	-1.58233700
H	4.48326900	0.74441900	-0.58891400
C	-6.56612200	1.17348300	-1.81561200
H	-7.53351700	1.68830300	-1.74379400
H	-6.54232800	0.36991000	-1.07018800
H	-6.51078100	0.71558000	-2.81032600
C	4.07156000	0.19809900	-2.62633000
H	4.37371200	0.46528300	-3.64785400
H	2.98158800	0.28009700	-2.56755600
H	4.35158700	-0.84830700	-2.45478700
C	-2.04184600	3.02966200	3.22566300
H	-1.05840200	3.31018100	3.62806300
H	-1.95854200	2.03912800	2.76261800
H	-2.74146100	2.94033000	4.06672900
C	3.91419600	6.48825400	0.87449100
H	4.18060500	7.19529500	0.07774000
H	4.82473500	5.95070300	1.16765700
H	3.55815300	7.06464400	1.73919000
C	-6.29798500	-0.98580700	1.72009600
H	-6.62830600	-1.30196700	2.71856600
H	-6.82064900	-1.60494200	0.98331500
H	-6.59957500	0.05892800	1.57704700
C	-3.91623400	-6.48639100	-0.87745900
H	-4.18218600	-7.19387400	-0.08094700
H	-3.56047500	-7.06229800	-1.74259700
H	-4.82698700	-5.94884400	-1.16997000
H	0.87272800	-5.05696900	2.42507400
H	-5.12592600	-1.20137700	-3.12359300

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Preface

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'En Route to Bis(carbene) Analogues of the Heavier Group 13 Elements: Consideration of Bridging Group and Metal(I) Source'
Chem. Eur. J. **2018**, *24*, 12397-12404.

Authors

Marcella E. Desat, Robert Kretschmer*

Author contributions

The preparation of the manuscript was done by the first author (M. E. Desat). R. Kretschmer supervised the research and revised the manuscript. Preparation and characterization (NMR, IR, EA, X-ray) of compound **1h**, **IIIb**-**h** and **Va** were done by the first author. Additionally, the calculation of all X-Ray structures herein was performed by the first author as well as the interpretation of the analytic data of the compounds. R. Kretschmer performed all DFT calculations and contributed the corresponding parts in the manuscript and the Supporting Information.

Acknowledgements

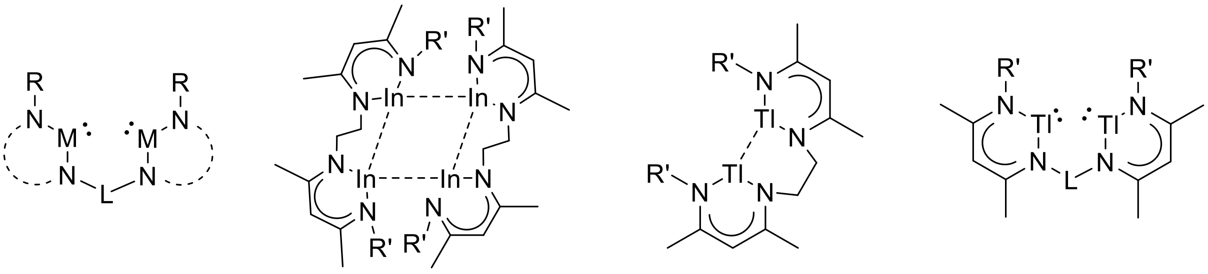
The project was financially supported by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft (DFG, KR4782/2-1), and the University of Regensburg. R. Kretschmer and M. E. Desat are grateful to the Stiftung Stipendien-Fonds des Verbands der Chemischen Industrie for a Liebig and PhD fellowship, respectively. We thank Professor T. Don Tilley (University of California, Berkeley) for use of laboratory space and equipment used to acquire some of the characterization data. Additionally, helpful discussions with Dr. Stefanie Gärtner and generous support from Professor Manfred Scheer is gratefully acknowledged.

4 *En Route* to Bis(carbene) Analogues of the Heavier Group 13 Elements: Consideration of Bridging Group and Metal(I) Source

Abstract: *Aiming to explore the effect of the steric constraints imposed on the metal-metal interaction of bis(carbene) analogues of thallium by the linking scaffold, we describe here the synthesis of seven dinuclear thallium diyls with a series of rigid, semi-rigid, and flexible bridging scaffolds. The molecular structure in the solid state was derived for four of these compounds by means of single crystal X-ray diffraction and compared with results from DFT calculations, which have been performed for all substances. The compounds serve as model compounds to investigate the metal-metal separation in the absence of co-coordinated molecules (additional ligands, solvent molecules). In addition, the effect of the metal(I) precursor, and more specifically the counter ion, on the synthetic access to bis(carbene) analogues of indium and thallium was investigated. For indium, only InI yields the desired dinuclear indium diyl. With InBr no reaction was observed and using InCl gives rise to a mononuclear indium(III) compound. For thallium, both TlI and TlBr allow access of the related bis(carbene) analogue, although the yield using the latter is significantly lower. In despite contrast, no reactions have been observed with TlCl and $TlBF_4$.*

4.1 Introduction

The last decades have seen a rapid development of the chemistry of low oxidation state Group 13 species[1] and numerous compounds have been synthesized since the seminal work on Group 13 diyls in the last century.[2] Although the first example of a stable Group 13 element analogue of carbenes[3] has not been isolated before 1999,[4] today, examples are known for aluminium,[5] gallium,[6] indium,[6c,6d,7] and thallium,[6c,6d,7c,8] and have found numerous applications either as ligands in transition-metal complexes,[3b,9] for the stabilization of unusual molecules,[10] or as reagents for the activation of small molecules and strong bonds.[5b,11] The corresponding neutral boron derivative, i.e., a borylene stabilized by one Lewis base, remains undiscovered to date.[12] In recent years, bimetallic species have been shown to be highly efficient catalysts in a variety of chemical transformations. They often display reactivities and selectivities that cannot be attained using their mononuclear congeners as the proximity of two (or more) metal centres gives rise to cooperative effects.[13] Compounds containing direct bonds between Group 13 centres in the oxidations state +1 have been studied to quite some extent,[1,14] but reports about Group 13 analogues of bis(carbene)s **I** lacked any precedence until our recent report about the dinuclear indium and thallium diyls **II** and **IIIa**, respectively (Figure 1).[15] However, both compounds **II** and **IIIa** exhibit metal-metal bonds in the solid state which benefit significantly from dispersion stabilization as revealed by computational studies. Noteworthy, London dispersion forces contribute critically to the thermodynamic stabilities of seemingly reactive main-group element compounds,[16] and also show large contributions to the dimerization enthalpies of Group 13 diyls.[6d]



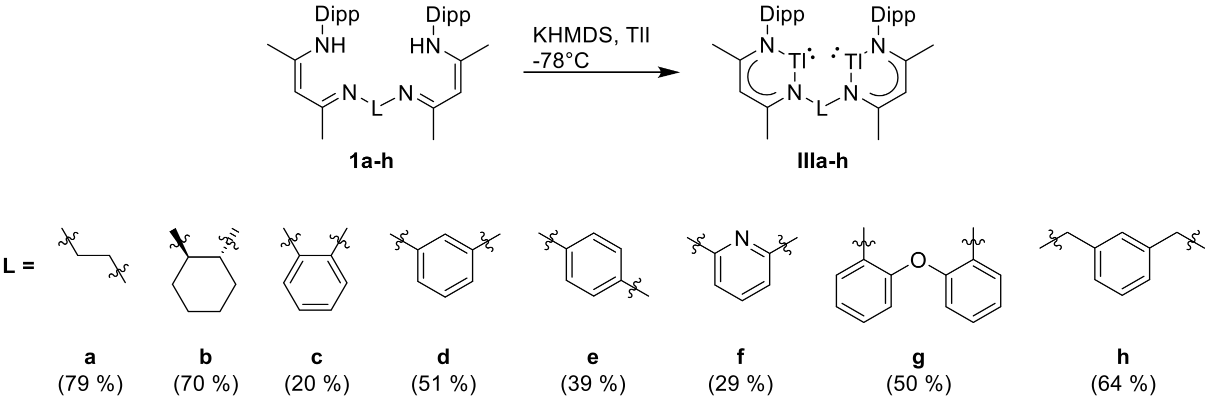
I **II** **IIIa** **III**

Figure 1. General structure of bis(carbene) analogues of the Group13 elements (M = B, Al, Ga, In, Tl) **I**. Schematic representation of the first isolated examples **II** and **IIIa**, respectively, and the general structure of the thallium(I) bis(*β*-diketiminates) **III** reported herein. (L = linker group, R' = Dipp = 2,6-diisopropylphenyl).

In continuation of our research efforts, we became interested how the three-dimensional structure, and more specifically the metal-metal interaction, is affected by the bridging scaffold. Starting from bis(*β*-diketimine)s bridged by different linker groups (L) we synthesized a variety of dinuclear thallium diyls **III**. Based on our previous results, we choose thallium over indium because of the increased stability and much better yields.[15] In addition, thallium diyls have been shown to serves as suitable precursors to access cobalt,[17] copper,[8b,18] and nickel[19] compounds, and the related dinuclear thallium diyls **III** are likely to serve as starting materials for bimetallic bis(*β*-diketiminate)-based 3d-metal species.[20] In addition, the low energy and s-type character of the thallium lone pair allows for the isolation of two-coordinated thallium species, which serve as model compounds to investigate the metal-metal interaction unperturbed by the electronics and sterics of additional ligands as observed for instance in the case of copper.[20d] When choosing the respective linker groups we did not primarily intend to derive compounds having thallium–thallium bonds, but to investigate the effect of both the flexibility and the number of bridging atoms to the Tl–Tl separation. Additionally, rigid ligands with well separated binding sites have been chosen to access thallium bis(carbene) analogues having two isolated diyl moieties. Finally, we also investigated the role of the metal(I) source concerning the accessibility of dinuclear species of indium(I) and thallium(I), respectively. Our efforts in both directions are reported herein.

4.2 Results and Discussion

The bis(β-diketimine)s **1a-g** have been synthesized according to published procedures,[20d,21] while compound **1h** was accessed in 30 % yield from the neat reaction of two equivalents of 4-((2,6-diisopropylphenyl)amino)pent-3-en-2-one with one equivalent of 1,3-bis(aminomethyl)benzene. Next, the bis(β-diketimine)s **1a-h** were treated in a one-pot reaction with potassium bis(trimethylsilyl)amide and thallium(I) iodide in THF at -78 °C and in the absence of light, Scheme 1.



Scheme 1. Syntheses of bis(carbene) analogues of thallium starting from bis(β-diketimine)s with different linker (L) groups. Dipp = 2,6-diisopropylphenyl.

A grey precipitate was characteristic for all reactions and the related dinuclear thallium diyls **IIIa-h** were isolated after work-up as (pale) yellow-coloured solids in yields ranging from 20 % to 79 %. Good yields were obtained in case of the 1,2-alkyl and 1,3-xylyl bridged bis(β-diketimine)s **1a**, **1b**, and **1h**, respectively, while with (hetero)aryl bridges, the isolated yields did not exceed 51 %. Noteworthy, the exclusion of light is crucial as solutions of **IIIa-h** are photo-labile depositing metallic thallium(0). In case of **IIIb**, **IIId**, **IIIe**, and **IIIg**, crystals suitable for an X-ray diffraction study were grown from saturated toluene solutions at room temperature; the molecular structures in the solid state are shown in Figures 2 - 4. In addition, all compounds have been studied by means of DFT calculations at the B3LYP-D3/LANL2DZ level of theory (see the supporting information for detailed information).

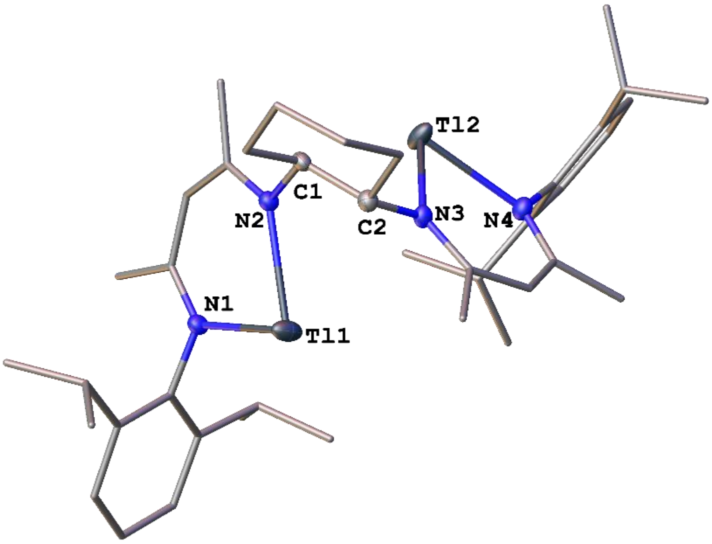


Figure 2. Solid-state structure of **IIIb** (hydrogen atoms are omitted for the sake of clarity). Selected bond lengths (Å) and angles (°) with calculated values (B3LYP-D3/LANL2DZ) in square brackets: Tl1–Tl2 4.294(8) [4.69], Tl1–N1 2.312(6) [2.45], Tl1–N2 2.378(5) [2.51], Tl2–N3 2.422(2) [2.56], Tl2–N4 2.380(2) [2.48]; N1–Tl1–N2 82.9(2) [77.0], N3–Tl3–N4 80.26(6) [75.6].

As shown before, the thallium bis(carbene) analogue **IIIa** characterizes an intramolecular thallium-thallium bond (3.5059(3) Å) in the solid state.[15] Computational investigations revealed that the metal-metal interactions benefit distinctly from London dispersion forces, wherefore the thallium-thallium bond formation becomes exergonic (-38.7 kJ mol^{-1}, B3LYP-D3/LAN2DZ). Due to the rather weak bonding interaction between the two thallium centres in **IIIa**, we wondered how increasing the rigidity of the C_2-bridge will affect the metal-metal interaction. Therefore, we applied the 1,2-*trans*-cyclohexylene bridge in which the rotation around the C–C bond is restricted, providing comparable electronic but different steric parameters. Indeed, no thallium-thallium bonding is observed in the solid-state structure of **IIIb**, Figure 2, and the Tl1–Tl2 separation (4.294(8) Å) excels the Tl1–Tl2 bond of **IIIa** by about 1 Å. Surprisingly, the N2–C1–C2–N3 dihedral angle within **IIIb** (54.8(2)°) is smaller compared with the corresponding angle in **IIIa** (56.805(2)°). In **IIIb**, free rotation along the C1–C2 axis is effectively cancelled out as the C2-bridge is part of a cyclohexane ring and both thallacycles are twisting away from each other. As rotation about the C1–N2 bond will affect the rotation around the C2–N3 bond and vice versa, a hindered conformational flexibility of both binding sites is expected and evidenced by the ^{1}H NMR spectrum of **IIIb**, which shows four separated groups of doublets (1.14, 1.16, 1.28, 1.30 ppm) and two groups of septets (3.14, 3.21 ppm) for the respective isopropyl methyl and methine proton resonances of the 2,6-diisopropyl substituents. In the energy-optimized gas-phase structure, the Tl–Tl distance amounts to 4.69 Å (Figure S32), thus being longer compared to the value observed in the solid-state structure. Noteworthy, also the calculated thallium-nitrogen bond distances are to some extent longer compared to the values obtained from single crystal X-ray diffraction.

The related dinuclear copper(I) complex reported by the group of Crimmin,[20d] shows a similar pattern of resonances, and in the solid state, an opposing orientation of the metal centres was observed. However, the metal-metal separation (5.4 Å) is significantly increased due to coordination to rather bulky triphenylphosphine ligands. This also effects the relative orientation of the two *β*-diketiminate pockets; a nearly co-planar orientation results for the copper(I) species while an almost perpendicular alignment is observed for the thallium compound **IIIb**. While for **IIIc**, crystal suitable for an X-ray diffraction study could not be obtained, the chemical integrity is established by spectroscopic data and accurate microanalysis. As for the pro-ligand **1c**, both, the ^{1}H and ^{13}C NMR spectrum of **IIIc** reveals one signal for the methine and two signals for the methyl group of the 2,6-diisopropylphenyl substituent, indicating a plane of symmetry within the molecule. According to our computational study, the energy minimum is reached at Tl1–Tl2 distance of 4.82 Å (Figures S29 and S33), which is by 0.13 Å longer compared to **IIIb**. Similar to **IIIb**, both thallacycles are facing away from each other, may prohibiting cooperative effects despite the close proximity of both metal centres.

Changing the substitution pattern of the phenylene bridge from *ortho* to *meta* and *para*, the metal-metal separation is increased as expected compared to the C_2-bridged species; for the 1,3-phenylene based compound **IIId**, the Tl–Tl distance amounts to 7.51(1) Å, while for the 1,4-substituted species **IIIe** the metals are separated by 8.4624(5) Å, Figure 3. Again, in both solid-state structures, an opposite orientation of the thallium centres is observed. DFT calculations result in thallium–thallium distances of 7.56 Å and 8.54 Å for **IIId** and **IIIe**, respectively, which are comparable close to the experimental values obtained from the solid-state structure analysis. The respective ^{1}H NMR spectra of **IIId** and **IIIe** give patterns with one isopropyl methine septet and two methyl doublets of the 2,6-diisopropylphenyl substituent, indicating pseudo C_{2v} symmetry in solution and thus chemical and magnetic equivalence of both binding sites due to free rotation along the bond between the *β*-diketiminate nitrogen atom and the carbon atom of phenylene bridge. In case of the 2,6-pyridine bridged species **IIIf**, for which, unfortunately, no crystals suitable for an X-ray analysis were obtained, the computational results (Figure S30), indicate that the energy-minimized structure corresponds to a heterobimetallic species with two different binding sites. While the Tl1 atom is ligated by three nitrogen atoms including the pyridine-based N3, Tl2 behaves as a carbene analogue being only chelated by N4 and N5, respectively, and the Tl1–Tl2 distance amounts to 5.04 Å. Additionally, the Tl1–N3 distance (2.69 Å) is slightly longer compared to the Tl1–N1 and Tl1–N2 distances of 2.56 Å and 2.63 Å, respectively. The ^{1}H NMR spectrum of **IIIf**, however, shows only one sets of doublets for the respective isopropyl methyl proton resonances of the 2,6-diisopropyl substituents, thus indicating magnetically equivalent binding sites in solution.

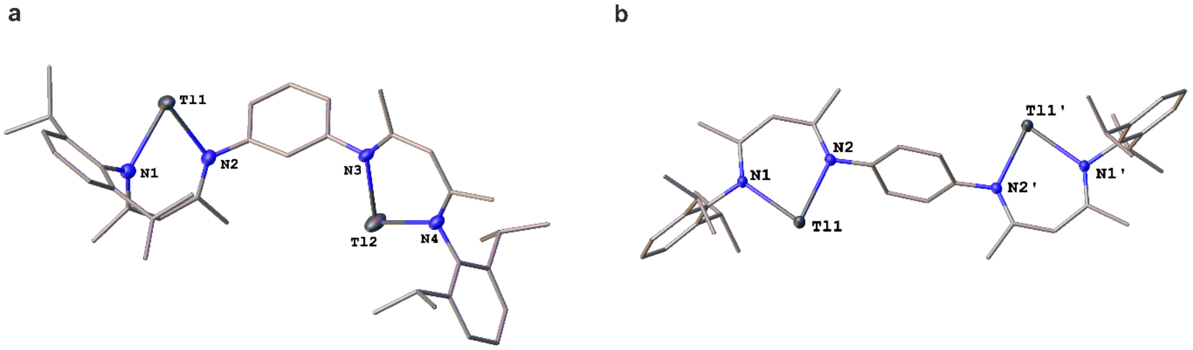


Figure 3. Solid-state structure of a) **IIId** and b) **IIIe** (hydrogen atoms are omitted for the sake of clarity). Selected bond lengths (Å) and angles (°) with calculated values (B3LYP-D3/LANL2DZ) in square brackets: a) Tl1–Tl2 7.51(1) [7.56], Tl1–N1 2.476(7) [2.47], Tl1–N2 2.384(6) [2.48], Tl2–N3 2.51(1) [2.49], Tl2–N4 2.48(1) [2.47]; N1–Tl1–N2 76.5(2) [75.9], N3–Tl3–N4 74.7(4) [75.9]; b) Tl1–Tl1' 8.4624(5) [8.54], Tl1–N1 2.401(2) [2.47], Tl1–N2 2.431(2) [2.49]; N1–Tl1–N2 77.98(9) [76.1].

The 2,2'-oxydiphenyl-bridged compound **IIIg** combines the advantage of an N,N'-diphenyl substitution of each *β*-diketiminate with the conformational flexibility due to the diphenyl ether moiety. In solution, the ^{1}H NMR spectrum shows the expected pattern of resonances for the 2,6-diisopropylphenyl groups (two methyl doublets, one methine septet), attributing for the chemically equivalent binding sites. In the solid state, Figure 4, both thallium centres are orthogonal directed, and the thallium-thallium separation adds up to 4.5266(1) Å. This is again significantly shorter compared with the related dicopper species reported by Crimmin and co-workers,[20d] in which the copper-copper distance is as long as 7.9 Å because of the coordinative saturation of the copper centres with triphenyl phosphine ligands. Noteworthy, no directed bonding between either Tl1 or Tl2 and the oxygen atom has been observed, although the Tl1–O separation (3.156(3) Å) is below the sum of the van-der-Waals radii. The computed minimum structure characterizes a shorter thallium-thallium separation of 4.44 Å (Figure S34) as well as a shorter Tl1–O1 distance (3.09 Å) compared to the values observed in the experimental solid-state structure.

Unfortunately, no crystal suitable for an X-ray diffraction analysis were obtained for the 1,3-xylylene-bridged derivative **IIIh** despite several attempts. However, accurate microanalysis and NMR data substantiate the chemical integrity. The ^{1}H and ^{13}C NMR spectra of **IIIh** give patterns consistent with a chemical and magnetic equivalence of the two binding sites. A potential-energy scan with respect to the thallium–thallium distance (Figure S35) revealed a rather flat potential between 3.6 Å and 5.3 Å and in the global energy minimum (Figure S31) the Tl1–Tl2 distance amounts to 4.53 Å; the local minimum of an isomeric species at the maximum Tl1–Tl2 separation (8.85 Å) is by 22.6 kJ mol^{-1} higher in energy.

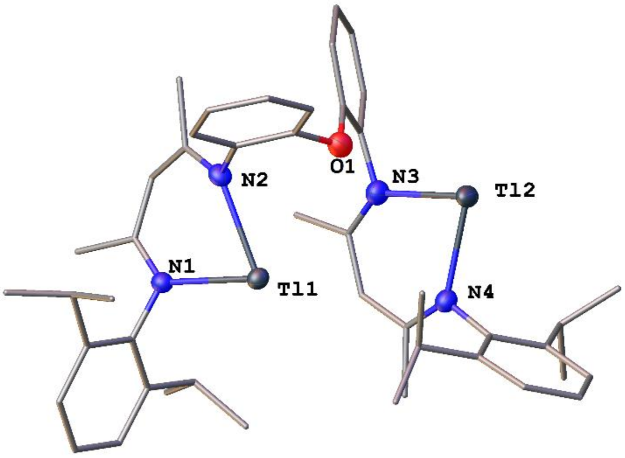
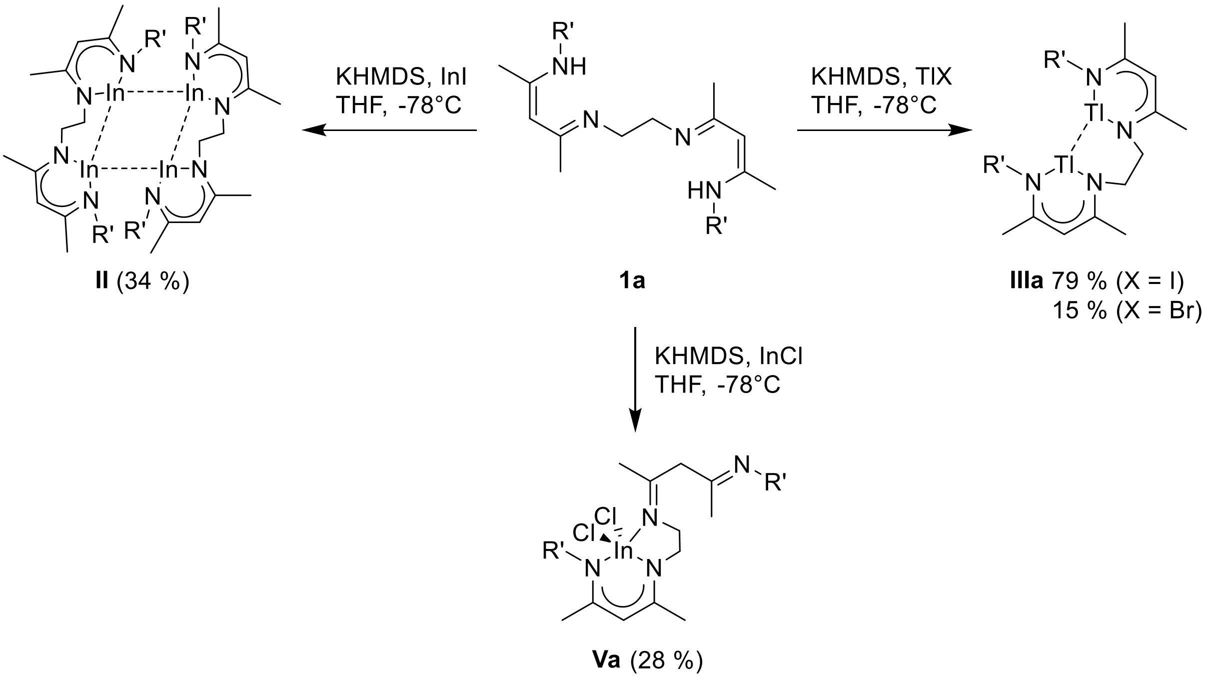


Figure 4. Solid-state structure of **IIIg** (hydrogen atoms are omitted for the sake of clarity). Selected bond lengths (Å) and angles (°) with calculated values (B3LYP-D3/LANL2DZ) in square brackets: Tl1–Tl2 4.5266(1) [4.44], Tl1–N1 2.47(1) [2.70], Tl1–N2 2.66(1) [2.71], Tl2–N3 2.448(4) [2.55], Tl2–N4 2.471(4) [2.52], N1–Tl1–N2 70.3(3) [68.8], N3–Tl3–N4 74.9(1) [74.3].

Across the series of **IIIa**, **IIIb**, **IIId**, **IIIe**, and **IIIg**, the thallium-thallium distances range from 3.5059(3) Å to 8.4624(5) Å. Due to the absence of co-ligands, the dinuclear thallium diyls serve as model compounds for studying the intramolecular metal-metal separation without being perturbed by coordinated solvents or other ligands. This information is of crucial importance for the design of new bimetallic catalysts as the optimum of the metal-metal separation has been proposed to be within 3.5 and 6 Å.[22] In consequence, and taking the results from the DFT calculation into account, bimetallic species based on the ligands **1g** and **1h** are the most promising candidates while employing **1d** and **1e** yields species with well separated metal sites (> 6 Å) for which cooperative effects may not arise. Although, using the ligands **1b** and **1c**, respectively, gives rise to compounds with thallium–thallium distances well within the range mentioned above, the opposing orientation of the thallacycles along with a hindered orientation may impedes cooperative effects. The N–Tl–N bite angles cover values from 70.3(3)° for **IIIg** up to 82.9(2)° in case of **IIIb**. Noteworthy, for **IIIb**, **IIId**, and **IIIg**, substantial differences in the N–Tl–N bite angles of the two bis(*β*-diketiminate)s are observed, most likely due to packing effects. Inequivalent values are also observed for the Tl–N bonds both within one N,N'-chelate and when comparing the two binding sites. The IR spectra of **IIIb-h** have the expected pattern characteristic for C–H and C–N stretching modes. The melting behavior differs for the investigated thallacycles: **IIIc** and **IIIh** melt at 82 °C and 87 °C, respectively, and decompose upon further heating above 100 °C. **IIIb**, **IIIc** - **IIIg** do not melt below 100 °C but decompose once the temperature exceed 100 °C.



Scheme 2. Impact of the metal(I) precursor on the synthesis of bis(carbene) analogues of indium and thallium starting from the ethylene bridged bis(*β*-diketimine) **1a**. R' = Dipp = 2,6-diisopropylphenyl.

Having studied the impact of the bridging scaffold to the three-dimensional structure we wondered whether the metal(I) source has an impact on the accessibility of the bis(carbene) analogues of indium and thallium, respectively. Therefore, the ethylene bridged bis(*β*-diketimine) **1a** was allowed to react with potassium bis(trimethylsilyl)amide and InCl, InBr, InI, TlCl, TlBr, TlI, and $TlBF_4$, respectively, in THF at -78 °C and in the absence of light, Scheme 2. For thallium, the counter ion strongly affects the yield of **IIIa**. While for the thallium(I) iodide, the related dinuclear thallium diyl is isolated in 79 % yield, using TlBr gives rise only to 15 %. Moreover, when TlCl or $TlBF_4$ are used, **IIIa** could not be isolated and the ^1H NMR spectrum only shows signal corresponding to the pro-ligand **1a**. The outcome of the reaction is more diverse when the indium(I) halogenides InX (X = Cl, Br, I) are employed. As reported previously,[15] using InI allows for the isolation of **II** in 34 % yield, which behaves as a four-membered metallacycle in the solid state due to intra- and intermolecular In–In bond formation. Substitution of InI by InBr does not allow for the isolation of **II** and gives rise to inseparable mixtures containing the pro-ligand **1a**; in this regard, the low solubility of InBr has to be taken into account.

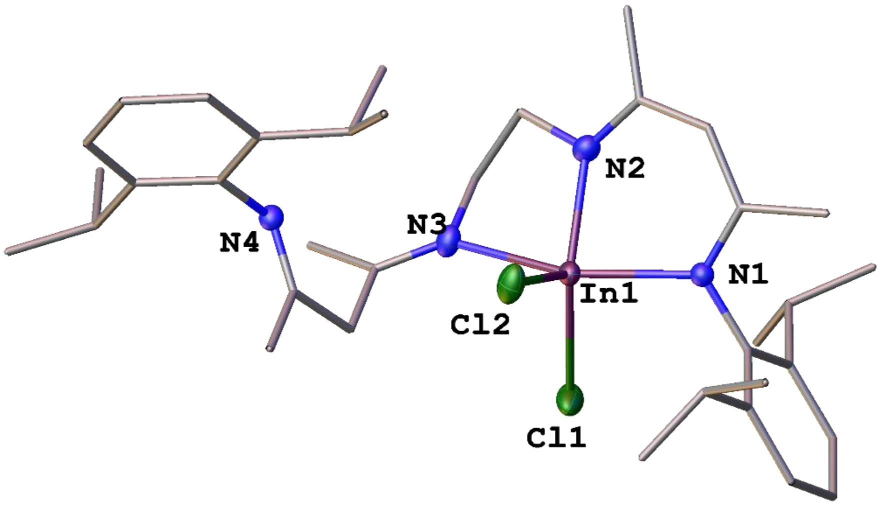


Figure 5. Solid-state structure of **Va** (hydrogen atoms are omitted for the sake of clarity). Selected bond lengths (Å) and angle (°): In1–Cl1 2.3873(5), In1–Cl2 2.3805(4), In1–N1 2.195(1), In1–N2 2.133(2), In1–N3 2.350(1); Cl1–In1–Cl2 114.29(2), N1–In1–N3 156.68(5), Cl1-In1-N2 131.76(4).

The reaction with InCl does also not yield the desired indium diyl but gives rise to the mononuclear indium(III) species **Va** in which the bis(β-diketiminate) behaves as a monotopic tridentate ligand. This observation is in line with the more distinct tendency of InCl to disproportionate to In(0) and In(III) compared to the more polarizable bromide and iodide counter ions.[23] Crystals of **Va** suitable for an X-ray diffraction study were obtained from a saturated *n*-hexane solution at room temperature; the molecular structure in the solid state is shown in Figure 5. The coordination geometry around the indium(III) centre is a distorted trigonal-bipyramid, in which the bis(β-diketiminate) ligand occupies the meridional positions; the equatorial positions are occupied by N2 and the two chlorine atoms. As expected, the longest indium-nitrogen bond (2.350(1) Å) is formed between In1 and the imine based nitrogen atom N3 and both In–Cl bonds are nearly equivalent (2.3873(5) and 2.3805(4) Å, respectively). To the best of our knowledge, only one compound in which an $InCl_2^+$ fragment is bound to a monoanionic N,N,N-tridentate ligand has been reported so far;[24] often the coordination sphere is saturated with an additional solvent molecule.[24a,25] However, cationic species composed of an $InCl_2^+$ fragment and a neutral N,N,N-tridentate ligand recently received considerable interest and the solid-state structures of two compounds have been reported.[26] The ^1H NMR spectrum of **Va** (as a C_6D_6 solution prepared by dissolving crystalline material) reveals the existence of a mixture of isomers in solutions.

4.3 Conclusion

In summary we have reported the synthesis of seven bis(carbene) analogues of thallium based on ditopic bis(*β*-diketiminate) ligands with different alkyl and (hetero)aryl bridges. The effect of the bridging unit to the intramolecular metal-metal separation has been studied and the first examples of dinuclear thallium diyls with two discrete metal centres are reported. The compounds serve as models for studying the metal-metal separation in the absence of co-ligands, which is valuable for the design of new catalyst aiming for cooperative effects. In addition, we investigated the synthetic access to bis(carbene) analogues of indium and thallium by using different metal(I) precursors. In case of indium, substitution of the iodide by the bromide prevents the isolation of the respective indium diyl and using InCl yields a mononuclear indium(III) compound. For thallium, yields of the respective dinuclear diyl decrease in going from TlI to TlBr; with TlCl or $TlBF_4$ no reaction could be observed. Currently, we are investigating the transformation of the thallium diyls to the corresponding dinuclear copper complexes.

4.4 References

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4.5 Supporting Information

General Considerations

All preparations were performed under an inert atmosphere of dinitrogen by means of both standard Schlenk line or glovebox techniques (GS-Systemtechnik and MBraun). Traces of oxygen and moisture were successively removed from the inert gas by passing it over a BASF R 3-11 ($CuO/MgSiO_3$) catalyst, through concentrated sulfuric acid, over coarsely granulated silica gel, and finally P_4O_{10}. *n*-Hexane, THF and Toluene were used as p.a. grade and distilled from Na/benzophenone prior to use. C_6D_6 and $CDCl_3$ were dried by distillation from potassium and calcium hydride, respectively. The metal(I) precursor were purchased from ABCR (TlCl, TlBr, TlI), and Onyxmet (InI) and used as delivered. Prior to use, InCl (Alfa Aesar) and InBr (Onyxmet) have been purified by high-vacuum distillation and sublimation, respectively. $TlBF_4$ was synthesized as described elsewhere.[S1]

Characterization

The NMR-spectra were recorded on BrukerAvance 400 spectrometers (T = 300 K) with δ (given in ppm) referenced to external tetramethylsilane (^1H and ^{13}C). ^1H and ^{13}C NMR spectra were calibrated using the solvent residual peak (δ ^1H (C_6D_5H) = 7.16, δ ^1H ($CHCl_3$) = 7.26) and the solvent peak (δ $^{13}C(CDCl_3)$ = 77.16, δ ^{13}C (C_6D_6) = 128.06), respectively. The coupling constants *J* are given in Hertz [Hz]. Infrared spectra were recorded on a Bruker ALPHA spectrometer equipped with a diamond ATR unit; the wavenumbers given in cm^{-1}. Elemental analysis were performed on a Vario micro cube (Elementar Analysensysteme GmbH); the presence of residual solvent molecules has been verified by ^1H NMR spectroscopy. Finally, (uncorrected) melting points were determined in sealed capillaries using an apotec melting point apparatus.

Ligand synthesis

4-((2,6-diisopropylphenyl)amino)pent-3-en-2-one[S2] and the bis(*β*-diketimine)s **1a-g**[S3] have been synthesized according to published procedures.

1h: A mixture of (*Z*)-4-(2,6-diisopropylphenyl)amino-3-penten-2-one (32.38 g, 125 mmol) and 1,3-bis(aminomethyl)benzene (8.51 g, 62.5 mmol) was stirred at 100 °C for 24 h. The orange oil was dissolved in hot methanol (20 mL) and cooled to -30 °C. The white precipitates were filtered off and washed with methanol (3 x 10 mL). Drying in vacuum yielded **1h** (12.29 g, 32 %)

as a colourless solid. ^{1}H-NMR: (400 MHz, CDCl$_3$): *δ* = 1.06 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.16 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.66 [s, 6H, C*Me*], 1.93 [s, 6H, C*Me*], 2.89 [sept, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*Me$_2$], 4.39 [s, 4H, C*H*$_2$], 4.72 [s, 2H, C*H*] 7.00 [t, 2H, $^3J_{HH}$ = 6.8 Hz, Ar*H*], 7.07-7.10 [m, 6H, Ar*H*], 7.12 [s, 1H, Ar*H*], 7.23 [t, 1H, $^3J_{HH}$ = 7.6 Hz, Ar*H*], 11.20 [s, 2H, N*H*]; ^{1}H-NMR: (400 MHz, C$_6$D$_6$): *δ* = 1.16 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.22 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.63 [s, 6H, C*Me*], 1.68 [s, 6H, C*Me*], 3.16 [sept, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*Me$_2$], 4.06 [s, 4H, C*H*$_2$], 4.74 [s, 2H, C*H*] 7.00 [s, 1H, Ar*H*], 7.08-7.13 [m, 5H, Ar*H*], 7.17-7.19 [m, 4H, Ar*H*], 11.43 [s, 2H, N*H*];^{13}C{^{1}H}-NMR: (101 MHz, C$_6$D$_6$): *δ* = 19.04 [C*Me*], 21.8 [C*Me*], 23.1 [CH*Me*$_2$], 24.2 [CH*Me*$_2$], 28.6 [C*H*Me$_2$], 46.83 [*C*H$_2$], 94.8 [*β*-*C*H], 123.3 [*m*-*C*(Dipp)], 123.5 [*p*-*C*(Dipp)], 125.0 [C(Aryl)], 125.4 [C(Aryl)], 129.3 [*o*-*C*(Dipp)], 138.2 [*i*-*C*(Dipp)], 140.8 [C(Aryl)], 147.3 [C(Aryl)], 155.6 [*C*N], 166.9 [*C*N]; ATR-IR: 2957, 2923, 2856, 1619, 1548, 1432, 1302, 1231, 784, 759, 724; Anal. Calc. (found) $C_{42}H_{58}N_4$: C 81.50 (81.35), H 9.45 (9.14), N 9.05 (8.98); Mp. 72 °C.

Synthesis of the indium and thallium compounds

General procedure for the synthesis employing thallium(I) iodide: THF (20 mL) was added to a mixture of TlI (1.33 g, 4.00 mmol), KHMDS (0.80 g, 4.00 mmol) and the respective bis(*β*-diketimine) (2.00 mmol) at -78 °C. Warming to room temperature and stirring in the absence of light for 22 h produced a dark brown suspension. The volatiles were removed in vacuum and the grey residue was extracted with toluene (20 mL). Concentration of the filtered extract yielded the products.

Crystals suitable for an X-ray diffraction analysis were obtained from concentrated toluene solutions of **IIIb**, **IIId**, **IIIe** and **IIIg** at room temperature.

IIIb, clear light-yellow crystals, 1.40 g (70 %). ^{1}H-NMR: (400 MHz, C$_6$D$_6$): *δ* = 1.14 [d, 6H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.16 [d, 6H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.20 [br, 2H, ring-C*H*$_2$], 1.28 [d, 6H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.30 [d, 6H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.56 [d, 2H, $^3J_{HH}$ = 6.9 Hz, ring-C*H*$_2$], 1.73 [s, 6H, C*Me*], 1.89 [br, 2H, ring-C*H*$_2$], 1.93 [s, 6H, C*Me*], 3.14 [sept, 2H, $^3J_{HH}$ = 6.9 Hz, C*H*Me$_2$], 3.21 [sept, 2H, $^3J_{HH}$ = 6.9 Hz, C*H*Me$_2$], 4.61 [s, 2H, C*H*], 4.99 [br, 2H, ring-C*H*$_2$], 7.10-7.22 [m, 6H, Ar*H*]; ^{13}C{^{1}H}-NMR: (101 MHz, C$_6$D$_6$): *δ* = 23.5 [C*Me*], 24.2 [C*Me*], 25.1 [CH*Me*$_2$], 26.1 [ring-*C*H$_2$], 27.8 [CH*Me*$_2$], 28.0 [C*H*Me$_2$], 38.4 [ring-*C*H$_2$], 66.1 [ring-*C*H], 101.5 [*β*-*C*H], 123.3 [*m*-*C*(Dipp)], 123.4 [*m*-*C*(Dipp)], 124.3 [*p*-*C*(Dipp)], 141.8 [*o*-*C*(Dipp)], 142.2 [*i*-*C*(Dipp)], 160.1 [*C*N], 162.9 [*C*N]; ATR-IR: 2955, 2919, 2862, 1541, 1518, 1434, 1383, 1363, 1317, 1307, 1230, 788, 759, 748; Anal. Calc. (found) $C_{40}H_{58}N_4Tl_2$: C 47.87 (48.00), H 5.82 (5.81), N 5.58 (5.46); Mp.: decomposition above 100 °C.

IIIc, yellow powder, 0.39 g (20 %). ^{1}H-NMR: (400 MHz, C_6D_6): δ = 1.15 [d, 12H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$], 1.17 [d, 12H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$], 1.82 [s, 6H, C*Me*], 2.11 [s, 6H, C*Me*], 3.19 [sept, 4H, $^3J_{HH}$ = 7.0 Hz, C*H*Me$_2$], 4.94 [s, 2H, C*H*], 6.94-7.02 [m, 6H, Ar*H*], 7.03-7.15 [m, 2H, Ar*H*], 7.16-7.21 [m, 2H, Ar*H*]; ^{13}C{^{1}H}-NMR: (101 MHz, C_6D_6): δ = 23.4 [C*Me*], 23.9 [C*Me*], 25.3 [CH*Me*$_2$], 25.6 [CH*Me*$_2$], 27.8 [C*H*Me$_2$], 101.1 [*β*-*C*H], 123.7 [*p*-*C*(Dipp)], 123.8 [*m*-*C*(Dipp)], 123.9 [*m*-*C*(Dipp)], 124.7 [C(Aryl)], 126.4 [C(Aryl)], 141.5 [*o*-*C*(Dipp)], 143.3 [C(Aryl)], 144.9 [C(Aryl)], 146.0 [*i*-*C*(Dipp)], 163.0 [*C*N], 163.3 [*C*N]; ATR-IR: 2958, 2866, 1545, 1433, 1381, 1361, 1318, 1170, 1099, 787, 757, 728; Anal. Calc. (found) $C_{40}H_{52}N_4Tl_2 \cdot 0.35\ C_7H_8$: C 49.51 (49.48), H 5.36 (5.27), N 5.44 (5.33); Mp. 82 °C.

IIId, clear light-yellow crystals, 1.02 g (51 %). ^{1}H-NMR: (400 MHz, C_6D_6): δ = 1.12 [d, 12H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$], 1.17 [d, 12H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$], 1.80 [s, 6H, C*Me*], 2.03 [s, 6H, C*Me*], 3.22 [br, 4H, C*H*Me$_2$], 4.88 [s, 2H, C*H*], 6.52 [s, 1H, Ar*H*], 6.63-6.66 [m, 2H, Ar*H*], 7.08-7.17 [m, 7H, Ar*H*]; ^{13}C{^{1}H}-NMR: (101 MHz, C_6D_6): δ = 21.0 [C*Me*], 23.7 [C*Me*], 25.1 [CH*Me*$_2$], 25.3 [CH*Me*$_2$], 27.8 [C*H*Me$_2$], 101.7 [*β*-*C*H], 117.4 [C(Aryl)], 119.1 [C(Aryl)], 123.8 [*m*-*C*(Dipp)], 124.8 [*p*-*C*(Dipp)], 141.3 [*o*-*C*(Dipp)], 142.8 [C(Aryl)], 146.3 [C(Aryl)], 153.0 [*i*-*C*(Dipp)], 161.2 [*C*N], 163.1 [*C*N]; ATR-IR: 2957, 2920, 2863, 1548, 1516, 1433, 1384, 1359, 1318, 1140, 788, 760, 743; Anal. Calc. (found) $C_{40}H_{52}N_4Tl_2 \cdot 0.65\ C_7H_8$: C 50.60 (50.99), H 5.45 (5.37), N 5.30 (5.70); Mp.: decomposition above 100 °C.

IIIe, clear light-yellow crystals, 0.78 g (39 %). ^{1}H-NMR: (400 MHz, C_6D_6): δ = 1.11 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.15 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.79 [s, 6H, C*Me*], 2.01 [s, 6H, C*Me*], 3.22 [sept, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*Me$_2$], 4.88 [s, 2H, C*H*], 6.81 [s, 4H, Ar*H*], 7.07-7.13 [m, 6H, Ar*H*]; ^{13}C{^{1}H}-NMR: (101 MHz, C_6D_6): δ = 22.9 [C*Me*], 23.7 [C*Me*], 24.4 [CH*Me*$_2$], 27.8 [CH*Me*$_2$], 28.8 [C*H*Me$_2$], 96.4 [*β*-*C*H], 123.5 [C(Aryl)], 123.8 [C(Aryl)], 124.1 [*m*-*C*(Dipp)], 124.8 [*p*-*C*(Dipp)], 140.6 [*o*-*C*(Dipp)], 141.5 [*i*-*C*(Dipp)], 142.8 [C(Aryl)], 161.8 [*C*N], 162.8 [*C*N]; ATR-IR: 2960, 2920, 2862, 1542, 1435, 1385, 1374, 1313, 1206, 1170, 792, 743; Anal. Calc. (found) $C_{40}H_{52}N_4Tl_2 \cdot 0.35\ C_7H_8$: C 49.51 (49.48), H 5.36 (5.27), N 5.44 (5.33); Mp.: decomposition above 100 °C.

IIIf, yellow powder, 0.58 g (29 %). ^{1}H-NMR: (400 MHz, C_6D_6): δ = 1.02 [d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.10 [d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.72 [s, 6H, C*Me*], 2.07 [s, 6H, C*Me*], 3.10 [sept, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 4.85 [s, 2H, C*H*], 6.21-6.24 [m, 2H, Ar*H*], 6.96-7.13 [m, 7H, Ar*H*]; ^{13}C{^{1}H}-NMR: (101 MHz, C_6D_6): δ = 21.8 [C*Me*], 22.8 [C*Me*], 23.8 [CH*Me*$_2$], 24.4 [CH*Me*$_2$], 28.0 [C*H*Me$_2$], 105.9 [*β*-*C*H], 110.7 [C(Pyr)], 111.4 [C(Pyr)], 123.9 [*m*-*C*(Dipp)], 124.6 [*p*-*C*(Dipp)], 138.4 [*o*-*C*(Dipp)], 138.9 [*o*-*C*(Dipp)], 140.6 [*i*-*C*(Dipp)], 151.8 [C(Pyr)], 154.6 [C(Pyr)], 159.3 [*C*N], 164.1 [*C*N]; ATR-IR: 2953, 2921, 2864, 1547, 1369, 1353, 1315, 1214, 1174, 1156, 1021, 787, 754, 610 ; Anal. Calc. (found) $C_{39}H_{51}N_5Tl_2 \cdot 0.35\ C_7H_8$: C 48.30 (48.50); H 5.26 (5.03); N 6.79 (6.78); Mp.: decomposition above 100 °C.

IIIg, clear yellow crystals, 1.08 g (50 %). ^{1}H-NMR: (400 MHz, C_6D_6): δ = 1.12 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me₂*], 1.15 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me₂*], 1.69 [s, 6H, C*Me*], 2.14 [s, 6H, C*Me*], 3.16 [sept, 4H, $^3J_{HH}$ = 7.0 Hz, C*H*Me₂], 4.87 [s, 2H, C*H*], 6.69-6.74 [m, 4H, Ar*H*], 6.86-6.93 [m, 4H, Ar*H*], 7.06-7.15 [m, 6H, Ar*H*]; ^{13}C{^{1}H}-NMR: (101 MHz, C_6D_6): δ = 23.9 [C*Me*], 24.5 [C*Me*], 24.8 [CH*Me₂*], 25.3 [CH*Me₂*], 27.7 [C*H*Me₂], 100.9 [*β*-*C*H], 123.8 [*m*-*C*(Dipp)], 124.2 [*m*-*C*(Dipp)], 124.5 [*p*-*C*(Dipp)], 124.8 [C(Aryl)], 126.0 [C(Aryl)], 129.3 [C(Aryl)], 141.4 [C(Aryl)], 142.5 [*o*-*C*(Dipp)], 143.4 [*i*-*C*(Dipp)], 146.4 [C(Aryl)], 150.4 [C(Aryl)], 162.8 [*C*N], 163.1 [*C*N]; ATR-IR: 2955, 2917, 2863, 1549, 1433, 1390, 1363, 1318, 1218, 1169, 785, 746; Anal. Calc. (found) $C_{46}H_{56}N_4OTl_2 \cdot 0.3\ C_7H_8$: C 51.70 (51.64), H 5.27 (5.24), N 5.01 (5.11); Mp.: decomposition above 100 °C.

IIIh, dark yellow powder, 1.31 g (64 %). ^{1}H-NMR: (400 MHz, C_6D_6): δ = 1.15 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me₂*], 1.21 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me₂*], 1.80 [s, 6H, C*Me*], 1.94 [s, 6H, C*Me*], 3.25 [sept, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*Me₂], 4.79 [s, 2H, C*H*], 4.82 [s, 4H, C*H₂*], 7.03-7.12 [m, 6H, Ar*H*], 7.13-7.20 [m, 4H, Ar*H*]; ^{13}C{^{1}H}-NMR: (101 MHz, C_6D_6): δ = 23.8 [C*Me*], 24.0 [C*Me*], 25.1 [CH*Me₂*], 26.1 [CH*Me₂*], 27.8 [C*H*Me₂], 54.5 [*C*H₂], 101.1 [*β*-*C*H], 123.7 [*m*-*C*(Dipp)], 124.6 [*p*-*C*(Dipp)], 127.0 [C(Aryl)], 129.5 [C(Aryl)], 141.6 [C(Aryl)], 143.8 [*o*-*C*(Dipp)], 146.7 [*i*-*C*(Dipp)], 161.2 [*C*N], 164.7 [*C*N]; ATR-IR: 2958, 2866, 1623, 1552, 1434, 1233, 818, 785, 758, 729, 697; Anal. Calc. (found) $C_{42}H_{56}N_4Tl_2 \cdot 0.75\ C_7H_8$: C 51.84 (52.26); H 5.71 (5.61); N 5.12 (5.52); Mp. 87 °C.

Va: THF (20 mL) was added to a mixture of InCl (0.27 g, 0.50 mmol), KHMDS (0.22 g, 1.10 mmol) and **1a** (0.17 g, 1.10 mmol) at -78 °C. Warming to room temperature and stirring in the absence of light for 20 h produced a dark grey suspension. The volatiles were removed in vacuum and the grey residue was extracted with *n*-hexane (20 mL). Filtration and concentration of the filtrate gave rise to **Va** as clear colorless crystals suitable for X-ray diffraction analysis. 0.10 g (28 %). ^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 1.06 [d, 6H, $^3J_{HH}$ = 6.8 Hz, CH*Me₂*], 1.10 [d, 6H, $^3J_{HH}$ = 6.8 Hz, CH*Me₂*], 1.24 [d, 6H, $^3J_{HH}$ = 6.8 Hz, CH*Me₂*], 1.28 [d, 6H, $^3J_{HH}$ = 6.8 Hz, CH*Me₂*], 1.54 [s, 1H, *β*-CH₂], 1.55 [s, 1H, *β*-CH₂] , 1.66 [s, 3H, C*Me*], 1.72 [s, 3H, C*Me*], 1.73 [s, 3H, C*Me*], 2.07-2.09 [m, 4H, C*H₂*], 2.45 [s, 3H, C*Me*], 2.78 [sept, 2H, $^3J_{HH}$ =

6.9 Hz, C*H*Me$_2$], 3.17 [sept, 2H, $^3J_{HH}$ = 6.9 Hz, C*H*Me$_2$], 4.88 [s, 1H, C*H*], 7.08-7.14 [m, 6H, Ar*H*]; ^{13}C{^{1}H}-NMR: (101 MHz, C_6D_6): ^{13}C{^{1}H}-NMR: (101 MHz, $CDCl_3$): δ = 21.1, 22.2, 23.0, 23.2, 23.4, 23.5, 23.6, 23.8, 24.4, 24.6, 24.7, 24.8, 25.1, 25.2, 25.5, 25.6, 25.8 [C*Me*], [CH*Me$_2$*], 27.4, 27.6, 27.7, 28.0, 28.2, 28.6 [*C*HMe$_2$], 47.8, 49.3, 50.9, 52.1, 52.4, 53.8 [*C*H$_2$], 95.1, 95.5, 96.9, 97.1, 97.6, 98.1[*β*-*C*H], 123.3, 123.4, 123.5, 123.6, 123.8, 124.2, 124.6, 125.0, 125.7, 125.9, 126.1, 126.9 [*C*(Aryl)], [*m*-*C*(Dipp)], [*p*-*C*(Dipp)], 136.3, 142.6, 142.9, 143.0, 144.3, 144.6, 144.8, 145.5, 145.9 [*C*(Aryl)], [*o*-*C*(Dipp)], [*i*-*C*(Dipp)], 168.1, 168.6, 168.8, 169.1, 169.9, 171.1, 172.0, 178.4 [*C*N]; ATR-IR: 2957, 2922, 1641, 1550, 1517, 1455, 1434, 1385, 1360, 1318, 1222, 1179, 1140, 1124, 1100, 886, 802, 788, 760, 744; Anal. Calc. (found) $C_{36}H_{53}Cl_2InN_4$: C 59.43 (59.68), H 7.34 (7.31), N 7.70 (7.62); Mp.: decomposition above 80 °C.

1h

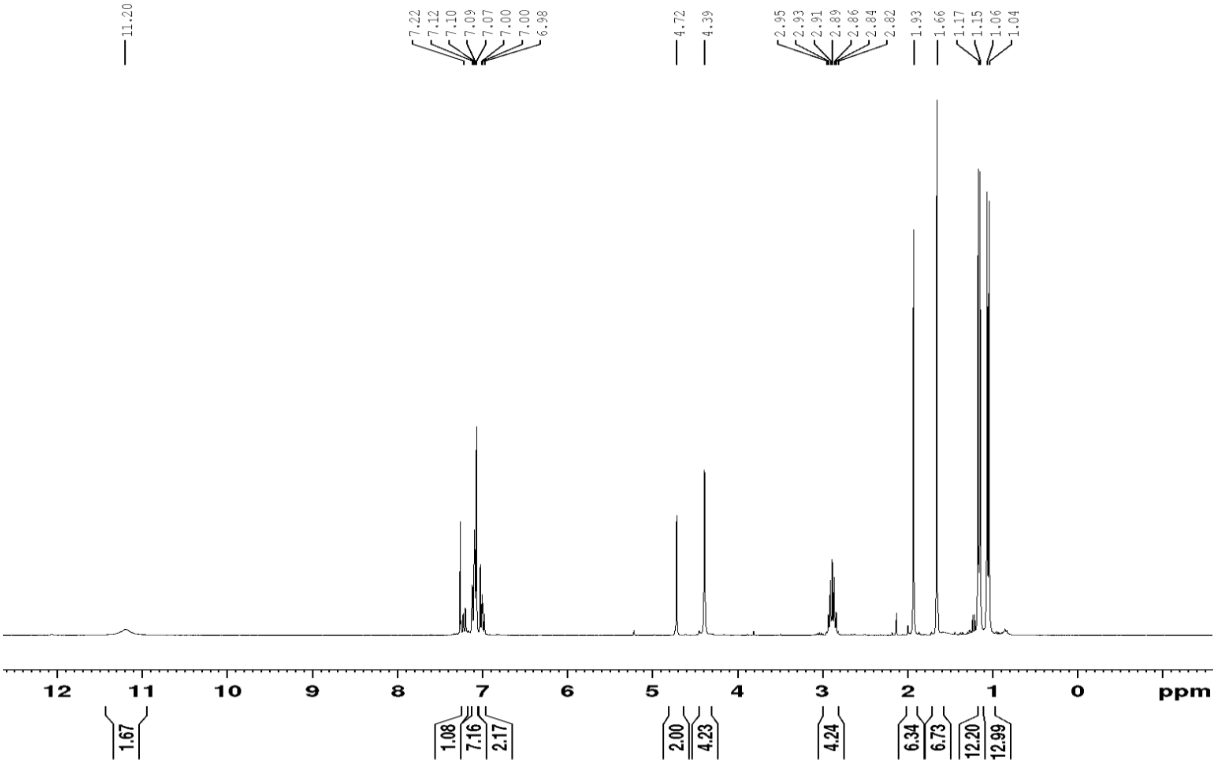

Figure S1. ^{1}H NMR spectrum (400 MHz) of **1h** in $CDCl_3$.

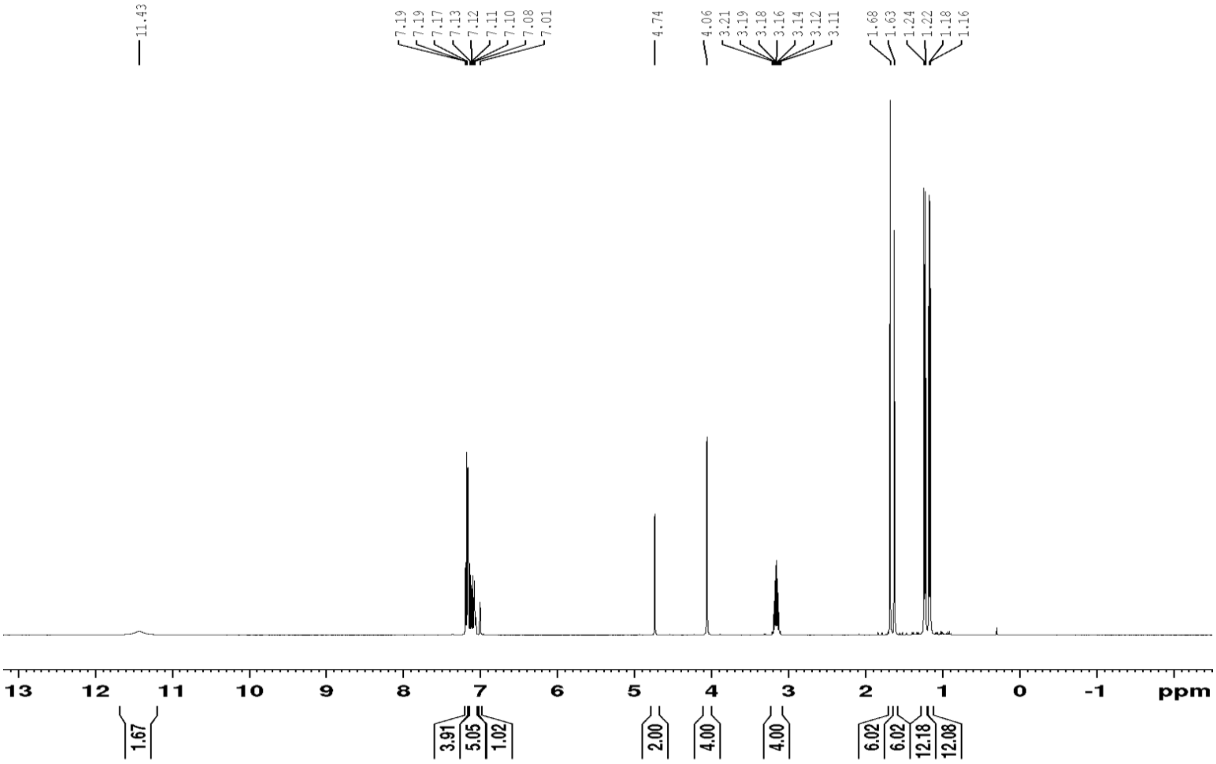

Figure S2. ^{1}H NMR spectrum (400 MHz) of **1h** in C_6D_6.

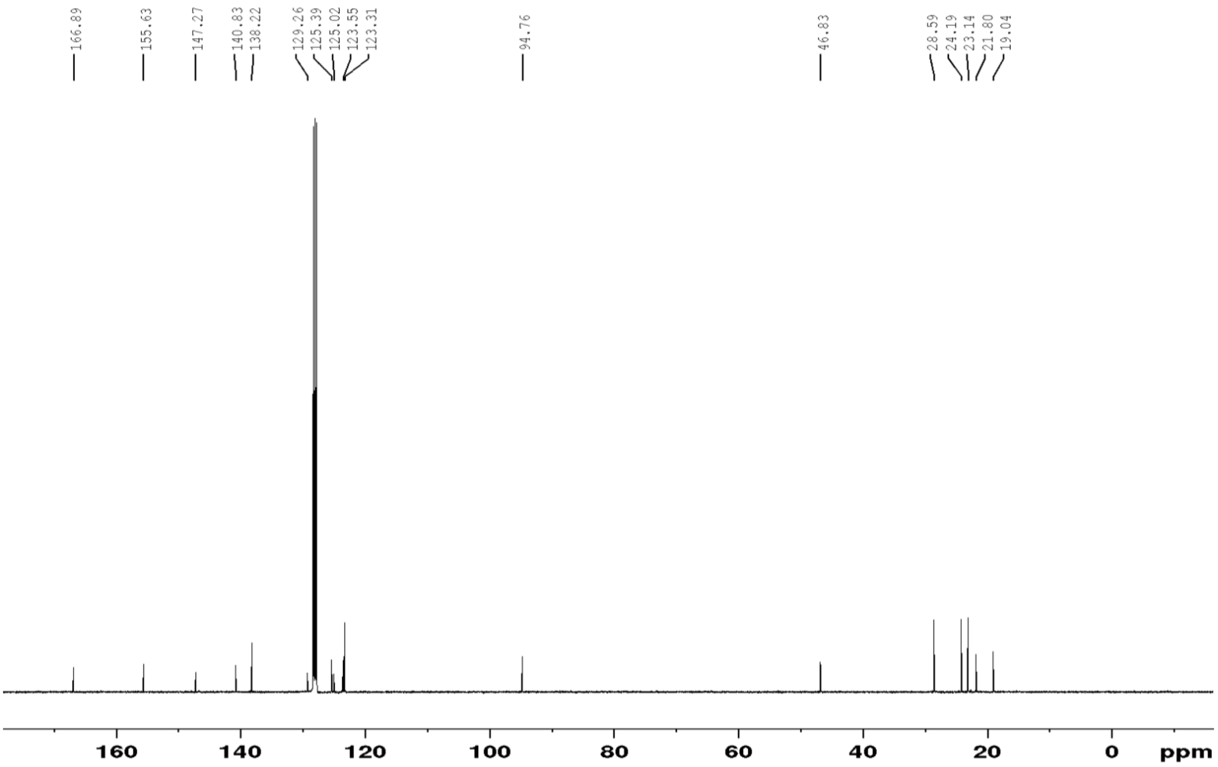

Figure S3. ^{13}C NMR spectrum (101 MHz) of **1h** in C_6D_6.

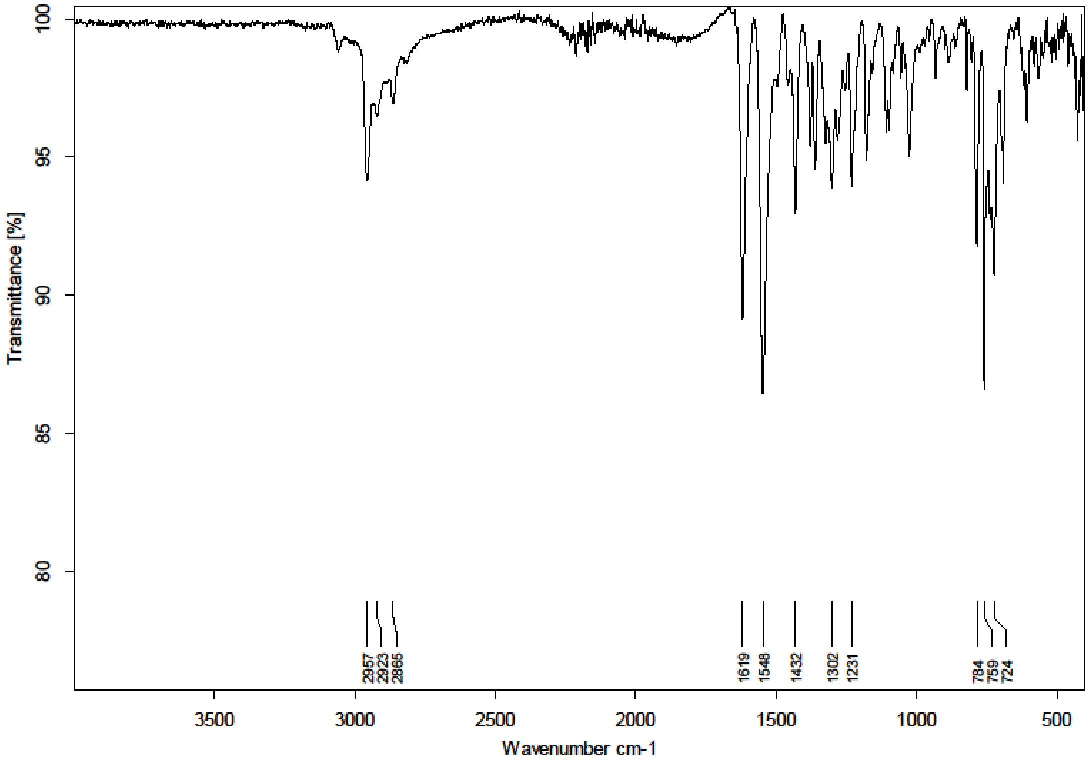

Figure S4. ATR-IR spectrum of **1h**.

IIIb

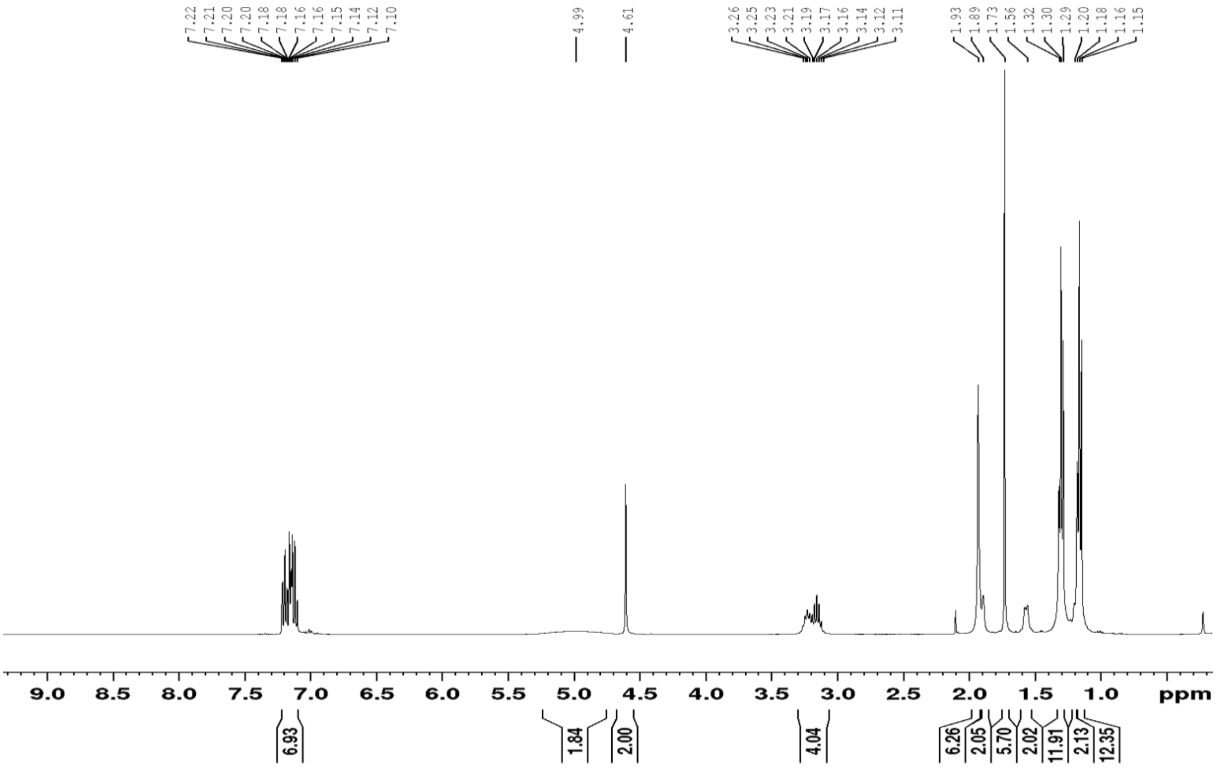

Figure S5. ^{1}H NMR spectrum (400 MHz) of **IIIb** in C_6D_6.

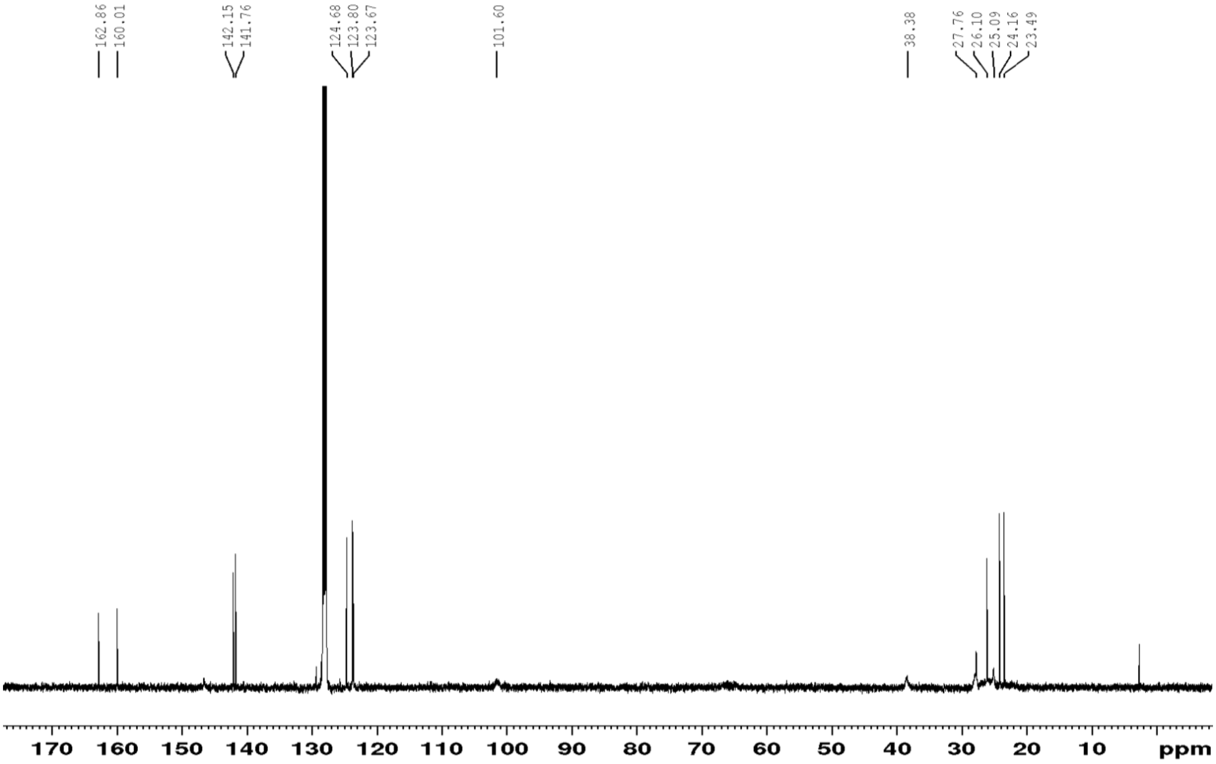

Figure S6. ^{13}C NMR spectrum (101 MHz) of **IIIb** in C_6D_6.

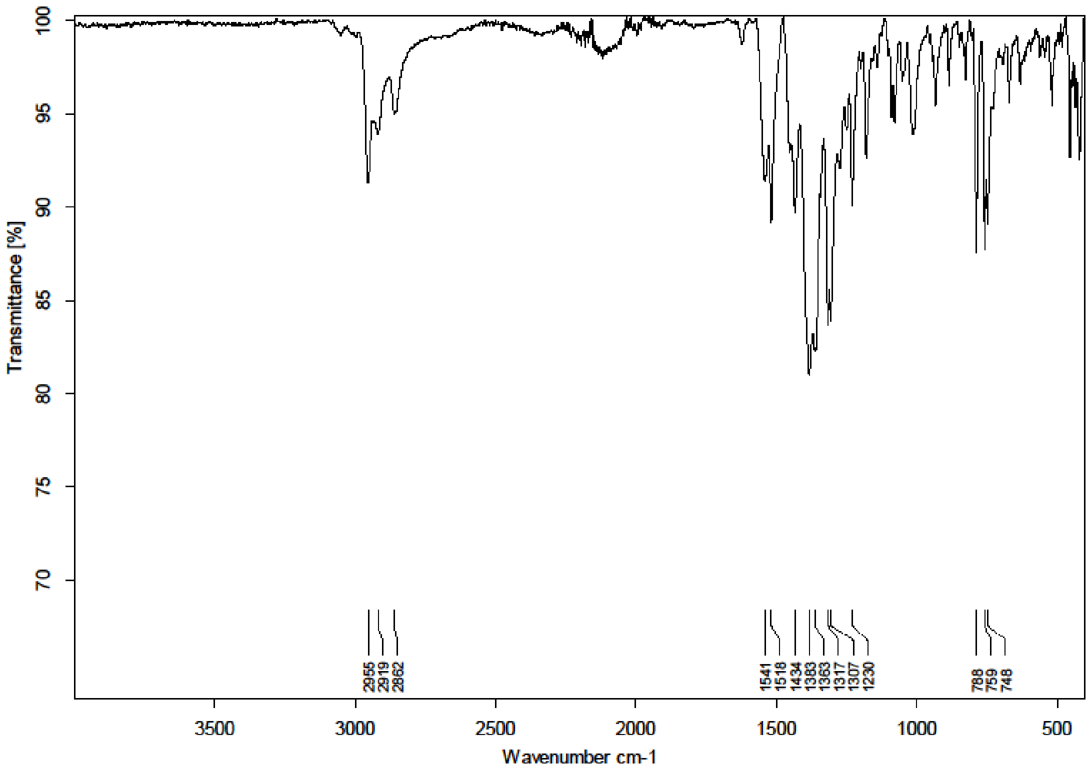

Figure S7. ATR-IR spectrum of **IIIb**.

IIIc

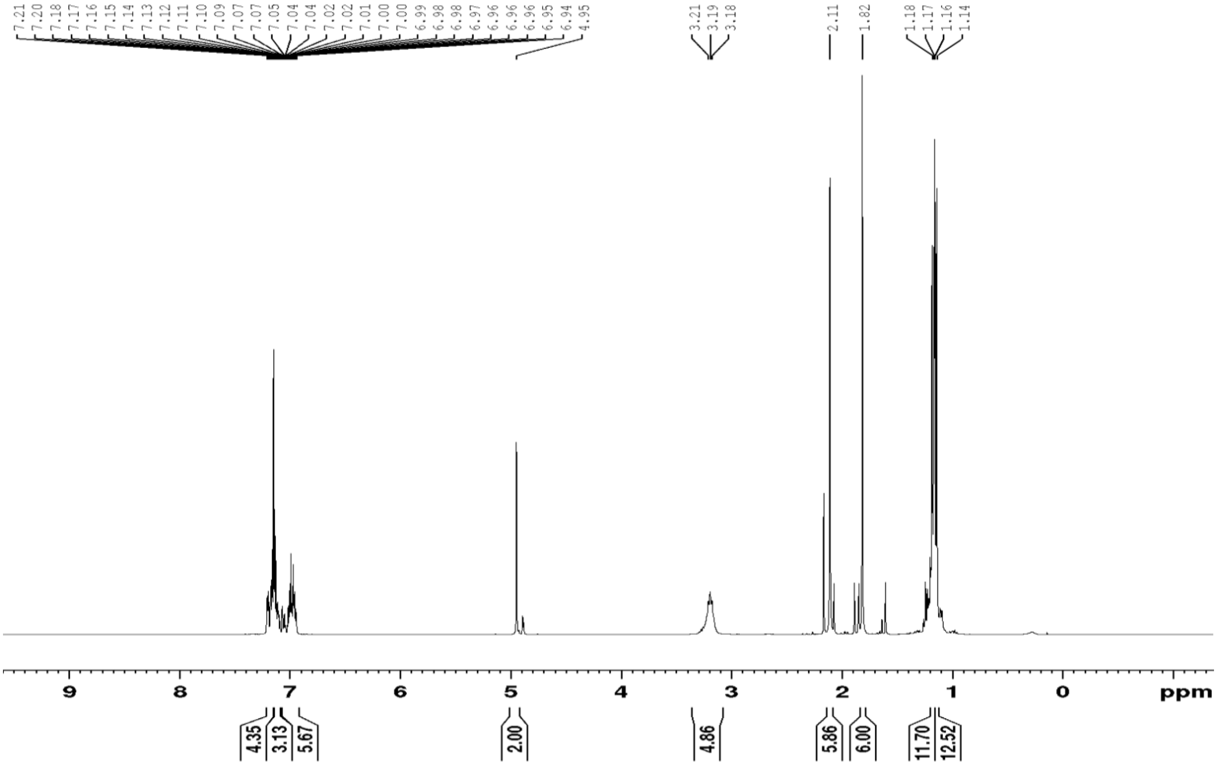

Figure S8. ^{1}H NMR spectrum (400 MHz) of **IIIc** in C_6D_6.

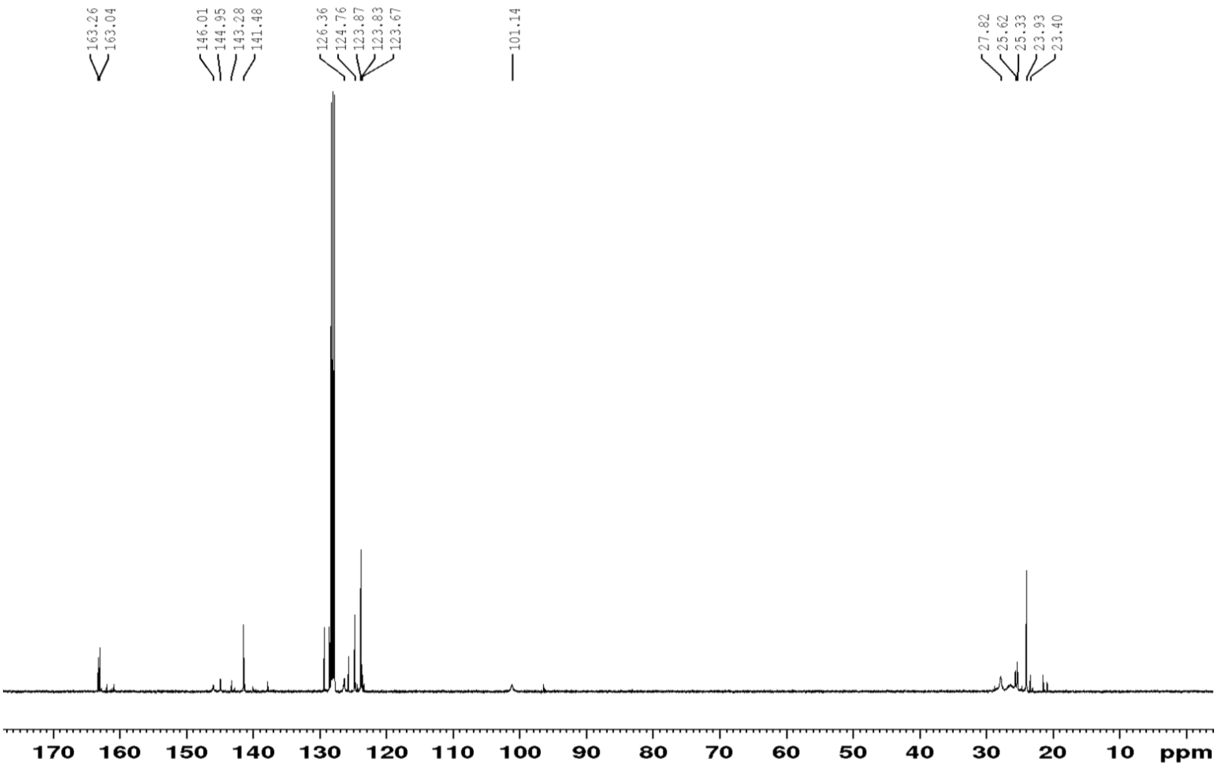

Figure S9. ^{13}C NMR spectrum (101 MHz) of **IIIc** in C_6D_6.

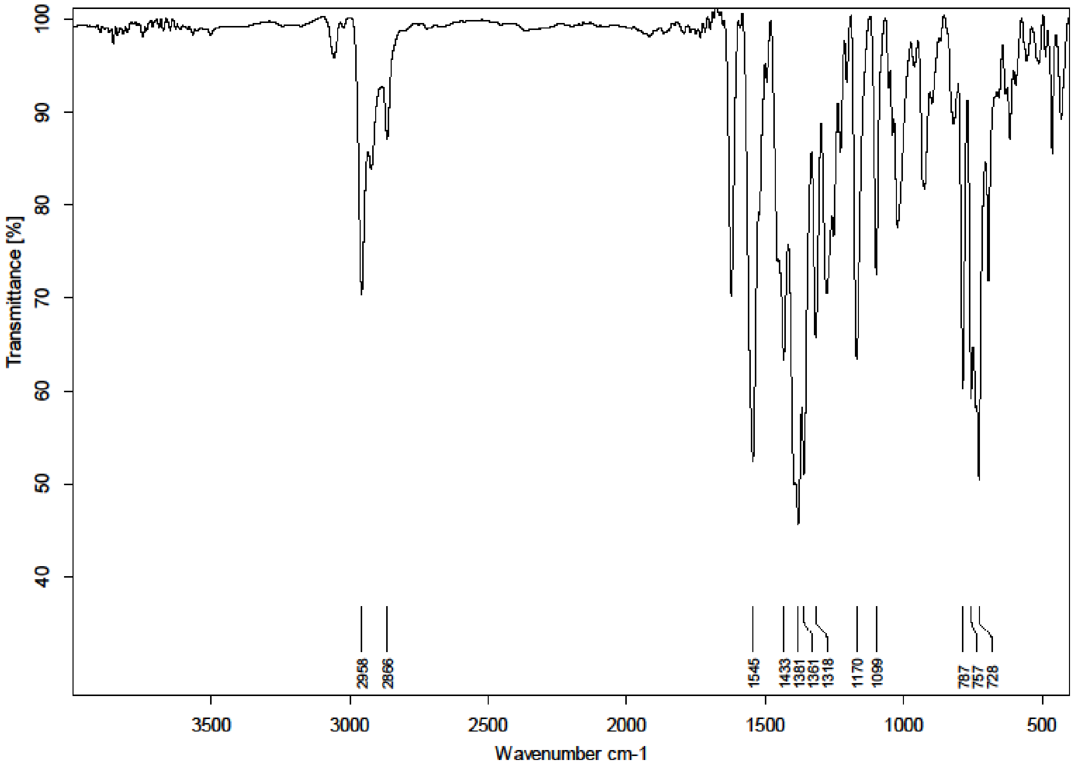

Figure S10. ATR-IR spectrum of **IIIc**.

IIId

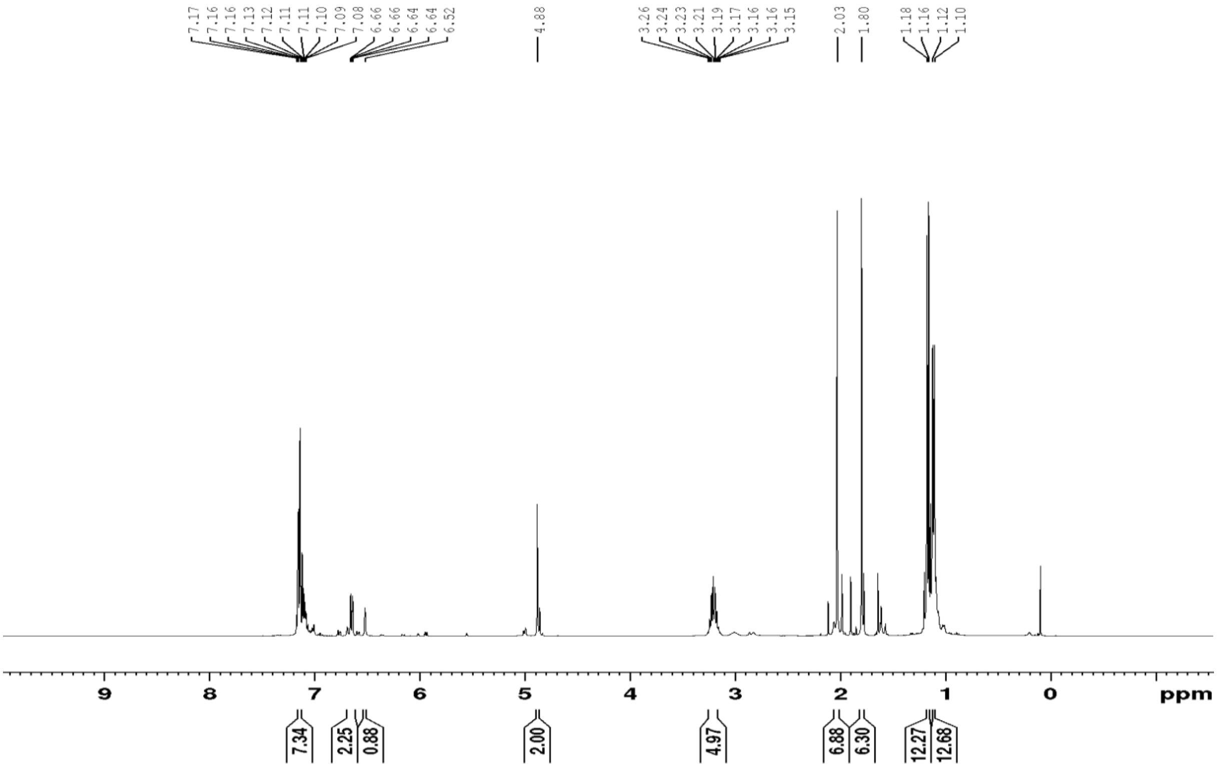

Figure S11. ^{1}H NMR spectrum (400 MHz) of **IIId** in C_6D_6.

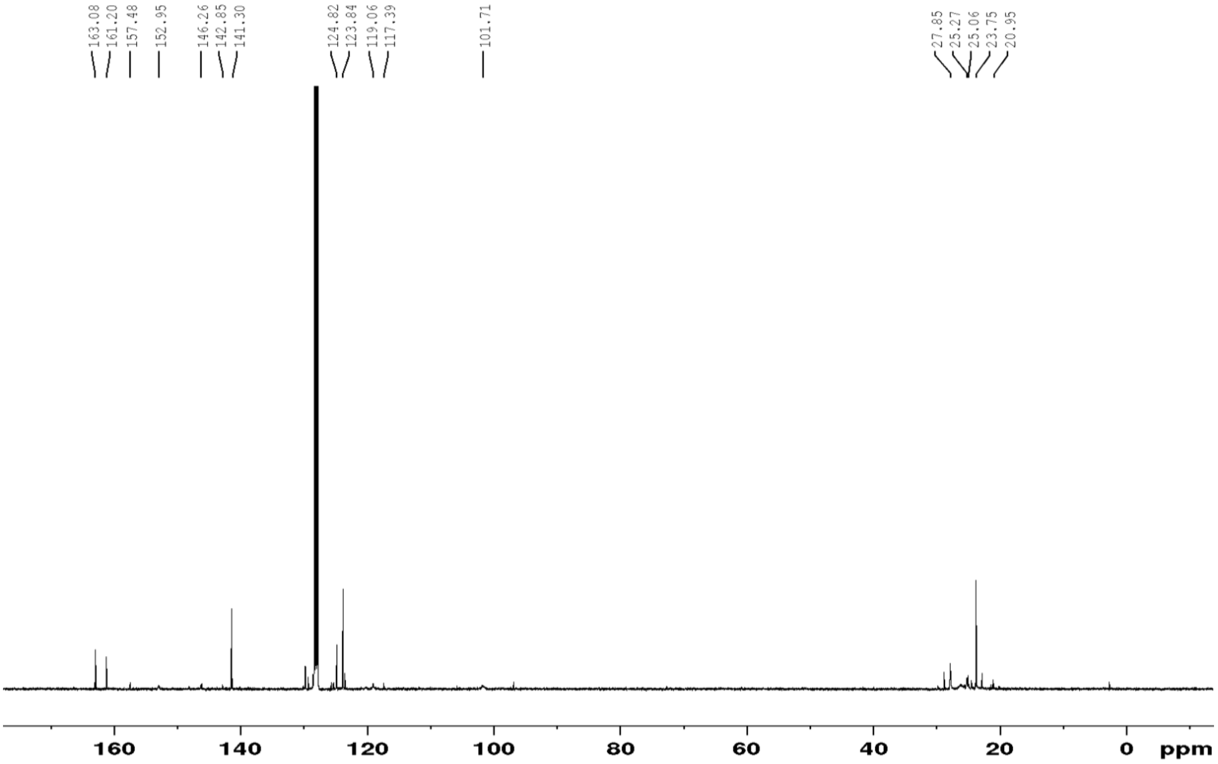

Figure S12. ^{13}C NMR spectrum (101 MHz) of **IIId** in C_6D_6.

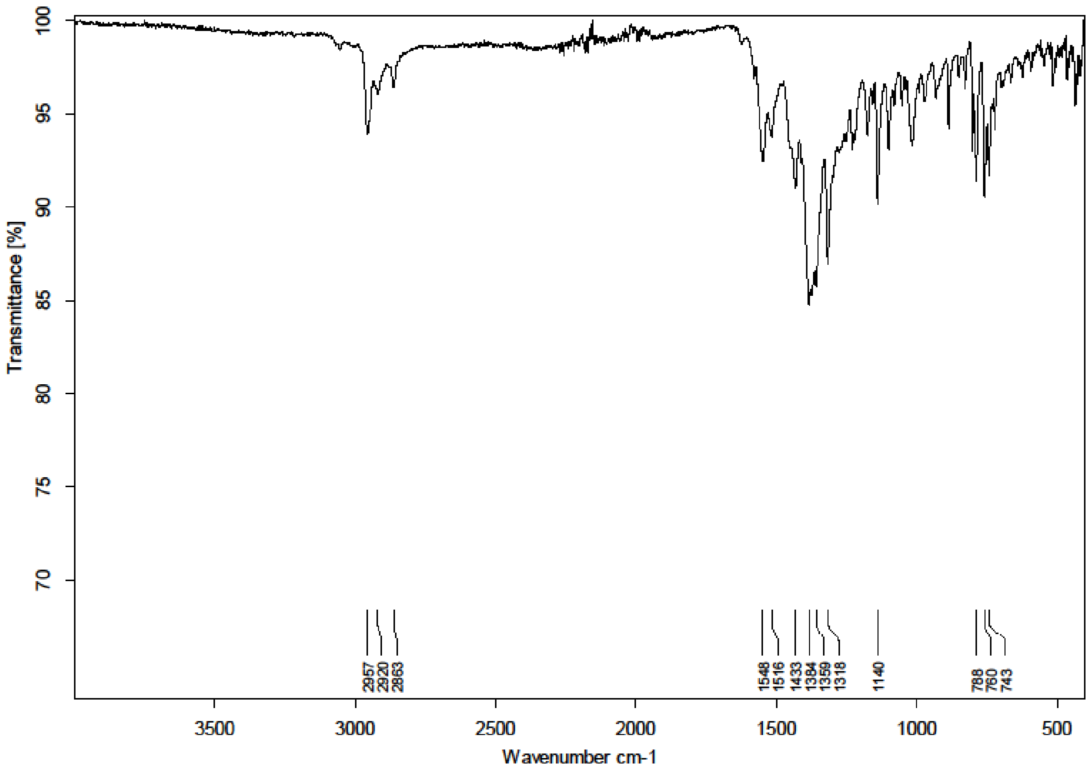

Figure S13. ATR-IR spectrum of **IIId**.

IIIe

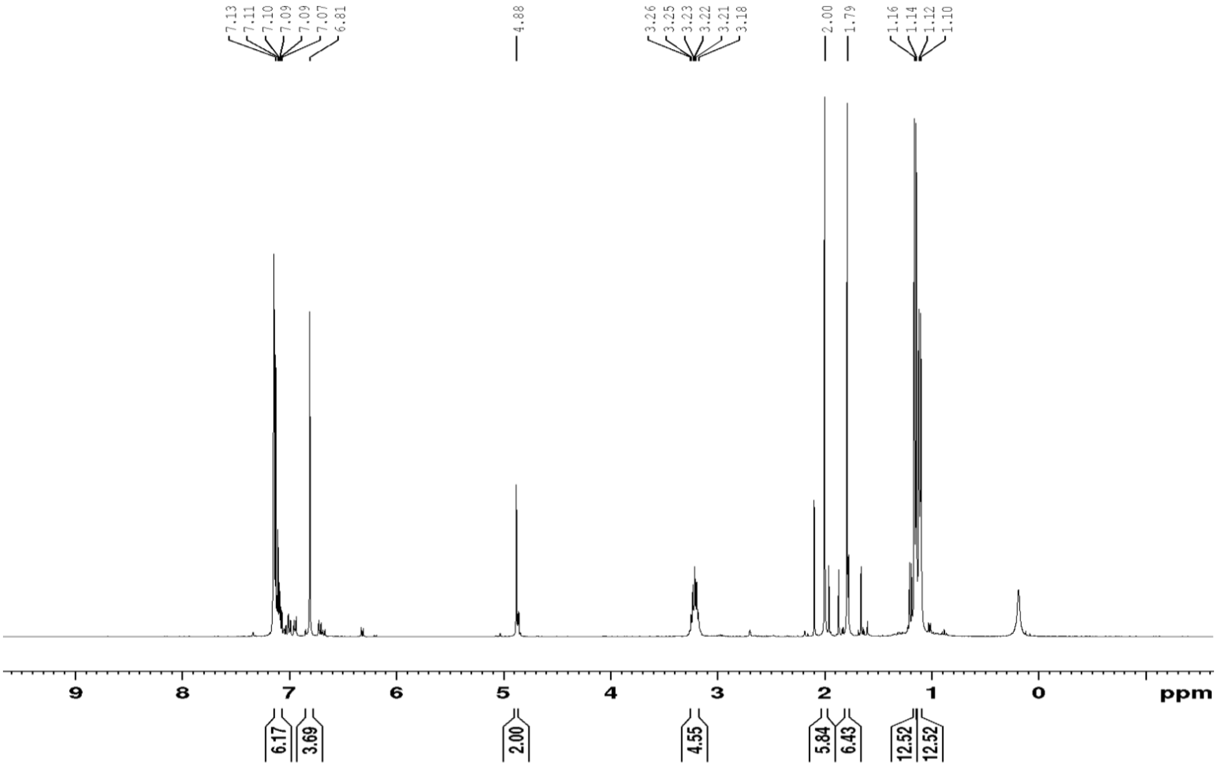

Figure S14. ^{1}H NMR spectrum (400 MHz) of **IIIe**.

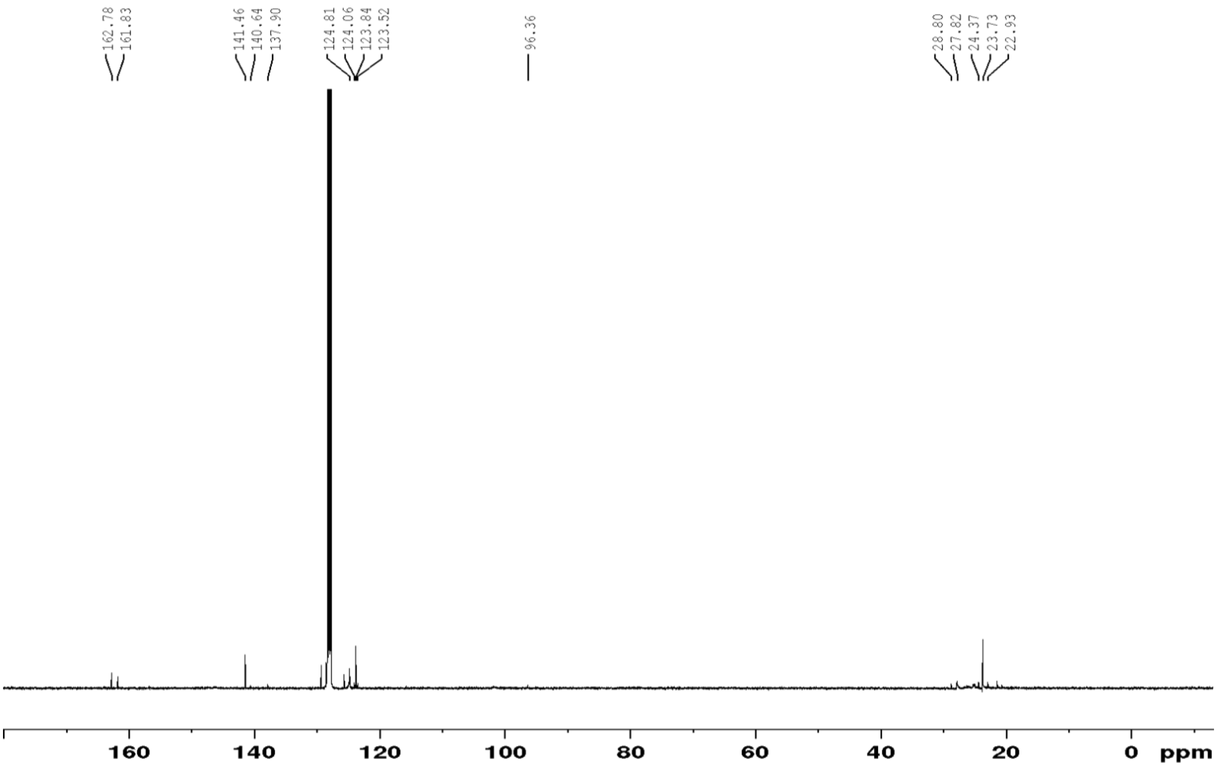

Figure S15. ^{13}C NMR spectrum (101 MHz) of **IIIe** in C_6D_6.

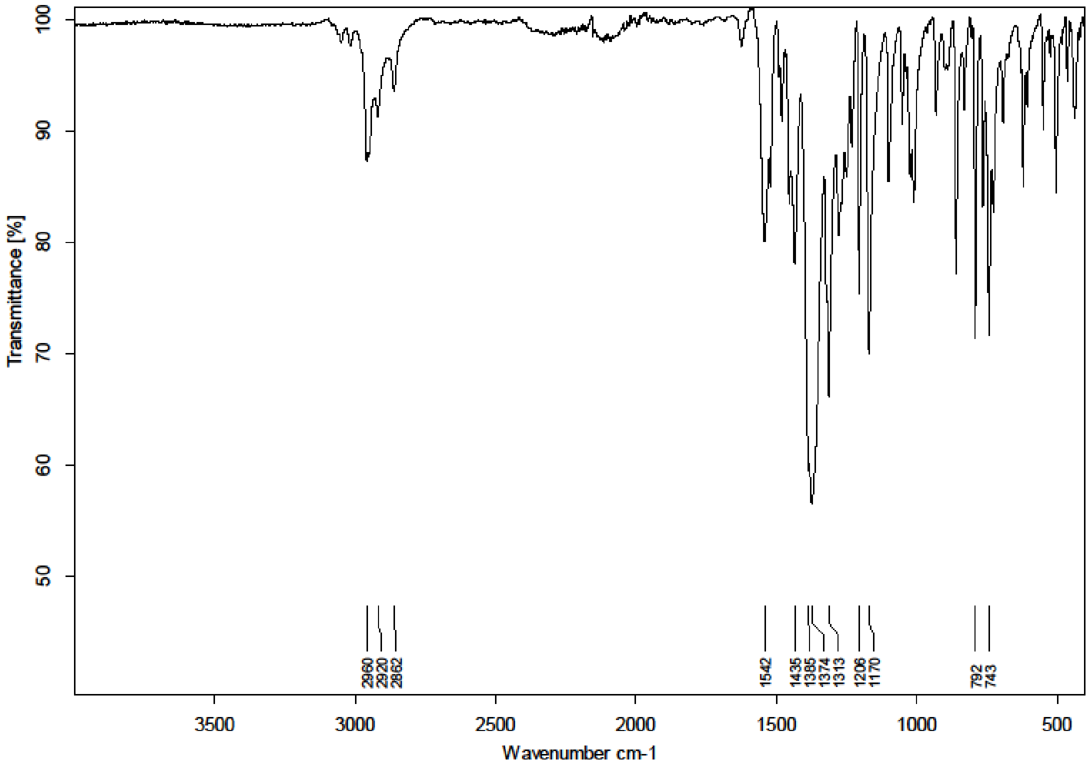

Figure S16. ATR-IR spectrum of **IIIe**.

IIIf

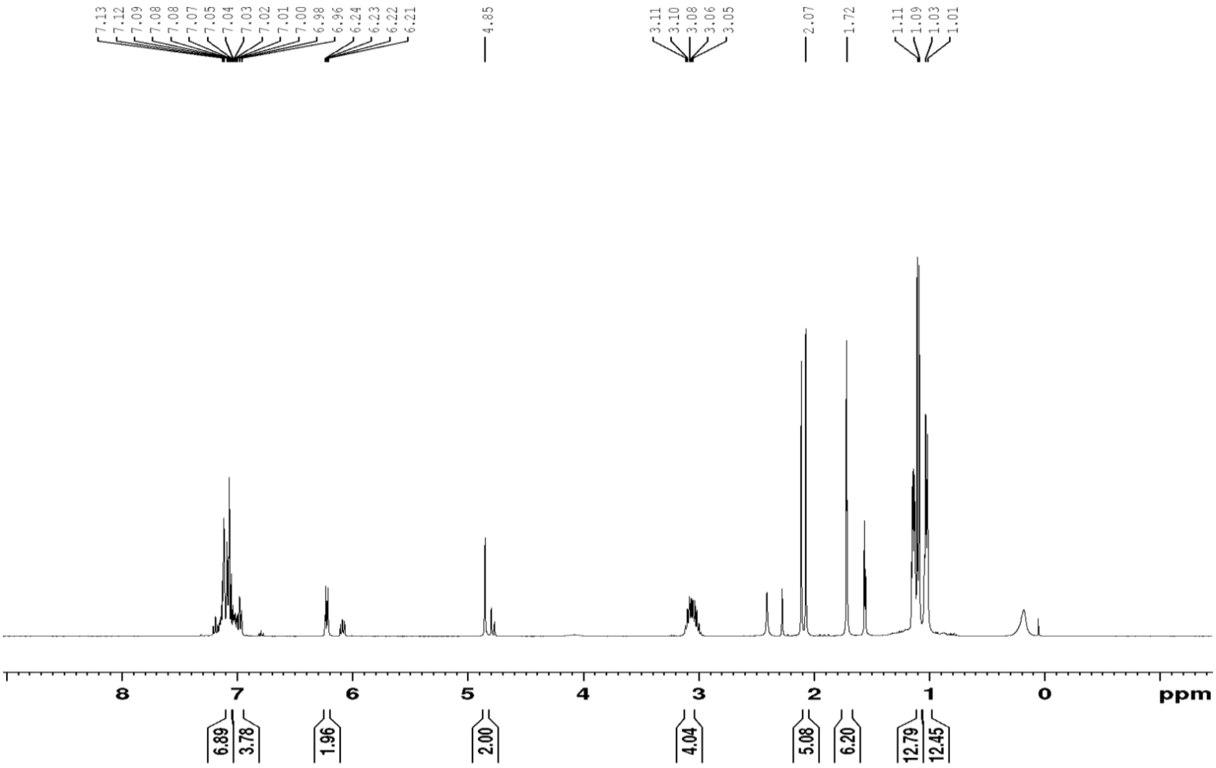

Figure S17. ^{1}H NMR spectrum (400 MHz) of **IIIf** in C_6D_6. The non-assigned peaks belong to a contamination with the ligand 1f.

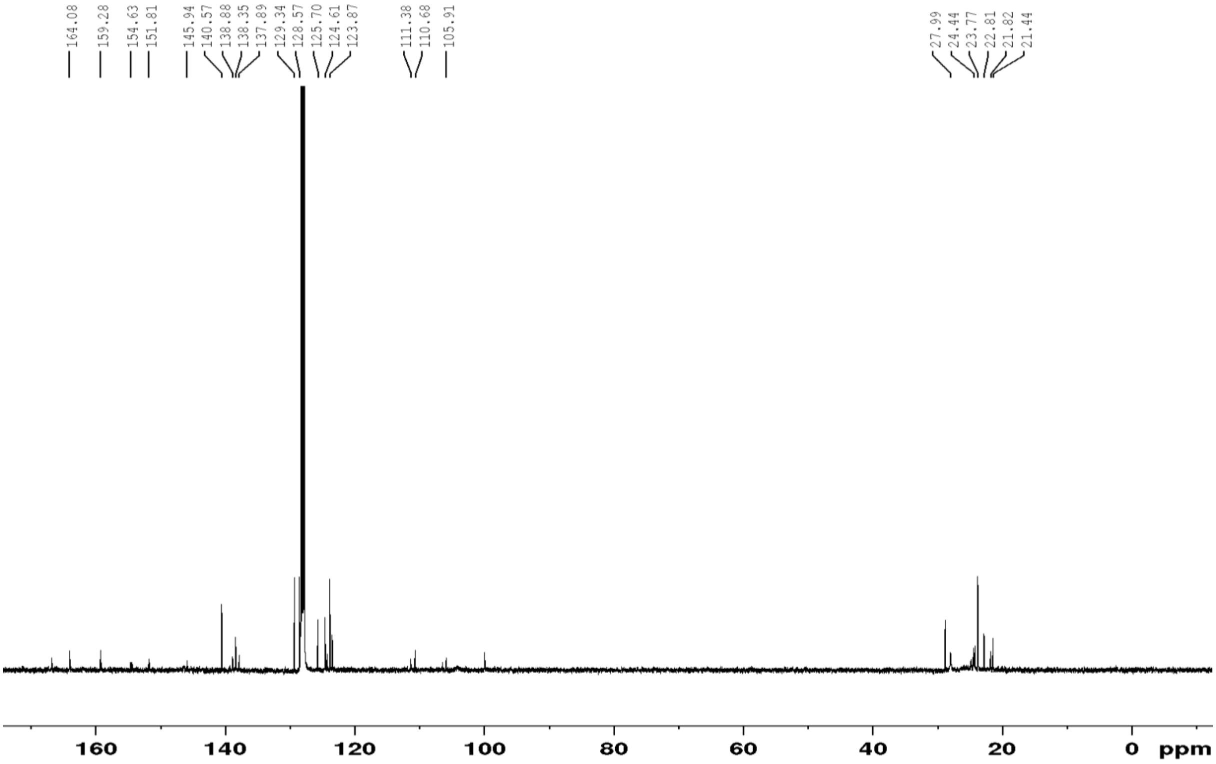

Figure S18. ^{13}C NMR spectrum (101 MHz) of IIIf in C_6D_6. The non-assigned peaks belong to a contamination with the ligand **1f**.

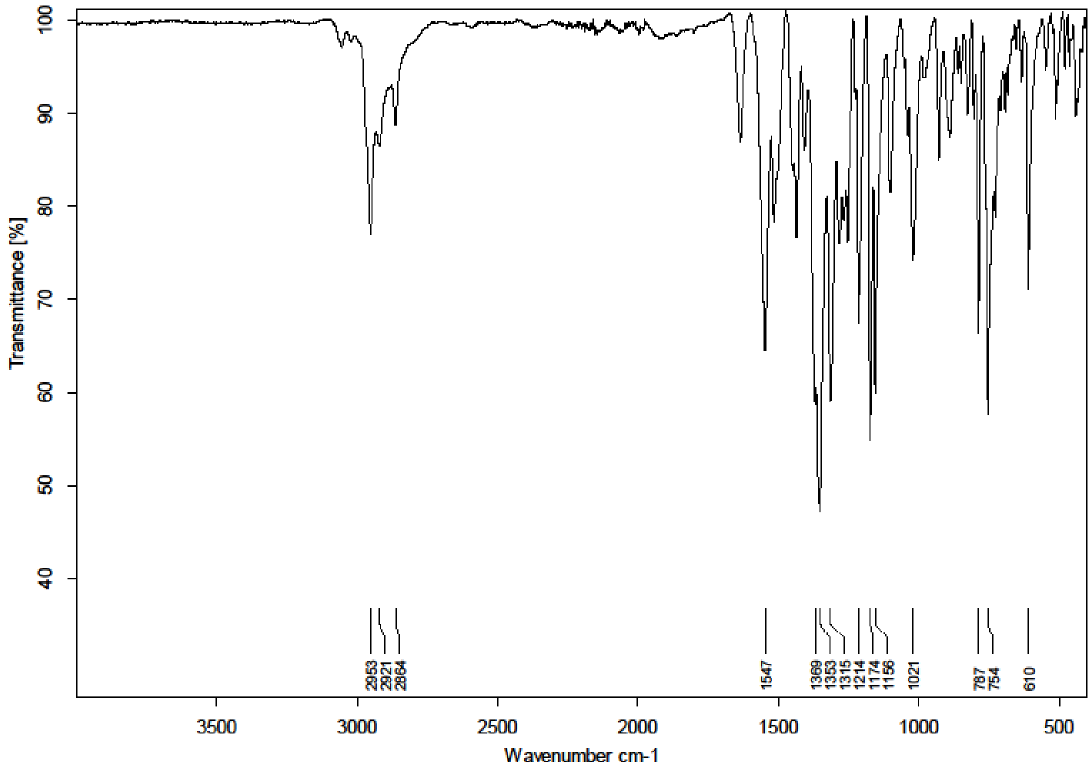

Figure S19. ATR-IR spectrum of **IIIf**.

IIIg

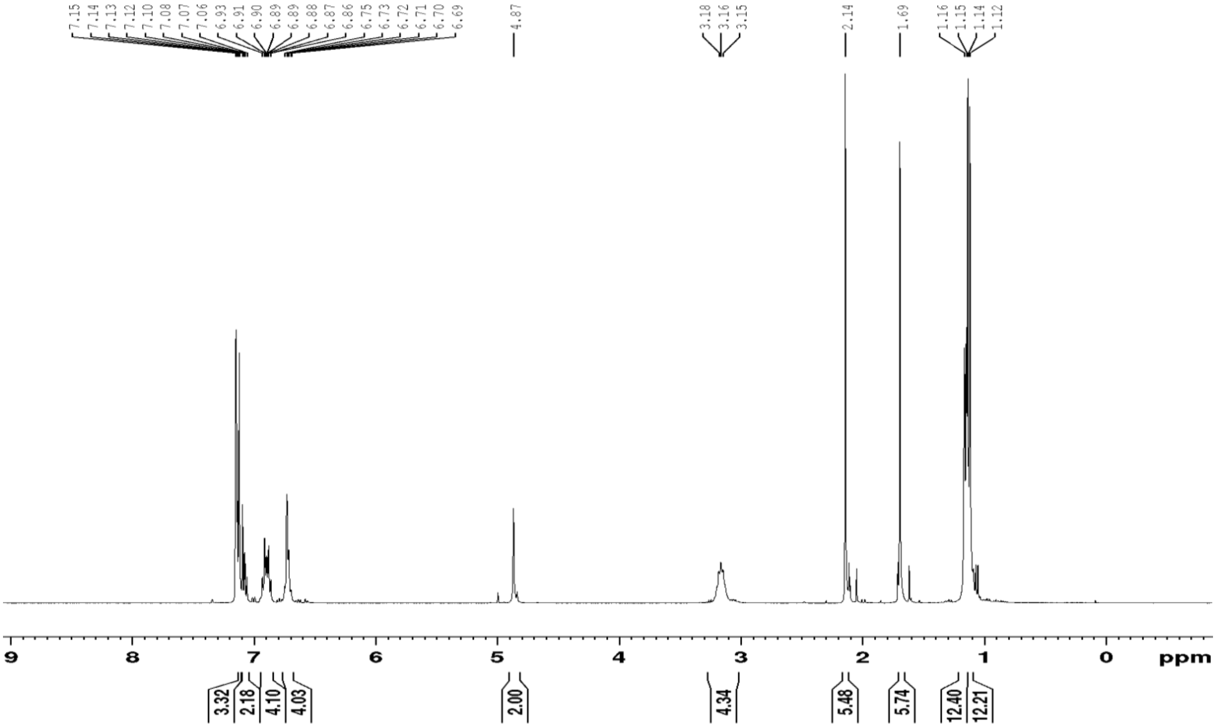

Figure S20. ^{1}H NMR spectrum (400 MHz) of **IIIg** in C_6D_6.

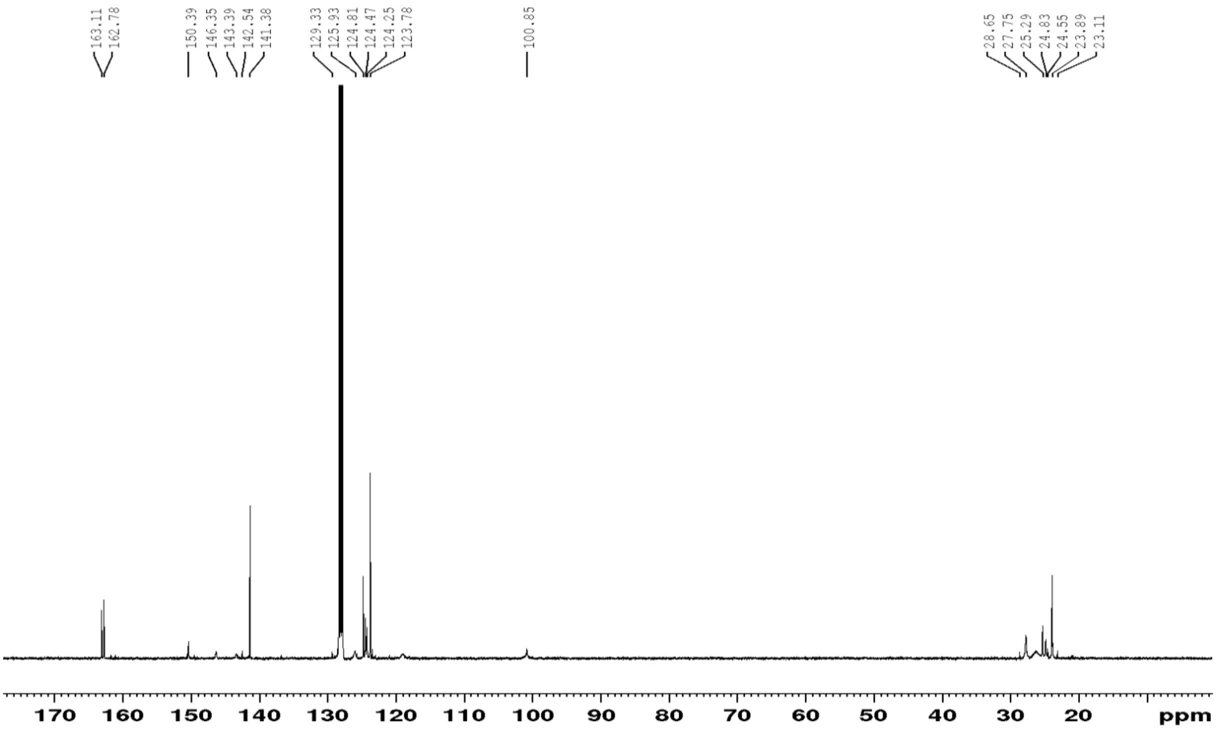

Figure S21. ^{13}C NMR spectrum (101 MHz) of **IIIg** in C_6D_6.

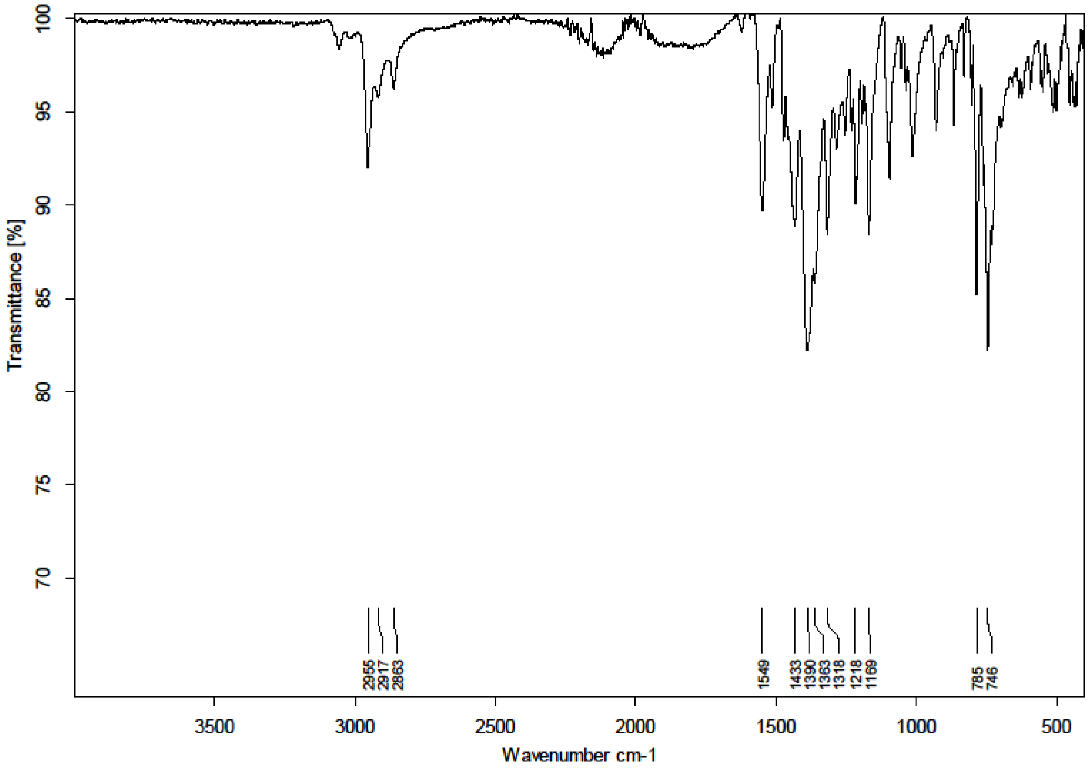

Figure S22. ATR-IR spectrum of **IIIg**.

IIIh

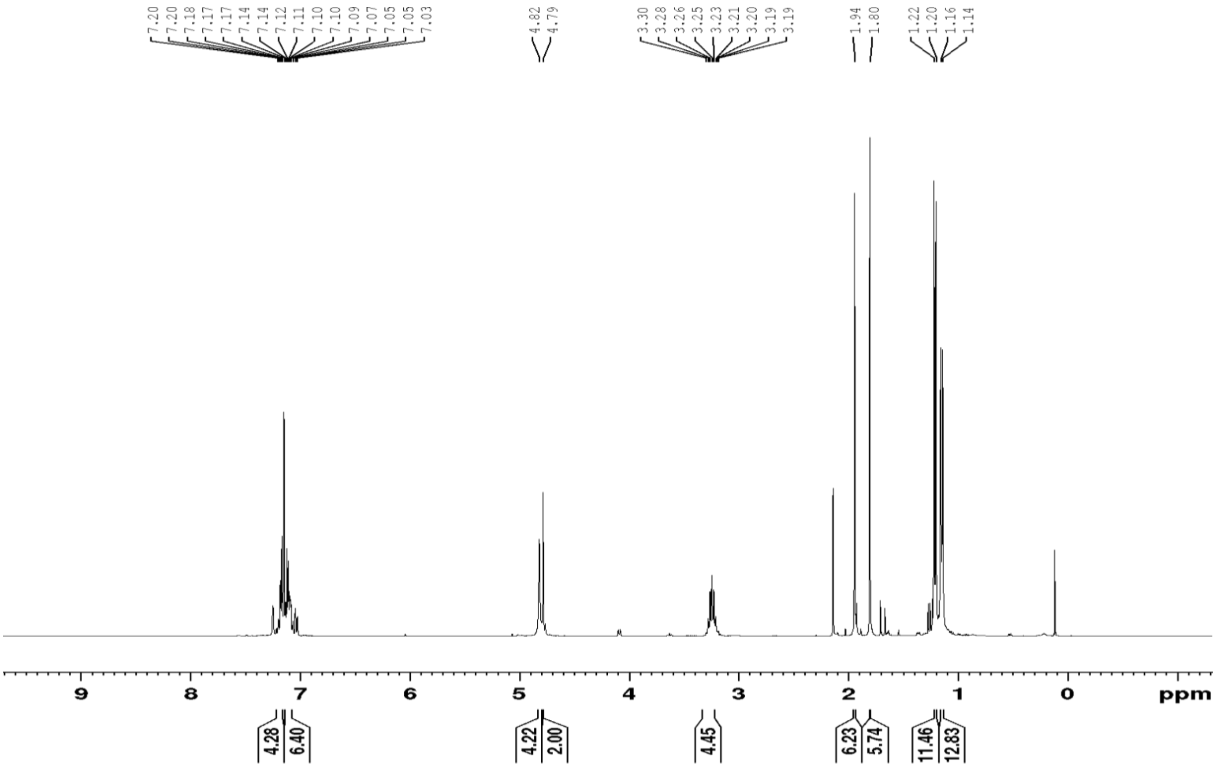

Figure S23. ^{1}H NMR spectrum (400 MHz) of **IIIh** in C_6D_6.

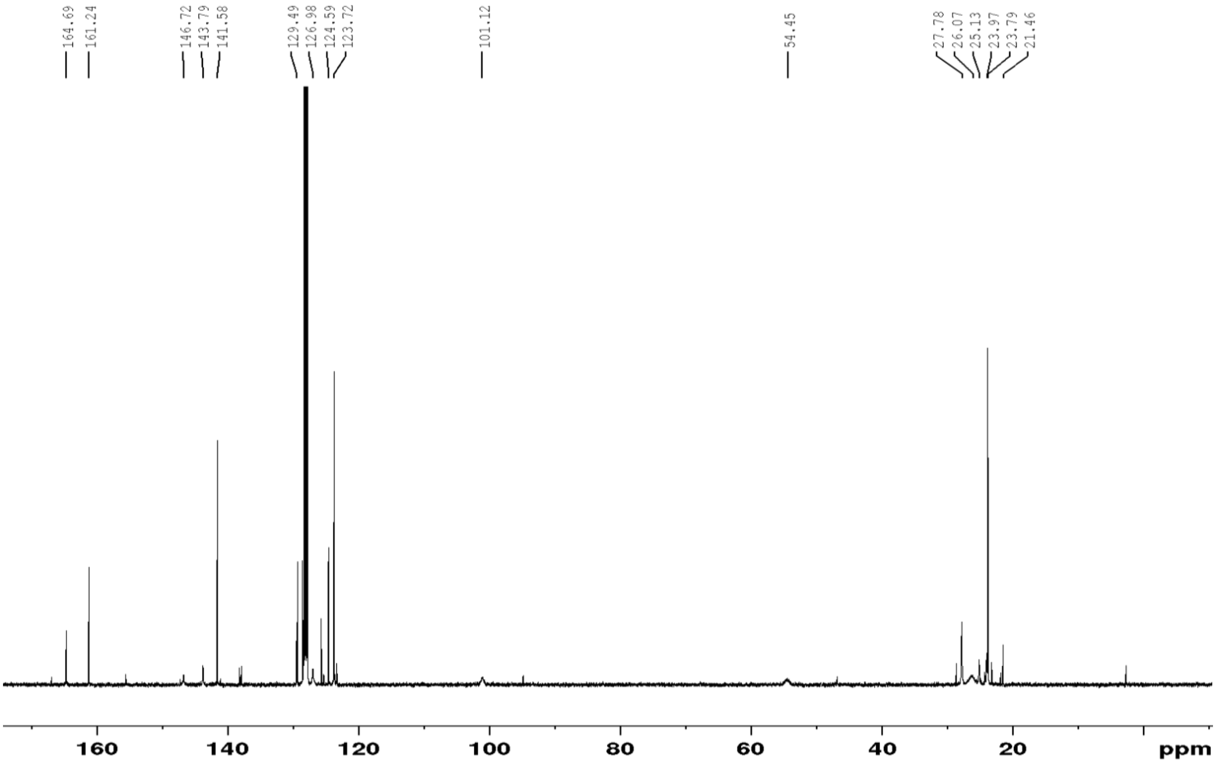

Figure S24. ^{13}C NMR spectrum (101 MHz) of **IIIh** in C_6D_6.

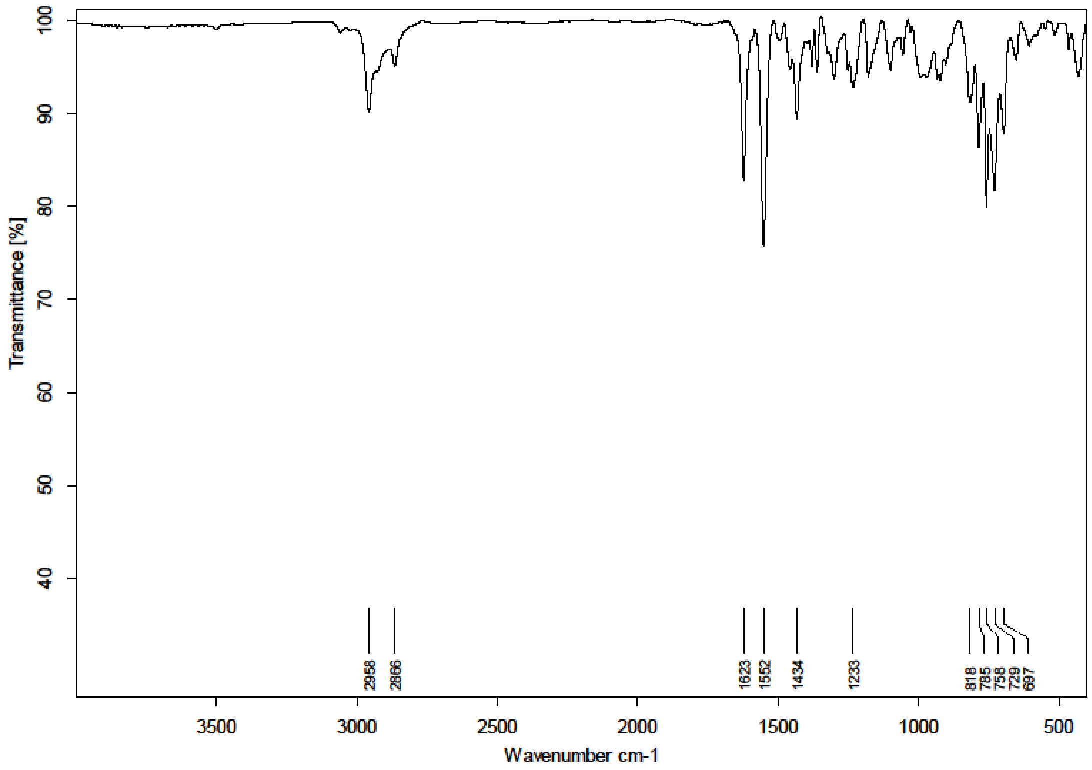

Figure S25. ATR-IR spectrum of **IIIh**.

Va

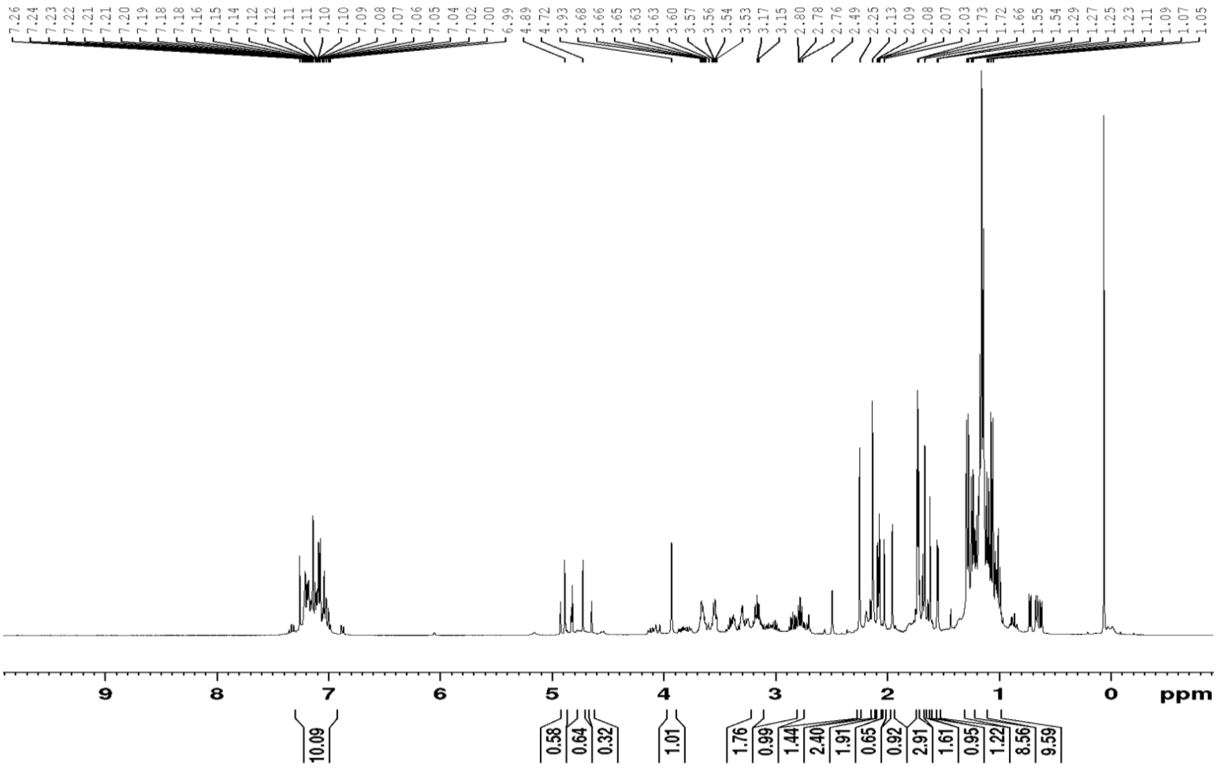

Figure S26. ^{1}H NMR spectrum (400 MHz) of **Va** in $CDCl_3$.

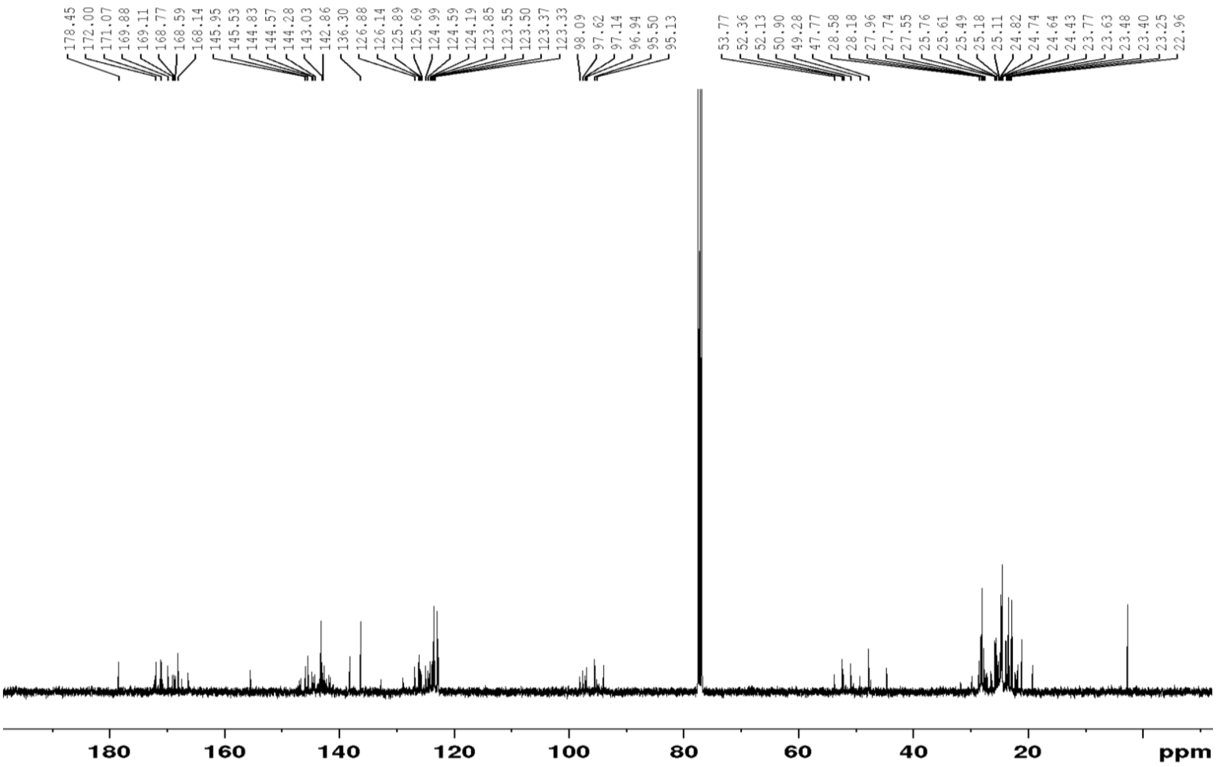

Figure S27. ^{13}C NMR spectrum (101 MHz) of **Va** in $CDCl_3$.

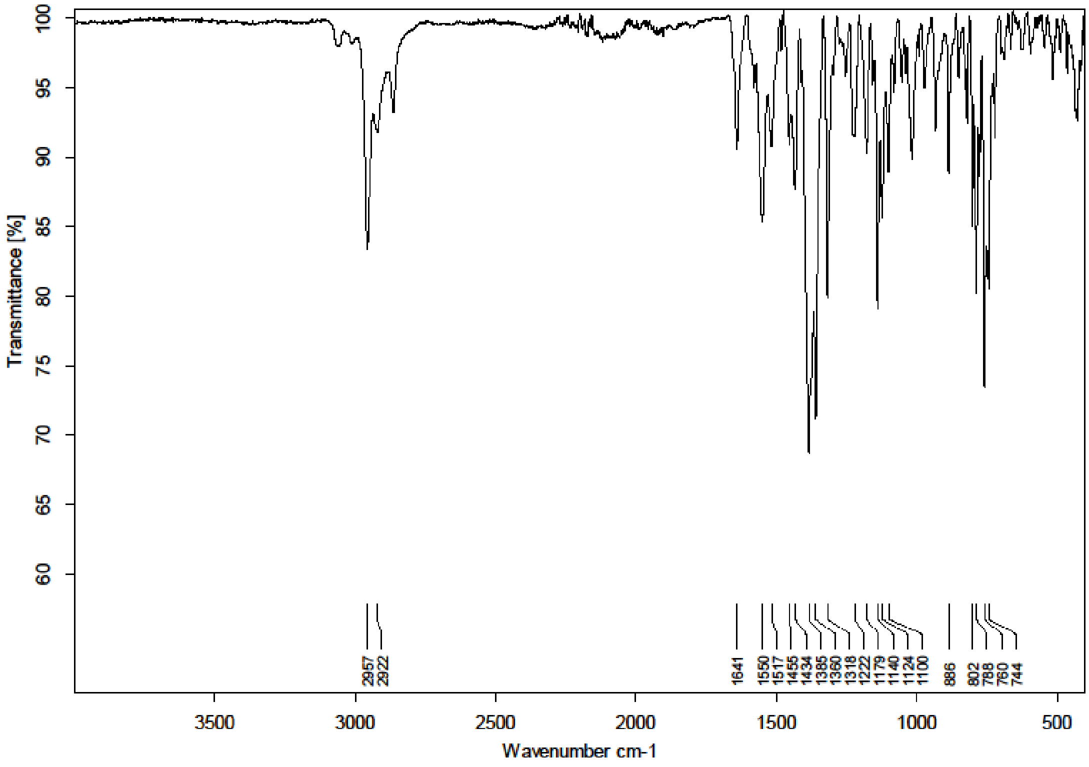

Figure S28. ATR-IR spectrum of **Va**.

Crystallographic Details

The single crystal X-ray diffraction data were recorded on either an Agilent Gemini R Ultra diffractometer with Mo K*α* radiation (λ = 0.71073 Å) **IIIb** and Cu K*α* radiation (λ = 1.54184 Å) **IIIe**, **IIIg**, a GV-50 diffractometer with Titan[S2] detector from Rigaku Oxford Diffraction (formerly Agilent Technologies) applying Cu Kβ radiation (λ = 1.39222 Å) **IIId** or SuperNova diffractometer with microfocus Cu K*α* radiation (λ = 1.54184 Å) **Va**. Empirical multi-scan[S4] and analytical absorption corrections[S5] were applied to the data. The structures were solved with SHELXT[S6] and least-square refinements on F^2 were carried out with SHELXL.[S7] For all single-crystal X-Ray structure determinations, the non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were located in idealized calculated positions and were refined isotropically according to the riding model. The crystals did not contain any solvent.

Single-crystal X-Ray structure determination of **IIIb** and **IIId**: The thallium atoms are disordered over two positions and could be refined by using the disorder model.

Single-crystal X-Ray structure determination of **IIIg**: The thallium atoms are disordered over two positions and could be refined with disorder model. The residual rest electron density of 2.2 is due to the heavy atoms thallium.

CCDC 1823060 (**IIIb**), 1822992 (**IIId**), 1822994 (**IIIe**), 1822993 (**IIIg**) and 1822995 (**Va**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data for $C_{40}H_{58}N_4Tl_2$ (**IIIb**), $C_{40}H_{52}N_4Tl_2$ (**IIId**), $C_{40}H_{52}N_4Tl_2$(**IIIe**).

	IIIb	**IIId**	**IIIe**
Empirical formula	$C_{40}H_{58}N_4Tl_2$	$C_{40}H_{52}N_4Tl_2$	$C_{40}H_{52}N_4Tl_2$
CCDC No.	1823060	1822992	1822994
Formula weight	1003.64	997.59	997.59
Temperature/K	123.3(2)	123.0(1)	123(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	11.8223(3)	11.2649(4)	11.4107(2)
b/Å	12.3605(3)	14.6040(7)	12.5545(2)
c/Å	27.0082(6)	23.9757(9)	13.8125(3)
α/°	90	90	90

β/°	97.309(2)	90.819(3)	110.420(2)
γ/°	90	90	90
Volume/Å^3	3914.63(16)	3943.9(3)	1854.38(6)
Z	4	4	2
ρ_{calc}g/cm^3	1.703	1.680	1.787
μ/mm^{-1}	8.254	12.169	16.730
F(000)	1952.0	1928.0	964.0
Crystal size/mm^3	0.27×0.21×0.15	0.19×0.08×0.05	0.27×0.13×0.08
Radiation	MoKα (λ = 0.71073)	CuKβ (λ = 1.39222)	CuKα (λ = 1.54184)
2Θ range for data collection/°	3.151 to 30.031	3.200 to 56.271	4.134 to 65.972
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -38 ≤ l ≤ 37	-13 ≤ h ≤ 12, -17 ≤ k ≤ 17, -28 ≤ l ≤ 19	-13 ≤ h ≤ 12, -14 ≤ k ≤ 14, -16 ≤ l ≤ 14
Reflections collected	37461	17728	11599
Independent reflections	11396 [R_{int} = 0.0369, R_{sigma} = 0.0451]	7032 [R_{int} = 0.0383, R_{sigma} = 0.0438]	3224 [R_{int} = 0.0288, R_{sigma} = 0.0248]
Data/restraints/parameters	11396/12/447	7032/12/447	3224/0/214
Goodness-of-fit on F^2	0.917	1.020	1.133
Final R indexes [I>=2σ (I)]	R_1 = 0.0227, wR_2 = 0.0357	R_1 = 0.0313, wR_2 = 0.0681	R_1 = 0.0205, wR_2 = 0.0479
Final R indexes [all data]	R_1 = 0.0373, wR_2 = 0.0373	R_1 = 0.0393, wR_2 = 0.0729	R_1 = 0.0220, wR_2 = 0.0486
Largest diff. peak/hole / e Å^{-3}	0.793/-0.995	1.115/-1.433	0.549/-0.540

Table S2. Crystallographic data for $C_{46}H_{56}N_4OTl_2$(**IIIg**), $C_{36}H_{53}Cl_2InN_4$(**Va**).

	IIIg	**Va**
Empirical formula	$C_{46}H_{56}N_4OTl_2$	$C_{36}H_{53}Cl_2InN_4$
CCDC No.	1822993	1822995
Formula weight	1089.68	727.54
Temperature/K	123(2)	123.0(1)
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a/Å	10.5625(3)	10.2950(2)
b/Å	12.8352(3)	16.7551(3)
c/Å	17.0017(4)	22.8038(4)
α/°	105.593(2)	75.0420(10)
β/°	91.493(2)	79.2910(10)
γ/°	107.245(2)	83.8490(10)
Volume/Å^3	2106.26(10)	3726.78(12)
Z	2	4
ρ_{calc}g/cm^3	1.718	1.297
μ/mm^{-1}	14.810	6.595
F(000)	1060.0	1520.0
Crystal size/mm^3	0.23×0.21×0.15	0.17×0.15×0.10
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)

2Θ range for data collection/°	3.767 to 72.958	3.786 to 73.526
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20	-12 ≤ h ≤ 12, -20 ≤ k ≤ 20, -28 ≤ l ≤ 28
Reflections collected	26609	90047
Independent reflections	8027 [R_{int} = 0.0438, R_{sigma} = 0.0363]	14859 [R_{int} = 0.0373, R_{sigma} = 0.0212]
Data/restraints/parameters	8027/6/500	14859/0/799
Goodness-of-fit on F^2	1.043	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0378, wR_2 = 0.1019	R_1 = 0.0222, wR_2 = 0.0540
Final R indexes [all data]	R_1 = 0.0408, wR_2 = 0.1044	R_1 = 0.0258, wR_2 = 0.0557
Largest diff. peak/hole / e Å^{-3}	2.188/-2.708	0.817/-0.414

Computational Details

Calculations have been performed with the Gaussian09 program package[S8] using the B3LYP functional[S9] and LANL2DZ basis sets[S10] in conjunction with the related quasi-relativistic pseudopotentials for thallium. To consider London dispersion, the D3 version of Grimme's dispersion with the original zero-damping function was used.[S11] The free energies (given in kJ mol^{-1}) were calculated for standard conditions, i.e., 298.15 K and 1 bar, and the absence of imaginary frequencies confirmed stationary points as minima. When X-ray data were available, the geometry optimization was performed using the XYZ coordinates as initial structures. In addition, relaxed PES scans were performed, which consists of geometry optimizations along selected Tl–Tl bond distances, for **IIIb**, **IIIc**, **IIIg**, and **IIIh**, respectively.

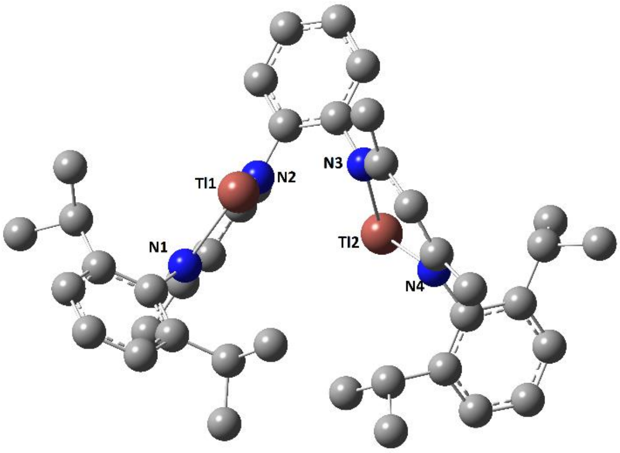

Figure S29. Geometry optimized structure (B3LYP-D3/LANL2DZ) of **IIIc** (hydrogen atoms are omitted for the sake of clarity). Selected calculated bond lengths (Å) and angles (°): Tl1–Tl2 4.82, Tl1–N1 2.48, Tl1–N2 2.54; N1–Tl1–N2 75.8.

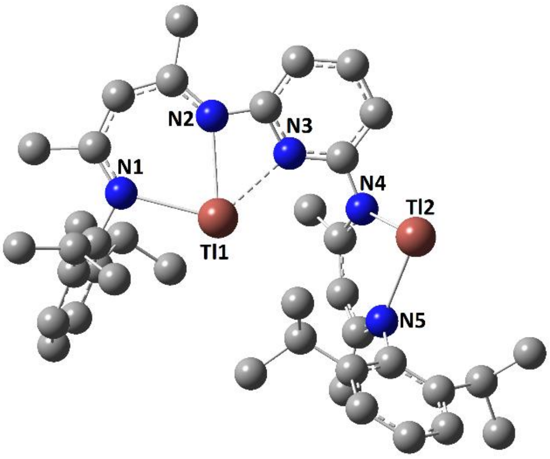

Figure S30. Geometry optimized structure (B3LYP-D3/LANL2DZ) of **IIIf** (hydrogen atoms are omitted for the sake of clarity). Selected calculated bond lengths (Å) and angles (°): Tl1–Tl2 5.04, Tl1–N1 2.56, Tl1–N2 2.63, Tl1–N3 2.69, Tl2–N4 2.51, Tl2–N5 2.48; N1–Tl1–N2 70.9, N1–Tl1–N3 114.9, N4–Tl2–N5 75.9.

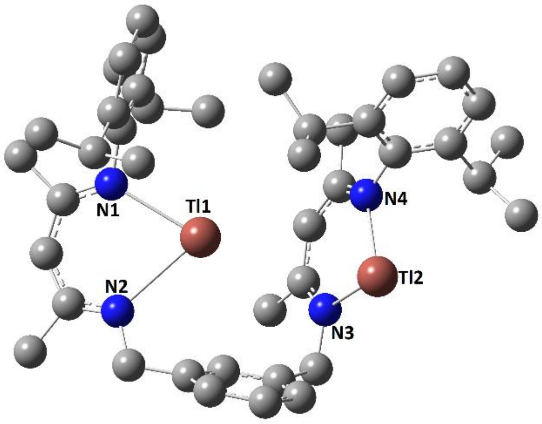

Figure S31. Geometry optimized structure (B3LYP-D3/LANL2DZ) of **IIIh** (hydrogen atoms are omitted for the sake of clarity). Selected calculated bond lengths (Å) and angles (°): Tl1–Tl2 4.53, Tl1–N1 2.76, Tl1–N2 2.63, Tl2–N3 2.52, Tl2–N4 2.44; N1–Tl1–N2 72.5, N3–Tl2–N4 77.0.

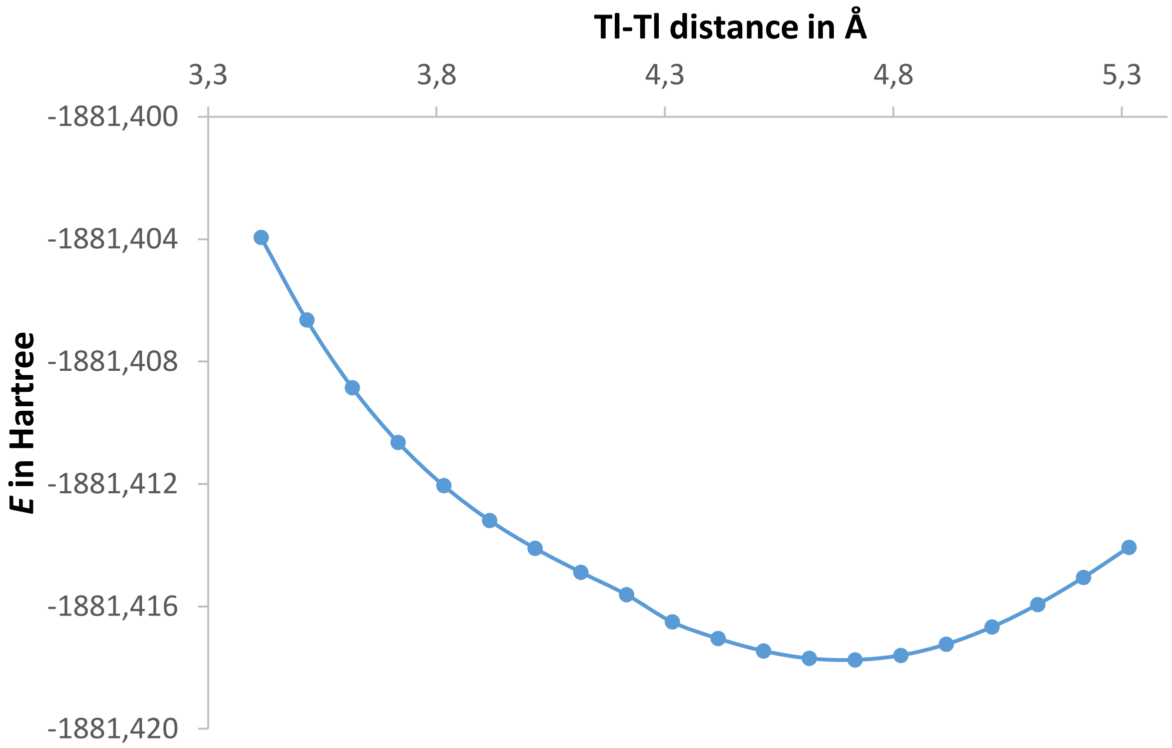

Figure S32. Energy scan (B3LYP-D3/LANL2DZ) of **IIIb** with respect to the thallium-thallium distance.

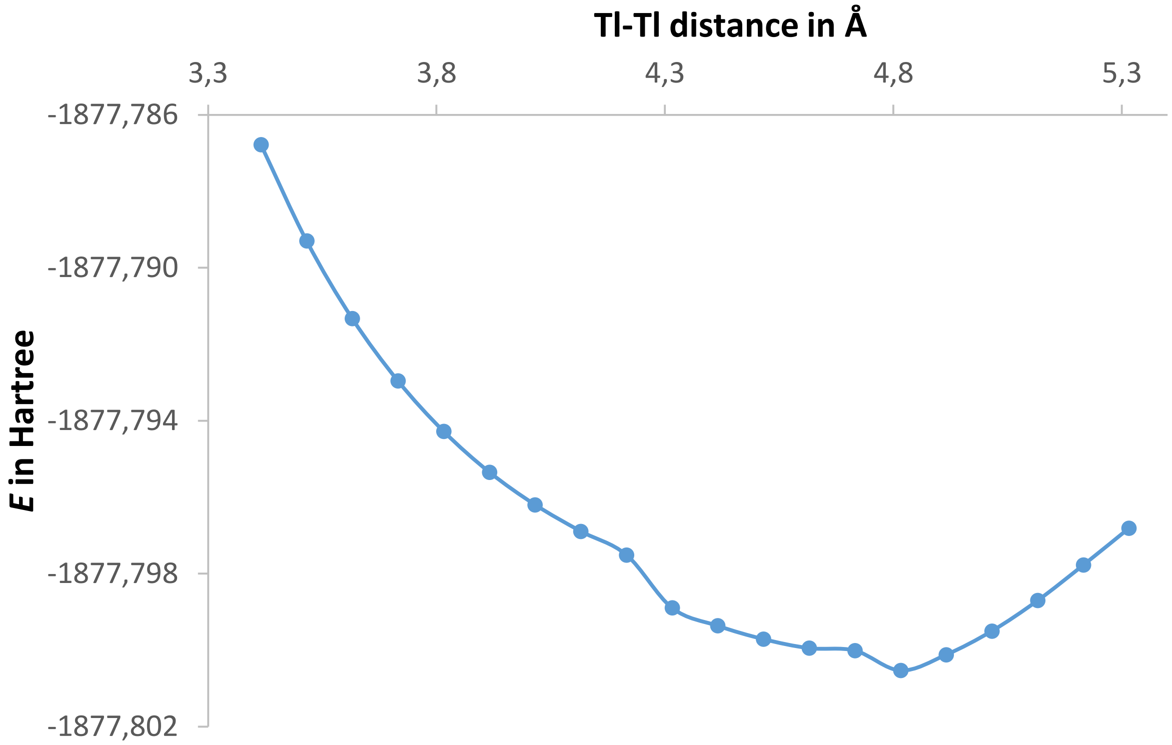

Figure S33. Energy scan (B3LYP-D3/LANL2DZ) of **IIIc** with respect to the thallium-thallium distance.

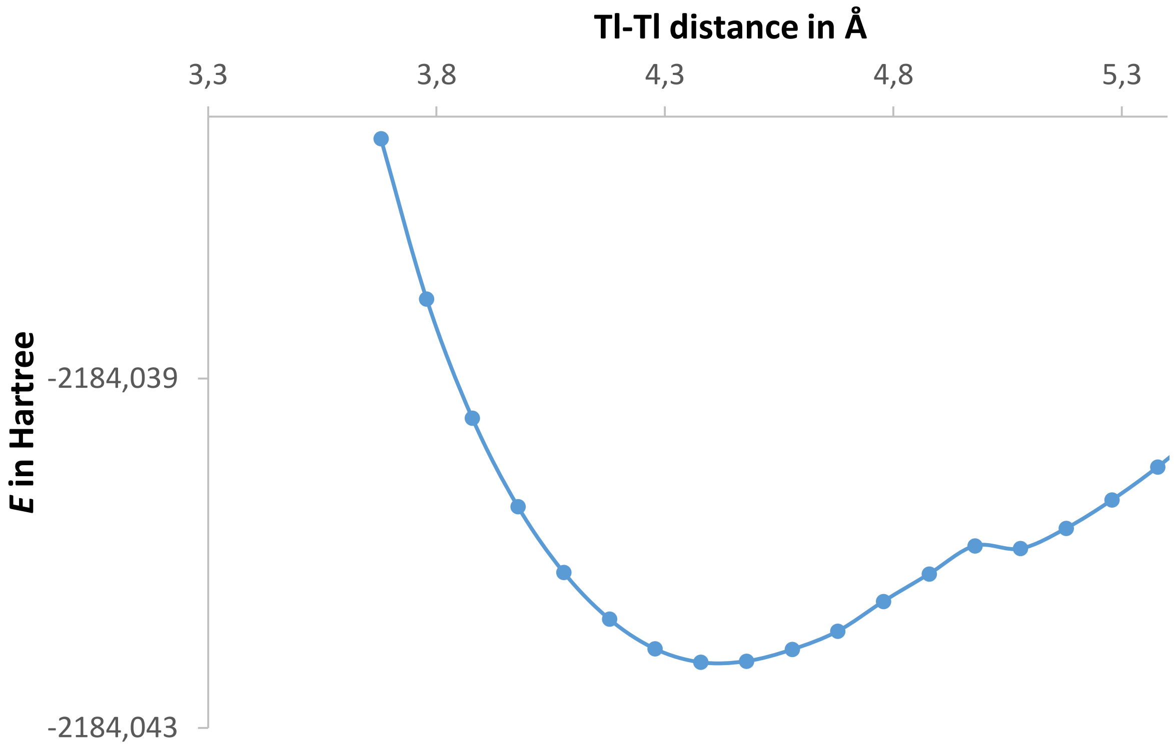

Figure S34. Energy scan (B3LYP-D3/LANL2DZ) of **IIIg** with respect to the thallium-thallium distance.

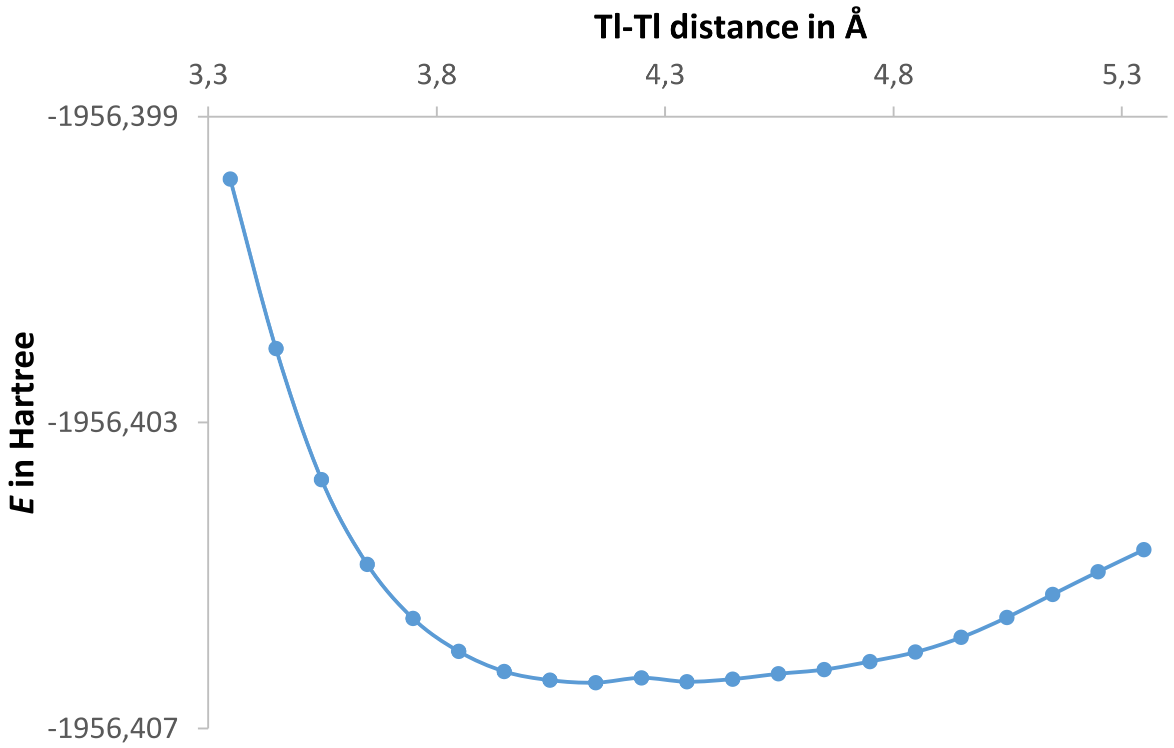

Figure S35. Energy scan (B3LYP-D3/LANL2DZ) of **IIIh** with respect to the thallium-thallium distance.

The coordinates of the geometry-optimized structures are given in the following:

IIIb

Tl	2.63253700	1.18572400	-0.85352800
Tl	-1.47223200	-0.04946500	1.04488100
N	-0.87468000	1.51273800	-0.88912200
N	1.26891200	1.82592500	1.15456100
N	3.06965400	-0.64409300	0.71522700
N	-3.02774800	-0.68950800	-0.76795700
C	1.42814700	1.39369900	2.42298200
C	2.20079100	0.26295300	2.81717700
H	2.20053600	0.06682100	3.88411700
C	-0.31655000	2.84542600	-0.54192600
H	0.48207000	3.14057300	-1.24445100
C	-1.82679300	0.15628300	-2.72139800
H	-1.75963500	0.02492400	-3.79614400
C	3.64082300	-1.74902100	-0.01087700
C	2.86522400	-0.72032000	2.04360000
C	-1.02347300	1.21185600	-2.19782400
C	-0.33240200	2.05841800	-3.28339300
H	-0.73567400	3.07779600	-3.32142800
H	-0.47706600	1.60721000	-4.26794200
H	0.74898900	2.13978300	-3.10909200
C	-2.84791600	-0.60324000	-2.09934400
C	2.77560600	-2.73511900	-0.56564700
C	-5.35182900	-0.18296900	-0.13372800
C	-1.42175100	3.93653700	-0.64062100
H	-1.91811500	3.86694100	-1.61653200
H	-2.19104100	3.71976900	0.11591600
C	4.70388500	-3.77326400	-1.66390200
H	5.11266200	-4.55040500	-2.30548700
C	-3.84090100	-1.30777700	-3.02506200
H	-4.05292400	-2.32452200	-2.67474000
H	-3.46373100	-1.35340700	-4.05096700
H	-4.79733400	-0.76748300	-3.03437000
C	0.67524300	2.06492200	3.58433000
H	0.75158800	3.15641500	3.56043300
H	1.06886800	1.71871000	4.54325200
H	-0.39349500	1.80572700	3.55582000
C	-4.44166300	-2.44151400	0.29610600
C	-4.28696000	-1.12996100	-0.23123900
C	5.54977200	-2.80261400	-1.10415700
H	6.61656600	-2.83633700	-1.31525200
C	5.03945200	-1.78323800	-0.27385200
C	1.26735800	-2.69498900	-0.30982800
H	1.08008100	-1.97237900	0.49301600
C	3.32588800	-3.73402200	-1.39318600
H	2.67296700	-4.48579200	-1.83095900
C	0.30186500	2.92115700	0.88698700
H	-0.54296200	2.88123200	1.59624900
C	7.09894600	-1.37307400	1.17535100
H	6.67425500	-1.99054900	1.97688300
H	7.72295500	-0.59537300	1.63580000
H	7.75343800	-2.01453500	0.57090200
C	-5.16664400	1.26291000	-0.60650600
H	-4.25394900	1.31838800	-1.20664500
C	-5.67242900	-2.79697800	0.88823500
H	-5.80267700	-3.80140100	1.28573800
C	-4.96166100	2.19966100	0.61380400
H	-5.85013000	2.20217100	1.25943900
H	-4.76969700	3.23001100	0.28412000
H	-4.10819600	1.87092900	1.22244200
C	-3.30659300	-3.46593300	0.24482800
H	-2.44609000	-2.99064600	-0.24053800
C	5.98464000	-0.73091800	0.30991600
H	5.39763800	-0.07277100	0.96024300
C	-0.84298100	5.35272300	-0.43101500
H	-0.15103200	5.58350500	-1.25656500

IIIc

Tl	2.11661800	-0.76988700	1.15501500
Tl	-2.11623800	-0.76995000	-1.15500600
N	-1.09298700	-1.84131300	0.90714100
N	1.09320100	-1.84129900	-0.90677100
N	2.94329200	0.62087500	-0.72750900
N	-2.94375700	0.62058200	0.72737400
C	1.17893900	-1.49025600	-2.20867900
C	1.81720700	-0.31645700	-2.69200800
H	1.70084300	-0.15259000	-3.75903800
C	-1.81772300	-0.31643700	2.69208600
H	-1.70156700	-0.15249200	3.75912600
C	3.92972500	1.51581300	-0.17838700
C	2.64885400	0.63115900	-2.03872200
C	-1.17900200	-1.49007400	2.20896500
C	-0.52910700	-2.35286700	3.30207400
H	-1.26670900	-3.03576800	3.74348900
H	-0.14555700	-1.71448500	4.10488200
H	0.29305100	-2.96337800	2.91767300
C	-2.64947200	0.63096900	2.03863700
C	3.53825100	2.76504000	0.37910200
C	-5.28115400	1.07197800	0.07662900
C	5.83877400	3.11996000	1.14715800
H	6.57219700	3.73648500	1.66143400
C	-3.26852800	1.71949000	2.91797900
H	-2.99707000	2.71456800	2.54380800
H	-2.93925400	1.63327600	3.95687400
H	-4.36378600	1.65975700	2.89017400
C	0.52933700	-2.35354900	-3.30154100
H	1.26705200	-3.03672300	-3.74236300
H	0.14607000	-1.71560100	-4.10482300
H	-0.29295300	-2.96384200	-2.91707300
C	-3.53880900	2.76507700	-0.37863300
C	-3.93015200	1.51550300	0.17815500
C	6.21817600	1.89024000	0.58551500
H	7.25151100	1.55972000	0.66747100
C	5.28088100	1.07259800	-0.07754400
C	2.09208500	3.25622100	0.28886800
H	1.54395000	2.58167100	-0.37918000
C	4.50526400	3.54715600	1.04337900
H	4.21364700	4.49876900	1.48197100
C	6.83555700	-0.11145900	-1.71471700
H	6.50942000	0.54839900	-2.52871900
H	7.10057000	-1.08535200	-2.14778000
H	7.74474200	0.32085800	-1.27657300
C	-5.72094600	-0.27783500	0.64913200
H	-4.85749500	-0.73743800	1.14115900
C	-4.50584100	3.54733100	-1.04271300
H	-4.21433800	4.49922900	-1.48075800
C	-6.18198300	-1.23763800	-0.47872200
H	-7.06155500	-0.83917800	-1.00119700
H	-6.44717500	-2.22055100	-0.06647100
H	-5.39024800	-1.38072300	-1.22669700
C	-2.09269300	3.25633000	-0.28814400
H	-1.54454600	2.58169200	0.37981000
C	5.72086100	-0.27683900	-0.65079100
H	4.85757900	-0.73618400	-1.14335400
C	3.26792500	1.71952100	-2.91822700
H	2.99934500	2.71471800	-2.54237400
H	2.93621600	1.63503100	-3.95649200
H	4.36314000	1.65752300	-2.89296100
C	-5.83923700	3.11989500	-1.14703700
H	-6.57268000	3.73655300	-1.66112500
C	-6.21848300	1.88975400	-0.58621600
H	-7.25171400	1.55902000	-0.66862600
C	-1.40187400	3.19646400	-1.67625400

H	-1.64805700	6.09967800	-0.47015900
C	3.35309200	-1.96528900	2.78596900
H	2.80488300	-2.85052000	2.43706000
H	3.20758600	-1.87119300	3.86548100
H	4.41459500	-2.15135200	2.58435300
C	-0.08202400	5.45294700	0.91022900
H	-0.80118400	5.37766700	1.74126300
H	0.40860100	6.43211700	0.99932100
C	-6.73079900	-1.87996100	0.97156200
H	-7.67317400	-2.17133500	1.42948700
C	0.96081300	4.32125500	1.04369300
H	1.73840700	4.43112200	0.27156400
H	1.47269900	4.38378300	2.01135100
C	-6.56137600	-0.57815600	0.46926800
H	-7.37717100	0.13639400	0.55205800
C	-2.88159100	-3.89536600	1.67319200
H	-2.53876000	-3.03327600	2.26003700
H	-2.06897400	-4.63244800	1.63539200
H	-3.72146800	-4.35186800	2.21225300
C	-6.33646200	1.76093000	-1.48858200
H	-6.48895000	1.09837400	-2.35033900
H	-6.12483600	2.77080000	-1.86503300
H	-7.27949000	1.80676800	-0.92848000
C	6.60647100	0.14435700	-0.80943900
H	7.21787900	-0.46370400	-1.48917700
H	7.24923100	0.92473300	-0.37969700
H	5.82806200	0.63144800	-1.41160200
C	0.71174700	-4.06213000	0.15478100
H	0.80416700	-4.82394700	-0.62998300
H	-0.35140500	-3.96990200	0.40214400
H	1.24364800	-4.42648700	1.04313600
C	0.51055100	-2.19895300	-1.56778300
H	0.82219600	-1.18756700	-1.85674300
H	-0.57259100	-2.16687500	-1.39899700
H	0.70107300	-2.86280900	-2.42121200
C	-3.68818900	-4.70664100	-0.60267500
H	-4.52974900	-5.24901600	-0.15224700
H	-2.83806600	-5.39862900	-0.67375000
H	-3.98163300	-4.41725200	-1.61950400
H	-1.42387000	2.17850800	-2.08782700
H	-0.35269900	3.50813200	-1.60707600
H	-1.90986000	3.85503200	-2.39307000
C	-6.83527700	-0.11308400	1.71353900
H	-6.50871400	0.54605700	2.52795400
H	-7.10034200	-1.08726100	2.14593100
H	-7.74450900	0.31977200	1.27602300
C	6.18155400	-1.23734300	0.47661600
H	7.06091700	-0.83915200	0.99964900
H	6.44693900	-2.21998300	0.06383900
H	5.38957100	-1.38095400	1.22422900
C	2.01634600	4.68510800	-0.30565500
H	2.49729300	5.41915200	0.35314300
H	0.97424400	4.99677500	-0.44111800
H	2.51763900	4.73341900	-1.28084400
C	1.40129800	3.19614100	1.67696800
H	1.42315400	2.17808300	2.08830300
H	0.35216000	3.50795400	1.60786700
H	1.90935400	3.85448000	2.39394100
C	-2.01694800	4.68512700	0.30657200
H	-2.49782300	5.41928900	-0.35214300
H	-0.97483500	4.99671800	0.44211900
H	-2.51828700	4.73333800	1.28174200
C	0.51878100	-3.08645800	-0.49469900
C	-0.51831500	-3.08642300	0.49534300
C	1.03428500	-4.32715100	-0.94060800
H	1.85361400	-4.31710900	-1.65501800
C	0.52450400	-5.54813700	-0.47066600
H	0.93959600	-6.48536000	-0.83327600
C	-0.52350800	-5.54813000	0.47182500
H	-0.93840900	-6.48535600	0.83464900
C	-1.03354600	-4.32715800	0.94150100
H	-1.85287500	-4.31713400	1.65591900

IIId

Tl	-3.88683600	-1.09924200	0.91263000
Tl	3.39229100	-0.48234200	-1.03082800
N	2.37828100	-1.37373900	1.06335500
N	-4.68230100	0.56690100	-0.73123100
N	4.95422300	0.22996900	0.74692600
N	-2.13935800	-1.10722300	-0.84864800
C	1.17475400	-2.04825700	0.68098900
C	5.98270100	1.02972000	0.12753200
C	-1.04303700	-1.90327000	-0.38016500
C	2.79612200	-1.34972700	2.34501600
C	-1.15007400	-3.31221700	-0.33810600
H	-2.04033800	-3.78840600	-0.74101300
C	5.76508400	2.42508200	-0.05766200
C	3.98812800	-0.72232500	2.79172000
H	4.16428800	-0.79225600	3.86002600
C	7.14997700	0.40472300	-0.39641400
C	-7.14254800	0.59623400	-0.41382700
C	0.11365500	-1.28586600	0.14529600
H	0.18067200	-0.20047000	0.15257600
C	-5.86640100	1.18549900	-0.18782900
C	-7.30187100	-0.63511000	-1.30905700
H	-6.33039200	-0.84988500	-1.76735900
C	-4.20802800	0.94504500	-1.93337900
C	-0.09535000	-4.07796000	0.19684300

IIIe

Tl	-4.13346500	-0.00791000	-1.08553200
N	-5.75070300	0.00834500	0.78174300
N	-2.69837300	-0.04816300	0.94780800
C	-0.55933200	1.15932500	0.55908400
H	-1.00196600	2.05989600	0.97870100
C	-7.69535100	1.24799800	-0.12816400
C	-3.00872800	-0.03354600	2.26054700
C	-7.01616300	2.58623200	0.17214800
H	-6.10656200	2.38407500	0.74801200
C	-1.87644500	-0.06494800	3.29224500
H	-1.16329700	-0.86498300	3.05771700
H	-2.26677900	-0.22392900	4.30111300
H	-1.31188400	0.87574400	3.28515300
C	-7.70983900	-1.22459900	-0.10155200
C	-1.32800200	-0.02711300	0.52334800
C	-4.32893600	-0.00993600	2.78142100
H	-4.38891600	-0.01371300	3.86460900
C	-7.04338300	-2.56342800	0.22403000
H	-6.13715100	-2.36047100	0.80474200
C	-6.82653600	0.02888200	3.01021900
H	-7.44200500	0.91103300	2.79479500
H	-6.55963200	0.03757800	4.07022100
H	-7.45416000	-0.84896100	2.81262100
C	0.74949700	1.18420700	0.04959800

H	-0.17465600	-5.16292400	0.21214400	**H**	1.33349100	2.10168600	0.07439300
C	-3.02380800	0.44274700	-2.53278900	**C**	-7.91476300	3.51700600	1.02474500
H	-2.80653700	0.84291200	-3.51746400	**H**	-8.82260300	3.80735300	0.47983900
C	-2.05434900	-0.46350900	-2.03178000	**H**	-7.37362900	4.43598100	1.28715000
C	8.08204600	1.19029400	-1.10463400	**H**	-8.22563400	3.02468300	1.95486900
H	8.97403500	0.72147200	-1.51450100	**C**	-7.95530500	-3.47718600	1.08044200
C	4.97268000	0.00632700	2.07499100	**H**	-8.27210600	-2.96994300	2.00050000
C	1.06479600	-3.46089000	0.69479000	**H**	-7.42161500	-4.39511900	1.36100000
H	1.88971500	-4.05529700	1.07853300	**H**	-8.85957900	-3.77070800	0.53134300
C	7.87737200	2.56705300	-1.29155200	**C**	-5.58324700	0.01037900	2.11836900
H	8.60650400	3.15866300	-1.84009600	**C**	-8.95883600	-1.20178500	-0.75481300
C	4.50511900	3.11017700	0.47767300	**H**	-9.44928400	-2.14045200	-1.00360200
H	3.93485200	2.37231300	1.05218500	**C**	-8.94469000	1.22549100	-0.78116600
C	-0.83607800	-0.71198300	-2.92729600	**H**	-9.42439200	2.16419200	-1.04998800
H	0.06217400	-0.24120600	-2.50712300	**C**	-9.57949000	0.01207500	-1.09149100
H	-0.99618200	-0.30716300	-3.93028600	**H**	-10.54350200	0.01223500	-1.59473900
H	-0.62444000	-1.78535400	-3.00654700	**C**	-7.07714100	0.01174800	0.21455200
C	-5.73417400	2.31652500	0.66794500	**C**	-6.61181900	-3.29081700	-1.07668000
C	6.72336600	3.17422500	-0.77042500	**H**	-7.48349700	-3.52558900	-1.70170400
H	6.56480700	4.24004600	-0.92047400	**H**	-6.09511300	-4.23160000	-0.84330400
C	-6.88748000	2.84000800	1.28681000	**H**	-5.93571800	-2.66557400	-1.67605900
H	-6.79603900	3.70128400	1.94520900	**C**	-6.59190300	3.29458400	-1.14128300
C	-4.36635600	2.94385700	0.94800800	**H**	-5.92448400	2.65848400	-1.73872300
H	-3.62646800	2.44430900	0.31370900	**H**	-6.06793900	4.23522100	-0.92413600
C	-8.27023900	1.15056100	0.22551800	**H**	-7.46764500	3.52673100	-1.76151800
H	-9.24934400	0.70517100	0.06271400	**Tl**	4.13347100	0.00776100	1.08554000
C	6.12680200	0.58362400	2.89711000	**N**	5.75069800	-0.00833400	-0.78174300
H	7.08777100	0.19808400	2.53470000	**N**	2.69835600	0.04794500	-0.94779000
H	6.02710100	0.33599900	3.95720100	**C**	0.55932100	-1.15956400	-0.55904700
H	6.16561300	1.67508400	2.79279500	**H**	1.00195600	-2.06013600	-0.97866200
C	-4.97904800	2.00222400	-2.72603600	**C**	7.69548400	-1.24778300	0.12817700
H	-6.01092600	1.67596500	-2.90392700	**C**	3.00870900	0.03336500	-2.26053200
H	-4.50374500	2.20632000	-3.68910100	**C**	7.01646200	-2.58610400	-0.17212800
H	-5.03842200	2.93942500	-2.15836400	**H**	6.10683400	-2.38406600	-0.74799000
C	-8.15079300	2.26651300	1.06945900	**C**	1.87643000	0.06478600	-3.29223400
H	-9.03083900	2.68166300	1.55497400	**H**	1.16322800	0.86475400	-3.05764300
C	7.38621900	-1.09856500	-0.23308500	**H**	2.26676200	0.22387900	-4.30108500
H	6.60963500	-1.49509500	0.42969200	**H**	1.31193000	-0.87594400	-3.28523100
C	-7.70999400	-1.87649600	-0.47313600	**C**	7.70970200	1.22481500	0.10152800
H	-6.97725400	-2.08107700	0.31941100	**C**	1.32799000	0.02687800	-0.52331900
H	-7.78447300	-2.76708700	-1.11169400	**C**	4.32891600	0.00987200	-2.78141200
H	-8.68358300	-1.72080700	0.01002600	**H**	4.38889100	0.01371200	-3.86459900
C	3.60311000	3.59714300	-0.68663800	**C**	7.04309000	2.56356000	-0.22407900
H	4.12006600	4.35045200	-1.29550300	**H**	6.13686300	2.36047900	-0.80475800
H	2.67858800	4.04669500	-0.29998200	**C**	6.82651800	-0.02869700	-3.01022600
H	3.32965400	2.76705900	-1.35271000	**H**	7.44209200	-0.91078100	-2.79482900
C	1.93515400	-2.00613000	3.42932300	**H**	6.55960800	-0.03739800	-4.07022700
H	2.24660300	-1.68083900	4.42580200	**H**	7.45404100	0.84921400	-2.81261100
H	2.01399400	-3.09958500	3.38648000	**C**	-0.74950700	-1.18444600	-0.04955800
H	0.87647200	-1.75641300	3.28990400	**H**	-1.33350300	-2.10192400	-0.07435500
C	-8.31928100	-0.39410600	-2.45292100	**C**	7.91518500	-3.51675900	-1.02472700
H	-9.32938400	-0.21972100	-2.05989200	**H**	8.82307500	-3.80696300	-0.47982800
H	-8.36404200	-1.26843500	-3.11605300	**H**	7.37418200	-4.43581700	-1.28711300
H	-8.04051600	0.47927200	-3.05614100	**H**	8.22597200	-3.02440400	-1.95486200
C	4.84435800	4.28420900	1.43027900	**C**	7.95488400	3.47738900	-1.08055000
H	5.47234900	3.94703000	2.26467800	**H**	8.27171100	2.97014900	-2.00060000
H	3.92491200	4.71795400	1.84588100	**H**	7.42108500	4.39525500	-1.36112200
H	5.38475500	5.08287600	0.90562600	**H**	8.85914400	3.77102900	-0.53149100
C	-3.94752900	2.71422300	2.42378100	**C**	5.58323400	-0.01035700	-2.11836800
H	-4.65178300	3.20001900	3.11189700	**C**	8.95870200	1.20214900	0.75478600
H	-2.94654200	3.12529800	2.61243000	**H**	9.44904800	2.14087500	1.00356000
H	-3.93177100	1.64352800	2.66988400	**C**	8.94482100	-1.22512800	0.78117800
C	7.25430400	-1.82603800	-1.59698500	**H**	9.42462700	-2.16377200	1.05001200
H	6.27007000	-1.64696600	-2.05097000	**C**	9.57948800	-0.01163700	1.09148500
H	7.38416700	-2.90979200	-1.47434200	**H**	10.54350000	-0.01168400	1.59473200
H	8.01361700	-1.46844500	-2.30490100	**C**	7.07713900	-0.01160400	-0.21455700
C	-4.33696200	4.45402200	0.60224900	**C**	6.61147900	3.29094200	1.07661900
H	-4.62269900	4.62613100	-0.44334000	**H**	7.48314800	3.52584100	1.70160700
H	-3.32854300	4.86160700	0.75406900	**H**	6.09465200	4.23165400	0.84322500

H	-5.02794000	5.02469900	1.23642600
C	8.75964600	-1.40834700	0.41381100
H	9.58852000	-1.08862800	-0.23109600
H	8.86662800	-2.48793600	0.58456400
H	8.86959900	-0.89596800	1.37799800

H	5.93547300	2.66563800	1.67604000
C	6.59230200	-3.29451600	1.14130100
H	5.92480800	-2.65850500	1.73875200
H	6.06845200	-4.23521700	0.92415100
H	7.46807700	-3.52656300	1.76152700

IIIf

Tl	-3.32309900	-1.41022300	0.71060200
Tl	1.54207800	-0.13320100	0.41277400
N	2.62329100	-2.52787700	0.53449300
N	-3.19918200	0.62124800	-0.71104500
N	4.08039400	0.07420600	0.11029500
N	-1.65403100	-2.00310700	-1.06047900
C	1.45374300	-3.26838400	0.36938200
C	4.26496300	1.41272300	-0.37711400
C	-0.75501800	-2.94888900	-0.51110700
C	3.88365000	-2.97760300	0.72989200
C	-1.16838200	-4.23109000	-0.07582000
H	-2.17335400	-4.58223100	-0.28454700
C	4.43571300	2.50149200	0.52567400
C	5.00329700	-2.11764900	0.71828500
H	5.95499300	-2.60400700	0.90859600
C	4.11321900	1.65200000	-1.77449100
C	-5.23373400	1.93315700	-0.15490700
C	-3.83763600	1.70388600	-0.00230000
C	-6.07504800	1.08765900	-1.11380100
H	-5.39385400	0.46391200	-1.70304800
C	-2.64864900	0.83185700	-1.91649900
C	-0.22497700	-5.02142500	0.60953200
H	-0.51228600	-6.00769500	0.96808500
C	-1.86579600	-0.12077600	-2.62896700
H	-1.54775600	0.20239500	-3.61484000
C	-1.32098600	-1.35227300	-2.20528000
C	4.17460000	2.97722400	-2.25020100
H	4.06783700	3.16654800	-3.31628800
C	5.11184300	-0.73381900	0.36425000
C	1.08221700	-4.56149700	0.84851200
H	1.76995200	-5.17173500	1.41600600
C	4.36558000	4.05519600	-1.37054100
H	4.41024200	5.07257100	-1.75198900
C	4.50789800	2.27893100	2.03850400
H	4.54800600	1.19980600	2.22397600
C	-0.27809200	-1.97791100	-3.13637900
H	0.73347600	-1.76076100	-2.77805700
H	-0.37896500	-1.58195800	-4.15160200
H	-0.38527800	-3.06880600	-3.16653400
C	-3.07361800	2.46328000	0.92966600
C	4.48419700	3.81149400	0.00759100
H	4.61278200	4.64946000	0.68941000
C	-3.72323700	3.46191200	1.68361900
H	-3.14822500	4.05261000	2.39361500
C	-1.58071600	2.19744300	1.13854300
H	-1.27977700	1.39919900	0.45196500
C	-5.84514300	2.93512500	0.62566700
H	-6.91246300	3.11765300	0.52160300
C	6.53477000	-0.18213300	0.23056600
H	6.69394500	0.21679300	-0.77953700
H	7.28737900	-0.95033800	0.42711500
H	6.69194700	0.64986700	0.92729600
C	-2.82454200	2.19831900	-2.58071800
H	-3.88766000	2.44498700	-2.68673800
H	-2.35500700	2.22689700	-3.56730300
H	-2.37859900	2.98448300	-1.95863300
C	-5.09872200	3.70296200	1.53478400
H	-5.58510200	4.47598800	2.12502400
C	3.86611300	0.49863500	-2.75064400
H	3.83521700	-0.43194500	-2.17381400

IIIg

Tl	-1.14182700	-0.35407200	-0.60866000
Tl	2.94214400	1.35779800	-0.36770800
O	0.17917500	2.71327900	-0.61620300
N	-3.40032000	-0.81971600	0.80276900
N	2.94518100	-1.03974300	0.41609900
N	-2.46293400	1.95452500	-0.08288300
N	1.20694600	1.23863100	1.49322100
C	3.91197600	-1.74861900	-0.38456800
C	1.24064700	-1.11267300	2.17815500
H	0.76600300	-1.80412800	2.86718000
C	2.28883400	-1.67693600	1.39956600
C	-3.78527300	-4.53851100	0.39766700
H	-3.28120000	-5.45766200	0.68861400
C	-4.98786300	-0.69393100	2.70434700
H	-5.97527000	-0.78100900	2.23091900
H	-5.09988300	-0.08698900	3.60825200
H	-4.67772900	-1.70566200	2.98758900
C	-3.26490900	-3.29805200	0.82541500
C	-3.94121400	-2.10203900	0.45843900
C	-4.94348600	-4.60556500	-0.38802800
H	-5.33599800	-5.56839000	-0.70689600
C	0.73135200	0.21042300	2.23112100
C	2.66109900	-3.12880600	1.70756500
H	2.41556100	-3.78333700	0.86220900
H	2.14398100	-3.49515900	2.59818400
H	3.74141800	-3.21540100	1.87013700
C	-0.85497300	3.15018700	-1.49066300
C	-3.98108800	-0.05693400	1.73851400
C	0.76568200	2.57261700	1.72756800
C	-5.59577700	-3.41724800	-0.76606900
H	-6.48770100	-3.48044200	-1.38216300
C	-3.79627500	1.34967100	1.87907800
H	-4.29815300	1.79185900	2.73417100
C	3.47341900	-2.46699000	-1.53481600
C	5.80933100	-2.95476700	-2.09079300
H	6.54038800	-3.41752700	-2.74944200
C	5.29950200	-1.63997500	-0.08612800
C	0.26434600	3.34982700	0.65341000
C	-0.51072700	3.84727100	-2.65296500
H	0.53772500	4.05676100	-2.84721600
C	-0.07374300	4.70221400	0.81253600
H	-0.45181700	5.26212800	-0.03748700
C	-3.25237700	2.27932700	0.95799300
C	6.23065800	-2.25000500	-0.95245900
H	7.29346600	-2.17366700	-0.73255300
C	-2.19881700	2.82812000	-1.15817500
C	-0.47280500	0.41962900	3.15742600
H	-0.17515000	0.85979300	4.11626800
H	-0.96396300	-0.53552800	3.36483200
H	-1.21326700	1.08776900	2.70367900
C	-5.11543200	-2.15778000	-0.36104800
C	-3.60887100	3.75141800	1.19215200
H	-2.73795900	4.39367000	1.02539800
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Preface

The following chapter has not been published until the submission of this thesis.

Authors

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Author contributions

The preparation of the manuscript was done by the first author (M. E. Desat). R. Kretschmer supervised the research and revised the manuscript. Preparation and single crystal X-Ray diffraction measurement of compound **IV** and **V** have been part of the first author's master thesis. Among them, the first author provides additional the characterisation (NMR, EA) of **IV** and **V**. A synthetic approach to **VI** as well as the complete characterization (NMR, EA, X-Ray) was done by the first author. Additionally, the calculation of all X-Ray structures herein was performed by the first author as well as the interpretation of the analytic data of the compounds. R. Kretschmer performed all DFT calculations and contributed the corresponding parts in the manuscript and the Supporting Information.

Acknowledgements

The project was financially supported by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft (DFG, KR4782/2-1 and KR4782/3-1), the University of Regensburg and the Friedrich-Schiller-Universität Jena. M. E. Desat is grateful to the Stiftung Stipendien-Fonds des Verbands der Chemischen Industrie for a PhD fellowship. Additionally, generous support from Professor Manfred Scheer is gratefully acknowledged and we thank Dr. Stefanie Gärtner, Dr. Helmar Görls, and Dr. Philipp Klahn for helpful discussions.

5 Facile Oxidative Addition of O_2 and S_8 by an Indium Bis(carbene) Analogue

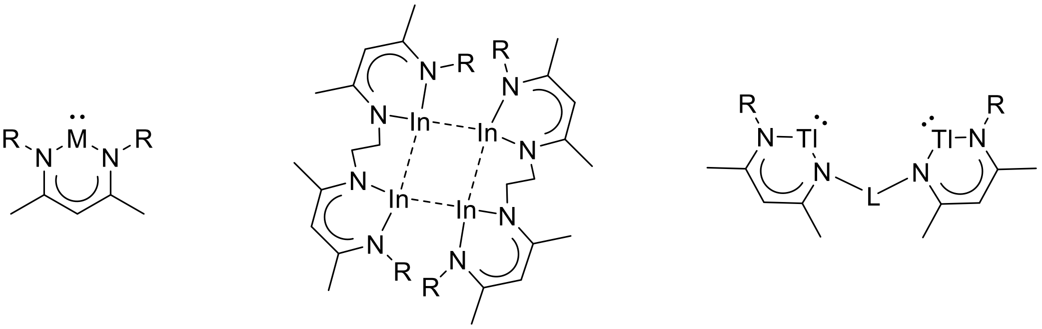
Abstract: *The oxidative addition of oxygen towards an indium bis(carbenoid) yields an almost planar In_4O_2 ring, an isovalence-electronic analogue of dioxane, in which the indium is in the formal oxidation state +II. The weaker oxidant sulfur, however, yields an eight-membered ring in a deck-chair conformation containing four indium(III) centres and four sulfides in an alternating fashion. According to DFT calculations, this reactivity difference originates from kinetic rather than thermodynamic reasons. When the reaction with S_8 is performed with the in situ generated bis(carbenoid), a novel β-diketimine (NacNac) incorporating an S_4-chain bridging the two γ-carbon atoms of each NacNac unit is derived.*

5.1 Introduction

For decades, oxidative addition reactions, which are key to many important catalytic transformations, have been believed to be limited to transition metals. In recent years, however, it was shown that low and subvalent species of the p-block elements readily oxidatively add small molecules, such as molecular hydrogen or ethylene, under mild conditions as they possess both, energetically close frontier orbitals and vacant coordination sites, thus mimicking the characteristics of transition-metal complexes.[1] Besides multiple-bonded unsaturated main group compounds,[2] carbenes[3] and their heavier Group 13 and 14 relatives[4] attracted particular attention as valuable reagents for the activation of small molecules, and belong, together with frustrated Lewis-pairs (FLPs),[5] to the most promising candidates for substituting transition-metal catalysts.

While carbenes, silylenes, and germylenes have been stabilized by various ligands, only the β-diketiminate (NacNac) ligand allowed for the isolation of carbenoids (**I**) of all four heavier triels, i.e., Al,[6] Ga,[7] In,[8] and Tl,[8b,9] Figure 1. Soon after their first isolation, the capability to oxidatively add small molecules such as N_2O and S_8 has been documented,[10] and reports on various oxidative addition reactions of the alanediyl **Ia** (M = Al),[11] the gallanadiyl **Ib** (M = Ga)[10,11d,11e,12] and the indanediyl **Ic** (M = In)[11d,11e,13] are found in the literature. The reactivity decrease in the order **Ia** > **Ib** > **Ic** is readily explained by DFT calculations, according to which, the oxidative addition of H–X σ-bonds becomes kinetically more demanding and less exothermic in going from aluminium to indium.[14] Following our recent reports on the heavier

Group 13 analogues (**II** and **III**) of bis(carbene)s,[15] Figure 1, we became interested in their capability to oxidative addition reactions.



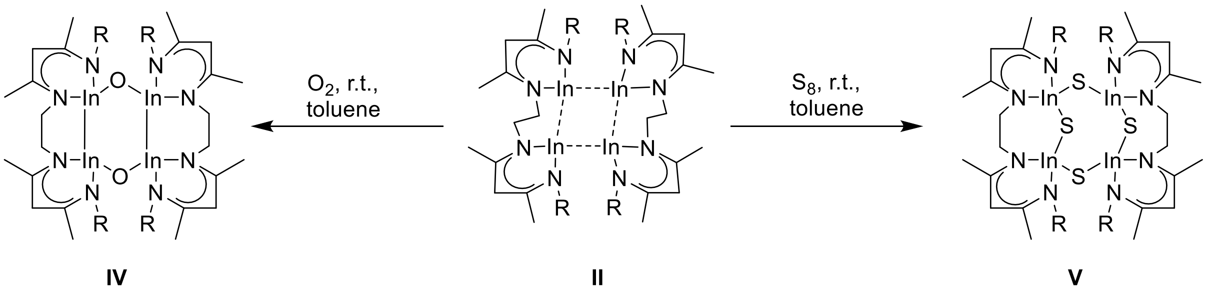
I **II** **III**

M = Al (**a**), Ga (**b**), In (**c**), Tl (**d**)

Figure 1. Mono- (**I**) and dinuclear (**II**, **III**) Group 13 diyls. R = aryl group, mostly 2,6-Diisopropylphenyl.

5.2 Results and Discussion

The reaction of a freshly-prepared toluene solution of the four-membered indium metallacycle **II** with a stream of dry oxygen or with sulfur, Scheme 1, proceeds smoothly at room temperature as indicated by an immediate color change from red to orange. After workup, we were able to isolate crystals of **IV** and **V**, respectively, suitable for an X-ray diffraction study, from a concentrated toluene solution at room temperature; noteworthy, in case of **V**, the addition of a few drops of THF was inevitable.



IV **II** **V**

Scheme 1. Reaction of the indium bis(carbenoid) **II** with oxygen and sulfur at room temperature.

The molecular structures of **IV** and **V**, are shown in Figure 2 and 4, respectively. Although, all manipulations have been performed under the strict exclusion of light, moisture and air, solutions of **IV** were always obtained as a mixture with the starting material, the respective protio-ligand and yet unidentified amorphous side products most likely as a result of the photoand thermo-lability of solutions of **II** or **IV** itself. While this unfortunately hampers the complete characterization and to obtain mechanistic insight (see SI), the reproducible synthesis of **IV** was unambiguously checked by repeated experiments and elemental and XRD analysis of the thus obtained crystals. Fortunately, compound **V** could be isolated in 52 % yield and the ^{1}H NMR spectrum reveals two groups of septets (3.54, 3.61 ppm) and two groups of doublets (1.17, 1.39, 1.46-1.49 ppm) along with a multiplet for the respective isopropyl methine and methyl proton resonances of the 2,6-diisopropylphenyl substituents, evidencing their asymmetric steric environment.

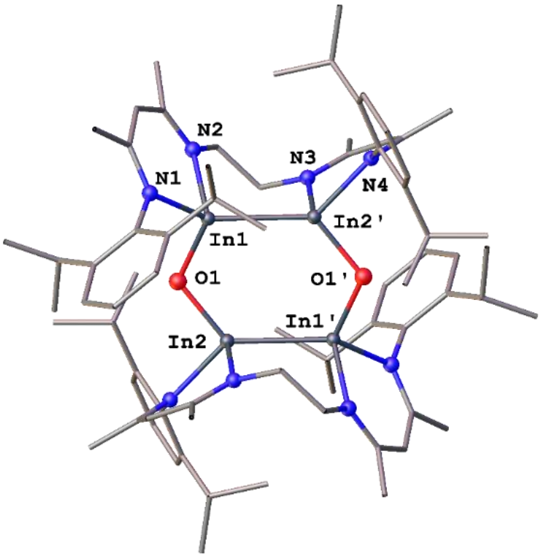
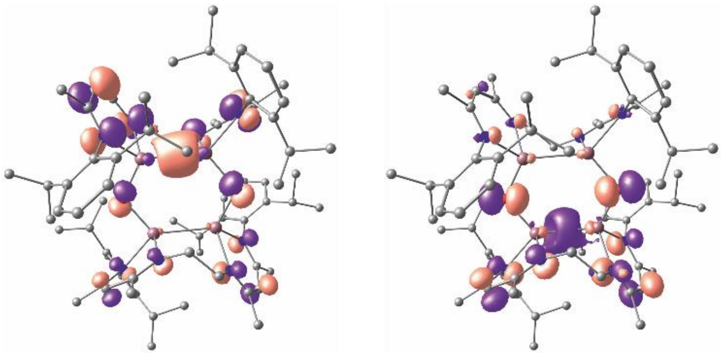


Figure 2. Solid-state structure of **IV** (hydrogen atoms and a co-crystallized second component are omitted for the sake of clarity).Selected bond lengths [Å] and angles [°] with calculated values (M06-GD3/def2-SVP) in square brackets: In1–In2' 2.7136(3) [2.743], In1–O1 2.003(2) [2.038], In2–O1 2.008(1) [2.024], In1–N1 2.140(2) [2.182], In1–N2 2.204(2) [2.243], In2'–N3 2.206(2) [2.233], In2'–N4 2.162(2) [2.162], In1–O1–In2 116.43(7) [112.82], N1–In1–N2 90.71(6) [87.58], N3–In2'–N4 88.30(6) [90.67].

As shown in Figure 2, **IV** contains an almost planar In_4O_2 six-membered ring, in which the oxygen atoms have a deviation of 0.519(2) Å from the In1-In2-In1'-In2' least-squares plane. The four indium atoms possess an oxidation state of +II and compound **IV** is an isovalence-electronic analogue of dioxane. The In–In bond lengths (2.7136(3) Å) are significantly shortened compared to the intramolecular In–In bonds within **II** (3.1095(3) Å)[15a] and the only other yet reported In(II) compounds incorporating β-dikeminate ligands (2.8343(7) Å and 2.7575(4) Å, respectively).[16] The In–O bond lengths of 2.003(2) Å and 2.008(1) Å, respectively, are comparable to those observed in other In(III) oxo-species, such as the In_3O_3 ring stabilized by three NacNac ligands with In–O bond distances in the range of 1.972(5) to 2.006(5) Å[13b] or the acyclic In–O–In species reported by Uhl *et al.* (1.981(2) Å to 1.989(2) Å).[17] In comparison with **II**, the In–N bond lengths are shortened by about 0.10 Å and the N1–In1–N2 angle is more obtuse, both aspects reflect well the increased oxidation state of the indium centre.

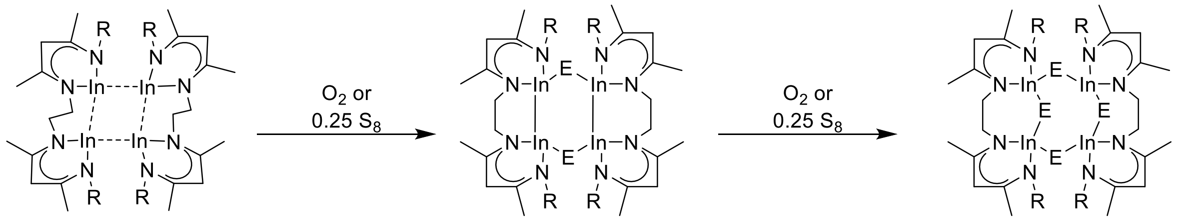


HOMO **HOMO-1**

Figure 3. Highest (HOMO) and second highest molecular orbital (HOMO-1) of **IV**, emphasizing σ-In–In bonds.

A qualitative molecular orbital analysis has been performed on the M06-GD3/def2-TZVP//M06-GD3/def2-SVP level of theory. The highest molecular orbital (HOMO) as well as the HOMO-1 are both involved in the In–In σ-bonding, Figure 3. A natural bond-orbital (NBO) analysis[18] revealed a covalent interaction between the indium atoms and the respective binding NBOs are mostly s-type orbitals (72.5 % to 83.54 %). The In–O interaction, however, is not characterized by binding NBOs, but rather by dative interaction of electron density from a formal O^{2-} fragment to the two neighbouring formal In^{+} atoms, as indicated by the natural charges of In (1.39 to 1.50) and O (-1.57), respectively. In order to understand whether kinetic or thermodynamic reasons account for the isolation of an indium(II) rather than an indium(III) species, we also calculated the Gibbs free energies, Table 1. Addition of one molecule of O_2 to compound **II** is exergonic by (527.1 kJ mol^{-1}) and as is the addition of a second molecule (by additional 433 kJ mol^{-1}). Hence, the respective indium(III) species should be accessible from a thermodynamic point of view, as observed in other reactions of indium(I),[13b, 19] wherefore its absence must be attributed to kinetic reasons.

Table 1. Gibbs free energies (given in kJ mol^{-1}) for the reaction of II with oxygen and sulfur as calculated on the M06-GD3/def2-TZVP//M06-GD3/def2-SVP level of theory. R = 2,6-Diisopropylphenyl



E = O	-527.1	-960.1
E = S	-236.1	-452.8

In contrast to the reaction with oxygen, the weaker oxidant S_8 gives rise to compound **IV**, possessing an In_4S_4 cycle in a “deck-chair” conformation containing four indium atoms in the oxidation state +III, Figure 4. The indium sulfur bond distances (2.3787(9) Å to 2.4156(8) Å) match well with values obtained for neutral dinuclear indium(III) sulfides (2.3640(8) – 2.3691(8) Å)[16b] or indium sulfide cluster (2.395(4) to 2.437(5) Å for μ_2-sulfide bridges).[20] As expected and as already observed in going from **II** to **IV**, the inner In–N bonds, i.e. In1–N2 and In2–N3, respectively, are further shortened in the indium(III) compound **V** by about 0.06 Å. According to DFT calculations, the formation of **V** is thermodynamically preferred over the formation of the respective indium(II) species by 216.7 kJ mol^{-1}. In comparison with the **II**/O_2 couple, both the oxidative addition steps are thermodynamically less pronounced emphasizing the higher oxidation potential of oxygen.

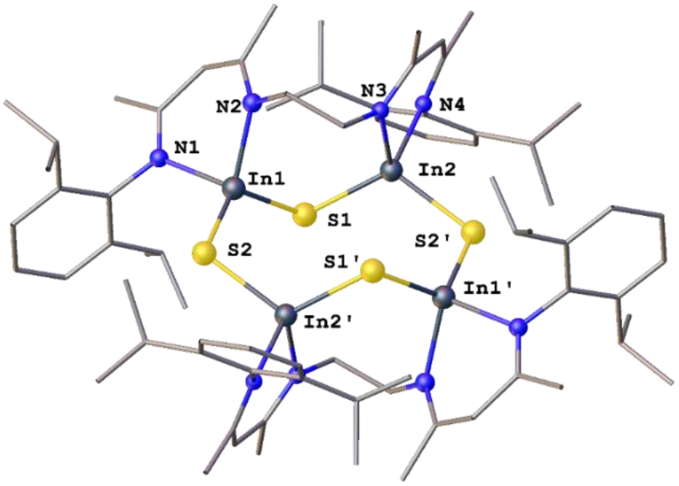
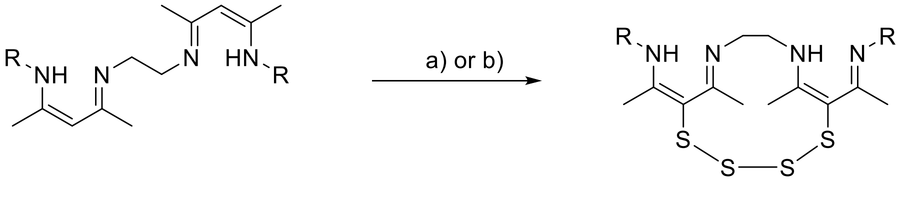


Figure 4. Solid-state structure of **V** (hydrogen atoms are omitted for the sake of clarity). Selected bond lengths [Å] and angles [°] with calculated values (M06-GD3/def2-SVP) in square brackets: In2–S1 2.3973(9) [2.424], In2–S2' 2.4156(8) [2.443], In1–S1 2.414(1) [2.444], In1–S2 2.3787(9) [2.410], In2–N3 2.139(3) [2.175], In2–N4 2.181(3) [2.208], In1–N1 2.153(3) [2.179], In1–N2 2.147(3) [2.186], N3–In2–N4 91.3(1) [89.53], N1–In1–N2 89.9(1) [86.76], S1–In2–S2'115.88(3) [116.76], S1–In1–S2 121.09(3) [121.65], In1–S1–In2 105.65(4) [101.92], In2'-S2-In1 102.31(3) [99.75].

Aiming to avoid the work-up of **II** and subsequent reactions, we intended to perform the oxidative addition of sulfur by directly using an *in situ* prepared toluene solution of **II** similar to trapping experiments with transient carbenes. Hence, the reaction of the protio-ligand **1** with potassium bis(trimethylsilyl)amide (KHMDS), indium(I) iodide, was performed in THF at -78 °C and after stirring the suspension for 24 h at room temperature, S_8 was directly added, Scheme 2a. After workup, yellow crystals were obtained from a concentrated toluene solution at room temperature. The ^1H NMR spectrum is essentially devoid of the corresponding signals for the *γ*-CH protons and contains a broad singlet at 13.36 ppm is indicative of NH protons. These observations are readily explained by the molecular structure obtained from an X-ray diffraction analysis, Figure 5. Instead of the desired indium sulfide **V**, the unreported protio-ligand **VI** in which the γ-carbon atoms of both β-dikemine unites are bridged by an S_4 chain, was obtained. To minimize the tension in the dodecacylcle, the two β-diketimine units are twisted towards each other, and N–H···N hydrogen bonds give rise to two almost planar C_3N_2-planes. The C–

S and S–S bond lengths within **VI** are comparable to those obtained for other intra- and intermolecular build S_4-bridges.[21]



1 **VI**

Scheme 2. Synthesis of the protio-ligand **VI**. Conditions: a) InI, KHMDS, THF , -78 °C -> r.t., S_8 and b) KHMDS, S_8, THF, r.t. R = 2,6-Diisopropylphenyl.

In order to elucidate the impact of indium to this reaction, we performed a one-pot reaction incorporating **1**, KHMDS, and S_8, Scheme 2b. Although the protio-ligand **VI** has also been obtained in similar crystalline yields, the ^{1}H-NMR spectra of the raw material is indicative of a much more complex reaction mixture. The behaviour of **1** and the formation of **VI** is a new example of the non-innocence of the NacNac ligand which founds more and more precedence in recent literature.[22] In search for a plausible reaction pathway towards **VI**, we found reports of Nicolao and co-workers about the reactions of alkaline metal salt of hexamethyldisilazane with S_8. The authors observed the formation of $(TMS)_2N\text{-}S_4\text{-}N(TMS)_2$ as the major product along with $(TMS)_2N\text{-}S_3\text{-}N(TMS)_2$ and $(TMS)_2N\text{-}S_5\text{-}N(TMS)_2$, respectively.[23] Hence, the observed reaction most likely proceeds through the initial formation of $(TMS)_2N\text{-SSSS-}N(TMS)_2$, which further reacts with the protio-ligand **1** affording **VI**. Hence, the desired formation of **II** as the initial step towards the generation of **V** competes with the reaction of KHMDS with S_8, wherefore the work-up of **II** seems inevitable to derive **V**.

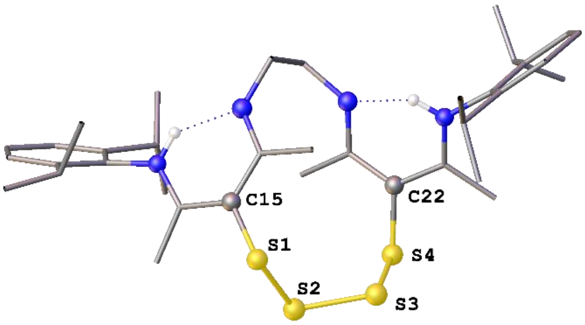


Figure 5. Solid-state structure of **VI** (hydrogen atoms and solvent molecule are omitted for the sake of clarity).Selected bond lengths [Å] and angles [°]:C15–S1 1.753(3), C22–S4 1.756(3), S1–S2 2.089(1), S2–S3 2.057(1), S3–S4 2.084(1), C15–S1–S2 108.7(1), C22–S4–S3 105.2(1), S1–S2–S3 111.28(5), S2–S3–S4 108.61(5).

5.3 Conclusion

In conclusion, oxidative addition reactions of a Group 13 bis(carbene) analogue has been investigated for the first time. Surprisingly, the stronger oxidant O_2 gives rise to an indium(II) species, which is isovalence-electronic to dioxane, while the weaker oxidant S_8 allows for the isolation of an In_4S_4 cycle possessing a deck-chair conformation and four indium(III) centre. However, the reaction conditions are of crucial importance as the *in situ* dinuclear indium diyl does not yield the indium sulfide but rather yields a new macrocyclic bis(β-diketimine).

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5.5 Supporting Information

General considerations

All preparations were performed under an inert atmosphere of dinitrogen by means of Standard Schlenk-line or glovebox (GS-Systemtechnik and MBraun) techniques. Traces of oxygen and moisture were removed from the inert gas by passing it over a BASF R 3-11 ($CuO/MgSiO_3$) catalyst, through concentrated sulfuric acid, over coarsely granulated silica gel, and finally P_4O_{10}. *n*-Hexane was freshly collected from a Solvent Purification System by M. Braun (MB SPS-800). THF and toluene were used as p.a. grade and distilled from Na/benzophenone prior to use. C_6D_6 was dried by distillation from Na/benzophenone. Indium(I) iodide was purchased from Onyxmet, while potassium bis(trimethylsilyl)amide (KHMDS) was purchased from Sigma Aldrich and Oxygen from Linde. These starting materials were used as delivered. Sulfur was sublimated before use. The ligand precursor **1** was prepared according to published procedures.[S1]

Characterization

The NMR spectra were recorded with a Bruker Avance 400 spectrometer (T = 300 K) with δ referenced to external tetramethylsilane (^{1}H and ^{13}C). ^{1}H and ^{13}C NMR spectra were calibrated by using the solvent residual peak (C_6D_5H: $\delta(^1H) = 7.16$) and the solvent peak (C_6D_6: $\delta(^{13}C) = 128.06$), respectively. Elemental analysis were performed with a Vario MICRO cube (Elementar Analysensysteme GmbH); the presence of residual solvent molecules was verified by ^{1}H NMR spectroscopy.

Synthetic procedures

IV: THF (15 mL) was added to a mixture of InI (0.97 g, 4.00 mmol), KHMDS (0.80 g, 4.00 mmol), and **1** (1.09 g, 2.00 mmol) at -78 °C. Warming to room temperature and stirring in the absence of light for 22 h produced a dark brown suspension. The volatiles were removed, and the grey residue was extracted with *n*-hexane (20 mL). The volatiles were removed in vacuum, yielding a red solid, which was redissolved in toluene (10 mL). Oxygen was bubbled through the toluene solution and the mixture was afterwards stirred for one day. Yellow crystals suitable for X-Ray diffraction analysis were obtained from a concentrated toluene solution at room temperature; elemental analysis calcd (found) $C_{72}H_{104}In_4N_8O_2 \cdot 0.60\ C_7H_8$: C 56.21 (56.44), H 6.74 (6.63), N 6.88 (7.15).

In-situ NMR experiment (**IV**): THF (15 mL) was added to a mixture of InI (0.97 g, 4.00 mmol), KHMDS (0.80 g, 4.00 mmol), and **1** (1.09 g, 2.00 mmol) at -78 °C. Warming to room temperature and stirring in the absence of light for 22 h produced a dark brown suspension. The volatiles were removed, and the grey residue was extracted with *n*-hexane (20 mL). The volatiles were removed in vacuum, yielding a red solid.

A portion of it was dissolved in C_6D_6 and transferred to a Young NMR tube. The inert gas atmosphere (N_2) was replaced by oxygen and the tube was immediately transferred to the NMR spectrometer. The respective spectrum is shown in Figure S1.

V: THF (50 mL) was added to a mixture of InI (2.42 g, 10.0 mmol), KHMDS (1.99 g, 10.0 mmol), and **1** (2.71 g, 5.00 mmol) at -78 °C. Warming to room temperature and stirring in the absence of light for 22 h produced a dark brown suspension. The volatiles were removed, and the grey residue was extracted with *n*-hexane (50 mL). The volatiles were removed in vacuum yielding a red solid. Sulfur (0.51 g, 2.00 mmol) and toluene (20 mL) were added to the solid and the mixture was stirred for eight days. Yellow crystals suitable for X-Ray diffraction analysis were obtained from a concentrated toluene solution containing five drops of THF at room temperature. (0.21 g, 0.13 mmol, 52%); ^{1}H NMR: (400 MHz, C_6D_6): δ = 1.17 [d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me₂*], 1.39 [d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me₂*], 1.43 [s, 12H, C*Me*], 1.46-1.49 [m, 24H, CH*Me₂*], 1.54-1.58 [m, 4H, C*H₂*], 1.64 [s, 12H, C*Me*], 3.41 [br, 4H, C*H₂*], 3.54 [sept, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*Me₂], 3.61 [sept, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*Me₂], 4.57 [s, 4H, *γ*-C*H*], 7.18-7.19 [m, 8H, Ar*H*], 7.21-7.23 [m, 4H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, C_6D_6): δ = 21.1 [C*Me*], 23.1 [C*Me*], 25.0 [CH*Me₂*], 25.1 [CH*Me₂*], 25.5 [CH*Me₂*], 26.6 [CH*Me₂*], 28.4 [*C*HMe₂], 28.6 [*C*HMe₂], 49.5 [*C*H₂], 97.5 [*γ*-*C*H], 123.5 [*m*-*C*(Dipp)], 124.9 [*m*-*C*(Dipp)], 126.2 [*p*-*C*(Dipp)], 142.9 [*o*-*C*(Dipp)], 144.8 [*o*-*C*(Dipp)], 145.5 [*ipso*-*C*(Dipp)], 166.7 [*C*N], 167.3 ppm [*C*N]. Despite repeated attempts, satisfactory elemental analyses could not be obtained.

VI:

<u>Route a:</u> THF (15 mL) was added to a mixture of InI (0.48 g, 2.00 mmol), KHMDS (0.40 g, 2.00 mmol), and **1** (0.54 g, 1.00 mmol) at -78 °C. Warming to room temperature and stirring in the absence of light for 22 h produced a dark brown suspension. The filtrate was added to sulfur (0.26 g, 1.00 mmol) and the reaction mixture was stirred for 6d. The volatiles were removed, and the green residue was extracted with toluene (20 mL). Filtration and concentration of the filtrate to about a half gave rise to **VI** as yellow crystals suitable for an X-ray diffraction analysis. (0.17 g, 0.25 mmol, 25%).

Route b: THF (20 mL) was added to a mixture of KHMDS (0.20 g, 1.00 mmol), S_8 (0.13 g, 0.50 mmol), and **1** (0.27 g, 0.50 mmol) at room temperature. The solution was stirred for one day. The volatiles were removed, and the residue was extracted with toluene (10 mL). Filtration and concentration of the filtrate to about one third gave rise to yellow crystals of **VI** suitable for an X-ray diffraction analysis. (0.09 g, 0.13 mmol, 27%).

^{1}H NMR: (400 MHz, C_6D_6): δ = 1.13-1.15 [m, 12H, CH*Me₂*], 1.21 ['t', 12H, CH*Me₂*], 2.20 [s, 6H, C*Me*], 2.31 [s, 6H, C*Me*], 2.50-2.54 [m, 2H, C*H₂*], 2.80-2.88 [m, 2H, C*H₂*], 2.91-3.07 [m, 4H, C*H*Me₂], 7.04-7.06 [m, 1H, Ar*H*], 7.11-7.15 [m, 2H, Ar*H*], 7.18-7.20 [m, 3H, Ar*H*], 13.36 ppm [br, 2H, N*H*]; ^{13}C{^{1}H} NMR: (101 MHz, C_6D_6): δ = 17.4 [C*Me*], 22.4 [C*Me*], 23.1 [CH*Me₂*], 23.3 [CH*Me₂*], 24.0 [CH*Me₂*], 24.7 [CH*Me₂*], 28.5 [*C*HMe₂], 28.9 [*C*HMe₂], 48.4 [*C*H₂], 96.4 [*γ-C*S], 123.6 [*m-C*(Dipp)], 123.7 [*m-C*(Dipp)], 124.5 [*p-C*(Dipp)], 138.2 [*o-C*(Dipp)], 138.3 [*o-C*(Dipp)], 145.5 [*ipso-C*(Dipp)], 166.5 [*C*N], 172.2 ppm [*C*N]; elemental analysis calcd (found) $C_{36}H_{52}N_4S_4 \cdot 0.80\ C_7H_8$: C 67.27 (66.99), H 7.92 (7.70), N 7.54 (7.30).

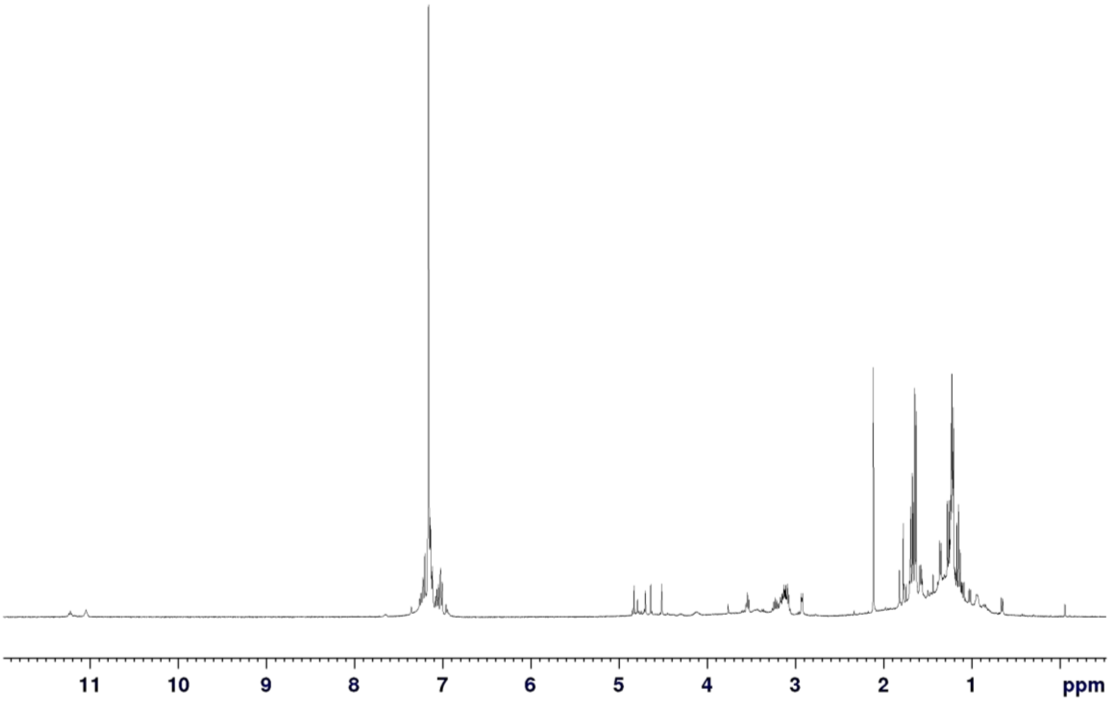

Figure S1: *In-situ* ^{1}H NMR spectrum (400 MHz) of the crude **IV** in C_6D_6.

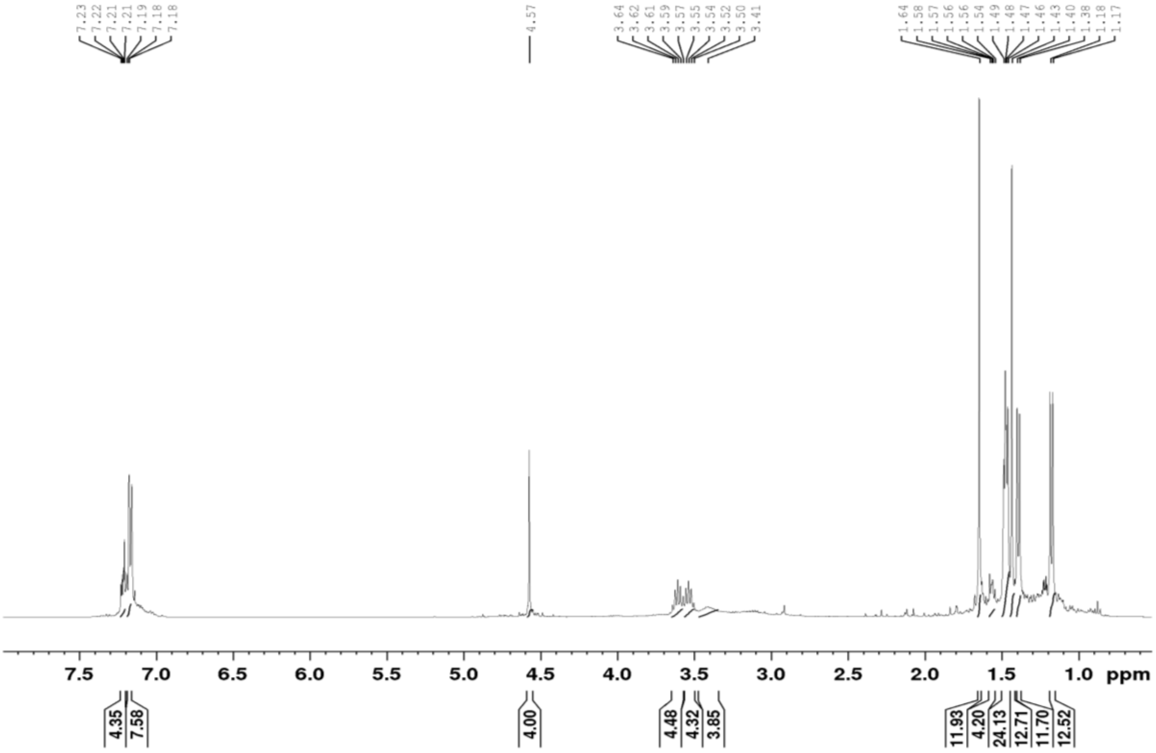

Figure S2: ^{1}H NMR spectrum (400 MHz) of **V** in C_6D_6.

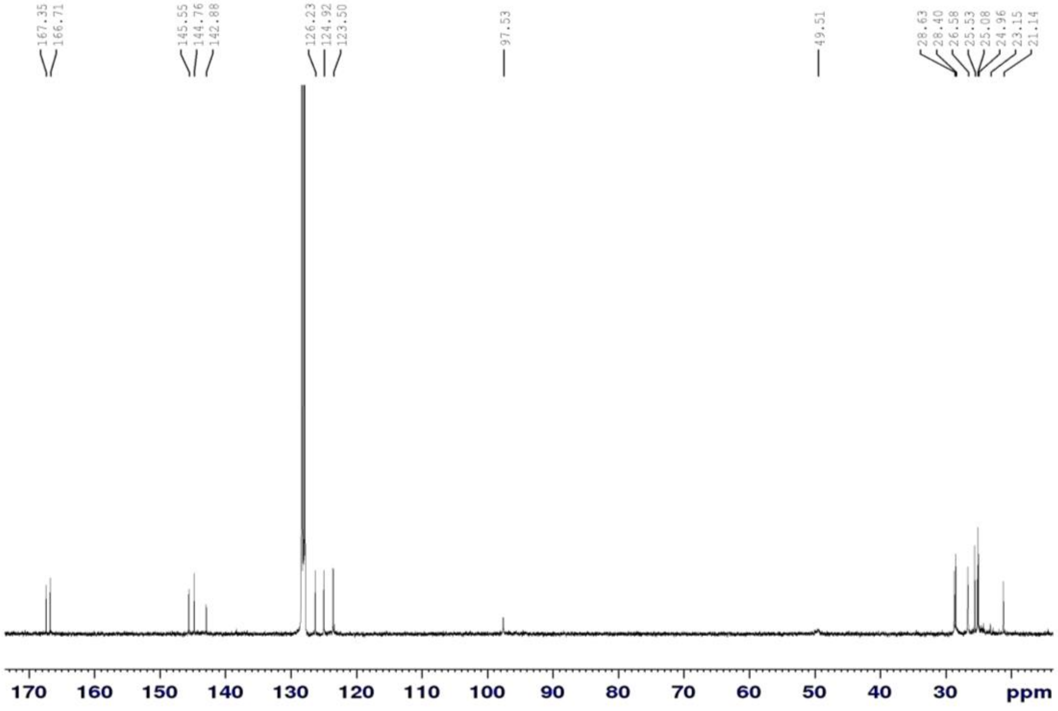

Figure S3: ^{13}C NMR spectrum (101 MHz) of **V** in C_6D_6.

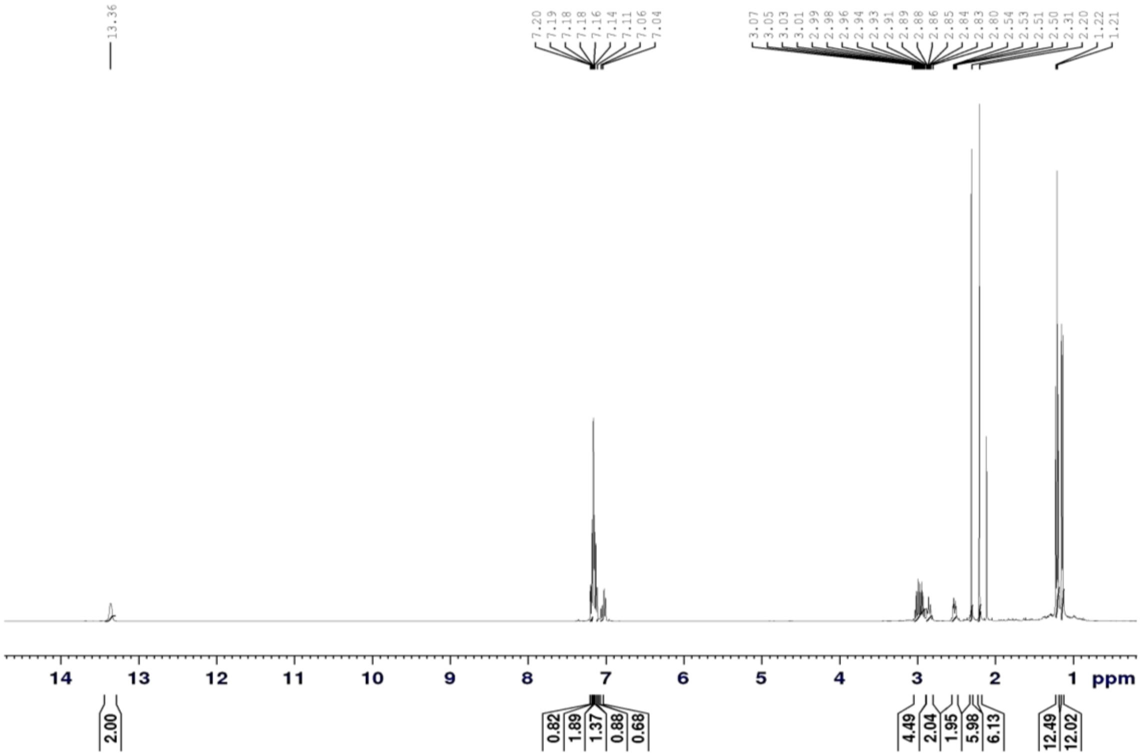

Figure S4: ^{1}H NMR spectrum (400 MHz) of **VI** in C_6D_6.

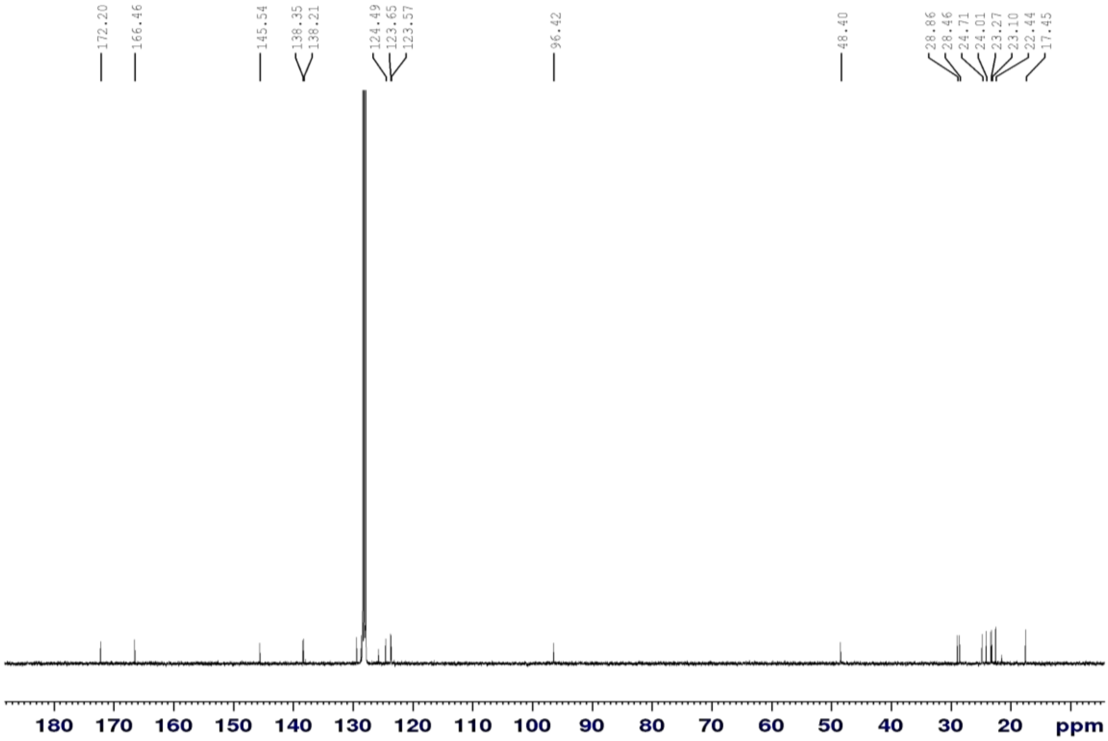

Figure S5: ^{13}C NMR spectrum (101 MHz) of **VI** in C_6D_6.

Crystallographic details

The single crystal X-ray diffraction data were recorded on a GV-50 diffractometer with Titan[S2] detector from Rigaku Oxford Diffraction (formerly Agilent Technologies) applying Cu K**α** radiation (λ = 1.54184 Å) **IV**, **V**, and **VI**. Empirical multi-scan[S2] and analytical absorption corrections[S3] were applied to the data. Using Olex2,[S4] the structures were solved with SHELXT[S5] structure solution program using Intrinsic Phasing and least-square refinements on F^2 were carried out with SHELXL.[S6] For all single-crystals X-Ray structure determinations, the non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were located in idealized calculated positions and were refined isotropically according to the riding model.

IV: Maxima in the Fourier difference maps of **IV** indicated the presence of a second species, which allowed for the refinement of a second In_4 ring (0.024(1)) without bridging oxygen atoms. In this compound, also unresolved residual electron density around a center of inversion was present, which could be assigned a disordered solvent molecule of toluene. The disorder could not be resolved completely, therefore the solvent mask of Olex2[4] was applied and the presence of a solvent accessible void including 54 electrons was confirmed, which we assign a fully occupied toluene molecule. In the subsequent refinement a modified reflection file without the contribution of the solvent was used.

V: The data reduction was calculated as a twin structure. In this compound, unresolved residual electron density around a center of inversion was present, which could be assigned two disordered solvent molecules of toluene. The disorder could not be resolved completely, therefore the solvent mask of Olex2[S4] was applied and the presence of a solvent accessible void including 106 electrons was confirmed, which we assign two fully occupied toluene molecules. In the subsequent refinement a modified reflection file without the contribution of the solvent was used. Additionally, the structure contains a THF molecule, in which all atoms were located in idealized calculated positions and were refined isotropically according to the riding model. The carbon atoms of one backbone and one diisopropylphenyl molecule are disordered over two positions and could be refined by using the disorder model.

IV: The structure contains a toluene molecule.

CCDC 1934795 (**V**), 1934796 (**IV**) and 1934797 (**VI**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data for $C_{72}H_{104}In_4N_8O_2$ (**IV**), $C_{72}H_{104}In_4N_8S_4$ (**V**), and $C_{36}H_{52}N_4S_4$ (**VI**).

	IV	**V**	**VI**
Empirical formula	$C_{72}H_{104}In_4N_8O_2$	$C_{76}H_{112}In_4N_8OS_4$	$C_{43}H_{60}N_4S_4$
CCDC No.	1934796	1934795	1934797
Formula weight	1572.91	1741.25	761.19
Temperature/K	123.0(2)	123.0(1)	123.0(1)
Crystal system	triclinic	monoclinic	orthorhombic
Space group	P-1	C2/c	$P2_12_12_1$
a/Å	11.7484(2)	16.2239(1)	9.2217(2)
b/Å	12.8340(3)	24.1502(2)	18.6267(5)
c/Å	14.8693(3)	23.9945(2)	24.4822(6)
α/°	106.288(2)	90	90
β/°	110.634(2)	100.9261(9)	90
γ/°	98.668(2)	90	90
Volume /Å^3	1934.67(8)	9230.9(2)	4205.3(2)
Z	1	4	4
ρ_{calc}g/cm^3	1.350	1.253	1.202
μ/mm^{-1}	9.745	9.034	2.328
F(000)	804.0	3568.0	1640.0
Crystal size/mm^3	0.166 x 0.06 x 0.056	0.148 x 0.08 x 0.06	0.26 x 0.083 x 0.077
Radiation	Cu K**α** (λ = 1.54184)	Cu K**α** (λ = 1.54184)	Cu K**α** (λ = 1.54184)
2Θ range for data collection/°	6.81 to 148.936	6.648 to 148.13	5962 to 134.988
Index ranges	-14≤h≤14, -16≤k≤15, -18≤l≤18	-18≤h≤19, -29≤k≤29, -29≤l≤25	-8≤h≤10, -20≤k≤22, -21≤l≤29
Reflections collected	41307	26078	12714
Independent reflections	7732 [R_{int}=0.0356, R_{sigma}=0.0236]	9159 [R_{int}=0.0398, R_{sigma}=0.0359]	7213 [R_{int}=0.0344, R_{sigma}=0.0472]

Data/restraints/parameters	7732/6/410	9159/489/580	7213/0/473
Goodness-of-fit on F^2	1.034	0.994	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0207, wR_2 = 0.0497	R_1 = 0.0365, wR_2 = 0.0995	R_1 = 0.0352, wR_2 = 0.0876
Final R indexes [all data]	R_1 = 0.0232, wR_2 = 0.0508	R_1 = 0.0455, wR_2 = 0.1024	R_1 = 0.0394, wR_2 = 0.0902
Largest diff. peak/hole / e Å^3	1.04/-0.66	1.83/-0.86	0.65/-0.28

Computational details

Calculations were performed with the Gaussian 09 program package[S7] and the M06 hybrid functional[S8] using def2-SVP basis sets[S9] for geometry optimizations and frequency calculations, and def2-TZVP basis sets[S9] for single-point calculations, in both cases in conjunction with the related quasi-relativistic pseudopotentials for indium.[S10] For **IV** and **V**, the geometry optimizations were performed using the XYZ coordinates derived from the XRD analysis as initial structures. The absence of imaginary frequencies confirmed stationary points as minima. To derive the contribution of London dispersion the D3 version of Grimme's dispersion with the original zero-damping function was used.[S11] Graphical representations of the frontier orbitals were generated using ChemCraft.[S12]

Thermal corrections obtained at the M06-GD3/def2-SVP level of theory were calculated for standard conditions, i.e.298.15 K and 1 bar. All energies are given in kJ mol^{-1}.

The coordinates of the optimized structures are given in the following:

In_4O_2 (**IV**)				In_4O_4			
In	1.85058100	0.94266800	0.25104200	In	0.68265100	1.50297800	0.40028700
N	1.51462300	1.40693700	2.42170500	In	-2.78117200	0.63859700	0.38062400
N	3.66425200	2.14766700	0.36755400	O	-2.53407700	-1.33806600	0.49485400
N	2.41817100	-3.45963300	0.47057000	O	-0.98888700	0.82100900	-0.64808500
N	1.93560400	-1.63726500	2.95874700	N	0.93437300	3.76110800	0.27181800
C	2.15132700	-4.02665200	-0.80595300	N	0.09244200	1.85261200	2.47111300
C	1.94512000	2.54287900	2.94060700	N	-4.62084900	1.54829700	-0.20228000
C	4.67790000	1.89183300	-0.59441700	N	-2.81041100	1.87100000	2.15074800
C	2.49638300	2.38249900	-3.40956000	C	1.23003100	4.19056400	-1.04995700
H	3.06368100	2.13472700	-4.32540800	C	4.78649700	3.28899400	-0.98386600
H	1.61920000	2.98723300	-3.69686300	H	5.26710200	3.57542200	-1.93694100
H	2.10571300	1.44697100	-2.97730800	H	5.58718300	3.18048000	-0.22959600
C	4.53470000	2.32007100	-1.93204300	H	4.28550600	2.31608800	-1.09881000
C	3.45045500	-1.20072700	-2.65366100	C	-0.74103600	0.83929400	3.08268500
H	3.41008300	-1.40478900	-3.73830200	H	-0.76124800	-0.05057200	2.42442400
H	4.16815400	-0.37628600	-2.50040800	H	-0.33790500	0.45948600	4.04220500

H	2.45203400	-0.84412300	-2.34700800
C	2.82932000	-2.50077900	3.41279500
C	0.64027200	0.50608100	3.14284800
H	-0.09839200	0.07150200	2.43447500
H	0.02185600	1.03099100	3.89455300
C	2.81078700	-3.52265300	-1.94888000
C	4.79714900	4.21065400	0.96165600
H	5.79989500	3.75381700	1.01202300
H	4.74693900	5.03196900	1.68801300
H	4.70015200	4.62750900	-0.05498600
C	5.79156500	1.11155300	-0.20119200
C	3.72892400	3.18253500	1.20550000
C	3.27376800	-3.97900000	1.34287800
C	5.92804100	0.61104300	1.22362500
H	5.32970700	1.27501300	1.87292800
C	3.35177600	3.14368900	-2.40126300
H	2.69826300	3.33920700	-1.53590600
C	4.13056300	-5.12473000	0.88728500
H	3.51684400	-5.94664500	0.48696700
H	4.76498700	-5.51303900	1.69403900
H	4.77713000	-4.79783800	0.05509100
C	1.43271300	3.00166800	4.27958900
H	0.33280200	3.07927500	4.26726400
H	1.83789200	3.98655000	4.54654400
H	1.70363800	2.29212300	5.07921000
C	1.35939600	-0.64224500	3.84983500
H	2.13355500	-0.19181900	4.50206900
H	0.62237000	-1.12331700	4.52692400
C	3.79030400	4.48700700	-2.97494100
H	4.38317600	4.36712600	-3.89850100
H	4.40644800	5.06022500	-2.26147400
H	2.91067800	5.10302100	-3.22687500
C	1.11830600	-4.98547000	-0.93025100
C	3.45502100	-3.53058000	2.66294000
H	4.20169300	-4.09722400	3.22412000
C	5.33530100	-0.78829200	1.35474000
H	4.27072800	-0.80379300	1.06050000
H	5.39717900	-1.16291200	2.39133100
H	5.87124600	-1.50654500	0.70546500
C	3.86106200	-2.43410200	-1.85821300
H	3.93931400	-2.13144100	-0.79883700
C	2.90015400	3.38875200	2.32230900
H	3.09299900	4.32156400	2.85761400
C	3.27054700	-2.40251300	4.84900800
H	3.79745700	-1.44903600	5.02927200
H	3.94695200	-3.22130300	5.12379100
H	2.40770600	-2.41997500	5.53425200
C	5.52188600	1.95632600	-2.85481800
H	5.42092100	2.28399800	-3.89562000
C	6.61470900	1.18462500	-2.48415100
H	7.37053000	0.90686100	-3.22472000
C	2.45555600	-4.02672100	-3.20389500
H	2.97117200	-3.65135700	-4.09537500
C	6.74244700	0.76540900	-1.16303000
H	7.60268700	0.15282200	-0.87291000
C	7.36080400	0.64152700	1.73771400
H	7.99973600	-0.10181100	1.23064800
H	7.38764700	0.40204900	2.81341300
H	7.82585600	1.63195400	1.59894400
C	1.45961900	-4.98653700	-3.33761900
H	1.19299100	-5.36955100	-4.32793800
C	0.79138000	-5.44575400	-2.20824200
H	-0.01455300	-6.17942500	-2.32031700
C	0.35914200	-5.52222500	0.26843900
H	0.64033500	-4.91327700	1.14628900
C	5.24261500	-2.91047700	-2.29319000
H	5.25327100	-3.20110900	-3.35816300
H	5.58080400	-3.78328400	-1.71034300
H	5.98375900	-2.10301900	-2.16006600
C	0.72700200	-6.97514800	0.55819200
H	0.44838800	-7.63269300	-0.28416800
H	0.19383500	-7.34008400	1.45187100
H	1.80647400	-7.11034700	0.73629200
C	-1.14515500	-5.36744700	0.08970700
H	-1.53521500	-6.00391700	-0.72532300
H	-1.37955300	-4.31326900	-0.12677300
H	-1.67379600	-5.65677500	1.01474600
C	0.52515200	2.88826100	3.19802200
C	3.76822500	4.33427100	-0.53521100
H	3.41523100	4.02191900	0.46348600
C	0.99860000	4.09142600	2.67132500
H	1.28590500	4.84497500	3.41072200
C	2.56721400	4.40615500	-1.46370600
C	-5.63099500	0.73065300	-0.77723300
C	1.08848600	4.53339400	1.32270100
C	-5.45338200	0.18008300	-2.05984800
C	0.49388700	2.80321500	4.70373400
H	0.96139200	1.87024900	5.05843900
H	1.03330900	3.64671400	5.15392200
H	-0.53285000	2.81665100	5.10484400
C	-4.79571300	2.84884800	0.04068800
C	-2.17362400	1.32611800	3.33275900
H	-2.19070100	2.04957000	4.16445400
H	-2.76547700	0.45319600	3.67295700
C	-1.27303600	4.13330700	-1.51582400
H	-1.28446700	3.45698900	-0.63947300
C	2.79385100	4.71804100	-2.80686400
H	3.82275300	4.88808200	-3.14254500
C	0.16424700	4.27838300	-1.97206600
C	-6.74790400	0.38040500	0.01699800
C	-7.70275300	-0.47982300	-0.52593500
H	-8.57484400	-0.76229000	0.07204900
C	0.44944800	4.58979300	-3.30337400
H	-0.36886200	4.67051500	-4.02526000
C	-5.89105500	3.56573700	-0.69312500
H	-6.87298500	3.36465800	-0.23066900
H	-5.73005600	4.65300700	-0.68131800
H	-5.95717900	3.21674000	-1.73646800
C	4.45104300	5.69579300	-0.40745700
H	4.90141900	5.99977100	-1.36855600
H	3.76032200	6.49971900	-0.10841000
H	5.26661700	5.65286200	0.33407800
C	-4.20197300	0.44873600	-2.86330200
H	-3.61434000	1.21077900	-2.32290400
C	-6.43224600	-0.68552300	-2.55724700
H	-6.30564000	-1.12129500	-3.55449400
C	-7.55468200	-1.00601000	-1.80632900
H	-8.31284100	-1.68255500	-2.21135000
C	1.36655800	6.00669300	1.18200600
H	1.39882300	6.34393000	0.13717200
H	0.58242200	6.57118600	1.71281400
H	2.32157100	6.26356400	1.66834000
C	-6.84048200	0.82196300	1.46511100
H	-6.35238500	1.80771600	1.56761200
C	1.75528700	4.80720500	-3.72452400
H	1.96390000	5.04868100	-4.77118300
C	-3.22063100	3.12225300	2.03091200
C	-4.03818700	3.58742400	0.96501100
H	-4.24796000	4.65932800	0.98326500
C	-2.18070800	3.51494600	-2.56652300
H	-1.77477200	2.55487700	-2.92885500
H	-3.18093600	3.32681100	-2.13730100
H	-2.33318600	4.18063300	-3.43411800
C	-4.49299800	1.02552200	-4.24213800
H	-5.07103800	1.96291600	-4.17793200
H	-3.55234800	1.24499600	-4.77500700
H	-5.06801600	0.32151500	-4.86822300
C	-1.81603700	5.48692100	-1.06497300
H	-1.72908800	6.23153300	-1.87615500
H	-2.87972200	5.41027900	-0.78254300
H	-1.26451400	5.87652800	-0.19315700
C	-6.06402100	-0.15589200	2.34534000
H	-5.01825300	-0.27488100	2.01290900
H	-6.04901800	0.17813600	3.39687900
H	-6.52225700	-1.15958800	2.30749600
C	-3.33732400	-0.80607300	-2.95098300
H	-3.79660600	-1.57448900	-3.59878100
H	-2.34363500	-0.55622700	-3.36151600
H	-3.18518100	-1.26382700	-1.95410800
C	-8.26754500	0.98140100	1.96677700
H	-8.79262900	0.01345100	2.03519000
H	-8.27089700	1.41617100	2.97939800
H	-8.86228600	1.63997600	1.31160500
C	-2.85640800	4.14537200	3.07105000

In	1.26181600	-1.67088500	0.82819000
O	-0.67221400	-2.26303800	0.74880300
In	-1.85810500	-0.95473700	-0.26823700
N	-1.53622800	-1.40412900	-2.44169400
N	-3.67037900	-2.16471200	-0.38165000
N	-2.41148000	3.47079800	-0.45405000
N	-1.96763000	1.64969800	-2.95657400
C	-2.13617100	4.03763100	0.82133700
C	-1.96861200	-2.53623900	-2.96764400
C	-4.67394200	-1.91618800	0.59222500
C	-2.46804100	-2.42890800	3.39020800
H	-3.02915000	-2.18863500	4.31191700
H	-1.58930100	-3.03650900	3.66717200
H	-2.08016200	-1.48968100	2.96333800
C	-4.51582000	-2.35005900	1.92625400
C	-3.34910600	1.15885100	2.70002500
H	-3.34933100	1.36728000	3.78472100
H	-4.03966400	0.31445600	2.52973100
H	-2.33144300	0.82621800	2.42896000
C	-2.85380000	2.52552800	-3.40087500
C	-0.67360600	-0.49272100	-3.16390100
H	0.06480000	-0.05441300	-2.45888900
H	-0.05823900	-1.00746100	-3.92425700
C	-2.74988600	3.49147100	1.97169600
C	-4.81398200	-4.21758100	-0.99014700
H	-5.81679100	-3.76200400	-1.05223800
H	-4.75689600	-5.04208000	-1.71245900
H	-4.72838500	-4.62905800	0.02955500
C	-5.79135500	-1.13371200	0.21383700
C	-3.74474100	-3.18951100	-1.23023200
C	-3.25802200	4.00830400	-1.32519500
C	-5.93889100	-0.62543200	-1.20730900
H	-5.36128100	-1.29720800	-1.86725300
C	-3.33103000	-3.18013000	2.38054200
H	-2.68269900	-3.37162200	1.50966200
C	-4.06901200	5.18899700	-0.87495700
H	-3.41443700	6.02040900	-0.56910900
H	-4.74976400	5.54468900	-1.65864800
H	-4.66020500	4.92529200	0.01792800
C	-1.45391100	-2.98724100	-4.30840000
H	-0.35478800	-3.07688300	-4.28771200
H	-1.86843300	-3.96464600	-4.58813000
H	-1.70978600	-2.26687200	-5.10314800
C	-1.40703200	0.65468400	-3.85783400
H	-2.19289700	0.20404700	-4.49602700
H	-0.68343800	1.13730000	-4.54815000
C	-3.77310600	-4.52475700	2.94869800
H	-4.37672600	-4.40597600	3.86538100
H	-4.38042100	-5.09872400	2.22823600
H	-2.89617600	-5.13980600	3.21225500
C	-1.15006400	5.04533900	0.93965400
C	-3.45864200	3.56236600	-2.64332000
H	-4.19814600	4.14358300	-3.19892600
C	-5.32088700	0.76259800	-1.34045500
H	-4.25472000	0.75533000	-1.05177200
H	-5.38113800	1.14123300	-2.37576200
H	-5.83817800	1.49000600	-0.68693500
C	-3.77122500	2.37524400	1.88479400
H	-3.83075900	2.05886200	0.82809500
C	-2.92361300	-3.38570300	-2.35489700
H	-3.11813000	-4.31463100	-2.89654400
C	-3.30532900	2.43784000	-4.83436900
H	-3.83561900	1.48689500	-5.01757700
H	-3.98077900	3.26043000	-5.09993800
H	-2.44662800	2.45689800	-5.52486100
C	-5.49195700	-1.98739300	2.86150600
H	-5.37932400	-2.31797900	3.90019600
C	-6.58841700	-1.21423100	2.50553600
H	-7.33560700	-0.93838200	3.25551500
C	-2.39165300	3.99415200	3.22622300
H	-2.86991900	3.58581000	4.12390900
C	-6.73175600	-0.79161200	1.18703500
H	-7.59531600	-0.17823900	0.90882300
C	-7.37839100	-0.62744100	-1.70258500
H	-7.99657400	0.12676500	-1.18592100
H	-7.41453200	-0.38473900	-2.77727300
H	-7.86026700	-1.60932000	-1.56023600
H	-1.76402300	4.17014800	3.22640300
H	-3.18006200	5.14771300	2.76207600
H	-3.33145300	3.92619300	4.04168500
In	-0.68393100	-1.50408500	-0.40044700
In	2.77823200	-0.63889700	-0.38969600
O	2.52801100	1.33772200	-0.50463100
O	0.98970100	-0.82311100	0.64564900
N	-0.93657900	-3.75950400	-0.25944100
N	-0.09730200	-1.86334000	-2.47031300
N	4.62146000	-1.54429000	0.19127500
N	2.80623000	-1.87659200	-2.15641900
C	-1.22832000	-4.18234600	1.06530700
C	-4.78827500	-3.29397900	0.99257400
H	-5.24906300	-3.55443500	1.96271700
H	-5.60362000	-3.21787400	0.25033100
H	-4.29509500	-2.31339500	1.06954100
C	0.73355900	-0.85166700	-3.08820800
H	0.75401900	0.04087600	-2.43341600
H	0.32818600	-0.47687700	-4.04879900
C	-0.53029000	-2.90338300	-3.19085000
C	-3.76709000	-4.34333900	0.56114300
H	-3.41711300	-4.04892700	-0.44450800
C	-0.99984200	-4.10502200	-2.65677000
H	-1.28721100	-4.86325700	-3.39134900
C	-2.56307300	-4.39647000	1.48675000
C	5.63251100	-0.72588600	0.76355900
C	-1.08961500	-4.53841800	-1.30548600
C	5.45822500	-0.17558100	2.04670500
C	-0.50133000	-2.82628900	-4.69699000
H	-0.97101100	-1.89605600	-5.05590400
H	-1.03976100	-3.67314700	-5.14203100
H	0.52492100	-2.83975200	-5.09944200
C	4.79740500	-2.84535100	-0.04816100
C	2.16637400	-1.33711100	-3.33913200
H	2.18316500	-2.06355400	-4.16818100
H	2.75624000	-0.46463000	-3.68381600
C	1.27627600	-4.12808400	1.51568400
H	1.28568700	-3.45147800	0.63951800
C	-2.78368900	-4.69263900	2.83456900
H	-3.81082300	-4.86012400	3.17689300
C	-0.15815500	-4.26314300	1.98325300
C	6.74898400	-0.37824400	-0.03246300
C	7.70724000	0.47870000	0.50959600
H	8.57956800	0.75863100	-0.08919400
C	-0.43688800	-4.55995300	3.31907700
H	0.38480900	-4.63384200	4.03783200
C	5.89507600	-3.55952100	0.68495900
H	6.87541800	-3.36187600	0.21765100
H	5.73263700	-4.64665900	0.67874500
H	5.96580700	-3.20606100	1.72645000
C	-4.44520700	-5.71015000	0.46309900
H	-4.90533300	-5.98878100	1.42720000
H	-3.74730900	-6.51903900	0.19509200
H	-5.25294700	-5.69084200	-0.28804900
C	4.20921500	-0.44550500	2.85352800
H	3.62257800	-1.21019400	2.31588800
C	6.43966200	0.68814900	2.54249300
H	6.31548900	1.12437500	3.53984500
C	7.56215700	1.00522900	1.79023100
H	8.32275100	1.67957400	2.19435300
C	-1.38259800	-6.00656100	-1.14943500
H	-1.28024200	-6.35322800	-0.11165500
H	-0.70026000	-6.58785100	-1.78941000
H	-2.40663300	-6.22688300	-1.49297700
C	6.83837800	-0.82081900	-1.48053200
H	6.35092100	-1.80711300	-1.58092100
C	-1.74122500	-4.77050900	3.74870600
H	-1.94537900	-4.99944600	4.79905400
C	3.21826900	-3.12704400	-2.03366800
C	4.03872400	-3.58784900	-0.96832200
H	4.25052800	-4.65938000	-0.98419500
C	2.19618100	-3.51616500	2.55914000
H	1.79854200	-2.55324200	2.92315600
H	3.19448000	-3.33460700	2.12289800
H	2.35032800	-4.18234200	3.42604700
C	4.50453900	-1.01885500	4.23291200
H	5.08534700	-1.95458900	4.16943400

C	-1.44176300	5.00051500	3.35329600	H	3.56552700	-1.24028400	4.76783600
H	-1.17485900	5.38470500	4.34305100	H	5.07824200	-0.31205100	4.85699800
C	-0.82320400	5.50767500	2.21720200	C	1.80476100	-5.48588300	1.05999800
H	-0.06183500	6.28830400	2.32292300	H	1.72442000	-6.22803900	1.87416500
C	-0.43377500	5.63774300	-0.25858400	H	2.86494100	-5.41630800	0.76271200
H	-0.81779800	5.13803600	-1.16605400	H	1.23917400	-5.87497100	0.19652900
C	-5.16782400	2.83343800	2.29268100	C	6.05901000	0.15520600	-2.36029800
H	-5.19706200	3.14911000	3.35015000	H	5.01350200	0.27277300	-2.02657600
H	-5.51510100	3.68544200	1.68476000	H	6.04293700	-0.17990700	-3.41146700
H	-5.89302600	2.01022300	2.17016300	H	6.51570200	1.15965900	-2.32422200
C	-0.70749200	7.13358600	-0.39192700	C	3.34162400	0.80723100	2.94067600
H	-0.27739000	7.69638100	0.45464900	H	3.80193500	1.57898900	3.58377600
H	-0.25111200	7.53193300	-1.31333500	H	2.35004900	0.55632400	3.35579800
H	-1.78543100	7.36546600	-0.42404500	H	3.18463100	1.26105200	1.94283600
C	1.06507200	5.36249700	-0.19767500	C	8.26436000	-0.97949200	-1.98546000
H	1.53299100	5.85201900	0.67560600	H	8.78826600	-0.01108800	-2.05653700
H	1.23851000	4.27430300	-0.14301600	H	8.26563500	-1.41566500	-2.99747600
H	1.56358800	5.75314100	-1.10258800	H	8.86136800	-1.63658900	-1.33085600
In	-1.27798200	1.66867700	-0.83271100	C	2.85345300	-4.15382300	-3.06997200
O	0.66539000	2.23599300	-0.78628300	H	1.76095400	-4.18022500	-3.22385900
				H	3.17821200	-5.15484100	-2.75791900
				H	3.32735400	-3.93749000	-4.04182000

In$_4$S$_2$				In$_4$S$_4$ (**V**)			
In	-1.73202600	1.07150700	-0.01174500	In	-0.92791700	2.33220900	-0.25856600
N	-0.88364100	1.36188500	-2.08201500	In	2.58174800	0.92950900	-0.37132300
N	-3.14254100	2.70262300	-0.53285200	S	3.09418700	-1.42532200	-0.41425000
N	-3.43256900	-3.04516500	-0.32085800	S	0.95258500	1.85922600	1.19596500
N	-2.17109900	-1.49895000	-2.72885500	N	-1.33239300	4.49133200	-0.47474900
C	-3.67332800	-3.51967100	1.00278200	N	-0.54303700	2.20863100	-2.39550400
C	-0.90785000	2.54274300	-2.67879800	N	4.47754600	1.95172600	-0.04016300
C	-4.44368900	2.73122200	0.04190100	N	2.43760600	2.06410100	-2.23469200
C	-3.29456900	3.05612800	3.43349900	C	-1.39942600	5.23981700	0.73942500
H	-4.18403200	3.02911200	4.08857200	C	-4.70364100	4.06098600	1.86705800
H	-2.46140500	3.49610500	4.00642700	H	-5.09741100	4.67635200	2.69486300
H	-3.00965300	2.01820800	3.19749800	H	-5.56138800	3.55848500	1.38843400
C	-4.66309600	3.24987600	1.33668600	H	-4.05770000	3.27659900	2.29145900
C	-4.48320500	-0.30358000	2.36851500	C	0.24848000	1.09979500	-2.89160300
H	-4.79669500	-0.40755600	3.42243700	H	0.31114200	0.33255600	-2.09727700
H	-4.83165100	0.68326900	2.01867300	H	-0.24235800	0.56807200	-3.72802900
H	-3.37827800	-0.30409500	2.35891200	C	-1.12680500	3.06225600	-3.23642200
C	-3.11113400	-2.21294400	-3.32504400	C	-3.95679300	4.90870100	0.84080000
C	-0.32199500	0.20731000	-2.75334900	H	-3.73574600	4.25293500	-0.02092100
H	0.18395900	-0.43886600	-2.00873500	C	-1.66437500	4.30830700	-2.87752900
H	0.47839900	0.49420000	-3.45625100	H	-2.07356600	4.88623400	-3.71104300
C	-4.46679500	-2.75997500	1.88986600	C	-2.64146700	5.43193800	1.38704100
C	-3.57621600	4.94443900	-1.37966500	C	5.50999000	1.22643000	0.61167700
H	-4.55077600	4.73881000	-1.85533500	C	-1.64871600	5.01137300	-1.64783800
H	-3.07416300	5.73852200	-1.94809700	C	5.40091700	0.92058200	1.98244400
H	-3.80014500	5.31432600	-0.36710100	C	-1.19384500	2.71618800	-4.69993800
C	-5.51296800	2.17917200	-0.70076100	H	-1.66884500	1.73212200	-4.84547100
C	-2.74416200	3.69314700	-1.33225900	H	-1.77090500	3.46349500	-5.25871600
C	-4.22847500	-3.39796200	-1.32795300	H	-0.19069300	2.65585600	-5.15328100
C	-5.31752500	1.64128700	-2.10467100	C	4.61744500	3.21789600	-0.40810400
H	-4.33418000	1.98744500	-2.47116500	C	1.66406600	1.48249300	-3.31059600
C	-3.55829600	3.86773200	2.16965600	H	1.64092900	2.13901300	-4.19626100
H	-2.62913900	3.85211200	1.57323900	H	2.16826200	0.55011000	-3.63451100
C	-5.46850400	-4.18802500	-1.01165400	C	1.13834100	5.53350400	0.62489600
H	-5.26894200	-5.03150300	-0.33436400	H	1.08211400	4.61184800	0.01575500
H	-5.95672800	-4.56202400	-1.92069200	C	-2.65558900	6.15077400	2.58673600
H	-6.18256800	-3.53654100	-0.47836500	H	-3.60917000	6.31540000	3.09965300
C	-0.17548400	2.75277000	-3.97787400	C	-0.19955700	5.72031500	1.31063400
H	0.88113000	2.44758800	-3.90253100	C	6.56778100	0.70835400	-0.16941500
H	-0.20204400	3.80799800	-4.27787500	C	7.49319200	-0.13587100	0.44659000
H	-0.63254500	2.15902400	-4.78753600	H	8.30925800	-0.56278300	-0.14517900
C	-1.31243000	-0.64959500	-3.53566300	C	-0.27318500	6.43309400	2.50962700
H	-1.91623700	0.02860400	-4.17511900	H	0.64554600	6.82293400	2.95782800
H	-0.71011400	-1.26815300	-4.23357900	C	5.78062300	3.99725100	0.13357300
C	-3.85891300	5.32066200	2.52474600	H	6.72356100	3.65528900	-0.32549500
H	-4.74478600	5.40660900	3.17783400	H	5.67694000	5.07259900	-0.06539300
H	-4.04880400	5.93859400	1.63113500	H	5.88706500	3.83575100	1.21849300
H	-3.00832900	5.76866400	3.06525400	C	-4.85931300	6.04130100	0.35590400

C	-3.06843100	-4.72499500	1.43090800
C	-4.04485900	-3.05792400	-2.67900300
H	-4.78426200	-3.49943500	-3.35090000
C	-5.27587800	0.11872900	-2.10079300
H	-4.41544900	-0.25664900	-1.52055900
H	-5.17868900	-0.28417900	-3.12365400
H	-6.19324400	-0.31291300	-1.65831600
C	-5.05563500	-1.42036300	1.50155900
H	-4.76253200	-1.21617300	0.45685600
C	-1.64425300	3.65479700	-2.20638700
H	-1.45308100	4.58929300	-2.74012600
C	-3.26232100	-2.11433100	-4.81924800
H	-3.48529700	-1.07789600	-5.12623400
H	-4.06518800	-2.76271100	-5.19136100
H	-2.32747500	-2.39455500	-5.33187600
C	-5.95351600	3.18194200	1.87211600
H	-6.13102600	3.57860700	2.87808800
C	-7.00504100	2.61471100	1.16483100
H	-8.00360500	2.56141100	1.60871600
C	-4.68810000	-3.24814900	3.18046400
H	-5.30928600	-2.66494000	3.86954800
C	-6.77948200	2.11892700	-0.11466300
H	-7.60876800	1.67574300	-0.67734900
C	-6.37378800	2.15924200	-3.07348100
H	-7.37834800	1.76833000	-2.83673600
H	-6.14080800	1.84623700	-4.10465300
H	-6.43545700	3.26017300	-3.05922900
C	-4.13293400	-4.44909800	3.60082600
H	-4.32168300	-4.82009800	4.61262000
C	-3.32351200	-5.17017600	2.73099300
H	-2.87342900	-6.11014500	3.06730100
C	-2.18470000	-5.56126900	0.52459700
H	-1.89796600	-4.93355500	-0.33667800
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H	-2.56572400	-4.01084100	4.27755900

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Preface

The following chapter has not been published until the submission of this thesis.

Authors

Marcella E. Desat, Robert Kretschmer*

Author contributions

The preparation of the manuscript was done by the first author (M. E. Desat). R. Kretschmer supervised the research and revised the manuscript. Preparation and characterization (NMR, X-Ray) of compound **IIb** and **IIk** have been part of the first author's master thesis. Among them, the first author provides additional the characterisation (IR, EA) of **IIb** and **IIk**. A synthetic approach to the other compounds **IIa**, **c-j** as well as the complete characterization (NMR, EA, IR, X-Ray) was done by the first author. Additionally, the calculation of all X-Ray structures herein was performed by the first author as well as the interpretation of the analytic data of the compounds.

Acknowledgements

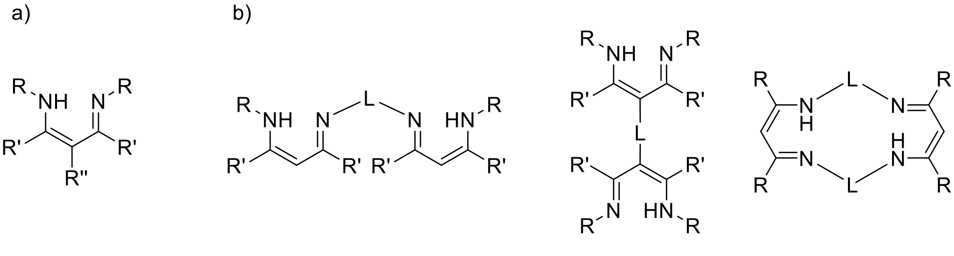
The project was financially supported by the *Fonds der Chemischen Industrie*, the *Deutsche Forschungsgemeinschaft* (DFG, KR4782/3-1), the University of Regensburg and the Friedrich Schiller University Jena. M.E.D. is grateful to the *Stiftung Stipendien-Fonds des Verbands der Chemischen Industrie* for a PhD fellowship. Additionally, helpful discussions with Dr. Stefanie Gärtner and generous support from Professor Manfred Scheer is gratefully acknowledged.

6 Synthesis and Structures of Dinuclear Aluminium Complexes Based on Bis(β-diketiminate) Ligands

Abstract: *A series of eleven dinuclear aluminium alkyl complexes based on rigid, semirigid, and flexible bis(β-diketiminate) ligands (NacNac) has been obtained from the reaction of trimethyl aluminium and the corresponding bis(β-diketimine)s. All compounds were fully characterized using NMR and IR spectroscopy and elemental analysis. The molecular structures of five compounds have been investigated by means of single-crystal X-ray diffraction analysis.*

6.1 Introduction

Since the first reports on transition-metal complexes of β-diketiminate ligands, also known as β-diiminate or NacNac ligands, in 1968,[1] these ligand class has been frequently used to stabilize a variety of elements from all sections of the periodic table and in unusual oxidation states.[2] Today, β-diketiminates belong to the most ubiquitous ligands in coordination chemistry, mostly because their electronic and steric features can readily be altered through variation of the ligand backbone and/or the terminal substituents at the nitrogen atoms, Figure 1a.[3] However, it has been shown that β-diketiminates do not necessarily behave as spectator ligands and their (hidden) non-innocence is an interesting feature in terms of reactivity.[3,4] Poly(β-diketiminate)s have been recently emerged as useful tools in coordination chemistry,[5] and the respective bis(β-diketiminate)s grant access to both, mono-[6] and dinuclear complexes,[7] not only depending on the respective element and the experimental protocol, but also on the ligand framework. In this regard, three types of bis(β-diketimine)s have to be considered: i) nitrogen-bridged, ii) backbone-bridged and iii) macrocyclic derivatives, Figure 1b.



nitrogen-bridged *backbone-bridged* *macrocyclic*

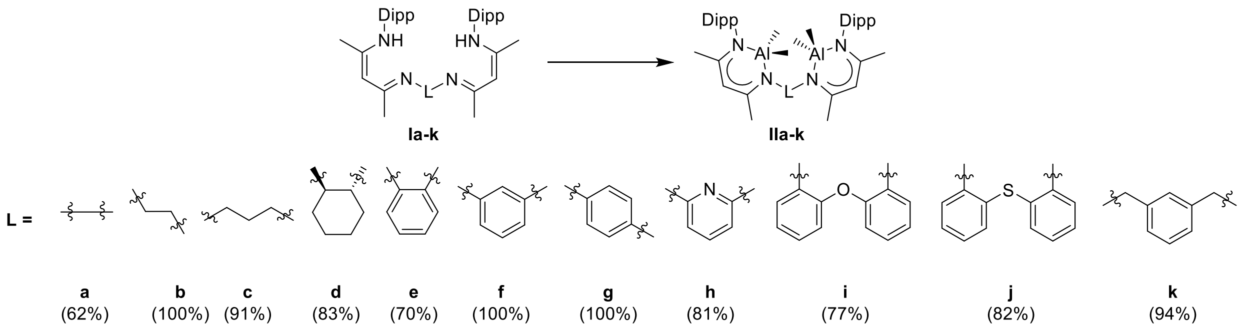
Figure 1. a) β-diketimines and b) various types of bis(β-diketimine)s.

The steric constraints of the ligand impact both, the element-element separation and the relative orientation of the two elemental centres. These aspects are very relevant in terms of cooperative catalysis, i.e. the concept of utilizing two or more catalytically active centres in one reaction system,[8] which is one of the most promising concepts in catalysis by main-group elements as it allows promoting chemical transformations that hitherto have been believed to be limited to transition metals. In their seminal work, Normand *et al.* could prove that a dinuclear aluminium complex excels its mononuclear counterpart in terms of activation free energy giving rise to a 5-to-10 fold increase in activity in the ring-opening polymerization (ROP) of racemic lactide.[9] Although in the following years various dinuclear aluminium(III) complexes have been probed as cooperative catalysts, mostly in the ROP of lactide,[10] systematic studies that investigate the role of the bridging unit and hence the metal-metal distance with respect to activity and selectivity are still missing to the best of our knowledge. Hence, the synthesis and structural characterization of a whole set of dinuclear aluminium alkyl complexes is worthy of pursuit as they are suitable pre-catalyst for the ROP of cyclic esters.[11]

Herein we report the synthesis of a library of eleven dinuclear aluminum complexes (**I**) based on bis(β-diketiminate) ligands and their structural characterization. We choose the β-diketiminate framework as the related mononuclear aluminium complexes have been shown to be active catalysts in polymerization reactions.[12]

6.2 Results and Discussion

The protio-ligands **Ia-k** have been synthesized by alkylation of 2-(2,6-di-isopropylphenyl)imido-2-penten-4-one using Meerwein's salt ($[O(C_2H_5)_3][BF_4]$) followed by condensation with various primary diamines as described before. [6b,6e,7b,7i,7l] The protio-ligands were subsequently converted to the respective dinuclear dimethyl aluminium complexes **IIa-k** using trimethyl aluminium, Scheme 1. All compounds were isolated in good to quantitative yields using a simple work-up procedure and were obtained as (pale) yellow (**IIa,b,c,e,g,h,i**,**k**), brown (**IIf**) or colourless (**IId**,**j**) powders. The species **IIa-k** were found to be thermally stable and melt without decomposition with values in between 162 °C and 296 °C; noteworthy, melting points above 200 °C were only found for bis(β-diketiminate) containing aryl linker.



Scheme 1. Syntheses of dinuclear organoaluminium complexes **II** starting from bis(β-diketimine)s **I** with different linker (L) groups. Dipp = 2,6-diisopropylphenyl.

Except for **IId**, **IIe**, **IIi**, and **IIj**, common features observed in the respective ^{1}H NMR spectra include one singlet for the aluminium methyl groups and one septet for the methine groups, Figure 2, consistent with a symmetrical substitution pattern at aluminium. Noteworthy, for **IIf** only one doublet (δ = 1.29 ppm) corresponding to the methyl protons of the isopropyl groups is observed, indicating a lower barrier of rotation about the C–N bond. In case of **IId** and **IIe**, respectively, the ^{1}H NMR spectrum shows two separated groups of septets and more complex peaks for the respective isopropyl methine and methyl proton resonances of the isopropyl groups, indicating a hindered conformational flexibility of both binding sites. A similar pattern has also been observed for the thallium(I)[7l] and copper(I)[7i] derivatives of **IId**. The thallium congener of **IIe**, however, gives a pattern comparable to that of the protio-ligand **Ie** with one isopropyl methine septet and two methyl doublets, demonstrating a symmetric or averaged structure in solution. This difference most likely arises from the increased steric demands of the $Al(CH_3)_2$ group in comparison with the “naked” Tl(I) centre bearing a diffuse s-type lone pair of electrons.

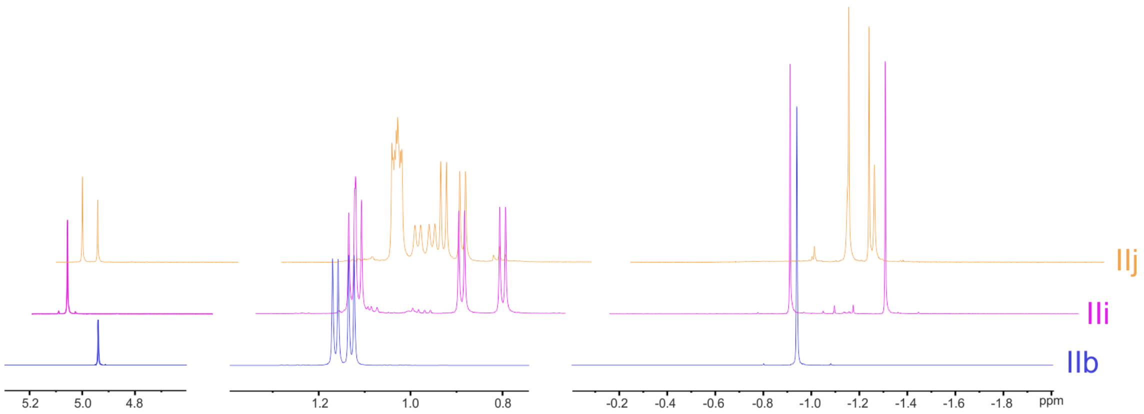


Figure 2. Selected areas of the room temperature ^{1}H-NMR spectra of **IIb**, **IIi**, and **IIj**.

The ^{1}H NMR spectra of **IIi** and **IIj** are more complex and differ from each other, Figure 2: In case of **IIi**, two distinct peaks corresponding to the $Al(CH_3)_2$ groups are observed at -0.77 and -1,18 ppm, respectively, and the signals associated with the methyl and methine group appear as four doublets and two septets, respectively. In case of **IIj** three resonances at -0.94, -1.02, and -1.04 ppm, respectively, are observed for the $Al(CH_3)_2$ groups. In case of **IIj**, two singlets (5.17 and 5.24 ppm) are observed for the γ-CH protons with an integration ratio of 43:57 indicating that two independent molecules exist in solution. Indeed, using this ratio allows for an assignment of some of the signals to two species. The major component is associated with well resolved signals at -1.02, 0.99, 1.04, 1.91, and 5.24 ppm, while for the minor component signals at -1.05, 1.08, 1.12, 1.95, and 5.17 ppm are observed. Furthermore, quite some signals are the result of overlapping resonances of both species. Variable temperature NMR studies in $CDCl_3$ at 253 K, 298 K, and 328 K provided arguments for a static relation of both molecules. While the resonance pattern of the major compound remains more or less unaffected, extensive line broadening is observed for the signals associated with the minor component. In addition, ^{27}Al-NMR resonances are only observed in case of **IIb**, **IIc**, **IId**, **IIh**, and **IIk** as broad signals with values in between 150.5 and 154.3 ppm.

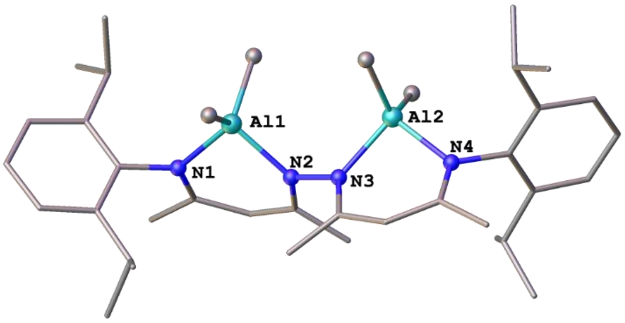


Figure 3. Solid state structures (hydrogen atoms are omitted for the sake of clarity) with selected bond lengths [Å] and angles [°] of IIa: Al1–Al2 3.8866(6), Al1–N1 1.917(1), Al1–N2 1.928(1), Al2–N3 1.929(1), Al2–N4 1.921(1), Al1–C18 1.965(1), Al1–C19 1.962(2), Al2–C25 1.967(2), Al2–C26 1.974(2), N2–N3 1.432(2), N1–Al1–N2 93.64(5), N3–Al2–N4 93.04(5), C18–Al1–C19 117.92(7), C25–Al2–C26 118.52(7).

Besides the behavior in solution, we became interested in the solid-state structures of the dinuclear complexes and crystals of **IIa**, **IIb**, **IIc**, **IIe**, and **IIi** were grown from toluene solutions at room temperature; their molecular structures are depicted in Figures 3 - 5. All structures feature two distorted tetrahedral aluminium centres that are projected out of the plane of each NacNac unit; the smallest and largest deviation from the least-squares N-C-C-C-N plane amount to 0.235(1) Å and 0.831(1) Å for **IIi** and **IId**, respectively. The N–Al–N bite angles with values between 93.04(5)° and 95.23(4)° are in the range regularly observed for mononuclear alkyl aluminium β-diketiminate complexes.[12,13] The same holds true for the Al–C bond lengths (1.958(1) Å – 1.975(2) Å) and the C–Al–C bond angles (113.22(5)° - 118.52(7)°) of the $Al(CH_3)_2$ group, whose values are comparable to those observed for the mononuclear counterparts.

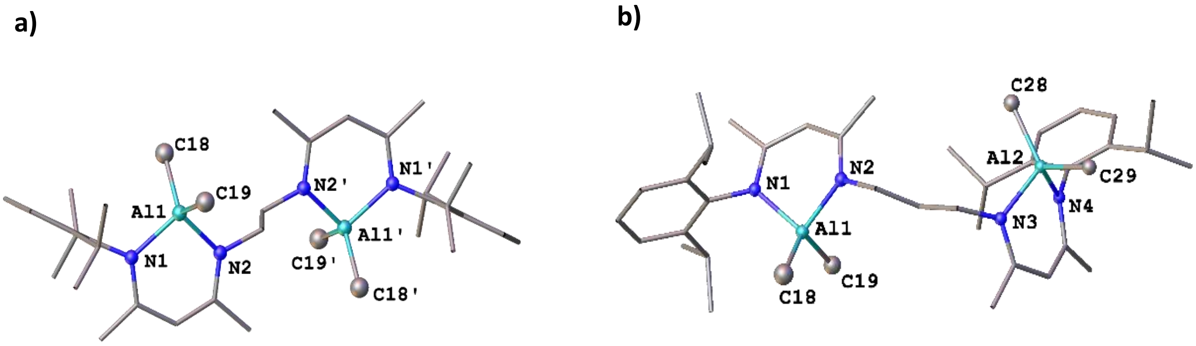


Figure 4. Solid state structures (hydrogen atoms are omitted for the sake of clarity) with selected bond lengths [Å] and angles [°] of a) IIb: Al1–Al1‘ 6.482(1), Al1–N1 1.918(1), Al1–N2 1.907(1), Al1–C18 1.969(2), Al1–C19 1.975(2), N1–Al1–N2 96.71(6), C18–Al1–C19 113.96(9); b) IIc: Al1–Al2 7.3823(4), Al1–N1 1.904(1), Al1–N2 1.915(1), Al2–N3 1.912(1), Al2–N4 1.911(1), Al1–C18 1.963(2), Al1–C19 1.974(2), Al2–C28 1.968(1), Al2–C29 1.967(1),N1–Al1–N2 95.02(5), N3–Al2–N4 94.22(4), C18–Al1–C19 116.53(8), C28–Al2–C29 117.85(6).

It is obvious that the Al–Al separations increase in the order **IIa** (3.8866(6) Å) < **IIe** (6.4023(8) Å) < **IIb** (6.482(1) Å) < **IIc** (7.3823(4) Å) < **IIi** (7.396(1) Å) as a result of the length and the rigidity of the bridging unit. The molecular structures also rationalize the respective ^{1}H resonance pattern observed in solution. For **IIa**, rotation about the N1–N2 is cancelled out due to the repulsion of the backbone CH_3 groups. In contrast, the alkyl bridges of **IIb** and **IIc** warrant conformational flexibility in agreement with chemically and magnetically equivalent binding sites in solution. For **IIe** and **IIi**, rotation about the N2–C_{bridge} bond becomes more restricted, which readily explains the diverse pattern of resonance in the ^{1}H NMR spectrum.

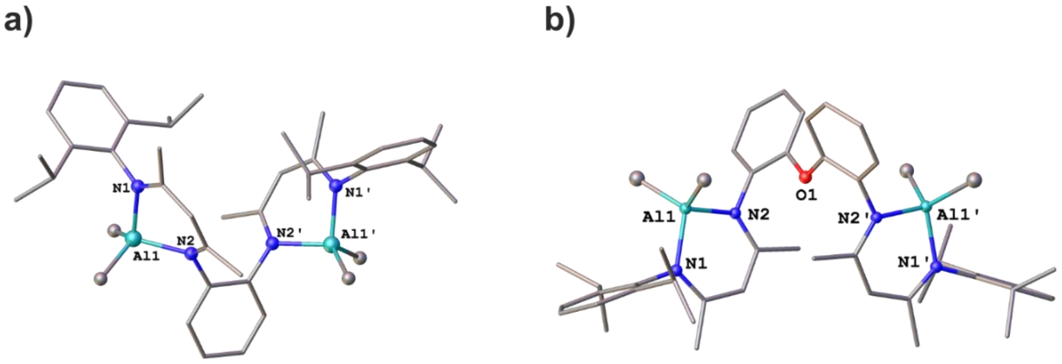


Figure 5. Solid state structures (hydrogen atoms are omitted for the sake of clarity) with selected bond lengths [Å] and angles [°] of a) IIe: Al1–Al1‘ 6.4023(8), Al1–N1 1.923(1), Al1–N2 1.927(1), Al1–C18 1.958(1), Al1–C19 1.973(1), N1–Al1–N2 95.14(4), C18–Al1–C19 115.14(6); b) Iii: Al1–Al1‘ 7.396(1), Al1–N1 1.930(1), Al1–N2 1.9193(9), Al1–C18 1.970(1), Al1–C19 1.967(1),N1–Al1–N2 95.23(4), C18–Al1–C19 113.22(5).

6.3 Conclusion

In summary, the synthesis of eleven dinuclear methylaluminium complexes based on bis(β-diketiminate) ligands with various alkylene and (hetero)arylene bridges is reported. The molecular structures of five compounds has been elucidated by X-ray diffraction techniques. In future experiment, we will investigate the impact of the metal-metal separation and the flexibility of the bridging unit on the catalytic performance in the ring-opening polymerization of cyclic esters.

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6.5 Supporting Information

General Considerations

All preparations were performed under an inert atmosphere of dinitrogen by means of Standard Schlenk-line or glovebox techniques (GS-Systemtechnik and MBraun). Traces of oxygen and moisture were removed from the inert gas by passing it over a BASF R 3-11 ($CuO/MgSiO_3$) catalyst, through concentrated sulfuric acid, over coarsely granulated silica gel, and finally P_4O_{10}. Dichloromethane was freshly collected from a Solvent Purification System by M. Braun (MB SPS-800). Toluene was used as p.a. grade and distilled from Na/benzophenone prior to use. $CDCl_3$ was dried by distillation from calcium hydride. Trimethylaluminum (2M in Toluene) was purchased from Sigma Aldrich.

Characterization

The NMR spectra were recorded with a Bruker Avance 400 spectrometer (T = 300 K) with δ referenced to external tetramethylsilane (^1H, ^{13}C and ^{27}Al). ^1H and ^{13}C NMR spectra were calibrated by using the solvent residual peak ($CHCl_3$: $\delta(^1H) = 7.26$) and the solvent peak (CDCl3: $\delta(^{13}C) = 77.16$), respectively. ^{27}Al NMR spectra were calibrated relative to external $Al(NO_3)_3 \cdot 9H_2O$. IR spectra were recorded with a Bruker ALPHA spectrometer equipped with a diamond ATR unit **IIb-k** and a Thermo Scientific Nicolet iS5 spectrometer with an ATR-coated diamond crystal **1e**, **1j** and **IIa**. Elemental analysis were performed with a Vario MICRO cube (Elementar Analysensysteme GmbH); the presence of residual solvent molecules was verified by ^1H NMR spectroscopy. Melting points were determined in sealed capillaries with an Apotec melting point apparatus.

Ligand synthesis: 4-[(2,6-diisopropylphenyl)amino]pent-3-en-2-one,[S1] triethyloxonium tetrafluoroborate[S2] and the bis(β-diketimine)s **Ia**-**d**,**f**-**i**, and **k**[S1,S3] were prepared according to published procedures.

Ie: A solution of $[Et_3O]^+[BF_4]^-$ (14.26 g, 75.0 mmol) in CH_2Cl_2 (40 mL) was added to a solution of 4-((2,6-diisopropylphenyl)amino)-pent-3-en-2-one (19.46 g, 75.0 mmol) in CH_2Cl_2 (70 mL) at 0 °C. The orange reaction mixture was stirred for 19 h at room temperature and then Et_3N (7.59 g, 75.0 mmol) was added. After 30 min a solution of *o*-phenylenediamine (4.06 g, 37.5 mmol) in Et_3N (24 g) was added to the mixture. After stirring at room temperature for 1 d all volatiles were removed in vacuo. Toluene (80 mL) was added to extract the product from the oily precipitate of $[Et_3NH]^+[BF_4]^-$. Toluene was removed from the extract and the crude product was dissolved in ethanol (3 mL). A yellow solid was obtained. Drying in vacuo gave 10.04 g (45 %) of the product. ^{1}H NMR: (400 MHz, $CDCl_3$): δ = 1.12 [d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me₂*], 1.21 [d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me₂*], 1.67 [s, 6H, C*Me*], 1.83 [s, 6H, C*Me*], 3.06 [sept, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*Me₂], 4.82 [s, 2H, C*H*], 6.87-6.90 [m, 2H, Ar*H*], 7.00-7.03 [m, 2H, Ar*H*], 7.14 [br, 6H, Ar*H*], 12.12 ppm [s, 2H, N*H*]; ^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$): δ = 20.9 [C*Me*], 23.0 [C*Me*], 24.5 [CH*Me₂*], 28.4 [*C*HMe₂], 95.3 [β-*C*H], 123.1 [*m*-*C*(Dipp)], 124.3 [*C*(Aryl)], 125.0 [*p*-*C*(Dipp)], 125.2 [*C*(Aryl)], 139.6 [*o*-*C*(Dipp)], 141.0 [*ipso*-*C*(Dipp)], 142.6 [*C*(Aryl)], 160.5 [*C*N], 160.8 ppm [*C*N]; ATR-IR: $\tilde{\nu}$ = 3066, 2958, 2923, 1622, 1542, 1501, 1439, 1361, 1255, 1175, 1103, 1022, 930, 789, 756, 701 cm^{-1}; elemental analysis calcd (found) $C_{40}H_{54}N_4$: C 81.31 (81.47), H 9.21 (8.97), N 9.48 (9.34); m.p. 135 °C.

Ij was synthesized by a procedure directly analogous to **1e**, employing 2,2'-thiodianiline (8.11 g, 37.5 mmol) instead of *o*-phenylenediamine. Yellow crystals were obtained after 2 months in ethanol (10 mL). Drying in vacuo gave 3.67 g (14 %) of the product. ^{1}H NMR: (400 MHz, $CDCl_3$): δ = 1.03 [d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me₂*], 1.17 [d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me₂*], 1.68 [s, 6H, C*Me*], 1.84 [s, 6H, C*Me*], 3.10 [sept, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*Me₂], 5.87 [s, 2H, C*H*], 6.82-6.86 [m, 4H, Ar*H*], 7.04-7.12 [m, 8H, Ar*H*], 7.15-7.19 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$): δ = 20.3 [C*Me*], 21.3 [C*Me*], 22.8 [CH*Me₂*], 24.6 [CH*Me₂*], 28.5 [*C*HMe₂], 94.9 [β-*C*H], 122.9 [*C*(Aryl)], 123.1 [*m*-*C*(Dipp)], 123.8 [*C*(Aryl)], 126.3 [*p*-*C*(Dipp)], 127.1 [*C*(Aryl)], 129.4 [*C*(Aryl)], 132.2 [*C*(Aryl)], 138.1 [*C*(Aryl)], 144.7 [*o*-*C*(Dipp)], 149.0 [*ipso*-*C*(Dipp)], 158.5 [*C*N], 163.8 ppm [*C*N]; ATR-IR: $\tilde{\nu}$ = 3051, 2962, 2924, 2864, 1617, 1539, 1485, 1456, 1362, 1320, 1273, 1178, 1021, 927, 904, 797, 749 cm^{-1}; elemental analysis calcd (found) $C_{46}H_{58}N_4S$: C 79.04 (79.23), H 8.36 (8.07), N 8.01 (7.84), S 4.59 (4.38); m.p. 143 °C.

General procedure for the synthesis employing trimethylaluminum: Trimethylaluminum (2.8 mL, 5.5 mmol, 2M in Toluene) was added dropwise to a solution of the respective bis(β-diketimine) (2.5 mmol) in Toluene (20 mL). The reaction solution was stirred for 16 h at 90 °C. The volatile substances were removed in vacuum and the residue was washed with pentane (3x10 mL). The residue was then extracted with toluene (20 mL) and the concentration of the filtered extract yielded the products. **IIc** has already reported in the literature.[S4]

Colorless crystals suitable for an X-ray diffraction analysis were obtained from concentrated toluene solutions of **IIa**, **IIb**, **IIc, IIe**, and **IIi** at room temperature.

IIa: pale yellow powder, 0.97 g (62%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ = -0.97 [s, 6H, Al*Me*$_2$], -0.73 [s, 6H, Al*Me*$_2$], 1.08 [d, 6H, $^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.17-1.21 [m, 18H, CH*Me*$_2$], 1.75 [s, 6H, C*Me*], 2.06 [s, 6H, C*Me*], 3.05 [sept, 2H, $^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 3.19 [sept, 2H, $^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 4.95 [s, 2H, C*H*], 7.13-7.15 [m, 2H, Ar*H*], 7.18-7.20 [m, 2H, Ar*H*], 7.22-7.27 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$): δ = -11.2 [Al*Me*$_2$], -8.6 [Al*Me*$_2$], 21.3 [C*Me*], 23.7 [C*Me*], 24.3 [CH*Me*$_2$], 24.6 [CH*Me*$_2$], 24.9 [CH*Me*$_2$], 25.9 [CH*Me*$_2$], 27.7 [*C*HMe$_2$], 28.0 [*C*HMe$_2$], 94.9 [β-*C*H], 124.1 [*m-C*(Dipp)], 124.3 [*m-C*(Dipp)], 126.7 [*p-C*(Dipp)], 140.8 [*o-C*(Dipp)], 143.6 [*o-C*(Dipp)], 144.8 [*ipso-C*(Dipp)], 168.0 [*C*N], 169.3 ppm [*C*N]; ATR-IR: $\tilde{\nu}$ = 2964, 2926, 2868, 1524, 1443, 1357, 1318, 1254, 1184, 1104, 1020, 925, 800, 764, 731, 676 cm^{-1}; elemental analysis calcd (found) $C_{38}H_{60}Al_2N_4\cdot 0.2C_7H_8$: C 73.33 (73.47), H 9.62 (9.79), N 8.68 (8.57); m.p. 201 °C.

IIb: yellow powder, 1.64 g (100%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ = -0.94 [s, 12H, Al*Me*$_2$], 1.12 [d, 12H, $^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.18 [d, 12H, $^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.68 [s, 6H, C*Me*], 2.16 [s, 6H, C*Me*], 3.01 [sept, 4H, $^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 3.43 [s, 4H, C*H*$_2$], 4.97 [s, 2H, C*H*], 7.13-7.15 [m, 4H, Ar*H*], 7.19-7.23 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$): δ = -10.5 [Al*Me*$_2$], 21.7 [C*Me*], 23.3 [C*Me*], 24.6 [CH*Me*$_2$], 24.9 [CH*Me*$_2$], 27.9 [*C*HMe$_2$], 48.1 [*C*H$_2$], 98.3 [β-*C*H], 123.9 [*m-C*(Dipp)], 126.4 [*p-C*(Dipp)], 140.9 [*o-C*(Dipp)], 144.2 [*ipso-C*(Dipp)], 168.3 [*C*N], 168.9 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, $CDCl_3$): δ = 154.0 ppm [*Al*Me$_2$]; ATR-IR: $\tilde{\nu}$ = 2963, 2925, 2869, 1552, 1522, 1441, 1380, 1312, 1294, 1261, 1184, 1098, 1014, 871, 798, 760, 668, 576 cm^{-1}; elemental analysis calcd (found) $C_{40}H_{64}Al_2N_4$: C 73.36 (73.25), H 9.85 (9.48), N 8.55 (8.36); m.p. 199 °C.

IIc: pale yellow powder, 1.53 g (91%). The analytic data are in agreement with published data.[S4] ^{1}H NMR: (400 MHz, $CDCl_3$): δ = -0.98 [s, 12H, Al*Me*$_2$], 1.12 [d, 12H, $^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.16[d, 12H, $^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.66 [s, 6H, C*Me*], 1.73-1.81 [m, 2H, C*H*$_2$], 2.09 [s, 6H, C*Me*], 3.01 [sept, 4H, $^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 3.33 [t, 4H, $^{3}J_{HH}$ = 8.1 Hz, C*H*$_2$], 4.94 [s, 2H, C*H*], 7.11-7.13 [m, 4H, Ar*H*], 7.18-7.21 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$): δ = -10.8 [Al*Me*$_2$], 20.8 [C*Me*], 23.3 [C*Me*], 24.5 [CH*Me*$_2$], 24.9 [CH*Me*$_2$], 27.9 [*C*HMe$_2$], 32.7 [*C*H$_2$], 45.5 [*C*H$_2$], 98.0 [β-*C*H], 123.9 [*m-C*(Dipp)], 126.3 [*p-C*(Dipp)], 141.1 [*o-C*(Dipp)], 144.4 [*ipso-C*(Dipp)], 167.8 [*C*N], 168.3 ppm [CN]; ^{27}Al{^{1}H} NMR: (104 MHz, $CDCl_3$): δ = 152.5 ppm [*Al*Me$_2$]; ATR-IR: $\tilde{\nu}$ = 2961, 2927, 2868, 1559, 1515, 1399, 1355, 1317, 1253, 1186, 1094, 1016, 800, 754, 670, 574 cm^{-1}; elemental analysis calcd (found) $C_{41}H_{66}Al_2N_4$: C 73.61 (73.42), H 9.94 (9.56), N 8.38 (8.07); m.p. 195 °C.

IId: colourless powder, 1.47 g (83%). ^{1}H NMR: (400 MHz, $CDCl_3$): *δ* = -0.85 [s, 6H, Al*Me*$_2$], -0.82 [s, 6H, Al*Me*$_2$], 1.04 [d, 6H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.15 [d, 6H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.17 [d, 6H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.19 [d, 6H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.30 [br, 2H, ring-C*H*$_2$], 1.58 [br, 2H, ring-C*H*$_2$], 1.66 [s, 6H, C*Me*], 1.72 [br, 4H, ring-C*H*$_2$], 2.24 [s, 6H, C*Me*], 2.84 [sept, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 3.23 [sept, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 4.24 [br, 2H, ring-C*H*], 5.05 [s, 2H, C*H*], 7.09-7.11 [m, 2H, Ar*H*], 7.15-7.23 ppm [m, 4H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$): *δ* = -9.8 [Al*Me*$_2$], -6.7 [Al*Me*$_2$], 23.4 [C*Me*], 24.2 [C*Me*], 24.3 [CH*Me*$_2$], 24.7 [CH*Me*$_2$], 25.4 [ring-*C*H$_2$], 25.5 [CH*Me*$_2$], 27.8 [*C*HMe$_2$], 27.9 [*C*HMe$_2$], 35.5 [ring-*C*H$_2$], 62.0 [ring-*C*H], 100.1 [β-*C*H], 123.6 [*m*-*C*(Dipp)], 123.7 [*m*-*C*(Dipp)], 126.1 [*p*-*C*(Dipp)], 141.7 [*o*-*C*(Dipp)], 144.1 [*o*-*C*(Dipp)], 145.1 [*ipso*-*C*(Dipp)], 166.9 [*C*N], 168.7 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, $CDCl_3$): *δ* = 153.9 ppm [*Al*Me$_2$]; ATR-IR: $\tilde{\nu}$ = 2965, 2926, 2868, 1546, 1526, 1459, 1382, 1316, 1251, 1189, 1091, 1021, 949, 800, 763, 673, 572 cm^{-1}; elemental analysis calcd (found) $C_{44}H_{70}Al_2N_4$: C 74.54 (74.17), H 9.95 (10.16), N 7.90 (7.64); m.p. 217 °C.

IIe: pale yellow powder, 1.23 g (70%). ^{1}H NMR: (400 MHz, $CDCl_3$): *δ* = -1.17 [s, 6H, Al*Me*$_2$], -0.81 [s, 6H, Al*Me*$_2$], 1.14-1.23 [m, 24H, CH*Me*$_2$], 1.76 [s, 6H, C*Me*], 1.88 [s, 6H, C*Me*], 2.98 [sept, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 3.25 [sept, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 5.21 [s, 2H, C*H*], 6.87-6.93 [m, 2H, Ar*H*], 7.11-7.22 ppm [m, 8H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$): *δ* = -10.0 [Al*Me*$_2$], -9.6 [Al*Me*$_2$], 23.7 [C*Me*], 24.6 [C*Me*], 24.6 [CH*Me*$_2$], 24.7 [CH*Me*$_2$], 25.4 [CH*Me*$_2$], 25.5 [CH*Me*$_2$], 27.9 [*C*HMe$_2$], 28.1 [*C*HMe$_2$], 99.2 [β-*C*H], 124.0 [*m*-*C*(Dipp)], 124.0 [*m*-*C*(Dipp)], 126.5 [*C*(Aryl)], 127.0 [*p*-*C*(Dipp)], 128.7 [*C*(Aryl)], 141.2 [*o*-*C*(Dipp)], 143.2 [*o*-*C*(Dipp)], 144.0 [*ipso*-*C*(Dipp)], 144.7 [*C*(Aryl)], 169.2 [*C*N], 169.8 ppm [*C*N]; ATR-IR: $\tilde{\nu}$ = 2962, 2923, 1542, 1521, 1448, 1364, 1318, 1185, 1109, 1042, 1021, 869, 802, 763, 750, 673, 583, 482, 440 cm^{-1}; elemental analysis calcd (found) $C_{44}H_{64}Al_2N_4$: C 75.18 (74.19), H 9.18 (8.73), N 7.97 (7.95) + silicon grease, shown in the NMR; m.p. 296 °C.

IIf: pale brown powder, 1.76 g (100%). ^{1}H NMR: (400 MHz, $CDCl_3$): *δ* = -0.94 [s, 12H, Al*Me*$_2$], 1.28 [d, 24H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.87 [s, 6H, C*Me*], 2.00 [s, 6H, C*Me*], 3.19 [sept, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 5.26 [s, 2H, C*H*], 6.69 [t, 1H, $^3J_{HH}$ = 2.0 Hz, Ar*H*], 6.92 [d, 1H, $^3J_{HH}$ = 2.0 Hz, Ar*H*], 6.94 [d, 1H, $^3J_{HH}$ = 2.0 Hz, Ar*H*], 7.24-7.25 [m, 4H, Ar*H*], 7.29-7.35 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$): *δ* = -10.9 [Al*Me*$_2$], 23.0 [C*Me*], 23.5 [C*Me*], 24.5 [CH*Me*$_2$], 24.8 [CH*Me*$_2$], 28.0 [*C*HMe$_2$], 98.5 [β-*C*H], 122.9 [*m*-*C*(Dipp)], 123.2 [*m*-*C*(Dipp)], 124.0 [*C*(Aryl)], 126.5 [*p*-*C*(Dipp)], 129.8 [*C*(Aryl)], 141.0 [*o*-*C*(Dipp)], 144.1 [*ipso*-*C*(Dipp)], 147.0 [*C*(Aryl)], 167.1 [*C*N], 169.6 ppm [*C*N]; ATR-IR: $\tilde{\nu}$ = 2962, 2928, 2868, 1551, 1521, 1441, 1376, 1317, 1252, 1185, 1106, 1018, 899, 798, 757, 674, 578, 443 cm^{-1}; elemental analysis calcd (found) $C_{44}H_{64}Al_2N_4$: C 75.18 (75.15), H 9.18 (9.12), N 7.97 (7.78); m.p. 199 °C.

IIg: pale yellow powder, 1.76 g (100%). ^{1}H NMR: (400 MHz, CDCl$_3$): δ = -1.06 [s, 12H, Al*Me*$_2$], 1.17 [d, 12H, $^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.18 [d, 12H, $^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.76 [s, 6H, C*Me*], 1.91 [s, 6H, C*Me*], 3.08 [sept, 4H, $^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 5.15 [s, 2H, C*H*], 6.94 [s, 4H, Ar*H*], 7.13-7.15 [m, 4H, Ar*H*], 7.19-7.23 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = -11.2 [Al*Me*$_2$], 22.8 [C*Me*], 23.4 [C*Me*], 24.4 [CH*Me*$_2$], 24.7 [CH*Me*$_2$], 27.9 [*C*HMe$_2$], 98.3 [β-*C*H], 123.8 [*m-C*(Dipp)], 126.2 [*C*(Aryl)], 126.3 [*p-C*(Dipp)], 140.9 [*o-C*(Dipp)], 143.2 [*ipso-C*(Dipp)], 144.0 [*C*(Aryl)], 167.1 [CN], 169.2 ppm [CN]; ATR-IR: $\tilde{\nu}$ = 2964, 2927, 2866, 1552, 1526, 1491, 1440, 1380, 1316, 1258, 1180, 1016, 893, 800, 759, 673, 577, 445 cm^{-1}; elemental analysis calcd (found) $C_{44}H_{64}Al_2N_4$: C 75.18 (75.20), H 9.18 (8.91), N 7.97 (7.74); m.p. 279 °C.

IIh: pale yellow powder, 1.43 g (81%). ^{1}H NMR: (400 MHz, CDCl$_3$): δ = -0.87 [s, 12H, Al*Me*$_2$], 1.25 [“t”, 24H, $^{3}J_{HH}$ = 6.5 Hz, $^{3}J_{HH}$ = 6.6 Hz, CH*Me*$_2$], 1.89 [s, 6H, C*Me*], 2.22 [s, 6H, C*Me*], 3.15 [sept, 4H, $^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 5.33 [s, 2H, C*H*], 6.82 [d, 2H, $^{3}J_{HH}$ = 7.8 Hz, Ar*H*], 7.24-7.26 [m, 4H, Ar*H*], 7.30-7.35 [m, 2H, Ar*H*], 7.69 ppm [t, 1H, $^{3}J_{HH}$ = 7.8 Hz, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = -11.6 [Al*Me*$_2$], 22.5 [C*Me*], 22.6 [C*Me*], 23.5 [CH*Me*$_2$], 23.7 [CH*Me*$_2$], 27.0 [*C*HMe$_2$], 99.4 [β-*C*H], 113.8 [*C*(Aryl)], 123.0 [*m-C*(Dipp)], 125.6 [*p-C*(Dipp)], 137.7 [*C*(Aryl)], 140.1 [*o-C*(Dipp)], 142.7 [*ipso-C*(Dipp)], 156.6 [*C*(Aryl)], 165.0 [*C*N], 169.7 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, CDCl$_3$): δ = 154.3 ppm [*Al*Me$_2$]; ATR-IR: $\tilde{\nu}$ = 2966, 2927, 2868, 1549, 1530, 1447, 1430, 1370, 1317, 1257, 1179, 1108, 1019, 934, 797, 759, 671, 583, 467 cm^{-1}; elemental analysis calcd (found) $C_{43}H_{63}Al_2N_5$: C 73.37 (73.27), H 9.02 (8.99), N 9.95 (9.66); m.p. 197 °C.

IIi: pale yellow powder, 1.54 g (77%). ^{1}H NMR: (400 MHz, CDCl$_3$): δ = -1.18 [s, 6H, Al*Me*$_2$], -0.77 [s, 6H, Al*Me*$_2$], 0.77 [d, 6H, $^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 0.89 [d, 6H, $^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.20 [d, 6H, $^{3}J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.22 [d, 6H, $^{3}J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.73 [s, 6H, C*Me*], 2.00 [s, 6H, C*Me*], 2.86 [sept, 2H, $^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 3.15 [sept, 2H, $^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 5.17 [s, 2H, C*H*], 6.81-6.83 [m, 2H, Ar*H*], 7.05-7.21 ppm [m, 12H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = -11.2 [Al*Me*$_2$], -8.9 [Al*Me*$_2$], 23.2 [C*Me*], 23.5 [C*Me*], 24.3 [CH*Me*$_2$], 24.7 [CH*Me*$_2$], 24.9 [CH*Me*$_2$], 25.7 [CH*Me*$_2$], 27.8 [*C*HMe$_2$], 27.8 [*C*HMe$_2$], 97.8 [β-*C*H], 120.0 [*C*(Aryl)], 123.8 [*m-C*(Dipp)], 124.1 [*m-C*(Dipp)], 126.6 [*p-C*(Dipp)], 126.9 [*C*(Aryl)], 127.3 [*C*(Aryl)], 137.0 [*C*(Aryl)], 140.6 [*C*(Aryl)], 143.9 [*o-C*(Dipp)], 144.3 [*ipso-C*(Dipp)], 151.5 [*C*(Aryl)], 169.3 [CN], 169.8 ppm [CN]; ATR-IR: $\tilde{\nu}$ = 3062, 2965, 2934, 2925, 2866, 1551, 1530, 1486, 1439, 1389, 1317, 1260, 1178, 1108, 1019, 796, 758, 671, 586, 467 cm^{-1}; elemental analysis calcd (found) $C_{50}H_{68}Al_2N_4O$: C 75.53 (75.43), H 8.62 (8.63), N 7.05 (7.00); m.p. 267 °C.

IIj: colourless powder, 1.67 g (82%). ^{1}H NMR: (400 MHz, CDCl$_3$): Spezies1:Spezies2 = 57:43

Species 1: δ = -1.02 [s, 6H, Al*Me*$_2$], -0.94 [s, 6H, Al*Me*$_2$], 0.99 [d, 6H, $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$], 1.04 [d, 6H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.17-1.20 [m, 12H, CH*Me*$_2$], 1.79 [s, 6H, C*Me*], 1.91 [s, 6H, C*Me*], 3.03-3.13 [m, 2H, C*H*Me$_2$], 3.19-3.33 [m, 2H, C*H*Me$_2$], 5.24 [s, 2H, C*H*], 7.00-7.24 ppm [m, 14H, Ar*H*];

Species 2: δ =-1.04 [s, 6H, Al*Me*$_2$], -0.94 [s, 6H, Al*Me*$_2$], 1.08 [d, 6H, $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$], 1.12 [d, 6H, $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$], 1.17-1.20 [m, 12H, CH*Me*$_2$], 1.78 [s, 6H, C*Me*], 1.95 [s, 6H, C*Me*], 3.03-3.13 [m, 2H, C*H*Me$_2$], 3.19-3.33 [m, 2H, C*H*Me$_2$], 5.17 [s, 1H, C*H*], 7.00-7.24 ppm [m, 14H, Ar*H*];

^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = -10.9 [Al*Me*$_2$], -10.2 [Al*Me*$_2$], -9.9 [Al *Me*$_2$], 23.3 [C*Me*], 23.5 [C*Me*], 24.6 [C*Me*], 24.7 [C*Me*], 24.7 [CH*Me*$_2$], 24.8 [CH*Me*$_2$], 24.8 [CH*Me*$_2$], 24.9 [CH*Me*$_2$], 25.3 [CH*Me*$_2$], 25.3 [CH*Me*$_2$], 27.9 [*C*HMe$_2$], 27.9 [*C*HMe$_2$], 28.0 [*C*HMe$_2$], 28.1 [*C*HMe$_2$], 98.4 [β-*C*H], 98.8 [β-*C*H], 123.9 [*C*(Aryl)], 123.9 [*C*(Aryl)], 124.0 [*m*-*C*(Dipp)], 124.1 [*m*-*C*(Dipp)], 126.5 [*m*-*C*(Dipp)], 126.6 [*m*-*C*(Dipp)], 126.8 [*p*-*C*(Dipp)], 127.4 [*p*-*C*(Dipp)], 127.5 [*C*(Aryl)], 132.8 [*C*(Aryl)], 133.6 [*C*(Aryl)], 140.7 [*C*(Aryl)], 140.9 [*C*(Aryl)], 144.0 [*o*-*C*(Dipp)], 144.2 [*ipso*-*C*(Dipp)], 144.5 [*C*(Aryl)], 145.9 [*C*(Aryl)], 167.7 [*C*N], 168.1 [*C*N], 169.9 [*C*N], 170.1 ppm [*C*N]; ATR-IR: $\tilde{\nu}$ = 3062, 2962, 2925, 2868, 1552, 1521, 1464, 1438, 1381, 1320, 1254, 1181, 1017, 943, 938, 887, 794, 758, 674, 577 cm^{-1}; elemental analysis calcd (found) $C_{50}H_{68}Al_2N_4S$: C 74.04 (74.11), H 8.45 (8.09), N 6.91 (6.83); m.p. 244 °C.

IIk: yellow powder, 1.72 g (94%). ^{1}H NMR: (400 MHz, CDCl$_3$): δ = -1.03 [s, 12H, Al*Me*$_2$], 1.14 [d, 24H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.70 [s, 6H, C*Me*], 2.00 [s, 6H, C*Me*], 3.09 [sept, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 4.58 [s, 4H, C*H*$_2$], 4.99 [s, 2H, C*H*], 7.07-7.14 [m, 7H, Ar*H*], 7.18-7.21 [m, 2H, Ar*H*], 7.24-7.28 ppm [m, 1H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = -10.8 [Al*Me*$_2$], 22.0 [C*Me*], 23.4 [C*Me*], 24.7 [CH*Me*$_2$], 24.9 [CH*Me*$_2$], 27.9 [*C*HMe$_2$], 50.9 [*C*H$_2$], 98.0 [β-*C*H], 123.9 [*m*-*C*(Dipp)], 125.0 [*m*-*C*(Dipp)], 125.5 [*C*(Aryl)], 126.4 [*p*-*C*(Dipp)], 128.9 [*C*(Aryl)], 140.0 [*o*-*C*(Dipp)], 141.0 [*ipso*-*C*(Dipp)], 144.3 [*C*(Aryl)], 168.6 [*C*N], 170.0 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, CDCl$_3$): δ = 150.5 ppm [*Al*Me$_2$]; ATR-IR: $\tilde{\nu}$ = 2962, 2928, 2868, 1555, 1520, 1466, 1439, 1389, 1319, 1258, 1184, 1099, 1015, 800, 763, 672, 441 cm^{-1}; elemental analysis calcd (found) $C_{46}H_{68}Al_2N_4$: C 75.58 (75.72), H 9.38 (9.50), N 7.66 (7.59); m.p. 162 °C.

1e

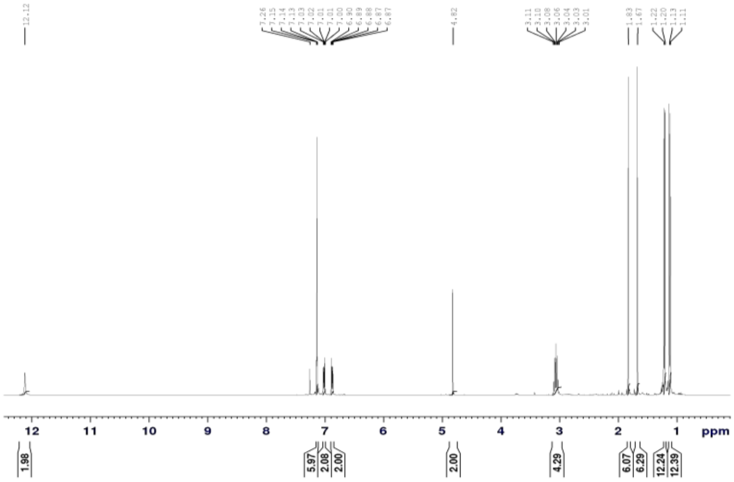

Figure S1: ^{1}H NMR spectrum (400 MHz) of **1e** in CDCl$_3$.

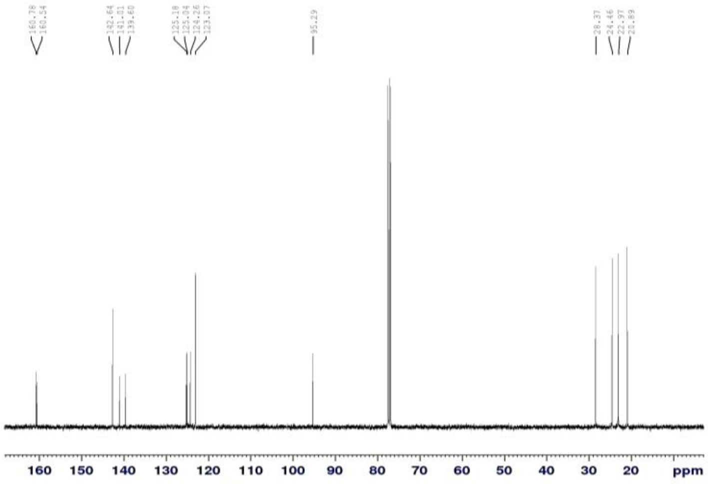

Figure S2: ^{13}C NMR spectrum (101 MHz) of **1e** in CDCl$_3$.

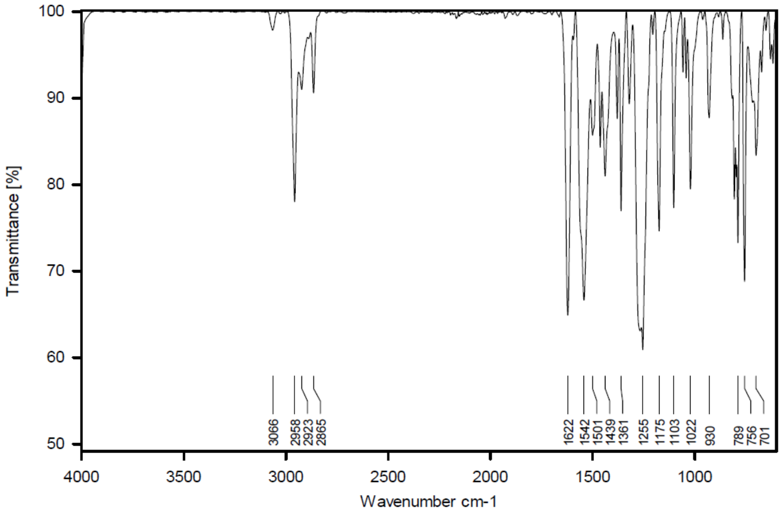

Figure S3: ATR-IR spectrum of **1e**.

1j

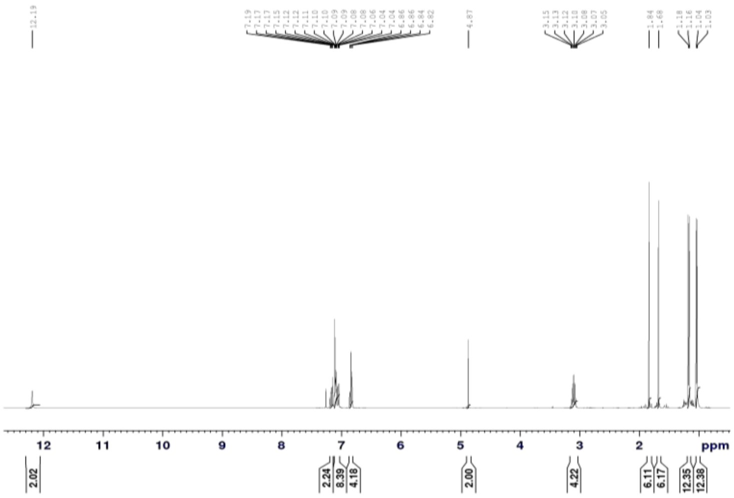

Figure S4: ^{1}H NMR spectrum (400 MHz) of **1j** in CDCl3.

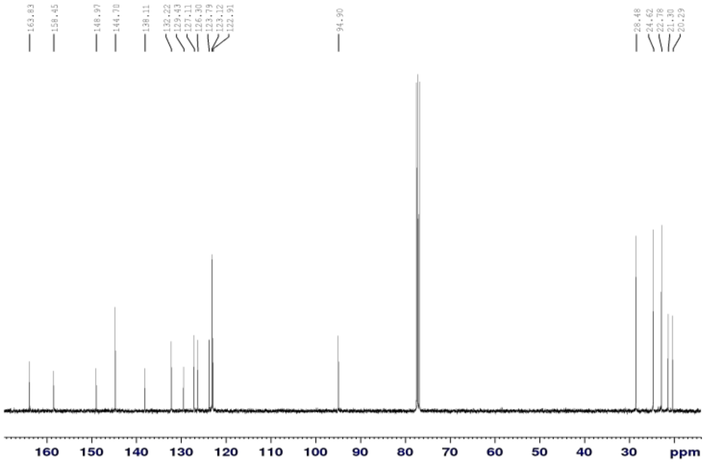

Figure S5: ^{13}C NMR spectrum (101 MHz) of **1j** in CDCl3.

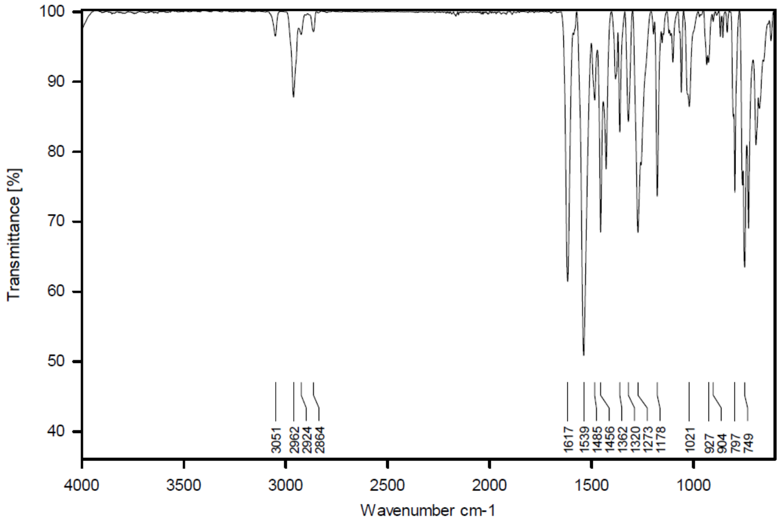

Figure S6: ATR-IR spectrum of **1j**.

IIa

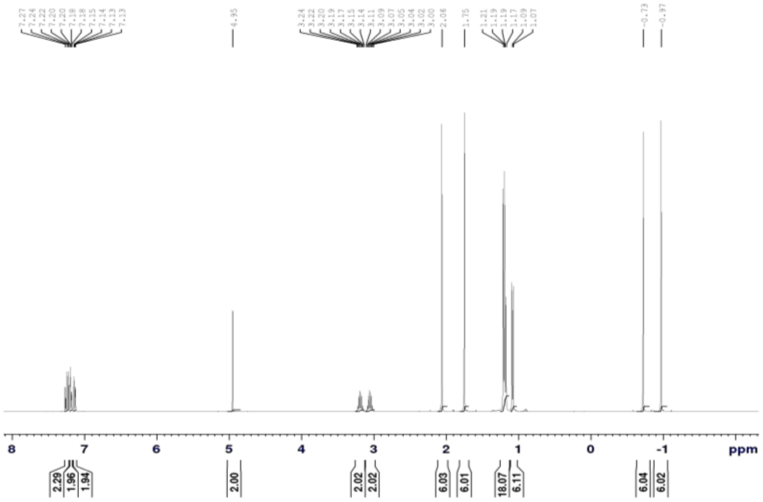

Figure S7: ^{1}H NMR spectrum (400 MHz) of **IIa** in CDCl$_3$.

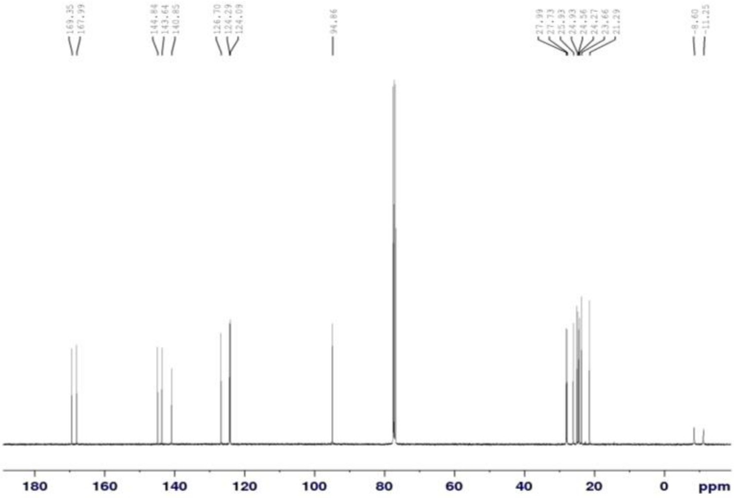

Figure S8: ^{13}C NMR spectrum (101 MHz) of **IIa** in CDCl$_3$.

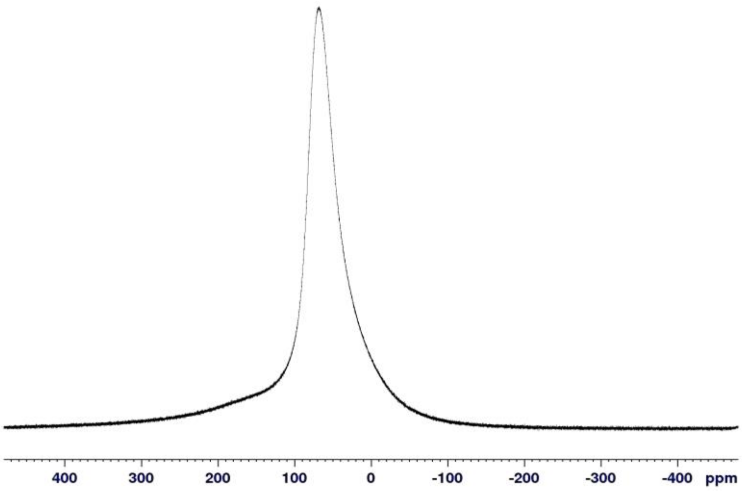

Figure S9: ^{27}Al NMR spectrum (104 MHz) of **IIa** in CDCl$_3$.

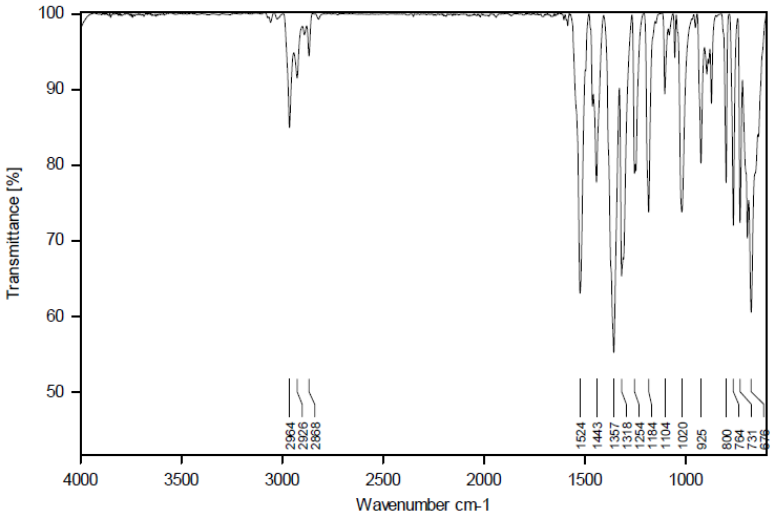

Figure S10: ATR-IR spectrum of **IIa**.

IIb

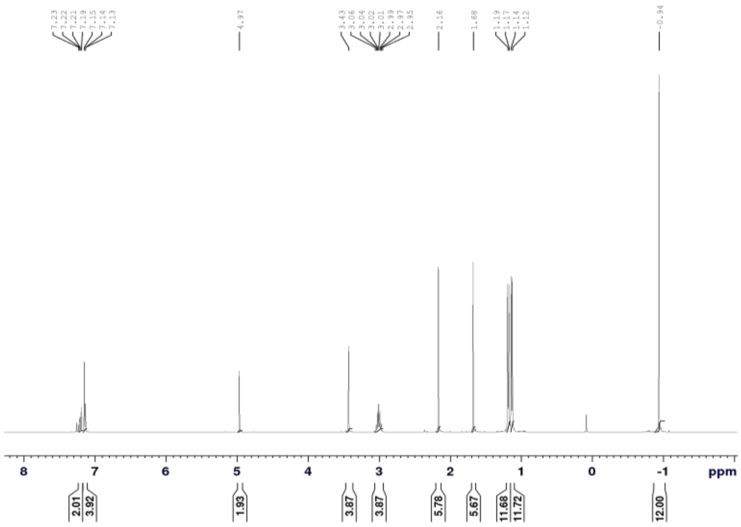

Figure S11: ^{1}H NMR spectrum (400 MHz) of **IIb** in $CDCl_3$.

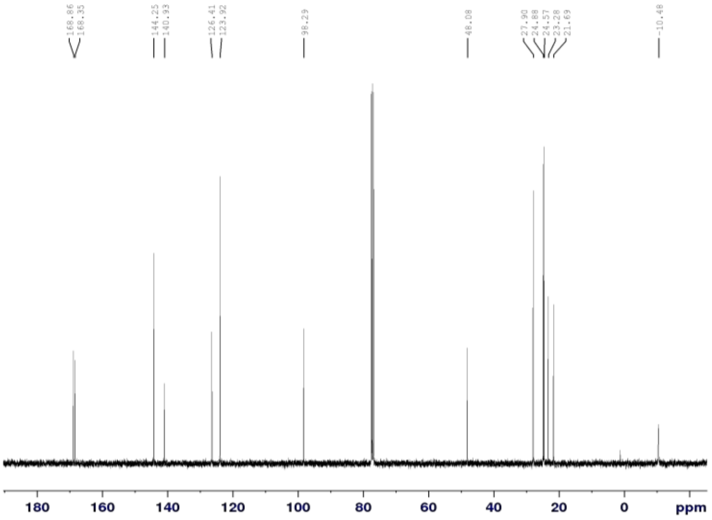

Figure S12: ^{13}C NMR spectrum (101 MHz) of **IIb** in $CDCl_3$.

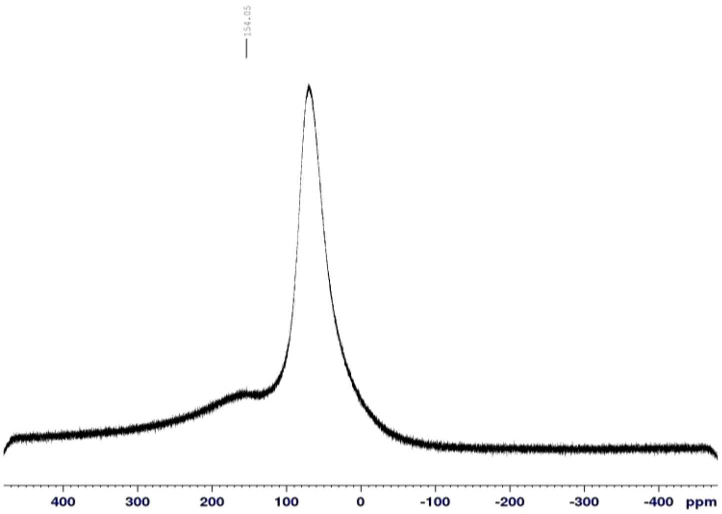

Figure S13: ^{27}Al NMR spectrum (104 MHz) of **IIb** in CDCl$_3$.

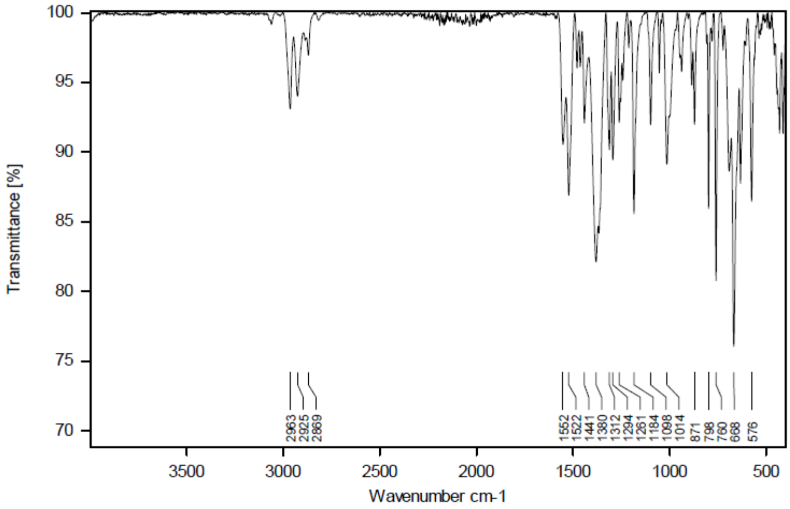

Figure S14: ATR-IR spectrum of **IIb**.

IIc

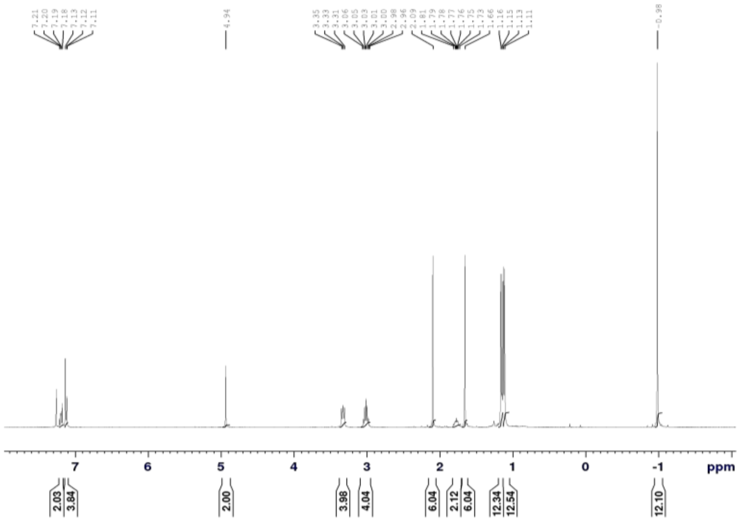

Figure S15: ^{1}H NMR spectrum (400 MHz) of **IIc** in CDCl$_3$.

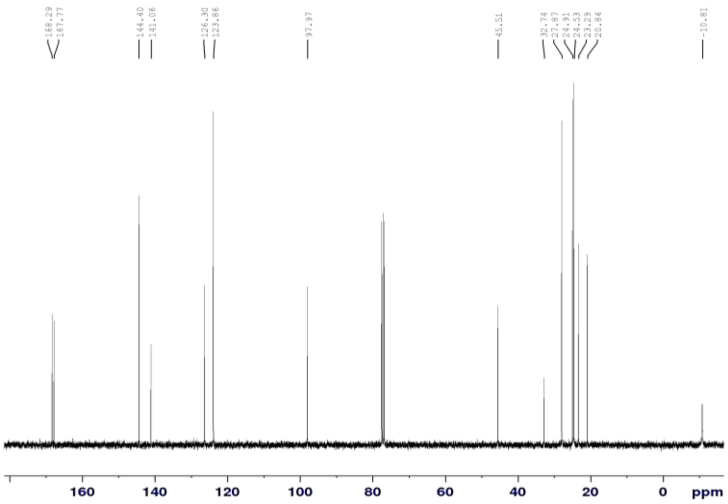

Figure S16: ^{13}C NMR spectrum (101 MHz) of **IIc** in CDCl$_3$.

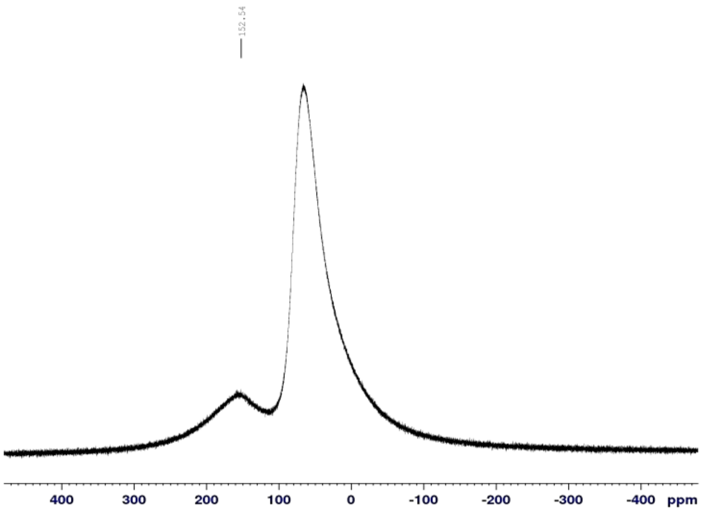

Figure S17: ^{27}Al NMR spectrum (104 MHz) of **IIc** in CDCl$_3$.

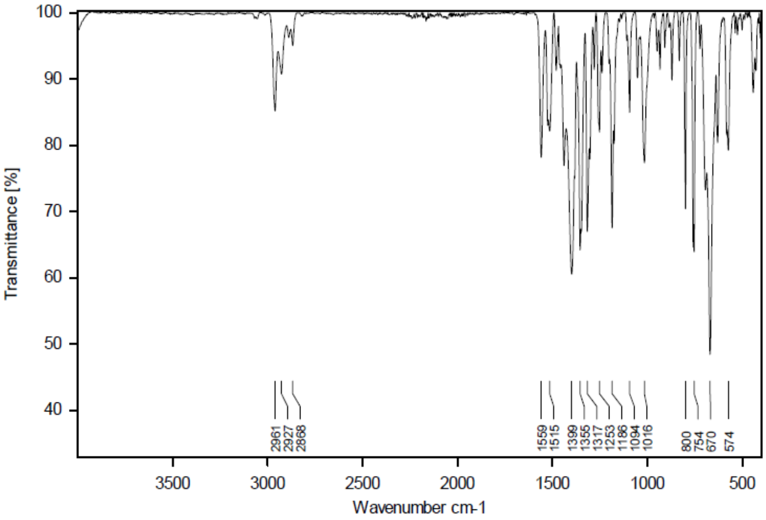

Figure S18: ATR-IR spectrum of **IIc**.

IId

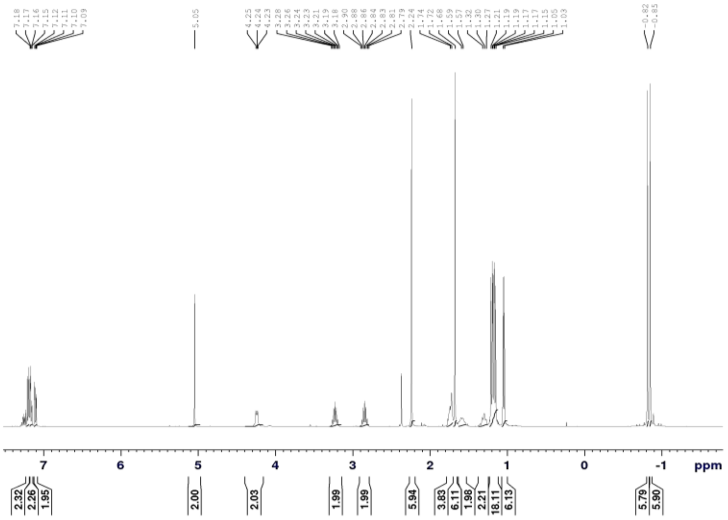

Figure S19: ^{1}H NMR spectrum (400 MHz) of **IId** in CDCl$_3$.

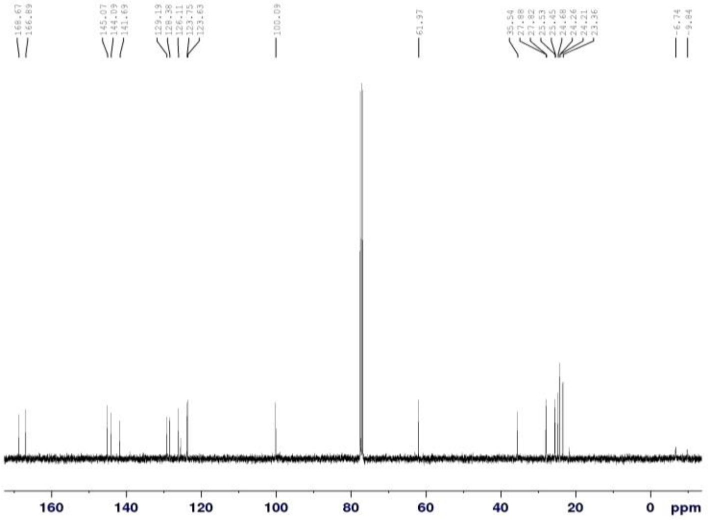

Figure S20: ^{13}C NMR spectrum (101 MHz) of **IId** in CDCl$_3$.

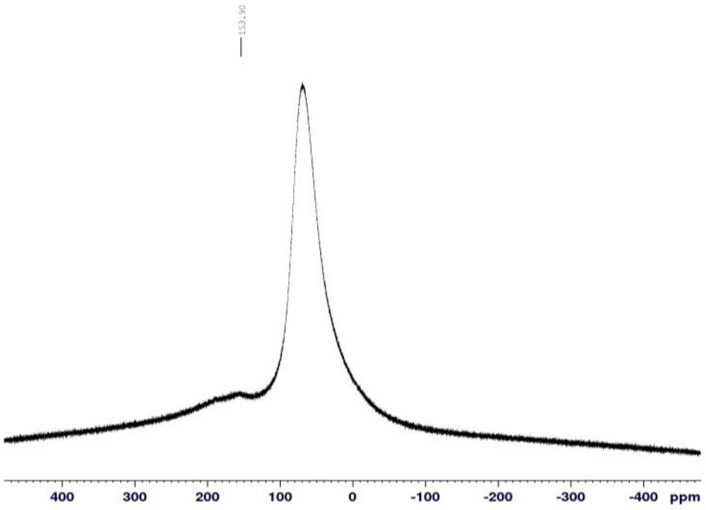

Figure S21: ^{27}Al NMR spectrum (104 MHz) of **IId** in CDCl$_3$.

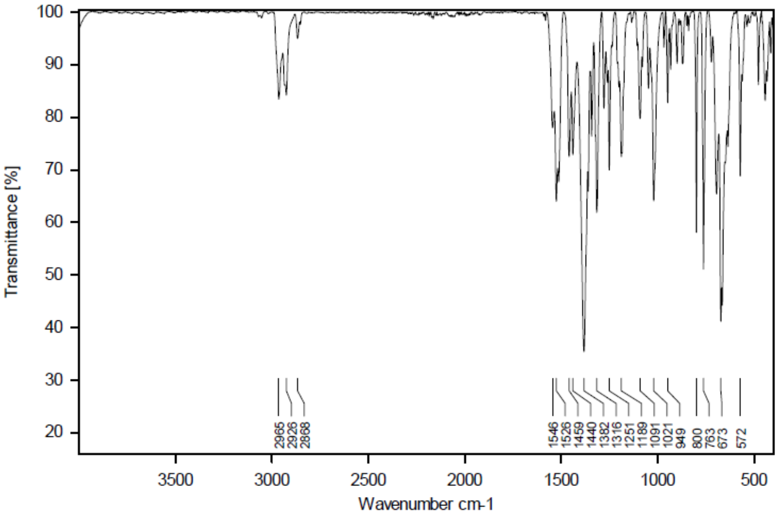

Figure S22: Figure S1: ATR-IR spectrum of **IId**.

IIe

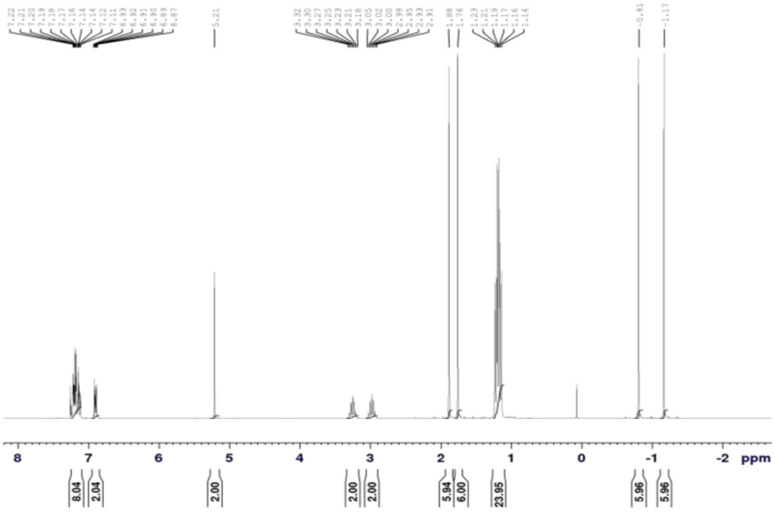

Figure S23: ^{1}H NMR spectrum (400 MHz) of **IIe** in CDCl$_3$.

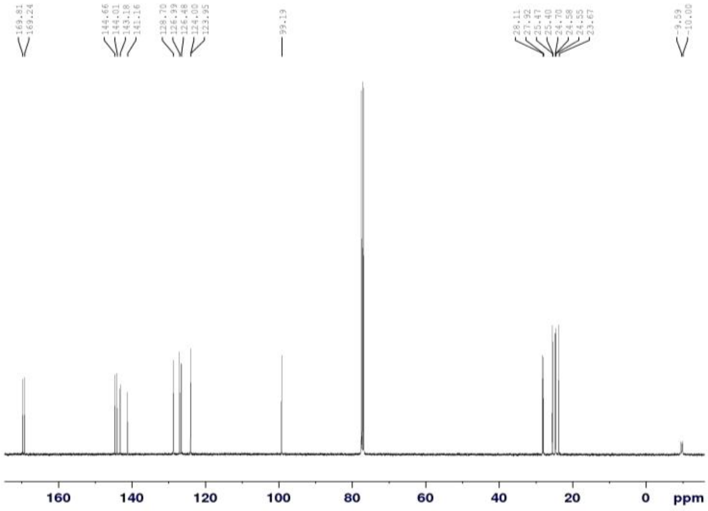

Figure S24: ^{13}C NMR spectrum (101 MHz) of **IIe** in CDCl$_3$.

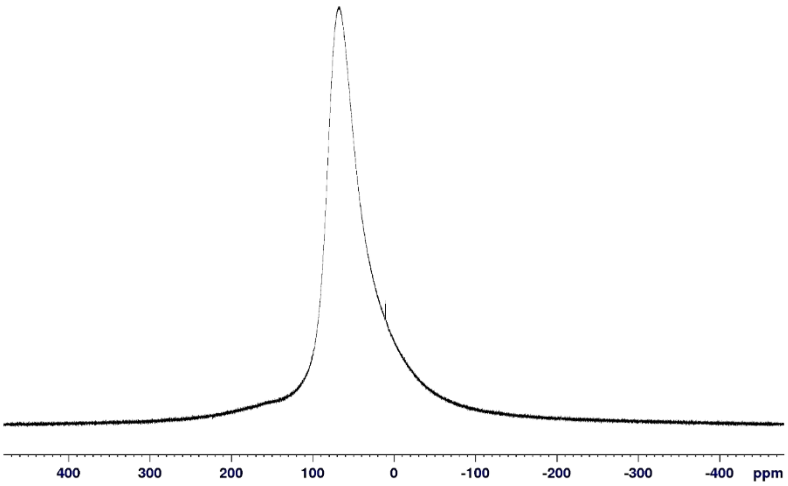

Figure S25: ^{27}Al NMR spectrum (104 MHz) of **IIe** in $CDCl_3$.

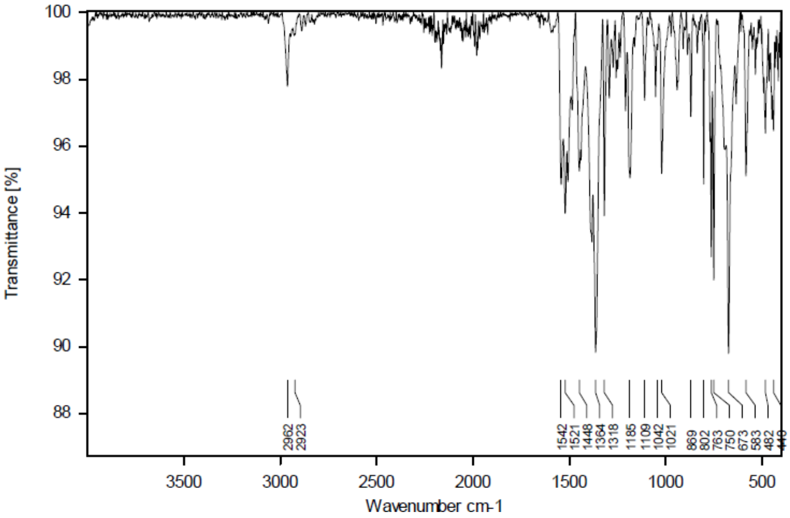

Figure S26: ATR-IR spectrum of **IIe**.

IIf

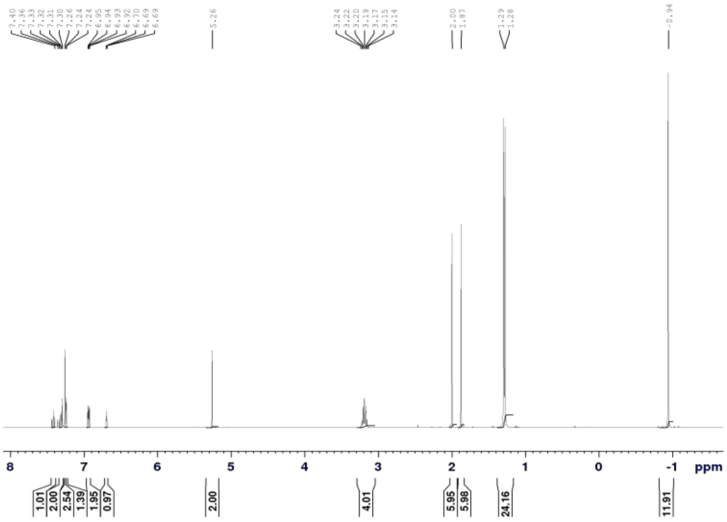

Figure S27: ^{1}H NMR spectrum (400 MHz) of **IIf** in $CDCl_3$.

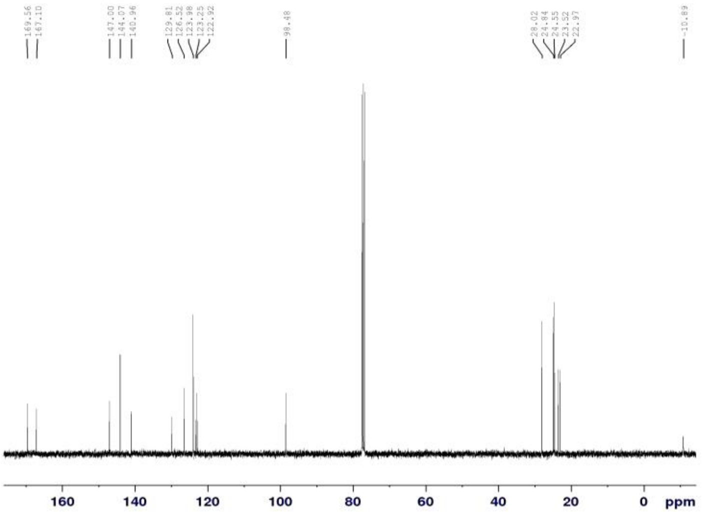

Figure S28: ^{13}C NMR spectrum (101 MHz) of **IIf** in $CDCl_3$.

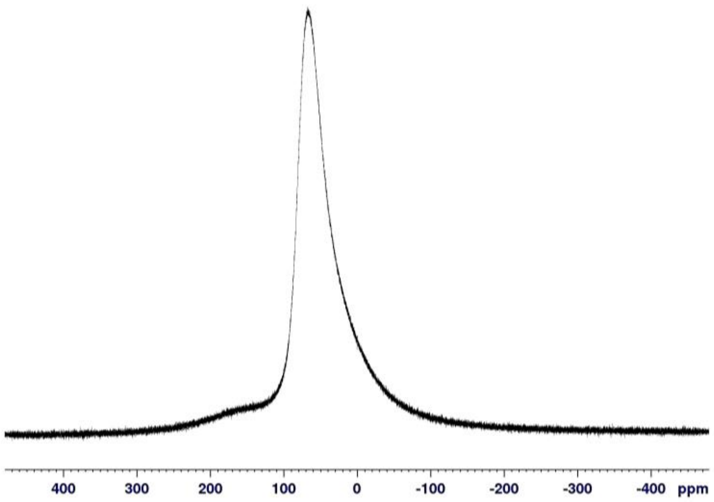

Figure S29: ^{27}Al NMR spectrum (104 MHz) of **IIf** in $CDCl_3$.

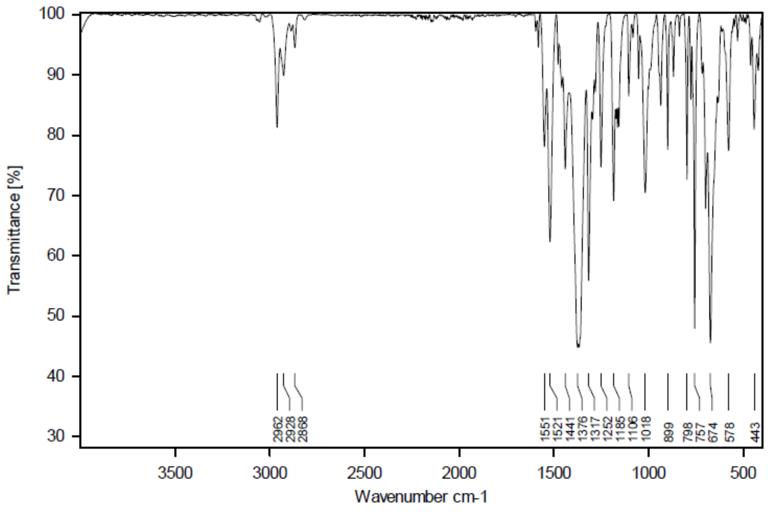

Figure S30: ATR-IR spectrum of **IIf**.

IIg

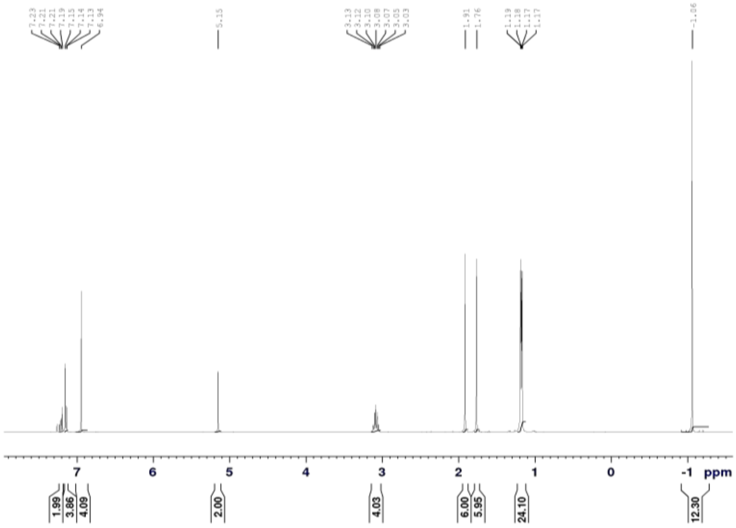

Figure S31: ^{1}H NMR spectrum (400 MHz) of **IIg** in $CDCl_3$.

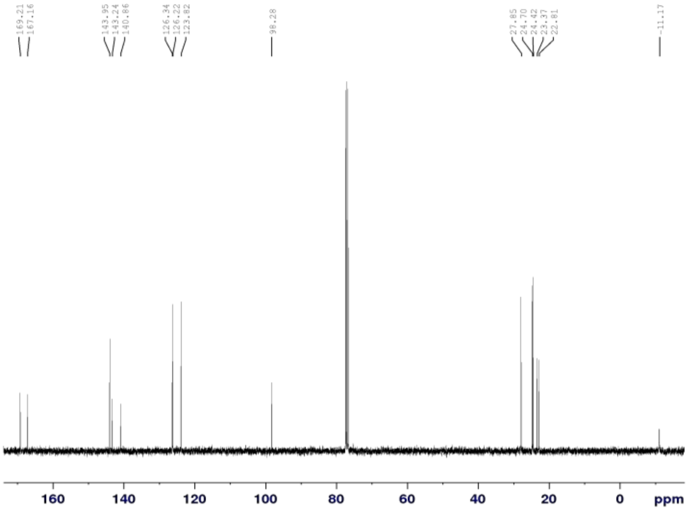

Figure S32: ^{13}C NMR spectrum (101 MHz) of **IIg** in $CDCl_3$.

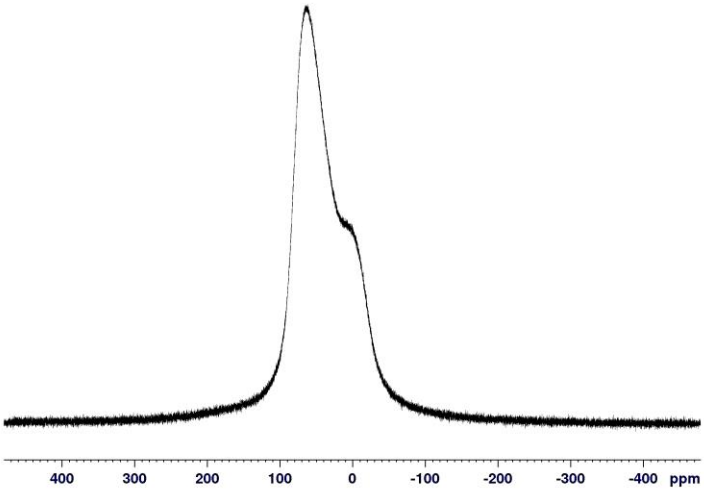

Figure S33: ^{27}Al NMR spectrum (104 MHz) of **IIg** in $CDCl_3$.

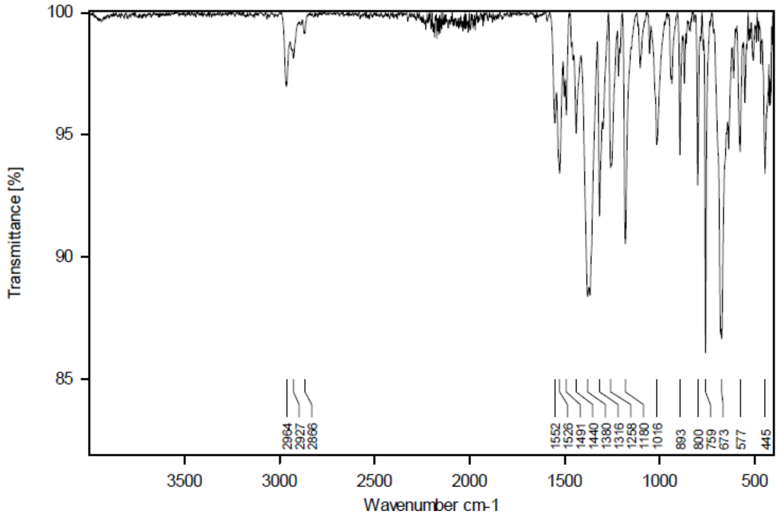

Figure S34: ATR-IR spectrum of **IIg**.

IIh

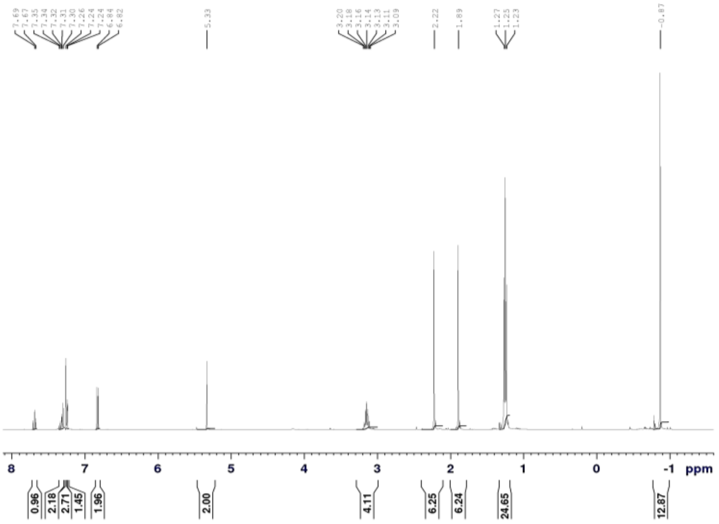

Figure S35: ^{1}H NMR spectrum (400 MHz) of **IIh** in CDCl$_3$.

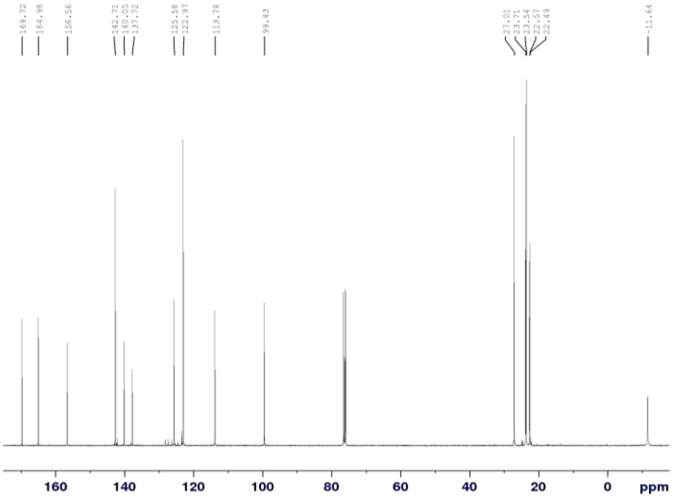

Figure S36: ^{13}C NMR spectrum (101 MHz) of **IIh** in CDCl$_3$.

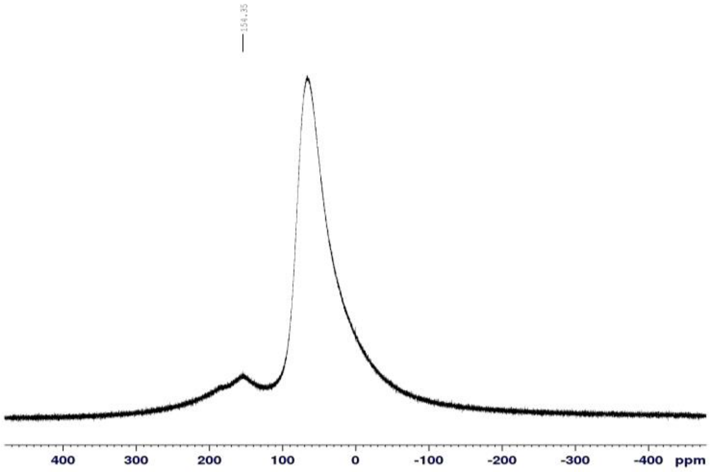

Figure S37: ^{27}Al NMR spectrum (104 MHz) of **IIh** in $CDCl_3$.

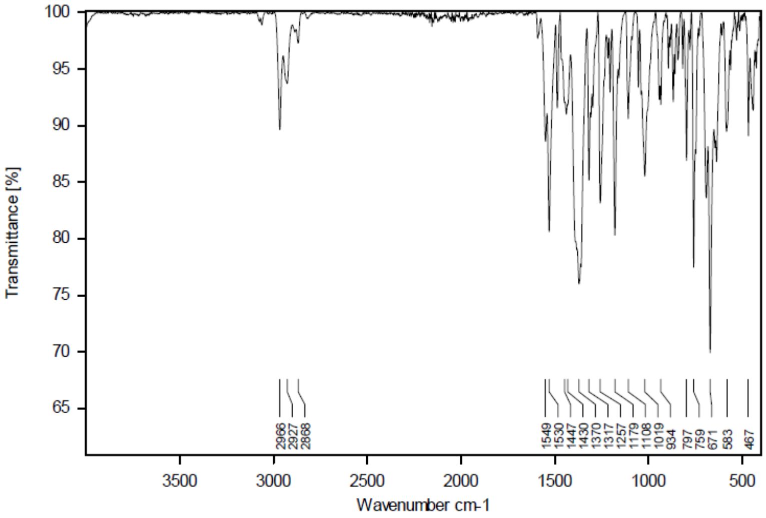

Figure S38: ATR-IR spectrum of **IIh**.

IIi

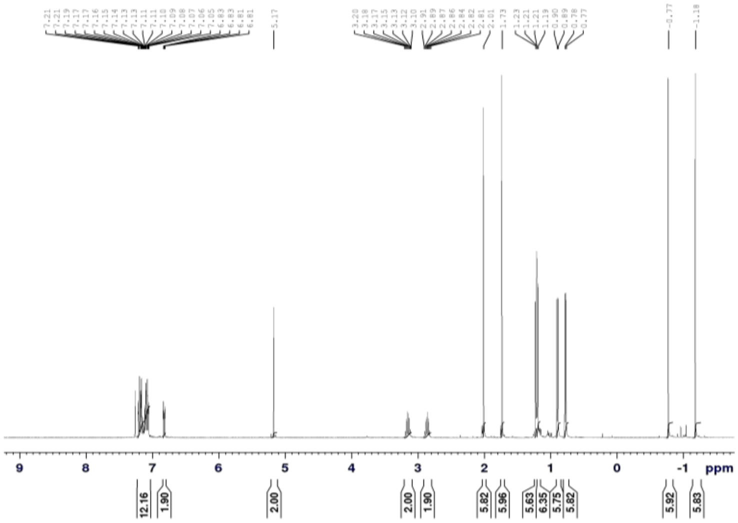

Figure S39: ^{1}H NMR spectrum (400 MHz) of **IIi** in $CDCl_3$.

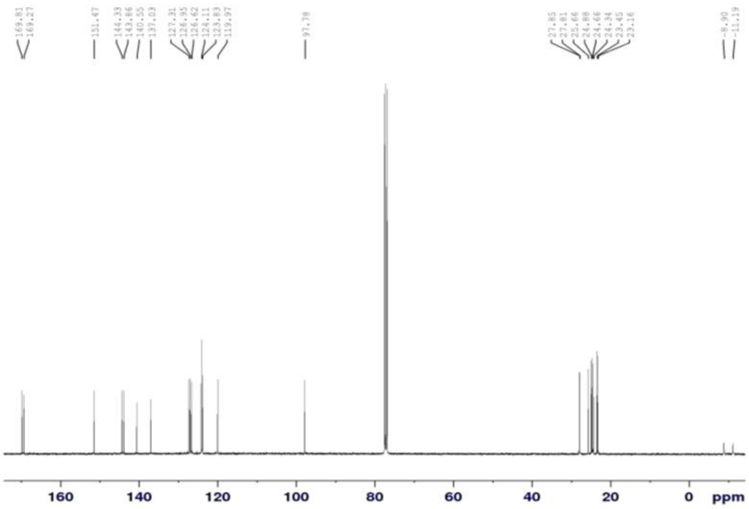

Figure S40: ^{13}C NMR spectrum (101 MHz) of **IIi** in $CDCl_3$.

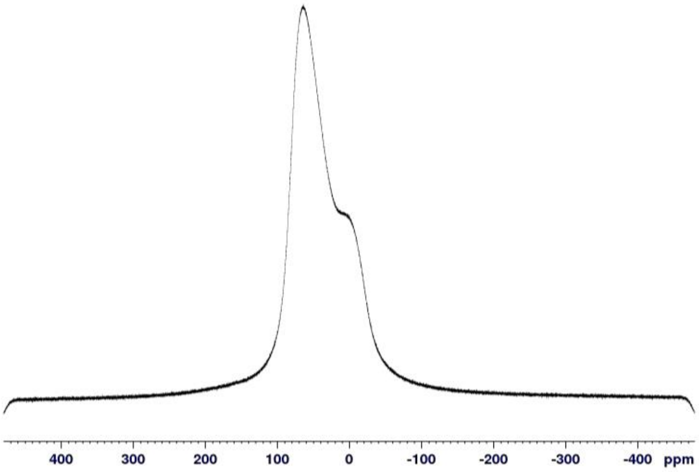

Figure S41: ^{27}Al NMR spectrum (104 MHz) of **IIi** in $CDCl_3$.

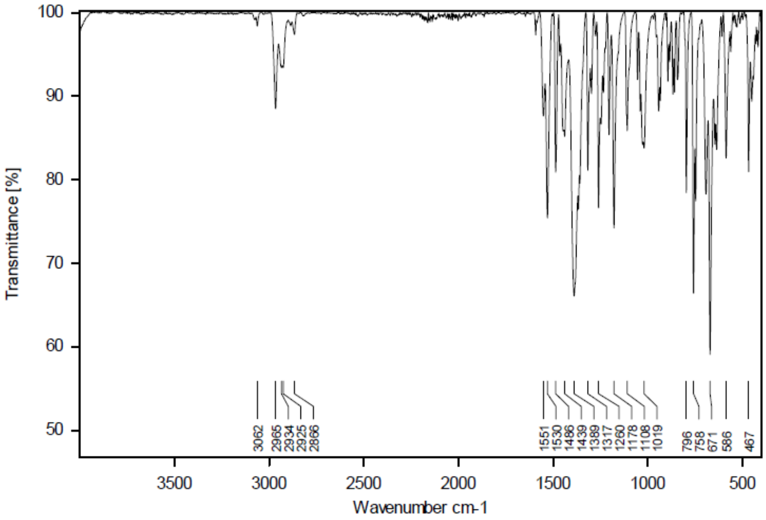

Figure S42: ATR-IR spectrum of **IIi**.

IIj

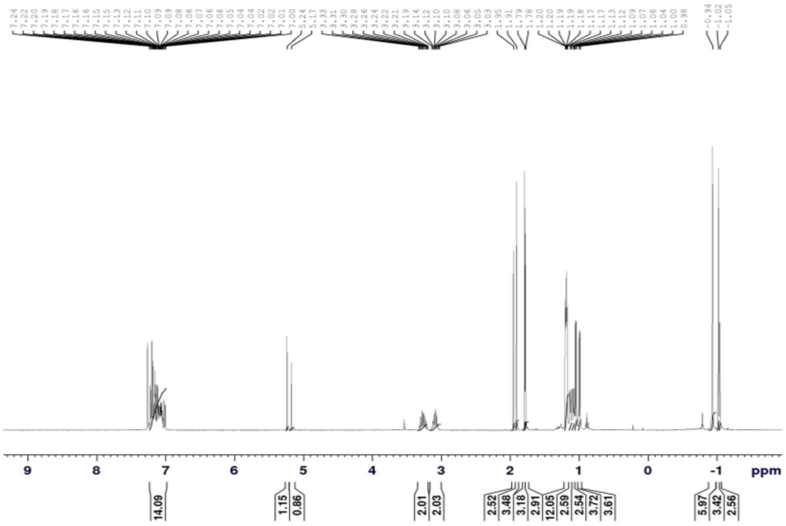

Figure S43: ^{1}H NMR spectrum (400 MHz) of **IIj** in CDCl$_3$.

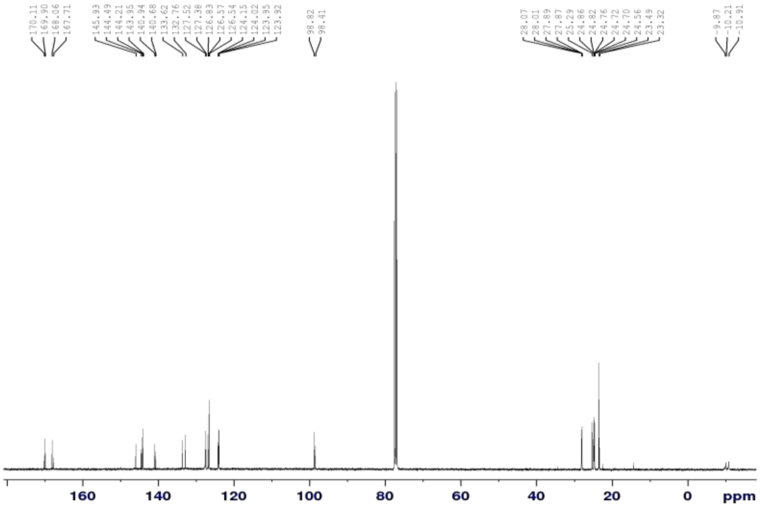

Figure S44: ^{13}C NMR spectrum (101 MHz) of **IIj** in CDCl$_3$.

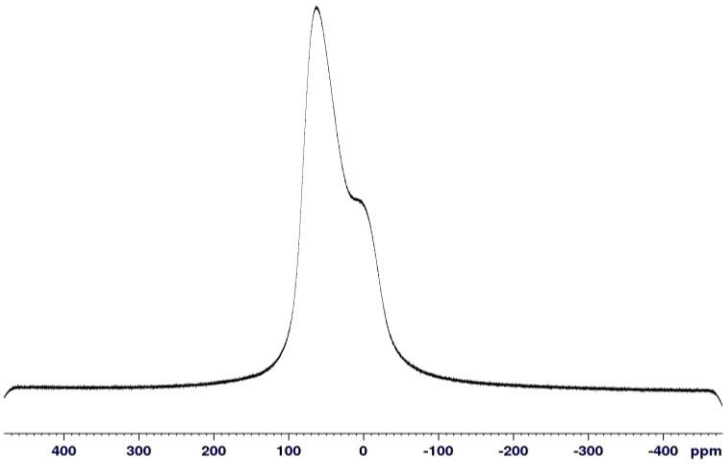

Figure S45: ^{27}Al NMR spectrum (104 MHz) of **IIj** in CDCl$_3$.

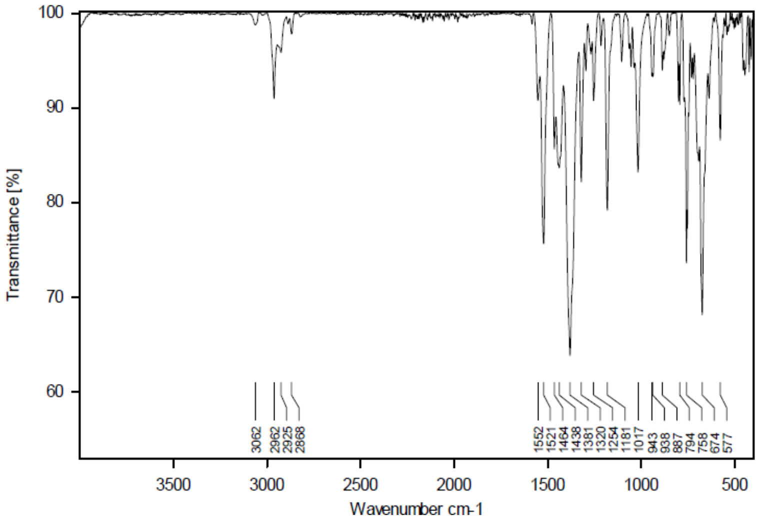

Figure S46: ATR-IR spectrum of **IIj**.

IIk

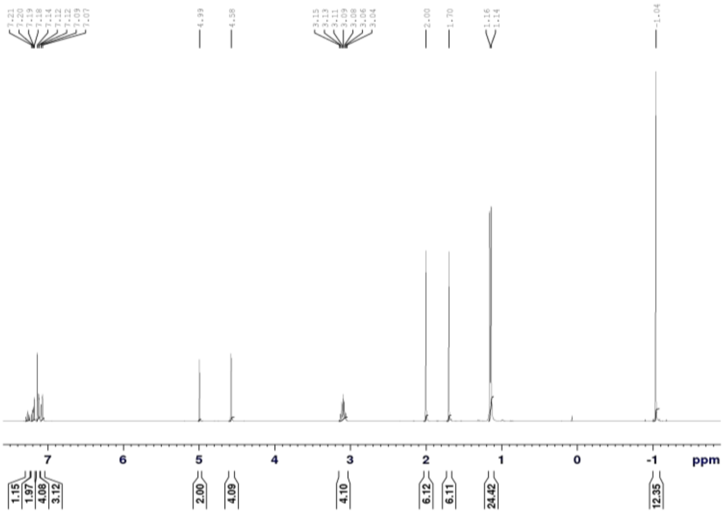

Figure S47: ^{1}H NMR spectrum (400 MHz) of **IIk** in $CDCl_3$.

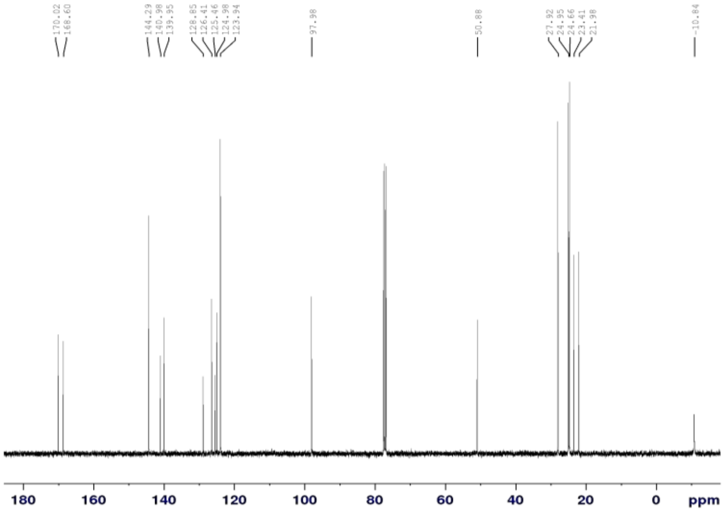

Figure S48: ^{13}C NMR spectrum (101 MHz) of **IIk** in $CDCl_3$.

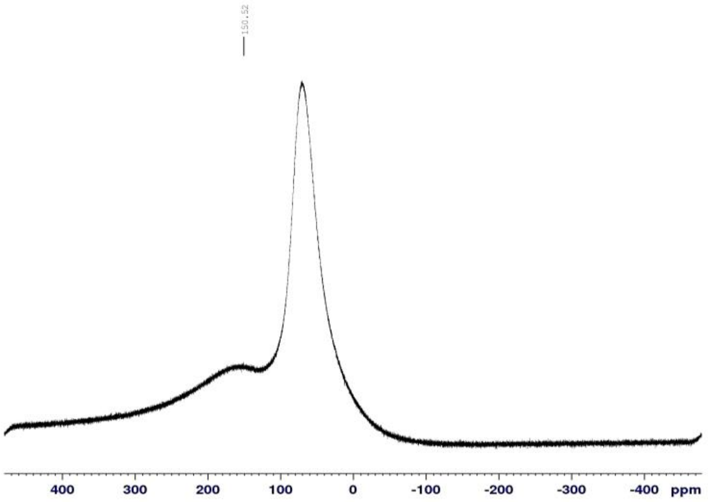

Figure S49: ^{27}Al NMR spectrum (104 MHz) of **IIk** in CDCl$_3$.

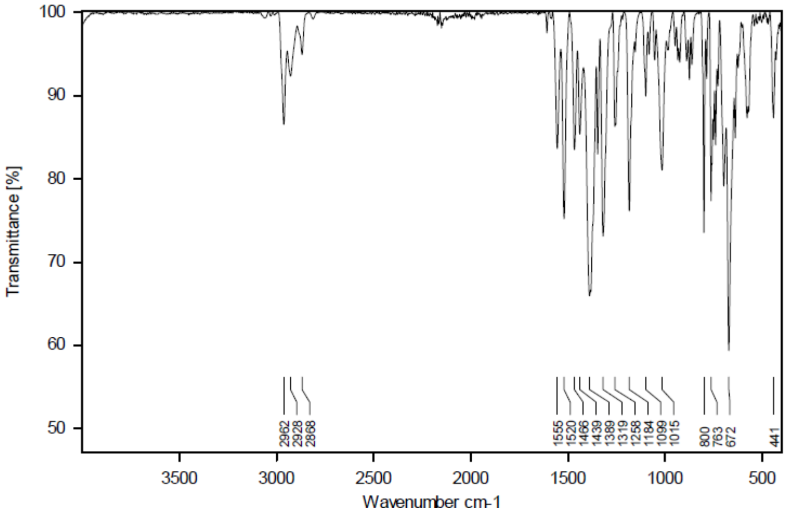

Figure S50: ATR-IR spectrum of **IIk**.

Crystallographic Details

The single crystal X-ray diffraction data were recorded on either a GV-50 diffractometer with Titan[S2] detector from Rigaku Oxford Diffraction (formerly Agilent Technologies) applying Cu K**α** radiation (λ = 1.54184 Å) **IIa**, **IIc**, **IIe**, and **IIi** and an Agilent Gemini R Ultra diffractometer with Cu K*α* radiation (λ = 1.54184 Å) **IIb**. Empirical multi-scan[S5] and analytical absorption corrections[S6] were applied to the data. Using Olex2,[S7] the structures were solved with SHELXT[S8] structure solution program using Intrinsic Phasing and least-square refinements on F^2 were carried out with SHELXL.[S9] For all single-crystals X-Ray structure determinations, the non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were located in idealized calculated positions and were refined isotropically according to the riding model.

Single-crystal X-Ray structure determination of **IIa**: In this compound, unresolved residual electron density around a center of inversion was present, which could be assigned two disordered solvent molecules of toluene. The disorder could not be resolved completely, therefore the solvent mask of Olex2[S7] was applied and the presence of a solvent accessible void including 104 electrons was confirmed, which we assign two fully occupied toluene molecules. In the subsequent refinement a modified reflection file without the contribution of the solvent was used.

Single-crystal X-Ray structure determination of **IIb**: The carbon and nitrogen atoms of the ethylene bridge unit are disordered over two positions and could be refined by using the disorder model.

CCDC 1922742 (**IIa**), 1922743 (**IIb**), 1922744 (**IIc**), 1922745 (**IIe**) and 1922746 (**IIi**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data for $C_{38}H_{60}Al_2N_4$ (**IIa**), $C_{40}H_{64}Al_2N_4$ (**IIb**), $C_{41}H_{66}Al_2N_4$ (**IIc**).

	IIa	**IIb**	**IIc**
Empirical formula	$C_{38}H_{60}Al_2N_4$	$C_{40}H_{64}Al_2N_4$	$C_{41}H_{66}Al_2N_4$
CCDC No.	1922742	1922743	1922744
Formula weight	626.86	654.91	668.93
Temperature/K	123.0(1)	123.0(1)	123.0(1)
Crystal system	triclinic	triclinic	monoclinic
Space group	P-1	P-1	$P2_1/c$
a/Å	11.3567(4)	8.8510(2)	16.2408(1)
b/Å	14.3346(3)	10.2167(2)	15.1517(1)
c/Å	15.6149(4)	11.4620(2)	17.2806(2)
α/°	107.401(2)	98.121(2)	90
β/°	108.855(3)	103.418(2)	105.354(1)
γ/°	96.901(2)	91.212(2)	90
Volume /Å^3	2228.4(1)	996.52(4)	4100.56(6)
Z	2	1	4
ρ_{calc}g/cm^3	0.934	1.091	1.084
μ/mm^{-1}	0.771	0.880	0.864
F(000)	684.0	358.0	1464.0
Crystal size/mm^3	0.12 x 0.104 x 0.073	0.431 x 0.241 x 0.203	0.214 x 0.198 x 0.15
Radiation	Cu K**α** (λ = 1.54184)	Cu K**α** (λ = 1.54184)	Cu K**α** (λ = 1.54184)
2Θ range for data collection/°	6.41 to 148.814	8.022 to 133.848	7.886 to 148.07
Index ranges	-13≤h≤13, -17≤k≤17, -19≤l≤18	-10≤h≤10, -12≤k≤12, -13≤l≤13	-20≤h≤20, -18≤k≤18, -21≤l≤15

Reflections collected	26689	36268	27386
Independent reflections	8794 [R_{int}=0.0440, R_{sigma}=0.0431]	3527 [R_{int}=0.0329, R_{sigma}=0.0146]	8071 [R_{int}=0.0290, R_{sigma}=0.0249]
Data/restraints/parameters	8794/0/413	3527/12/235	8071/0/440
Goodness-of-fit on F^2	1.045	1.051	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0415, wR_2 = 0.1068	R_1 = 0.0393, wR_2 = 0.1064	R_1 = 0.0370, wR_2 = 0.0987
Final R indexes [all data]	R_1 = 0.0505, wR_2 = 0.1127	R_1 = 0.0421, wR_2 = 0.1095	R_1 = 0.0410, wR_2 = 0.1020
Largest diff. peak/hole / e Å^3	0.29/-0.33	0.25/-0.18	0.30/-0.28

Table S2. Crystallographic data for $C_{44}H_{64}Al_2N_4$ (**IIe**) and $C_{50}H_{68}Al_2N_4O$ (**IIi**).

	IIe	**IIi**
Empirical formula	$C_{44}H_{64}Al_2N_4$	$C_{50}H_{68}Al_2N_4O$
CCDC No.	1922745	1922746
Formula weight	702.95	795.04
Temperature/K	123.0(1)	123.0(1)
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
a/Å	14.7748(2)	18.2589(2)
b/Å	17.2244(2)	8.9930(1)
c/Å	18.0957(3)	29.1015(3)
α/°	90	90
β/°	113.682(2)	106.922(1)
γ/°	90	90
Volume /Å^3	4217.3(1)	4571.63(9)
Z	4	4
ρ_{calc}g/cm^3	1.107	1.155
μ/mm^{-1}	0.866	0.873
F(000)	1528.0	1720.0
Crystal size/mm^3	0.231 x 0.191 x 0.163	0.272 x 0.188 x 0.142
Radiation	Cu K**α** (λ = 1.54184)	Cu K**α** (λ = 1.54184)
2Θ range for data collection/°	8.31 to 146.976	6.35 to 148.026
Index ranges	-18≤h≤18, -16≤k≤21, -22≤l≤21	-22≤h≤22, -7≤k≤11, -36≤l≤35
Reflections collected	13320	15251
Independent reflections	4047 [R_{int}=0.0190, R_{sigma}=0.0133]	4531 [R_{int}=0.0225, R_{sigma}=0.0183]
Data/restraints/parameters	4047/0/234	4531/0/266
Goodness-of-fit on F^2	1.063	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0346, wR_2 = 0.0945	R_1 = 0.0335, wR_2 = 0.0876
Final R indexes [all data]	R_1 = 0.0456, wR_2 = 0.0955	R_1 = 0.0352, wR_2 = 0.0891
Largest diff. peak/hole / e Å^3	0.26/-0.23	0.28/-0.24

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Preface

The following chapter has not been published until the submission of this thesis.

Authors

Marcella E. Desat, Robert Kretschmer*

Author contributions

The preparation of the manuscript was done by the first author (M. E. Desat). R. Kretschmer supervised the research and revised the manuscript. Preparation and characterization (NMR, X-Ray) of compound **IIa**, **IIi**, **IVa** and **IVi** have been part of the first author's master thesis. Among them, the first author provides additional the characterisation (IR, EA) of **IIa**, **IIi**, **IVa** and **IVi**. A synthetic approach to the other compounds **IIb**-**h**, **IIIa**-**i** and **IVb**-**h** as well as the complete characterization (NMR, EA, IR, X-Ray) was done by the first author. Additionally, the calculation of all X-Ray structures herein was performed by the first author as well as the interpretation of the analytic data of the compounds.

Acknowledgements

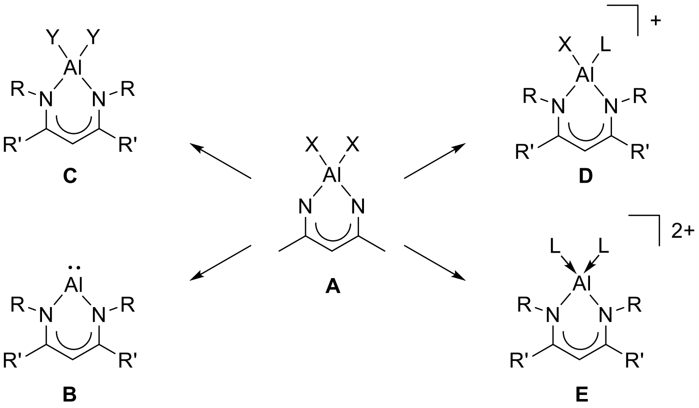
The project was financially supported by the *Fonds der Chemischen Industrie*, the *Deutsche Forschungsgemeinschaft* (DFG, KR4782/2-1 and KR4782/3-1), the University of Regensburg and the Friedrich Schiller University Jena. M.E.D. is grateful to the *Stiftung Stipendien-Fonds des Verbands der Chemischen Industrie* for a PhD fellowship. Additionally, generous support from Professor Manfred Scheer is gratefully acknowledged and we thank Dr. Stefanie Gärtner and Dr. Helmar Görls for helpful discussions.

7 Dinuclear Aluminium Halide Complexes Based on Bis(β-diketiminate) Ligands: Synthesis, Structures and Electrochemical Characterization

Abstract: *23 dinuclear aluminium halide complexes based on bis(β-diketiminate) ligands have been synthesized and fully characterized including NMR and IR spectroscopy, cyclic voltammetry, and elemental analysis. In addition, nine complexes were structurally characterized by means of single-crystal X-ray diffraction. Attempts to reduce the dinuclear species using* C_8K *remained unsuccessful but according to the reduction potentials obtained by cyclic voltammetry indicate the principle feasibility.*

7.1 Introduction

Since the first report on aluminium halide complexes supported by sterically encumbered β-diketiminate ligands in 1998,[1] these compounds found widespread applications in catalysis and as precursors for species with unusual chemical properties.[2] With respect to the latter, they not only serve as precursors for a unique alane diyl (**B**),[3] but also for new neutral (**C**),[4] mono- (**D**) and dicationic (**E**) aluminium complexes, Scheme 1,[5] that exhibit promising reactivity.[6] The respective aluminum halide complexes **A** are readily obtained by salt metathesis using AlX_3 (X = Cl, Br, I) and the related deprotonated β-diketiminates.[1,5b,7] However, aluminium fluorides and iodides are regularly synthesized by nucleophilic substitution starting from the respective alanes[7b,7e,8] or from alkyl alanes.[3a,3b,9] Furthermore, the reaction of the protio-ligand with alkyl aluminium (di)halogenides is an additional route[10] and aluminium difluorides were also recently obtained from the reaction of the aluminium diyl **B** with fluoroalkenes.[11]

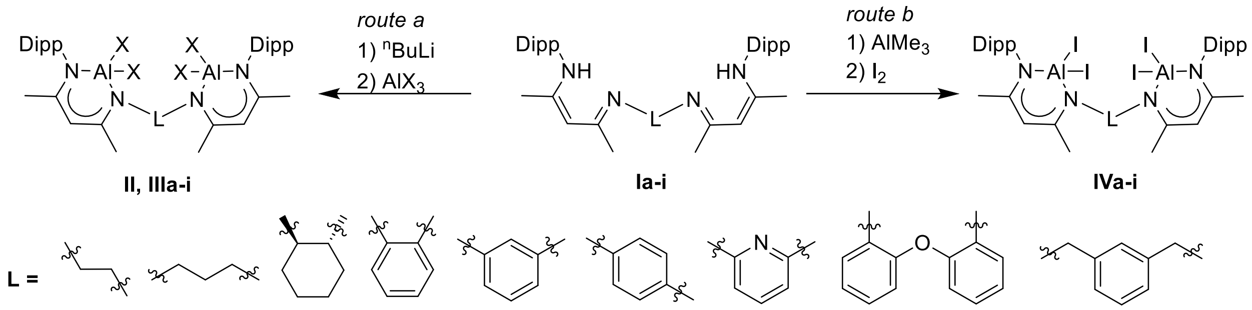


Scheme 1. Aluminium halide complexes based on β-diketiminate ligands are valuable precursors.

As outlined by the group of Roesky, the halide substituent has a crucial impact on the reactivity: While the aluminium dichloride does not allow for the isolation of the aluminium carbene analogue **B**,[7a] the aluminium diiodide is the only suitable precursor to derive **B** in up to 21 % yield.[3a] In recent years, dinuclear complexes, in which two metal centres are framed by one ligand, received increasing attention because of their promising catalytic application.[12] New reactivity and selectivity patterns are expected to arise from cooperative effects between two metal atoms in close proximity.[13] This has already been proven for dinuclear aluminium complexes, which show a significantly increased activity in the ring-opening polymerization (ROP) of racemic lactide compared to their mononuclear counterparts.[14] In consequence, the synthesis of dinuclear aluminium halide complexes is a desirable task as these compounds may find a variety of applications in catalysis and serve a suitable precursors for the synthesis of the aluminium analogues of bis(carbene)s or dinuclear mono- and polycationic aluminium complexes. This prompted us to prepare a whole series of 23 dinuclear aluminum halide complexes based on bis(β-diketiminate) ligands and their synthesis and characterization is reported herein.

7.2 Results and Discussion

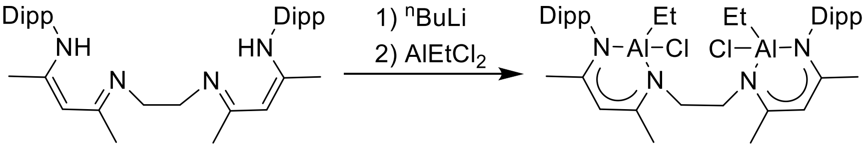
Starting from the bis(β-diketimine)s **Ia-i**, which are readily available using established protocols,[15] the dinuclear aluminium chloride (**II**), bromide (**III**), and iodide (**IV**) complexes have been obtained using the two synthetic protocols outlined in Scheme 2. While derivatives of **II** and **III** have been accessed by transmetalation of the respective lithium bis(β-diketiminate)s (route a), the aluminium iodides **IV** were obtained through the respective dinuclear methyl alanes[15f] and iodine (route b).



	X	a	b	c	d	e	f	g	h	i
II	Cl	(15%)	(21%)	(-)	(30%)	(76%)	(22%)	(30%)	(-)	(52%)
III	Br	(37%)	(17%)	(-)	(35%)	(60%)	(26%)	(25%)	(-)	(52%)
IV	I	(42%)	(43%)	(41%)	(50%)	(71%)	(-)	(83%)	(25%)	(79%)

Scheme 2. Synthetic access to the dinuclear aluminium chlorides (**II**), bromides (**III**), and iodides (**IV**) originating from bis(β-diketimine)s (**I**).

The yields differ to quite some extent, ranging from only 15 % (**IIa**) up to 83 % (**IVg**), but overall, better yields are obtained on route b especially as the respective dinuclear aluminium alkyl complexes are obtained in almost quantitative yields.[15f] The rather low yields as compared to those obtained for the mononuclear counterparts might be explained by the well-known non-innocence of the bis(β-diketimine)s,[16] and we already experienced that certain alkaline metal precursors such as *n*-butyl lithium or lithium bis(trimethylsilyl)amide give rise to products with a ligand-to-metal ratio higher than 1:2, due to deprotonation of the ligand backbone.[17] Very unfortunately, we have not been able to isolate pure samples of **IIc**, **IIIc**, **IIh**, as well as **IIIh** from the raw products, which appear as brown oils, reluctant to crystalize despite several efforts; the same holds true for **IVf**. In addition, the deprotonated ligand **Ia** was treated with ethylaluminium dichloride and the respective dinuclear alkyl aluminium chloride **Va** was obtained in 23 % yield, Scheme 3.



1a **Va**

Scheme 3. Synthetic route to **V** originating from the bis(β-diketimine)s **Ia**.

The room temperature ^{1}H NMR spectra of the dinuclear aluminium halides reflect well the expected behavior in solution and are comparable to those obtained for the dinuclear aluminium alkyl complexes[15f] and to some extent to those of the respective dinuclear indium[18] and thallium diyls.[15e] Hence, a simple set of one isopropyl methine septet and two methyl doublets of the isopropyl groups is observed for all complexes incorporating ethylene (**a**), propylene (**b**), 1,3-phenylene (**e**), 1,4-phenylene (**f**), 2,6-pyridylene (**g**), and 1,3-xylylene (**i**) bridges, indicating conformational averaging on the NMR time scale. More complex resonance pattern are characteristic for the 1,2-phenylene bridged bromide (**IId**), chloride (**IIId**), and iodide (**IVd**) as well as for the *trans*-1,2-cyclohexylene- (**IVc**) and the 2,2'-oxydiarylene-bridged (**IVh**) iodide. Here, two septets for the Dipp methine groups are observed, while the Dipp methyl groups show more complex and partially overlapping resonance pattern. This indicates a conformational rigidity, which is in agreement with the previously observed magnetic inequivalence in case of the respective dinuclear copper(I)[15d] and thallium(I) compounds.[15e] ^{27}Al-NMR resonances of the bromides (81.5 – 102.9 ppm) and chlorides (89.2 – 103.2 ppm) are found in the typical range of mononuclear four-coordinate aluminum compounds,[19] while the resonances of the iodides (-23.9 - -24.8 ppm) are significantly shifted to higher field compared to their mononuclear relatives;[7b] for **IVb** and **IVc**, ^{27}Al resonances were not detected despite extended numbers of scans. The ^{1}H NMR spectrum of **Va** includes two unresolved multiplets for the isopropyl methine groups and a set of one doublet and two multiplets, integrating to 6:6:12 protons for the germinal methyl groups, consistent with an unsymmetrical substitution pattern at aluminium. Its ^{27}Al spectrum shows a singlet in the expected range, i.e., at 102.6 ppm.

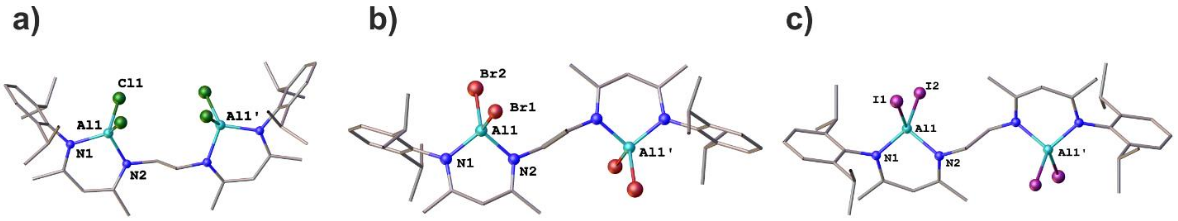


Figure 1. Solid-state structure (hydrogen atoms are omitted for the sake of clarity) with selected bond lengths [Å] and angles [°]:a) **IIa**: Al1–Al1' 5.269(2), Al1–N1 1.865(3), Al1–N2 1.882(5), Al1–Cl1 2.119(1), N1–Al1–N2 100.7(2), Cl1–Al1–Cl1 107.79(6); b) **IIIa**: Al1–Al1' 6.273(2), Al1–N1 1.859(2), Al1–N2 1.867(2), Al1–Br1 2.2924(8), Al1–Br2 2.2717(7), N1–Al1–N2 99.75(8), Br1–Al1–Br2 110.97(3); c) **IVa**: Al1–Al1' 6.393(2), Al1–N1 1.860(3), Al1–N2 1.872(3), Al1–I1 2.527(2), Al1–I2 2.528(7), N1–Al1–N2 99.5(1), I1–Al1–I2 107.288(2).

The molecular structures of the compounds **IIa**, **IId**, **IIIa**, **IIId**, **IIIi**, **IVa**, **IVe**, **IVi** and **Va** are depicted in Figures 1 - 4. Distorted tetrahedral aluminium centres that are projected out of the almost planar C_3N_2 ring of the β-diketiminate unit are characteristic for all structures. For obvious reasons, the aluminium–aluminium separation increases in the following order as a result of the geometric constraints of the bridge: **IIa** (5.259(2) Å) < **IId** (6.223(2) Å) < **IIIa** (6.273(2) Å) < **IIId** (6.308(1) Å) < **V** (6.368(4) Å) < **IVa** (6.393(2) Å) < **IVe** (6.747(2) Å) < **IIIi** (7.119(1) Å) < **IVi** (7.479(4) Å).

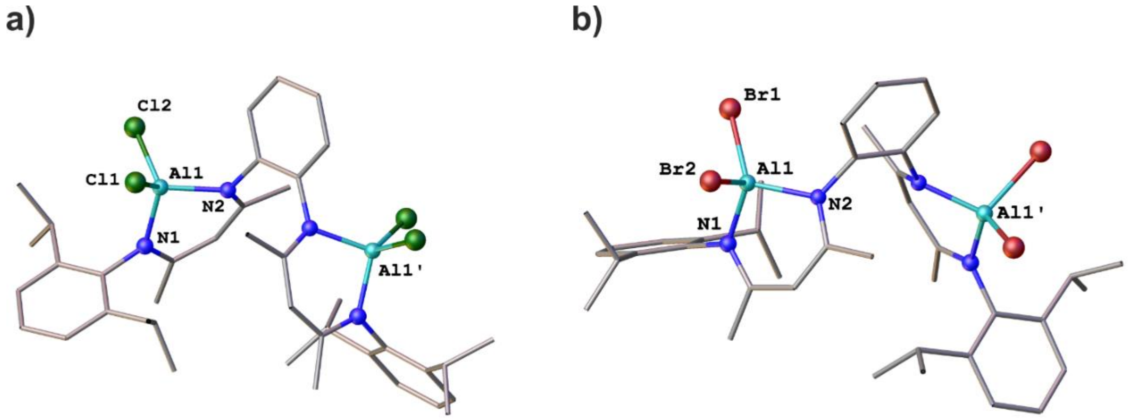


Figure 2. Solid-state structure (hydrogen atoms are omitted for the sake of clarity) with selected bond lengths [Å] and angles [°]:a) **IId**: Al1–Al1' 6.223(2), Al1–N1 1.874(2), Al1–N2 1.883(2), Al1–Cl1 2.1058(9), Al1–Cl2 2.1286(7), N1–Al1–N2 98.3(8), Cl1–Al1–Cl2 110.24(4); b) **IIId**: Al1–Al1' 6.308(1), Al1–N1 1.873(2), Al1–N2 1.875(2), Al1–Br1 2.2578(7), Al1–Br2 2.2983(7), N1–Al1–N2 98.84(8), Br1–Al1–Br2 110.88(3).

It seems probable that the aluminum chloride, bromide and iodide derivatives exhibit close structural resemblance as illustrated by the Al–N bonds with values in between 1.855(4) Å and 1.883(2) Å, which are comparable to those obtained for their mononuclear counterparts with an average distance of 1.88(1) Å.[7a] The same holds true for the N1-Al1-N2 angles with values between 97.5(2)° and 100.7(2)° and angles between the halogen atom, which have values between 105.6(3)° and 110.97(3)°.

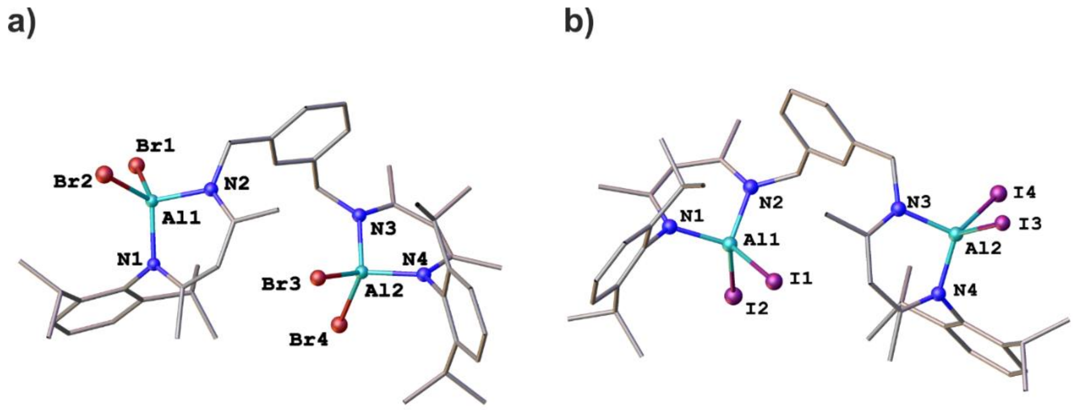


Figure 3. Solid-state structure (hydrogen atoms are omitted for the sake of clarity) with selected bond lengths [Å] and angles [°]:a) **IIIi**: Al1–Al2 7.119(1), Al1–N1 1.867(2), Al1–N2 1.856(2), Al2–N3 1.862(2), Al2–N4 1.857(2), Al1–Br1 2.2752(7), Al1–Br2 2.2934(7), Al2–Br3 2.2752(7), Al2–Br4 2.2987(7), N1–Al1–N2 100.32(9), N3–Al2–N4 98.9(1), Br1–Al1–Br2 110.39(3), Br3–Al2–Br4 110.52(3); b) **IVi**: Al1–Al2 7.479(4), Al1–N1 1.875(8), Al1–N2 1.867(8), Al2–N3 1.862(8), Al2–N4 1.860(9), Al1–I1 2.56(2), Al1–I2 2.524(3), Al2–I3 2.50(2), Al2–I4 2.496(3), N1–Al1–N2 97.7(4), N3–Al2–N4 99.6(4), I1–Al1–I2 109.2(5), I3–Al2–I4 105.6(3).

In comparison with the respective dinuclear alkyl aluminium complexes[15f] certain trends are observed: a) the Al–N bonds in the halide complexes are shorter compared to their alkyl relatives (1.907(1) Å - 1.930(1) Å), most likely due to the more ionic Al–N bonding as a result of the increased positive charge on the metal. b) The N–Al–N bond angles are more obtuse than those of the alkyl substituted aluminium complexes for which values between 93.04(5)° and 95.23(4)° were reported.[15f] Similar trends have been reported for the mononuclear derivatives.[7a] Furthermore, the values of the mixed alkyl halide complex **Va**, Figure 4b, resemble more those obtained for the halide complexes **IIa**, **IIIa**, and **IVa**, rather than those of the respective alkyl alane complex.[15f]

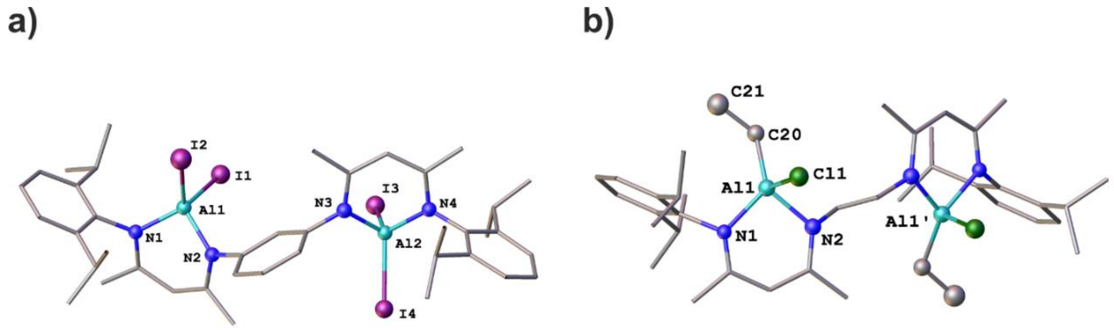


Figure 4. Solid-state structure (hydrogen atoms are omitted for the sake of clarity) with selected bond lengths [Å] and angles [°]:a) **IVe**: Al1–Al2 6.747(2), Al1–N1 1.858(4), Al1–N2 1.860(4), Al2–N3 1.874(5), Al2–N4 1.855(4), Al1–I1 2.521(2), Al1–I2 2.463(1), Al2–I3 2.496(1), Al2–I4 2.503(1), N1–Al1–N2 97.5(2), N3–Al2–N4 97.5(2), I1–Al1–I2 108.96(5), I3–Al2–I4 109.94(5); b) **Va**: Al1–Al1' 6.368(4), Al1–N1 1.954(2), Al1–N2 1.877(2), Al1–Cl1 2.175(1), Al1–C20 1.951(3), C20–C21 1.534(4), N1–Al1–N2 95.60(8).

Due to the unique reactivity of the alane diyl (**B**)[3] and our interest in group 13 bis(carbene) analogues, which have so far only been isolated for indium[18] and thallium,[15e] we attempted the reduction using potassium graphite (C_8K). In NMR experiments, the diiodides **IVa**, **IVe**, **IVh**, and **IVi** were treated with an excess of C_8K. However, the ^1H NMR spectra measured after 2 hours or one day at 65 °C, did not differ significantly from the spectra of the respective dinuclear aluminium(III) complexes **IV**, Figures S93 – S97; noteworthy, no color change of the golden C_8K flakes was observed. We next explored the reduction of **IIa**, **IIb**, **IId**, **IIe**, **IIg**, **IIIa**, **IIIb**, **IIId**, **IVa**, **IVb**, **IVe**, and **IVg** in a 10:1 toluene diethyl ether mixture with an excess of potassium graphite. NMR spectra recorded in C_6D_6 after filtration and evaporation of the volatiles are mostly characterized by solvent signals and only for **IIb**, **IId**, **IIIb**, **IVb**, and **IVg**, weak and rather broad signals appeared in the aliphatic region, Figures S98 – S102. Unfortunately, all our attempts to isolate pure compounds from the yellow/orange colored raw materials by crystallization remained unsuccessful.

In order to rationalize the findings and evaluate whether the dinuclear aluminium halides **II**, **III**, and **IV** are suitable precursors to access the aluminium analogues of bis(carbene)s, we performed cyclic voltammetry experiments. The reduction potentials, referenced to the ferrocene/ferrocenium redox couple,[20] are given in Table 1. Furthermore, we also analyzed the mononuclear compound [$\{CH(CMeNDipp)_2\}AlI_2$], which is regularly used to obtain the respective aluminium diyl **B**.[3a] To our surprise, its reduction potential (-3.16 V against Fc/Fc^+) appears at only slightly more positive values than potassium (-3.24 V versus Fc/Fc^+).[21] The reduction potentials of dinuclear aluminium complexes reported herein, are in most of the cases irreversible. Only for the 1,3-and 1,4-phenylene bridged bromide and chloride complexes (**IIe**, **IIf**, **IIIe**, **IIIf**) and the 2,6-pyridylene bridged chloride complex **IIg** (poorly) reversible reduction events are observed. Overall, the reduction potential strongly depends on the bridging group as well as on the halogen substituent. Besides the complexes based on the bis(β-diketimine) **If**, the reduction potentials are shifted to more negative values in the order Cl < Br < I. This unfortunately prohibits the two-electron reduction of quite some of the dinuclear aluminium iodide complexes if potassium is used. However, reduction of the iodides **IVc**, **IVe**, **IVh**, **IVi**, and of all aluminium chlorides **II** and bromides **III** investigated in here is expected to occur according to the reported potentials. The non-occurrence of any reduction event in case of diiodides **IVe**, **IVh**, and **IVi** in the NMR experiments reported above can be explained by solvent effects, which strongly impact the reduction potential. Noteworthy, the mononuclear alane diyl **B** readily reacts with tetrahydrofuran,[22] which excludes its use in here. For compound **Va**, the reduction events take place at -2.49 V and -3.14 V (versus Fc/Fc^+), respectively.

Table 1. Reduction potentials (given in Volts) of the dinuclear aluminium chloride (**II**), bromide (**III**), and iodide (**IV**) complexes. The values are referenced to the Fc/Fc$^+$ redox couple. Conditions: 0.1 mM in THF at 298 K, 0.1 M Bu_4NPF_6.

	II	**III**	**IV**
a	-2.92	-3.05	-3.39
b	-2.77	-3.07	-3.25
c	-	-	-2.74 -3.02
d	-2.59	-3.05	-3.35
e	-2.40 -2.69	-2.53 -2.88	-3.22
f	-2.31 -2.58	-2.25 -2.55	-
g	-2.32 -2.65	-2.52 -3.04	-2.78 -3.31
h	-	-	-1.88 -3.13
i	-2.30	-2.97	-3.19

7.3 Conclusion

In summary, 23 dinuclear aluminum halide complexes (X = Cl, Br, I) based on bis(β-diketiminate) ligands have been synthesized and characterized by NMR and IR spectroscopy as well as elemental analysis. In addition, the molecular structures in the solid state are reported for nine compounds. Attempts to reduce the dinuclear aluminium complexes by using potassium graphite remained unsuccessful, but cyclic voltammetry experiments revealed that reduction should be possible for certain dinuclear complexes. Based on these findings we continue to explore the development dinuclear aluminium complexes aiming to access dinuclear alane diyls.

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7.5 Supporting Information

General considerations

All preparations were performed under an inert atmosphere of dinitrogen by means of standard Schlenk-line or glovebox techniques (GS-Systemtechnik and MBraun). Traces of oxygen and moisture were removed from the inert gas by passing it over a BASF R 3-11 ($CuO/MgSiO_3$) catalyst, through concentrated sulfuric acid, over coarsely granulated silica gel, and finally P_4O_{10}. Dichloromethane, diethyl ether and *n*-pentane were freshly collected from a Solvent Purification System by M. Braun (MB SPS-800). Toluene was used as p.a. grade and distilled from Na/benzophenone prior to use. $CDCl_3$ was dried by distillation from calcium hydride. *n*-Butyllithium (1.6M in Hexane), Trimethylaluminum (2M in Toluene), Iodine and ethylaluminium dichloride (1.8M in Toluene) were purchased from Sigma Aldrich, $AlCl_3$ from BASF, and $AlBr_3$ from Merck. The bis(β-diketimine)s **1a**-**i**[S1] were prepared according to published procedures.

Characterization

The NMR spectra were recorded with a Bruker Avance 400 spectrometer (T = 300 K) with *δ* referenced to external tetramethylsilane (^1H, ^{13}C and ^{27}Al). ^1H and ^{13}C NMR spectra were calibrated by using the solvent residual peak ($CHCl_3$: $\delta(^1H) = 7.26$) and the solvent peak (CDCl3: $\delta(^{13}C) = 77.16$), respectively. ^{27}Al NMR spectra were calibrated relative to external $Al(NO_3)_3 \cdot 9H_2O$. IR spectra were recorded with a Bruker ALPHA spectrometer equipped with a diamond ATR unit. Elemental analysis were performed with a Vario MICRO cube (Elementar Analysensysteme GmbH); the presence of residual solvent molecules was verified by ^1H NMR spectroscopy.

General procedure for the synthesis employing aluminum chloride

n-Butyllithium (6.9 mL, 11.0 mmol, 1.6M in Hexane) was added dropwise to a solution of the respective bis(*β*-diketimine) (5.0 mmol) in Toluene (20 mL). After additional stirring for 3 h, the solution was added to $AlCl_3$ (1.47 g, 11.0 mmol) in diethyl ether (20 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 16 h. The volatile substances were removed in vacuum and the residue was extracted with toluene (20 mL). Concentration of the filtered extract yielded the products. Crystals of **IIa** and **IId**, suitable for an x-ray diffraction analysis were obtained from concentrated dichloromethane solutions upon layering with *n*-pentane.

IIa: colourless powder, 0.55 g (15%). ^{1}H NMR: (400 MHz, CDCl$_3$): δ = 1.14 [d, 12H, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, CH*Me*$_2$], 1.27 [d, 12H, $^{3}J_{\mathrm{HH}}$ = 6.7 Hz, CH*Me*$_2$], 1.79 [s, 6H, C*Me*], 2.38 [s, 6H, C*Me*], 3.02 [sept, 4H, $^{3}J_{\mathrm{HH}}$ = 6.7 Hz, C*H*Me$_2$], 3.80 [s, 4H, C*H*$_2$], 5.24 [s, 2H, C*H*], 7.17-7.22 [m, 4H, Ar*H*], 7.28-7.32 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = 22.6 [C*Me*], 23.7 [C*Me*], 24.9 [CH*Me*$_2$], 25.0 [CH*Me*$_2$], 28.3 [*C*HMe$_2$], 47.3 [*C*H$_2$], 99.9 [*β*-*C*H], 124.7 [*m*-*C*(Dipp)], 128.0 [*p*-*C*(Dipp)], 137.4 [*o*-*C*(Dipp)], 144.8 [*ipso*-*C*(Dipp)], 171.6 [*C*N], 172.6 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, CDCl$_3$): δ = 102.7 ppm [*Al*Cl$_2$]; ATR-IR: $\tilde{\nu}$ = 2962, 2926, 2867, 1591, 1527, 1441, 1384, 1276, 1188, 1164, 1099, 1019, 801, 490 cm^{-1}; elemental analysis calcd (found) $C_{36}H_{52}Al_2Cl_4N_4\cdot 0.35C_7H_8$: C 60.07 (60.11), H 7.18 (7.16), N 7.29 (7.18).

IIb: yellow powder, 0.79 g (21%). ^{1}H NMR: (400 MHz, CDCl$_3$): δ = 1.15 [d, 12H, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, CH*Me*$_2$], 1.28 [d, 12H, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, CH*Me*$_2$], 1.79 [s, 6H, C*Me*], 2.09-2.17 [m, 2H, C*H*$_2$], 2.27 [s, 6H, C*Me*], 3.05 [sept, 4H, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, C*H*Me$_2$], 3.58-3.62 [m, 4H, C*H*$_2$], 5.21 [s, 2H, C*H*], 7.21 [d, 4H, $^{3}J_{\mathrm{HH}}$ = 7.8 Hz, Ar*H*], 7.28-7.32 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = 21.6 [C*Me*], 23.6 [C*Me*], 24.8 [CH*Me*$_2$], 25.0 [CH*Me*$_2$], 28.2 [*C*HMe$_2$], 32.2 [*C*H$_2$], 45.2 [*C*H$_2$], 99.6 [*β*-*C*H], 124.6 [*m*-*C*(Dipp)], 127.8 [*p*-*C*(Dipp)], 137.6 [*o*-*C*(Dipp)], 144.9 [*ipso*-*C*(Dipp)], 170.9 [*C*N], 171.8 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, CDCl$_3$): δ = 102.3 [*Al*Cl$_2$], 104.3 ppm [*Al*Cl$_2$]; ATR-IR: $\tilde{\nu}$ = 2964, 2928, 2868, 1539, 1440, 1397, 1347, 1304, 1278, 1256, 1099, 1002, 971, 935, 888, 803, 765, 731, 696, 644, 610, 551, 497, 466, 431 cm^{-1}; elemental analysis calcd (found) $C_{37}H_{54}Al_2Cl_4N_4\cdot 0.75C_7H_8$: C 61.91 (61.93), H 7.38 (7.23), N 6.83 (6.82).

IId: yellow powder, 1.19 g (30%). ^{1}H NMR: (400 MHz, CDCl$_3$): δ = 1.17 [d, 12H, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, CH*Me*$_2$], 1.28 [‘t’, 12H, $^{3}J_{\mathrm{HH}}$ = 6.2 Hz, CH*Me*$_2$], 1.87 [s, 6H, C*Me*], 2.09 [s, 6H, C*Me*], 3.00 [sept, 2H, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, C*H*Me$_2$], 3.31 [sept, 2H, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, C*H*Me$_2$], 5.47 [s, 2H, C*H*], 7.17-7.23 [m, 6H, Ar*H*], 7.28-7.32 [m, 2H, Ar*H*], 7.35-7.37 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = 23.8 [C*Me*], 24.8 [C*Me*], 24.8 [CH*Me*$_2$], 25.3 [CH*Me*$_2$], 26.3 [CH*Me*$_2$], 28.1 [*C*HMe$_2$], 28.4 [*C*HMe$_2$], 100.8 [*β*-*C*H], 124.4 [*C*(Aryl)], 124.6 [*C*(Aryl)], 127.8 [*m*-*C*(Dipp)], 128.3 [*m*-*C*(Dipp)], 130.2 [*p*-*C*(Dipp)], 137.7 [*C*(Aryl)], 140.2 [*o*-*C*(Dipp)], 144.4 [*ipso*-*C*(Dipp)], 144.8 [*C*(Aryl)], 172.5 [*C*N], 173.9 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, CDCl$_3$): δ = 100.3 ppm [*Al*Cl$_2$]; ATR-IR: $\tilde{\nu}$ = 2960, 2929, 2866, 1534, 1523, 1511, 1441, 1357, 1319, 1249, 1178, 1107, 1019, 935, 891, 804, 778, 763, 642, 585, 562, 537, 525, 479, 451, 418, 407 cm^{-1}; elemental analysis calcd (found) $C_{40}H_{52}Al_2Cl_4N_4$: C 61.23 (61.52), H 6.68 (6.49), N 7.14 (7.01).

IIe: pale brown powder, 2.99 g (76%). ^{1}H NMR: (400 MHz, CDCl$_3$): δ = 1.19 [d, 12H, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, CH*Me*$_2$], 1.30 [d, 12H, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, CH*Me*$_2$], 1.89 [s, 6H, C*Me*], 2.00 [s, 6H, C*Me*], 3.13

[sept, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*Me$_2$], 5.37 [s, 2H, C*H*], 6.97 [t, 1H, $^4J_{HH}$ = 2.0 Hz, Ar*H*], 7.17 [dd, 2H, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 2.0 Hz, Ar*H*], 7.21-7.23 [m, 4H, Ar*H*], 7.29-7.33 [m, 2H, Ar*H*], 7.46 ppm [t, 1H, $^3J_{HH}$ = 7.9 Hz, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = 23.6 [C*Me*], 23.9 [C*Me*], 24.9 [CH*Me$_2$*], 25.0 [CH*Me$_2$*], 28.3 [*C*HMe$_2$], 99.5 [*β*-*C*H], 124.7 [*m*-*C*(Dipp)], 125.2 [*m*-*C*(Dipp)], 125.7 [*C*(Aryl)], 128.1 [*p*-*C*(Dipp)], 130.4 [*C*(Aryl)], 137.5 [*o*-*C*(Dipp)], 143.8 [*ipso*-*C*(Dipp)], 144.7 [*C*(Aryl)], 170.9 [*C*N], 173.0 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, CDCl$_3$): δ = 100.2 ppm [*Al*Cl$_2$]; ATR-IR: $\tilde{\nu}$ = 2965, 2928, 2868, 1520, 1439, 1358, 1321, 1252, 1162, 1021, 925, 800, 759, 725, 695, 574, 531, 466 cm^{-1}; elemental analysis calcd (found) $C_{40}H_{52}Al_2Cl_4N_4\cdot 0.10C_7H_8$: C 61.75 (61.40), H 6.72 (6.50), N 7.02 (6.79).

IIf: pale yellow powder, 0.85 g (22%). ^{1}H NMR: (400 MHz, CDCl$_3$): δ = 1.18 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me$_2$*], 1.28 [d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me$_2$*], 1.88 [s, 6H, C*Me*], 2.00 [s, 6H, C*Me*], 3.11 [sept, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*Me$_2$], 5.38 [s, 2H, C*H*], 7.20-7.22 [m, 8H, Ar*H*], 7.28-7.32 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = 23.6 [C*Me*], 24.0 [C*Me*], 24.9 [CH*Me$_2$*], 25.0 [CH*Me$_2$*], 28.4 [*C*HMe$_2$], 99.6 [*β*-*C*H], 124.7 [*m*-*C*(Dipp)], 127.7 [*C*(Aryl)], 128.0 [*p*-*C*(Dipp)], 137.7 [*o*-*C*(Dipp)], 141.7 [*ipso*-*C*(Dipp)], 144.7 [*C*(Aryl)], 170.8 [*C*N], 172.9 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, CDCl$_3$): δ = 100.3 ppm [*Al*Cl$_2$]; ATR-IR: $\tilde{\nu}$ = 2963, 2928, 2869, 1533, 1504, 1440, 1360, 1318, 1253, 1180, 1103, 1015, 943, 907, 804, 781, 763, 730, 647, 570, 530, 516, 493, 449 cm^{-1}; elemental analysis calcd (found) $C_{40}H_{52}Al_2Cl_4N_4\cdot 0.25C_7H_8$: C 62.09 (62.11), H 6.74 (6.72), N 6.94 (6.86).

IIg: yellow powder, 1.16 g (30%). ^{1}H NMR: (400 MHz, CDCl$_3$): δ = 1.09 [d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me$_2$*], 1.22 [d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me$_2$*], 1.86 [s, 6H, C*Me*], 2.29 [s, 6H, C*Me*], 3.07 [sept, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 5.37 [s, 2H, C*H*], 7.16-7.20 [m, 6H, Ar*H*], 7.25-7.28 [m, 2H, Ar*H*], 7.82 ppm [t, 1H, $^3J_{HH}$ = 7.9 Hz, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = 24.1 [C*Me*], 24.7 [C*Me*], 24.8 [CH*Me$_2$*], 24.9 [CH*Me$_2$*], 28.3 [*C*HMe$_2$], 101.6 [*β*-*C*H], 114.6 [*C*(Aryl)], 124.4 [*m*-*C*(Dipp)], 127.7 [*p*-*C*(Dipp)], 139.2 [*C*(Aryl)], 142.7 [*o*-*C*(Dipp)], 144.0 [*ipso*-*C*(Dipp)], 155.8 [*C*(Aryl)], 166.1 [*C*N], 174.9 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, CDCl$_3$): δ = 89.2 [*Al*Cl$_2$], 104.3 ppm [*Al*Cl$_2$]; ATR-IR: $\tilde{\nu}$ = 2968, 2928, 2870, 1588, 1541, 1524, 1435, 1355, 1320, 1256, 1218, 1181, 1008, 799, 758, 657, 563, 533, 485 cm^{-1}; elemental analysis calcd (found) $C_{39}H_{51}Al_2Cl_4N_5\cdot 0.10\ C_7H_8$: C 59.99 (60.22), H 6.57 (6.29), N 8.81 (8.67).

IIi: pale orange powder, 2.11 g (52%). ^{1}H NMR: (400 MHz, CDCl$_3$): δ = 1.16 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me$_2$*], 1.27 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me$_2$*], 1.82 [s, 6H, C*Me*], 2.11 [s, 6H, C*Me*], 3.11 [sept, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 4.80 [s, 4H, C*H$_2$*], 5.26 [s, 2H, C*H*], 7.20-7.22 [m, 6H, Ar*H*], 7.28-7.35 ppm [m, 4H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): *δ* = 22.8 [C*Me*], 23.7 [C*Me*], 24.9 [CH*Me*$_2$], 25.1 [CH*Me*$_2$], 28.3 [*C*HMe$_2$], 50.8 [*C*H$_2$], 99.8 [*β*-*C*H], 124.6 [*m*-*C*(Dipp)], 125.7 [*m*-*C*(Dipp)], 126.1 [*C*(Aryl)], 127.9 [*p*-*C*(Dipp)], 129.2 [*C*(Aryl)], 137.7 [*o*-*C*(Dipp)], 138.7 [*ipso*-*C*(Dipp)], 144.7 [*C*(Aryl)], 171.6 [*C*N], 173.2 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, CDCl$_3$): *δ* = 103.2 ppm [*Al*Cl$_2$]; ATR-IR: $\tilde{\nu}$ = 2960, 2928, 2865, 1525, 1438, 1384, 1301, 1280, 1097, 1034, 924, 806, 756, 695, 547, 428, 411 cm^{-1}; elemental analysis calcd (found) $C_{42}H_{56}Al_2Cl_4N_4 \cdot 0.45\ CH_2Cl_2$: C 59.92 (60.04), H 6.74 (6.83), N 6.58 (6.35).

General procedure for the synthesis employing aluminium bromide

n-Butyllithium (6.9 mL, 11.0 mmol, 1.6M in Hexane) was added dropwise to a solution of the respective bis(*β*-diketimine) (5.0 mmol) in Toluene (20 mL). After additional stirring for 3 h, the solution was added to AlBr$_3$ (2.93 g, 11.0 mmol) in diethyl ether (20 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 16 h. The volatile substances were removed in vacuum and the residue was extracted with toluene (20 mL). Concentration of the filtered extract yielded the products. Crystals of **IIIa, IIId**, and **IIIi** suitable for an X-ray diffraction analysis were obtained from concentrated dichloromethane solutions layered with *n*-pentane.

IIIa: colourless powder, 1.69 g (37%). ^{1}H NMR: (400 MHz, CDCl$_3$): *δ* = 1.15 [d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.28 [d, 12H, $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$], 1.81 [s, 6H, C*Me*], 2.43 [s, 6H, C*Me*], 3.04 [sept, 4H, $^3J_{HH}$ = 6.7 Hz, C*H*Me$_2$], 3.86 [s, 4H, C*H*$_2$], 5.33 [s, 2H, C*H*], 7.21 [d, 4H, $^3J_{HH}$ = 7.7 Hz, Ar*H*], 7.29-7.33 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): *δ* = 23.2 [C*Me*], 23.9 [C*Me*], 24.7 [CH*Me*$_2$], 25.3 [CH*Me*$_2$], 28.4 [*C*HMe$_2$], 47.5 [*C*H$_2$], 100.6 [*β*-*C*H], 124.6 [*m*-*C*(Dipp)], 128.0 [*p*-*C*(Dipp)], 137.8 [*o*-*C*(Dipp)], 144.7 [*ipso*-*C*(Dipp)], 171.6 [*C*N], 172.5 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, CDCl$_3$): *δ* = 102.4 ppm [*Al*Br$_2$]; ATR-IR: $\tilde{\nu}$ = 2962, 2926, 2867, 1524, 1463, 1439, 1376, 1365, 1302, 1261, 1217, 1183, 1100, 1021, 894, 801, 780, 760, 727, 676, 551, 487, 440, 413 cm^{-1}; elemental analysis calcd (found) $C_{36}H_{52}Al_2Br_4N_4 \cdot 0.25\ C_7H_8$: C 48.37 (48.33), H 5.81 (5.78), N 5.98 (5.93).

IIIb: pale yellow powder, 0.79 g (17%). ^{1}H NMR: (400 MHz, CDCl$_3$): *δ* = 1.14 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.26 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.79 [s, 6H, C*Me*], 2.07-2.15 [m, 2H, C*H*$_2$], 2.27 [s, 6H, C*Me*], 3.04 [sept, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 3.59-3.63 [m, 4H, C*H*$_2$], 5.29 [s, 2H, C*H*], 7.19 [d, 4H, $^3J_{HH}$ = 7.8 Hz, Ar*H*], 7.27-7.31 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): *δ* = 21.8 [C*Me*], 23.9 [C*Me*], 24.7 [CH*Me*$_2$], 25.3 [CH*Me*$_2$], 28.4 [*C*HMe$_2$], 32.1 [*C*H$_2$], 45.3 [*C*H$_2$], 100.4 [*β*-*C*H], 124.5 [*m*-*C*(Dipp)], 127.9 [*p*-*C*(Dipp)], 138.0 [*o*-*C*(Dipp)], 144.8 [*ipso*-*C*(Dipp)], 170.8 [*C*N], 171.6 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, CDCl$_3$): *δ* = 102.6 ppm [*Al*Br$_2$]; ATR-IR: $\tilde{\nu}$ = 2964, 2925, 2868, 1517, 1473, 1437, 1382, 1350, 1321, 1282, 1250, 1191, 1094, 1017, 934, 896, 877, 799, 759, 727, 679, 644, 601, 555, 478, 438, 426 cm^{-1}; elemental analysis calcd (found) $C_{37}H_{54}Al_2Br_4N_4$: C 47.87 (47.62), H 5.86 (5.88), N 5.71 (6.03).

IIId: yellow powder, 1.68 g (35%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ = 1.18 [d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.30 [‘t’, 12H, $^3J_{HH}$ = 6.2 Hz, CH*Me*$_2$], 1.89 [s, 6H, C*Me*], 2.16 [s, 6H, C*Me*], 3.03 [sept, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 3.32 [sept, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 5.54 [s, 2H, C*H*], 7.16-7.24 [m, 4H, Ar*H*], 7.29-7.39 ppm [m, 6H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$): δ = 24.1 [C*Me*], 24.8 [C*Me*], 25.0 [CH*Me*$_2$], 25.3 [CH*Me*$_2$], 25.6 [CH*Me*$_2$], 27.4 [CH*Me*$_2$], 28.4 [*C*HMe$_2$], 28.6 [*C*HMe$_2$], 101.5 [*β*-CH], 124.6 [*C*(Aryl)], 128.0 [*m*-*C*(Dipp)], 128.6 [*m*-*C*(Dipp)], 130.0 [*p*-*C*(Dipp)], 138.2 [*C*(Aryl)], 140.5 [*o*-*C*(Dipp)], 144.5 [*ipso*-*C*(Dipp)], 144.8 [*C*(Aryl)], 172.6 [*C*N], 174.1 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, $CDCl_3$): δ = NMR 99.6 ppm [*A*lBr$_2$]; ATR-IR: $\tilde{\nu}$ = 2965, 2926, 2868, 1511, 1460, 1438, 1360, 1314, 1288, 1271, 1255, 1181, 1100, 1055, 1022, 978, 945, 890, 864, 849, 800, 788, 755, 709, 639, 566, 545, 506, 477, 441, 416 cm^{-1}; elemental analysis calcd (found) $C_{40}H_{52}Al_2Br_4N_4 \cdot 0.20\ C_7H_8$: C 50.69 (50.72), H 5.51 (5.41), N 5.71 (5.79).

IIIe: pale brown powder, 2.89 g (60%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ = 1.19 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.29 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.90 [s, 6H, C*Me*], 2.02 [s, 6H, C*Me*], 3.13 [br, 4H, C*H*Me$_2$], 5.47 [s, 2H, C*H*], 6.97 [t, 1H, $^4J_{HH}$ = 2.0 Hz, Ar*H*], 7.16-7.22 [m, 6H, Ar*H*], 7.29-7.33 [m, 2H, Ar*H*], 7.48 ppm [t, 1H, $^3J_{HH}$ = 7.9 Hz, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$): δ = 23.8 [C*Me*], 24.2 [C*Me*], 24.8 [CH*Me*$_2$], 25.2 [CH*Me*$_2$], 28.5 [*C*HMe$_2$], 100.4 [*β*-*C*H], 124.6 [*m*-*C*(Dipp)], 125.2 [*m*-*C*(Dipp)], 125.3 [*C*(Aryl)], 128.0 [*p*-*C*(Dipp)], 130.5 [*C*(Aryl)], 138.0 [*o*-*C*(Dipp)], 144.0 [*ipso*-*C*(Dipp)], 144.6 [*C*(Aryl)], 170.7 [*C*N], 172.8 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, $CDCl_3$): δ = 100.5 ppm [*A*lBr$_2$]; ATR-IR: $\tilde{\nu}$ = 2963, 2928, 2868, 1674, 1599, 1589, 1525, 1468, 1442, 1355, 1324, 1029, 1002, 895, 803, 762, 730, 692, 564, 465, 432, 417 cm^{-1}; elemental analysis calcd (found) $C_{40}H_{52}Al_2Br_4N_4 \cdot 0.60\ C_7H_8$: C 52.16 (52.13), H 5.63 (5.48), N 5.51 (5.38).

IIIf: colourless powder, 1.25 g (26%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ = 1.19 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.29 [d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.90 [s, 6H, C*Me*], 2.02 [s, 6H, C*Me*], 3.12 [sept, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*Me$_2$], 5.48 [s, 2H, C*H*], 7.20-7.24 [m, 8H, Ar*H*], 7.29-7.33 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$): δ = 23.7 [C*Me*], 24.2 [C*Me*], 24.7 [CH*Me*$_2$], 25.3 [CH*Me*$_2$], 28.5 [*C*HMe$_2$], 100.4 [*β*-*C*H], 124.6 [*m*-*C*(Dipp)], 127.6 [*C*(Aryl)], 128.0 [*p*-*C*(Dipp)], 138.1 [*o*-*C*(Dipp)], 141.8 [*ipso*-*C*(Dipp)], 144.5 [*C*(Aryl)], 170.5 [*C*N], 172.7 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, $CDCl_3$): δ = 100.8 ppm [*A*lBr$_2$]; ATR-IR: $\tilde{\nu}$ = 2963, 2927, 2868, 1532, 1496, 1439, 1358, 1322, 1252, 1184, 1100, 1016, 944, 902, 805, 790, 766, 724, 646, 612, 544, 522, 477, 454, 442, 414 cm^{-1}; elemental analysis calcd (found) $C_{40}H_{52}Al_2Br_4N_4 \cdot 0.55\ C_7H_8$: C 51.99 (51.96), H 5.61 (5.69), N 5.53 (5.57).

IIIg: yellow powder, 1.22 g (25%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ = 1.12 [d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me₂*], 1.24 [d, 12H, $^3J_{HH}$ = 6.8 Hz, CH*Me₂*], 1.89 [s, 6H, C*Me*], 2.27 [s, 6H, C*Me*], 3.11 [sept, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*Me₂], 5.48 [s, 2H, C*H*], 7.18-7.20 [m, 5H, Ar*H*], 7.26-7.30 [m, 3H, Ar*H*], 7.83 ppm [t, 1H, $^3J_{HH}$ = 7.8 Hz, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$): δ = 24.5 [C*Me*], 24.8 [C*Me*], 24.8 [CH*Me₂*], 25.2 [CH*Me₂*], 28.5 [*C*HMe₂], 102.0 [*β*-CH], 116.1 [*C*(Aryl)], 124.6 [*m*-*C*(Dipp)], 127.9 [*p*-*C*(Dipp)], 139.1 [*C*(Aryl)], 141.8 [*o*-*C*(Dipp)], 144.1 [*ipso*-*C*(Dipp)], 155.6 [*C*(Aryl)], 167.3 [*C*N], 174.6 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, $CDCl_3$): δ = 81.5 [*Al*Br₂], 90.5 ppm [*Al*Br₂]; ATR-IR: $\tilde{\nu}$ = 2968, 2925, 2869, 1587, 1539, 1524, 1435, 1352, 1319, 1255, 1217, 1180, 1007, 799, 758, 656, 563, 468, 443, 419 cm^{-1}; elemental analysis calcd (found) $C_{39}H_{51}Al_2Br_4N_5 \cdot 0.30\ C_7H_8$: C 49.81 (49.67), H 5.43 (5.41), N 7.07 (6.84).

IIIi: pale brown powder, 2.58 g (52%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ = 1.17 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me₂*], 1.27 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me₂*], 1.83 [s, 6H, C*Me*], 2.13 [s, 6H, C*Me*], 3.14 [sept, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*Me₂], 4.82 [s, 4H, C*H₂*], 5.34 [s, 2H, C*H*], 7.16-7.24 [m, 7H, Ar*H*], 7.28-7.34 ppm [m, 3H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$): δ = 23.0 [C*Me*], 24.0 [C*Me*], 24.8 [CH*Me₂*], 25.4 [CH*Me₂*], 28.4 [*C*HMe₂], 50.9 [*C*H₂], 100.5 [*β*-*C*H], 124.6 [*m*-*C*(Dipp)], 125.7 [*m*-*C*(Dipp)], 126.3 [*C*(Aryl)], 127.9 [*p*-*C*(Dipp)], 129.2 [*C*(Aryl)], 138.0 [*o*-*C*(Dipp)], 138.5 [*ipso*-*C*(Dipp)], 144.7 [*C*(Aryl)], 171.6 [*C*N], 173.0 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, $CDCl_3$): δ = 102.9 ppm [*Al*Br₂]; ATR-IR: $\tilde{\nu}$ = 2965, 2925, 2868, 1515, 1463, 1438, 1381, 1320, 1255, 1018, 887, 805, 762, 740, 702, 551, 437, 413 cm^{-1}; elemental analysis calcd (found) $C_{42}H_{56}Al_2Br_4N_4 \cdot 0.15\ C_7H_8$: C 51.48 (51.27), H 5.74 (5.50), N 5.58 (5.24).

General procedure for the synthesis employing trimethylaluminum and iodine

Trimethylaluminum (5.5 mL, 11 mmol, 2M in Toluene) was added dropwise to a solution of the respective bis(*β*-diketimine) (5 mmol) in Toluene (20 mL). The reaction solution was stirred for 16 h at 90 °C. Iodine (5.84 g, 23 mmol) was added and the red solution was stirred for 5d at room temperature. The volatile substances were removed in vacuum. The residue was then extracted with dichloromethane (20 mL) and the concentration of the filtered extract was layered with *n*-pentane yielding the products. In case of **IVa**, **IVe**, and **IVi**, the product was obtained as single-crystal suitable for an X-ray diffraction.

IVa: pale brown powder, 2.33 g (42%). ^{1}H NMR: (400 MHz, CDCl$_3$): δ = 1.14 [d, 12H, $^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.28 [d, 12H, $^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.85 [s, 6H, C*Me*], 2.49 [s, 6H, C*Me*], 3.03 [sept, 4H, $^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 3.91 [s, 4H, C*H*$_2$], 5.47 [s, 2H, C*H*], 7.20 [d, 4H, $^{3}J_{HH}$ = 7.7 Hz, Ar*H*], 7.29-7.32 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = 24.3 [C*Me*], 24.4 [C*Me*], 24.6 [CH*Me*$_2$], 25.6 [CH*Me*$_2$], 28.6 [*C*HMe$_2$], 47.8 [*C*H$_2$], 101.5 [*β*-*C*H], 124.6 [*m*-*C*(Dipp)], 128.0 [*p*-*C*(Dipp)], 138.6 [*o*-*C*(Dipp)], 144.7 [*ipso*-*C*(Dipp)], 171.5 [*C*N], 172.3 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, CDCl$_3$): δ = -24.5 ppm [*Al*I$_2$]; ATR-IR: $\tilde{\nu}$ = 2962, 2925, 2866, 1517, 1440, 1364, 1317, 1256, 1099, 1013, 891, 805, 777, 762, 671, 642, 549, 480, 427 cm^{-1}; elemental analysis calcd (found) $C_{36}H_{52}Al_2I_4N_4 \cdot 0.20\ CH_2Cl_2$: C 38.84 (38.84), H 4.72 (4.73), N 5.01 (4.97).

IVb: pale brown powder, 2.39 g (43%). ^{1}H NMR: (300 MHz, CDCl$_3$): δ = 1.13 [d, 12H, $^{3}J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.26 [d, 12H, $^{3}J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.82 [s, 6H, C*Me*], 2.05-2.14 [m, 2H, C*H*$_2$], 2.29 [s, 6H, C*Me*], 3.03 [sept, 4H, $^{3}J_{HH}$ = 6.9 Hz, C*H*Me$_2$], 3.60-3.65 [m, 4H, C*H*$_2$], 5.42 [s, 2H, C*H*], 7.17-7.20 [m, 4H, Ar*H*], 7.27-7.31 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = 22.1 [C*Me*], 24.2 [C*Me*], 24.5 [CH*Me*$_2$], 25.7 [CH*Me*$_2$], 28.6 [*C*HMe$_2$], 31.9 [*C*H$_2$], 45.5 [*C*H$_2$], 101.3 [*β*-*C*H], 124.5 [*m*-*C*(Dipp)], 127.9 [*p*-*C*(Dipp)], 138.7 [*o*-*C*(Dipp)], 144.8 [*ipso*-*C*(Dipp)], 170.7 [*C*N], 171.2 ppm [*C*N]; ATR-IR: $\tilde{\nu}$ = 2959, 2923, 2870, 1560, 1514, 1465, 1438, 1388, 1348, 1317, 1277, 1257, 1245, 1233, 1175, 1091, 1053, 1019, 946, 893, 872, 806, 775, 766, 738, 707, 643, 553, 528, 499, 465, 438 cm^{-1}; elemental analysis calcd (found) $C_{37}H_{54}Al_2I_4N_4 \cdot 0.30\ CH_2Cl_2$: C 39.23 (39.23), H 4.82 (4.83), N 4.91 (4.88).

IVc: pale brown powder, 1.98 g (41%). ^{1}H NMR: (400 MHz, CDCl$_3$): δ = 0.98 [d, 6H, $^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.14 [d, 6H, $^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.19-1.22 [m, 12H, CH*Me*$_2$], 1.43-1.48 [m, 2H, ring-C*H*$_2$], 1.75 [br, 2H, ring-C*H*$_2$], 1.79 [s, 6H, C*Me*], 1.87 [br, 2H, ring-C*H*$_2$], 2.16 [br, 2H, ring-C*H*$_2$], 2.62 [s, 6H, C*Me*], 2.69 [sept, 2H, $^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 3.38 [sept, 2H, $^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 5.12-5.20 [m, 2H, ring-C*H*], 5.47 [s, 2H, C*H*], 7.08-7.10 [m, 2H, Ar*H*], 7.16-7.14 [m, 2H, Ar*H*], 7.22-7.24 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = 24.4 [C*Me*], 24.4 [C*Me*], 24.5 [CH*Me*$_2$], 24.8 [CH*Me*$_2$], 25.0 [ring-*C*H$_2$], 26.4 [CH*Me*$_2$], 27.5 [CH*Me*$_2$], 28.5 [*C*HMe$_2$], 28.6 [*C*HMe$_2$], 36.2 [ring-*C*H$_2$], 63.1 [ring-*C*H], 103.1 [*β*-*C*H], 124.1 [*m*-*C*(Dipp)], 124.4 [*m*-*C*(Dipp)], 127.6 [*p*-*C*(Dipp)], 139.5 [*o*-*C*(Dipp)], 144.4 [*o*-*C*(Dipp)], 145.8 [*ipso*-*C*(Dipp)], 169.7 [*C*N], 173.2 ppm [*C*N]; ATR-IR: $\tilde{\nu}$ = 2958, 2933, 2860, 1538, 1496, 1439, 1369, 1346, 1323, 1277, 1256, 1231, 1178, 1076, 1053, 1020, 973, 949, 936, 895, 851, 801, 786, 764, 725, 694, 643, 600, 570, 553, 480, 451, 432, 411 cm^{-1}; elemental analysis calcd (found) $C_{40}H_{58}Al_2I_4N_4$: C 41.54 (41.64), H 5.06 (4.85), N 4.84 (4.80).

IVd: colourless powder, 2.88 g (50%). ^{1}H NMR: (400 MHz, CDCl$_3$): δ = 1.18 [d, 12H, ${}^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.31-1.33 [m, 12H, CH*Me*$_2$], 1.92 [s, 6H, C*Me*], 2.22 [s, 6H, C*Me*], 3.09 [sept, 2H, ${}^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 3.30 [sept, 2H, ${}^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 5.65 [s, 2H, C*H*], 7.20-7.24 [m, 4H, Ar*H*], 7.30-7.33 [m, 2H, Ar*H*], 7.37-7.40 [m, 2H, Ar*H*], 7.57-7.59 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = 24.4 [C*Me*], 24.5 [C*Me*], 25.0 [CH*Me*$_2$], 25.7 [CH*Me*$_2$], 25.9 [CH*Me*$_2$], 28.5 [CH*Me*$_2$], 28.7 [*C*HMe$_2$], 28.8 [*C*HMe$_2$], 102.2 [*β*-*C*H], 124.5 [*m*-*C*(Dipp)], 124.6 [*m*-*C*(Dipp)], 127.9 [*C*(Aryl)], 128.5 [*C*(Aryl)], 129.5 [*p*-*C*(Dipp)], 138.6 [*C*(Aryl)], 140.5 [*o*-*C*(Dipp)], 144.4 [*ipso*-*C*(Dipp)], 172.7 [*C*N], 173.9 ppm [*C*N]; Due to the poor solubility in different solvents (CDCl$_3$, C$_6$D$_6$, CH$_2$Cl$_2$, THF, Toluene), no signals were visible in the ^{13}C{^{1}H} NMR spectrum by the measurement with 1k scans. The same applies for the ^{27}Al{^{1}H} NMR spectrum. At a scan number of 8k very small signals could be obtained for the ^{13}C{^{1}H} NMR spectrum. ATR-IR: $\tilde{\nu}$ = 2960, 2924, 2866, 1538, 1504, 1440, 1348, 1318, 1296, 1250, 1234, 1203, 1179, 1117, 1018, 935, 891, 845, 803, 784, 771, 761, 727, 639, 581, 560, 533, 486, 450, 431 cm^{-1}; elemental analysis calcd (found) C$_{40}$H$_{52}$Al$_2$I$_4$N$_4$·0.10 C$_7$H$_8$: C 42.15 (42.11), H 4.59 (4.67), N 4.83 (4.88).

IVe: pale brown powder, 4.10 g (71%). ^{1}H NMR: (400 MHz, CDCl$_3$): δ = 1.19 [d, 12H, ${}^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.29 [d, 12H, ${}^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.93 [s, 6H, C*Me*], 2.05 [s, 6H, C*Me*], 3.13 [br, 4H, C*H*Me$_2$], 5.62 [s, 2H, C*H*], 7.02 [t, 1H, ${}^{3}J_{HH}$ = 2.0 Hz, Ar*H*], 7.18-7.21 [m, 6H, Ar*H*], 7.30 [t, 2H, ${}^{3}J_{HH}$ = 7.8 Hz, Ar*H*], 7.50 ppm [t, 1H, ${}^{3}J_{HH}$ = 7.8 Hz, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = 24.2 [C*Me*], 24.5 [C*Me*], 24.6 [CH*Me*$_2$], 25.4 [CH*Me*$_2$], 28.7 [*C*HMe$_2$], 101.4 [*β*-*C*H], 124.6 [*m*-*C*(Dipp)], 124.9 [*C*(Aryl)], 125.3 [*p*-*C*(Dipp)], 128.0 [*C*(Aryl)], 130.7 [*o*-*C*(Dipp)], 138.8 [*ipso*-*C*(Dipp)], 144.4 [*C*(Aryl)], 170.4 [*C*N], 172.6 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, CDCl$_3$): δ = -23.9 ppm [*Al*I$_2$]; ATR-IR: $\tilde{\nu}$ = 2961, 2925, 2866, 1598, 1585, 1520, 1440, 1355, 1321, 1259, 1247, 1026, 1001, 799, 757, 692, 562, 457, 425 cm^{-1}; elemental analysis calcd (found) C$_{40}$H$_{52}$Al$_2$I$_4$N$_4$·0.25 C$_7$H$_8$: C 42.73 (42.70), H 4.64 (4.67), N 4.77 (4.92).

IVg: yellow powder, 4.78 g (83%). ^{1}H NMR: (400 MHz, CDCl$_3$): δ = 1.17 [d, 12H, ${}^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.26 [d, 12H, ${}^{3}J_{HH}$ = 6.8 Hz, CH*Me*$_2$], 1.95 [s, 6H, C*Me*], 2.16 [s, 6H, C*Me*], 3.13 [sept, 4H, ${}^{3}J_{HH}$ = 6.8 Hz, C*H*Me$_2$], 5.65 [s, 2H, C*H*], 7.20 [d, 4H, ${}^{3}J_{HH}$ = 7.7 Hz, Ar*H*], 7.28-7.32 [m, 2H, Ar*H*], 7.36 [d, 2H, ${}^{3}J_{HH}$ = 7.7 Hz, Ar*H*], 7.87 ppm [t, 1H, ${}^{3}J_{HH}$ = 7.8 Hz, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = 24.6 [C*Me*], 24.7 [C*Me*], 25.6 [CH*Me*$_2$], 28.7 [*C*HMe$_2$], 102.2 [*β*-*C*H], 118.9 [*C*(Aryl)], 124.6 [*m*-*C*(Dipp)], 128.0 [*p*-*C*(Dipp)], 139.0 [*C*(Aryl)], 140.4 [*o*-*C*(Dipp)], 144.4 [*ipso*-*C*(Dipp)], 155.4 [*C*(Aryl)], 169.4 [*C*N], 173.7 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, CDCl$_3$): δ = -24.8 ppm [*Al*I$_2$]; ATR-IR: $\tilde{\nu}$ = 2967, 2925, 2867, 1587, 1537, 1434, 1350, 1317, 1297, 1253, 1216, 1178, 1106, 1052, 1005, 933, 889, 818, 798, 757, 715, 655, 602, 562, 535, 516, 490, 437 cm^{-1}; elemental analysis calcd (found) $C_{39}H_{51}Al_2I_4N_5$: C 40.68 (40.55), H 4.46 (4.53), N 6.08 (5.97).

IVh: pale brown powder, 1.56 g (25%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ = 0.71 [d, 6H, $^3J_{HH}$ = 6.8 Hz, CH*Me₂*], 0.93 [d, 6H, $^3J_{HH}$ = 6.8 Hz, CH*Me₂*], 1.22 [d, 6H, $^3J_{HH}$ = 6.9 Hz, CH*Me₂*], 1.30 [d, 6H, $^3J_{HH}$ = 6.9 Hz, CH*Me₂*], 1.89 [s, 6H, C*Me*], 2.15 [s, 6H, C*Me*], 2.72 [sept, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*Me₂], 3.40 [sept, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*Me₂], 5.62 [s, 2H, C*H*], 7.07-7.12 [m, 4H, Ar*H*], 7.18-7.24 [m, 6H, Ar*H*], 7.29-7.30 [m, 2H, Ar*H*], 7.86-7.88 ppm [m, 2H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$): δ = 24.2 [C*Me*], 24.5 [C*Me*], 24.6 [CH*Me₂*], 25.0 [CH*Me₂*], 27.5 [CH*Me₂*], 28.5 [*C*HMe₂], 28.6 [*C*HMe₂], 100.3 [*β-C*H], 121.4 [*C*(Aryl)], 124.4 [*m-C*(Dipp)], 124.7 [*m-C*(Dipp)], 125.0 [*p-C*(Dipp)], 127.5 [*C*(Aryl)], 128.2 [*C*(Aryl)], 128.9 [*C*(Aryl)], 134.3 [*C*(Aryl)], 138.2 [*o-C*(Dipp)], 143.8 [*o-C*(Dipp)], 145.0 [*ipso-C*(Dipp)], 151.6 [*C*(Aryl)], 171.4 [*C*N], 173.0 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, $CDCl_3$): δ = -24.8 ppm [*Al*I₂]; ATR-IR: $\tilde{\nu}$ = 3061, 2961, 2926, 2868, 1590, 1536, 1484, 1464, 1439, 1364, 1313, 1274, 1259, 1232, 1197, 1173, 1151, 1109, 1032, 1017, 942, 892, 874, 859, 848, 796, 774, 755, 729, 644, 593, 562, 553, 534, 502, 477, 436 cm^{-1}; elemental analysis calcd (found) $C_{46}H_{56}Al_2I_4N_4O\cdot0.70\ CH_2Cl_2$: C 43.08 (42.75), H 4.44 (4.36), N 4.30 (4.32).

IVi: pale yellow powder, 4.64 g (79%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ = 1.17 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me₂*], 1.27 [d, 12H, $^3J_{HH}$ = 6.9 Hz, CH*Me₂*], 1.86 [s, 6H, C*Me*], 2.15 [s, 6H, C*Me*], 3.15 [sept, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*Me₂], 4.84 [s, 4H, C*H₂*], 5.45 [s, 2H, C*H*], 7.16-7.22 [m, 6H, Ar*H*], 7.24 [br, 1H, Ar*H*], 7.28-7.34 ppm [m, 3H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, $CDCl_3$): δ = 23.4 [C*Me*], 24.4 [C*Me*], 24.7 [CH*Me₂*], 25.8 [CH*Me₂*], 28.6 [*C*HMe₂], 50.9 [*C*H₂], 101.3 [*β-C*H], 124.6 [*m-C*(Dipp)], 125.7 [*m-C*(Dipp)], 126.5 [*C*(Aryl)], 127.9 [*p-C*(Dipp)], 129.2 [*C*(Aryl)], 138.3 [*o-C*(Dipp)], 138.7 [*ipso-C*(Dipp)], 144.7 [*C*(Aryl)], 171.6 [*C*N], 172.8 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, $CDCl_3$): δ = -24.2 ppm [*Al*I₂]; ATR-IR: $\tilde{\nu}$ = 2962, 2925, 2867, 15, 1464, 1437, 1377, 1346, 1334, 1320, 1256, 1099, 1017, 933, 894, 864, 803, 762, 737, 705, 646, 592, 550, 481, 447, 420, 404 cm^{-1}; elemental analysis calcd (found) $C_{42}H_{56}Al_2I_4N_4\cdot0.65\ CH_2Cl_2$: C 41.52 (41.25), H 4.68 (4.57), N 4.54 (4.49).

Synthesis of Va

n-Butyllithium (6.9 mL, 11.0 mmol, 1.6M in Hexane) was added dropwise to a solution of **Ia** (2.71g, 5.0 mmol) in Toluene (20 mL). After additional stirring for 1 h, $EtAlCl_2$ (6.7 ml, 12.0 mmol, 1.8M in Toluene) was added to the solution at -30 °C. The orange mixture was allowed to warm to room temperature and stirred for 19 h. The volatile substances were removed in vacuum and the residue was extracted with toluene (20 mL). Crystals of **Va** (0.84 g, 23%) suitable for an X-ray diffraction analysis were obtained from the concentrated extract as colourless blocks.

^{1}H NMR: (400 MHz, CDCl$_3$): δ = -0.14 - -0.03 [m, 2H, AlCH_2CH$_3$], 0.02-0.13 [m, 2H, AlCH_2CH$_3$], 0.74-0.81 [m, 6H, AlCH$_2$$CH_3$], 1.13 [d, 6H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$], 1.20-1.23 [m, 6H, CH*Me*$_2$], 1.26-1.31 [m, 12H, CH*Me*$_2$], 1.80 [s, 6H, C*Me*], 2.32 [s, 6H, C*Me*], 2.83-2.92 [m, 2H, C*H*Me$_2$], 3.22-3.33 [m, 2H, C*H*Me$_2$], 3.59-3.74 [m, 4H, CH_2], 5.19 [s, 2H, C*H*], 7.18-7.32 ppm [m, 6H, Ar*H*]; ^{13}C{^{1}H} NMR: (101 MHz, CDCl$_3$): δ = 8.6, 13.6 [AlCH$_2$CH$_3$], 22.0, 22.1, 23.2, 23.2, 24.0, 24.1, 24.6, 24.7, 24.8, 25.3, 25.4, 25.4, 27.3, 27.9, 28.1, 28.4 [C*Me*, CH*Me*$_2$, *C*HMe$_2$], 48.0 [*C*H$_2$], 99.3, 99.4 [*β*-*C*H], 123.8, 123.9, 124.5, 124.6, 127.2 [*m*-*C*(Dipp), *p*-*C*(Dipp)], 139.1, 143.6, 143.8, 144.9, 145.9 [*o*-*C*(Dipp), *ipso*-*C*(Dipp)], 169.9, 170.0, 170.5, 170.6 ppm [*C*N]; ^{27}Al{^{1}H} NMR: (104 MHz, CDCl$_3$): δ = 102.6 ppm [*AlCl*]; ATR-IR: $\tilde{\nu}$ = 3067, 2965, 2928, 2898, 2864, 1518, 1440, 1371, 1316, 1295, 1260, 1187, 1097, 1054, 1018, 933, 890, 801, 778, 760, 725, 672, 647, 610, 535, 455, 418 cm^{-1}; $C_{40}H_{62}Al_2Cl_2N_4 \cdot 0.35\ C_7H_8$: C 67.44 (67.38), H 8.64 (8.59), N 7.41 (7.41).

IIa

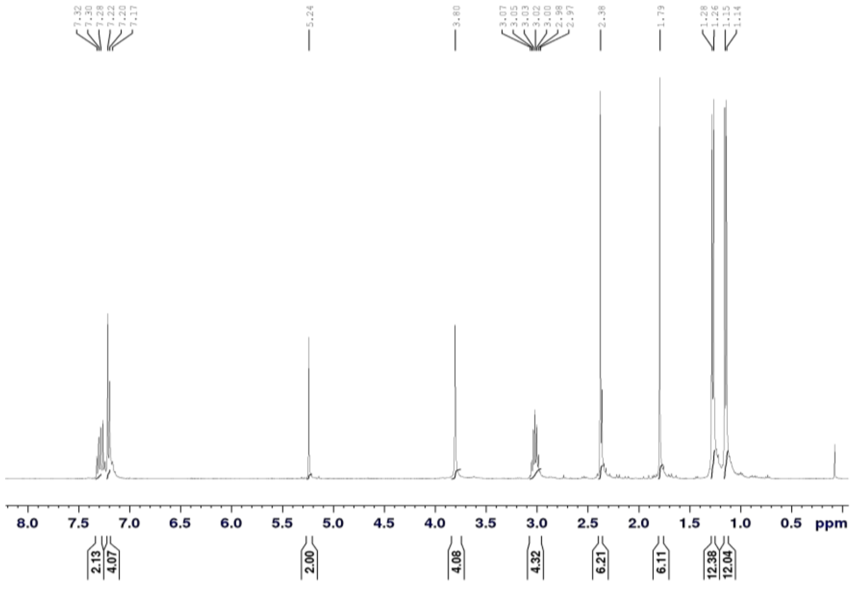


Figure S1: ^{1}H NMR spectrum (400 MHz) of **IIa** in CDCl$_3$.

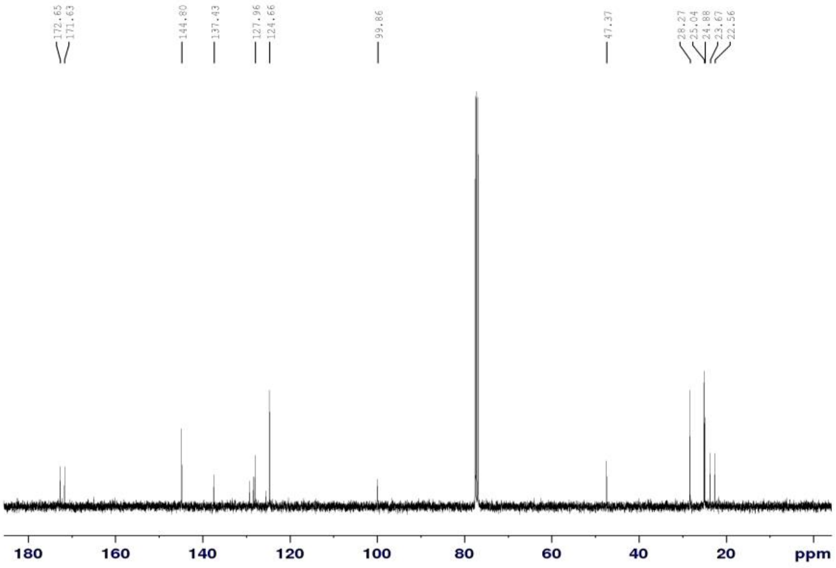


Figure S2: ^{13}C NMR spectrum (101 MHz) of **IIa** in CDCl$_3$.

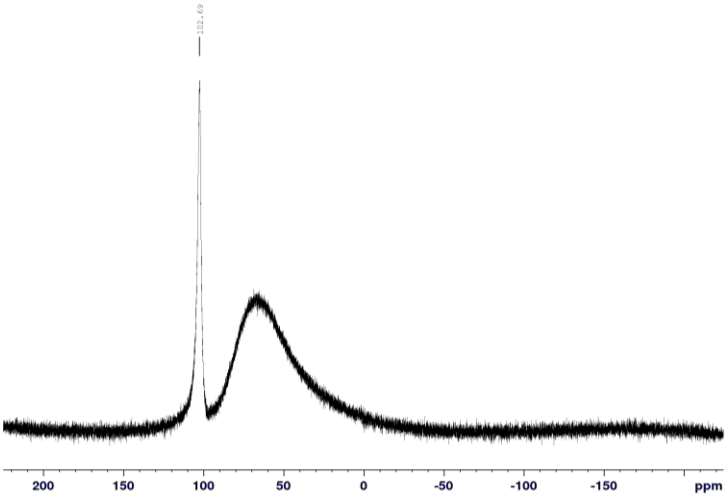


Figure S3: ^{27}Al NMR spectrum (104 MHz) of **IIa** in CDCl$_3$.

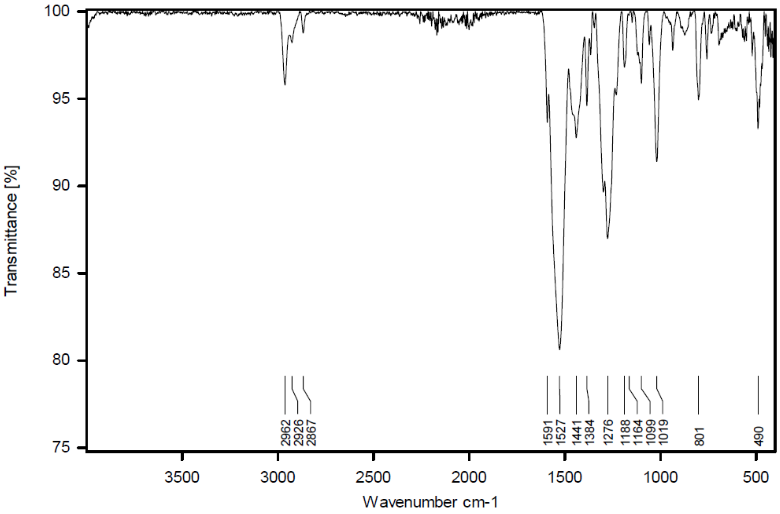


Figure S4: ATR-IR spectrum of **IIa**.

IIb

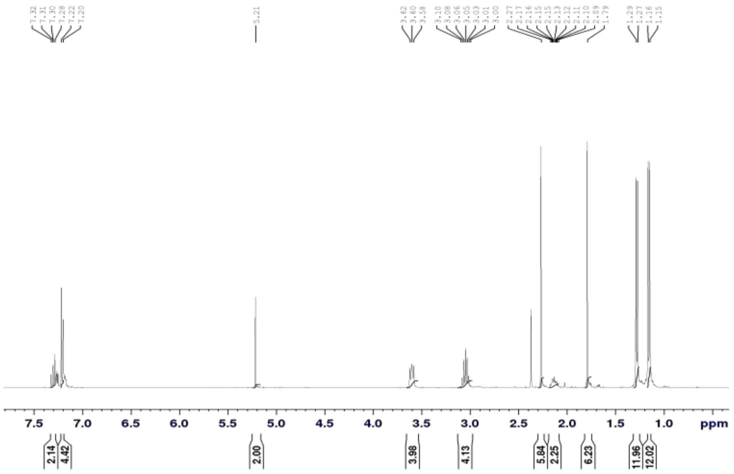


Figure S5: ^{1}H NMR spectrum (400 MHz) of **IIb** in $CDCl_3$.

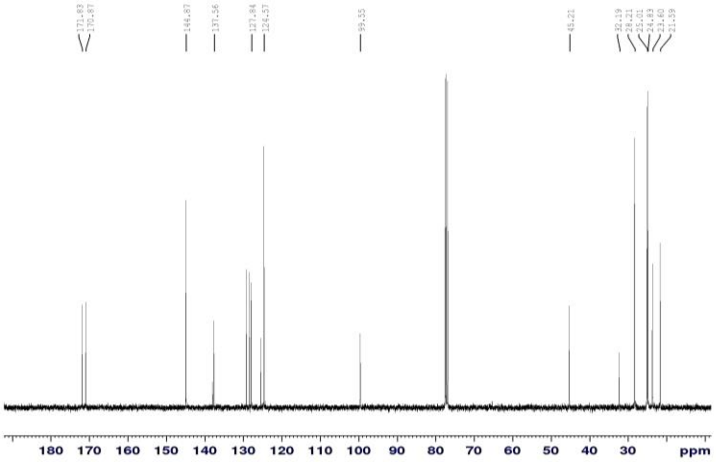


Figure S6: ^{13}C NMR spectrum (101 MHz) of **IIb** in $CDCl_3$.

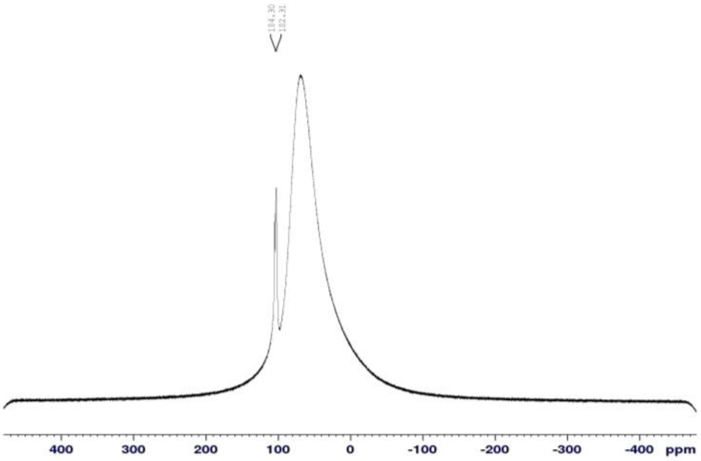


Figure S7: ^{27}Al NMR spectrum (104 MHz) of **IIb** in $CDCl_3$.

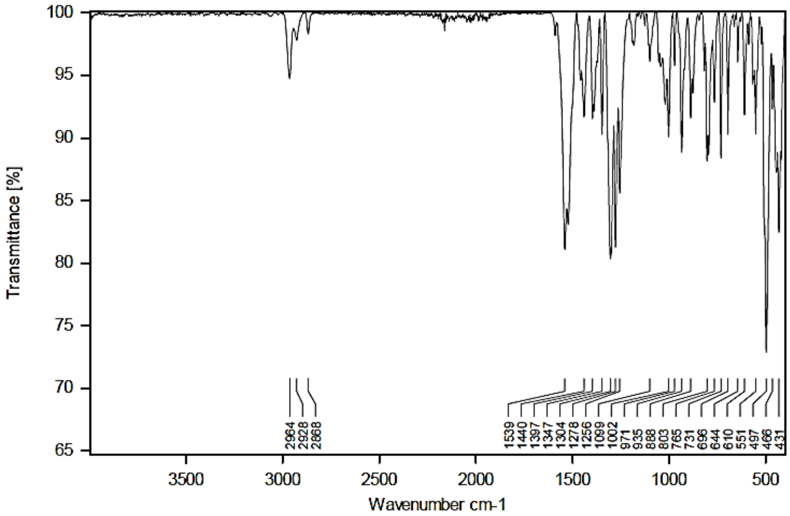


Figure S8: ATR-IR spectrum of **IIb**.

IId

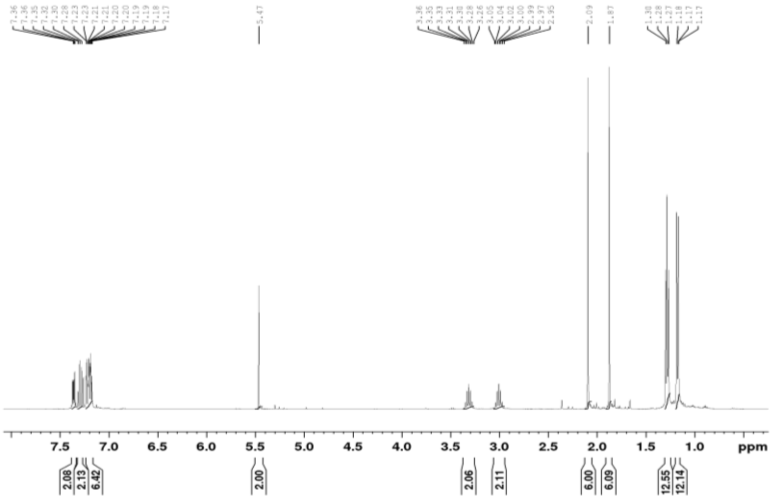


Figure S9: ^{1}H NMR spectrum (400 MHz) of **IId** in $CDCl_3$.

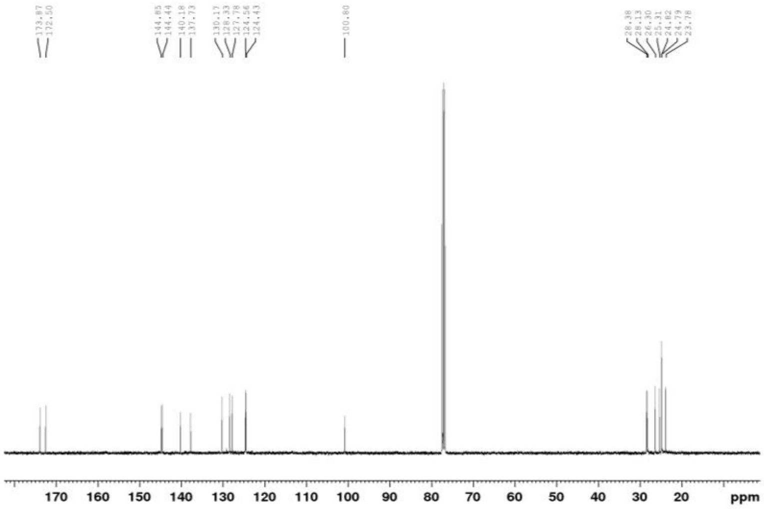


Figure S10: ^{13}C NMR spectrum (101 MHz) of **IId** in $CDCl_3$.

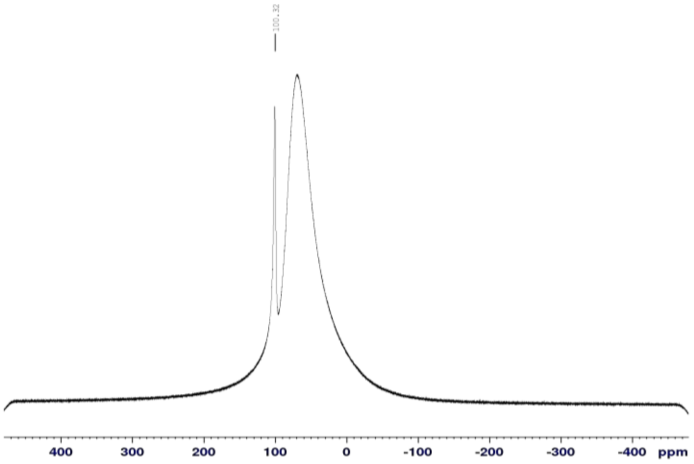


Figure S11: ^{27}Al NMR spectrum (104 MHz) of **IId** in CDCl$_3$.

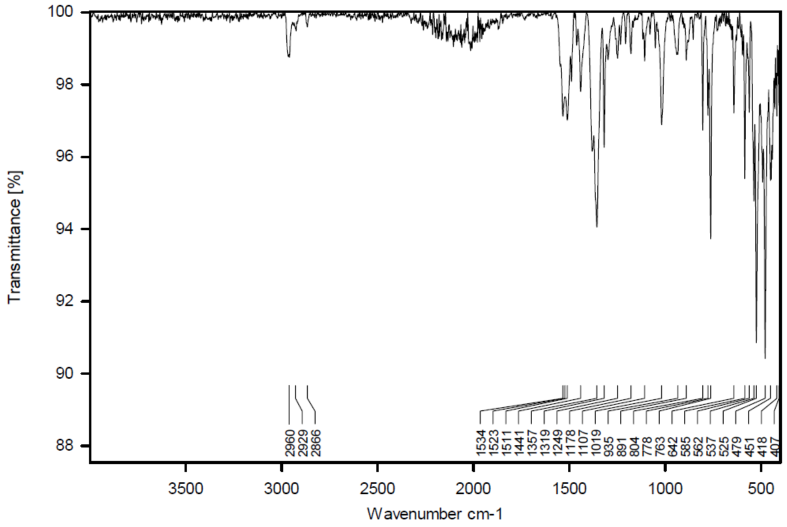


Figure S12: ATR-IR spectrum of **IId**.

IIe

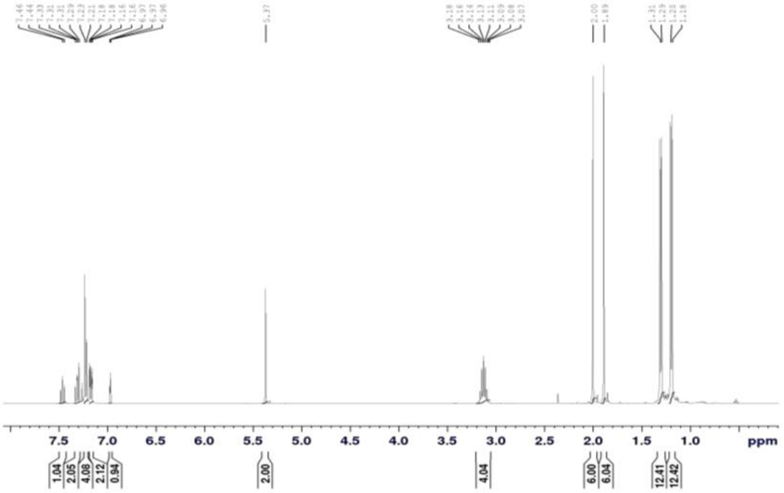


Figure S13: ^{1}H NMR spectrum (400 MHz) of **IIe** in CDCl$_3$.

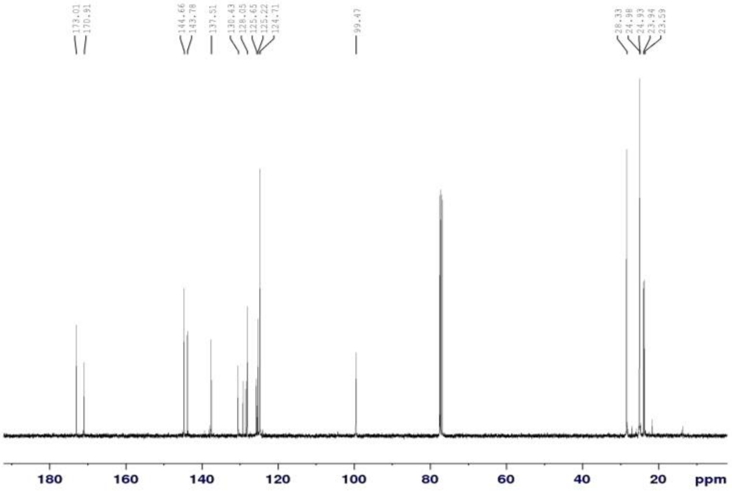


Figure S14: ^{13}C NMR spectrum (101 MHz) of **IIe** in $CDCl_3$.

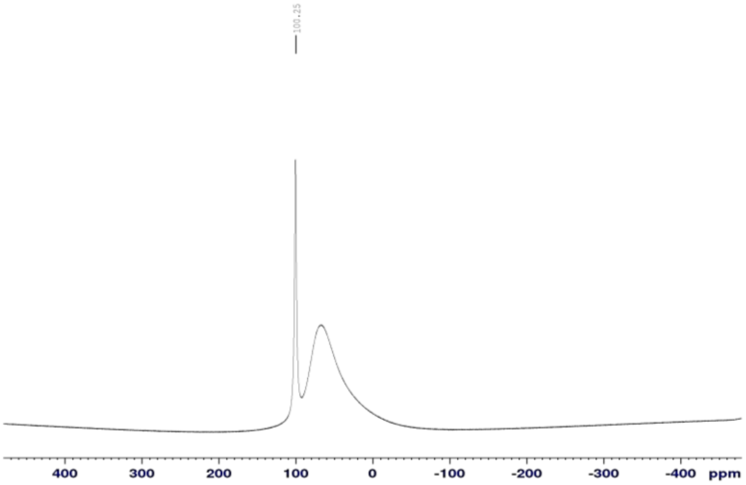


Figure S15: ^{27}Al NMR spectrum (104 MHz) of **IIe** in $CDCl_3$.

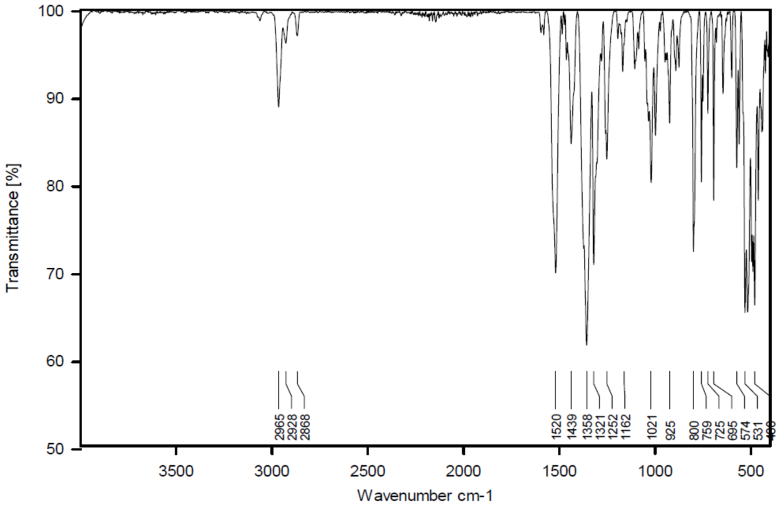


Figure S16: ATR-IR spectrum of **IIe**.

IIf

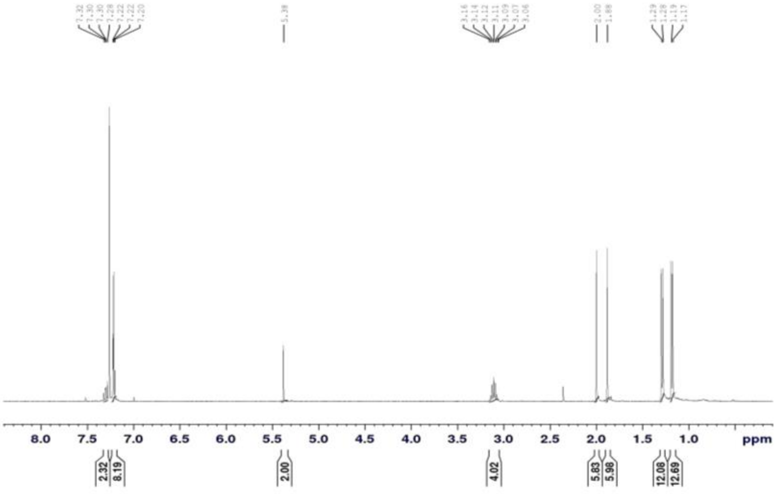


Figure S17: ^{1}H NMR spectrum (400 MHz) of **IIf** in $CDCl_3$.

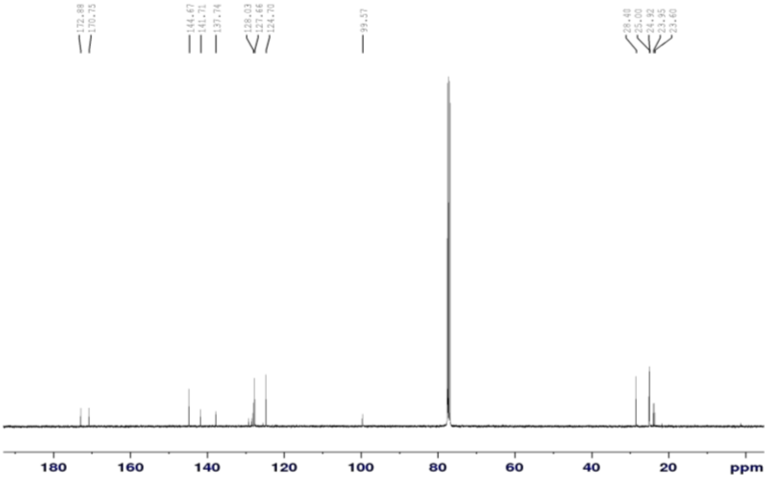


Figure S18: ^{13}C NMR spectrum (101 MHz) of **IIf** in $CDCl_3$.

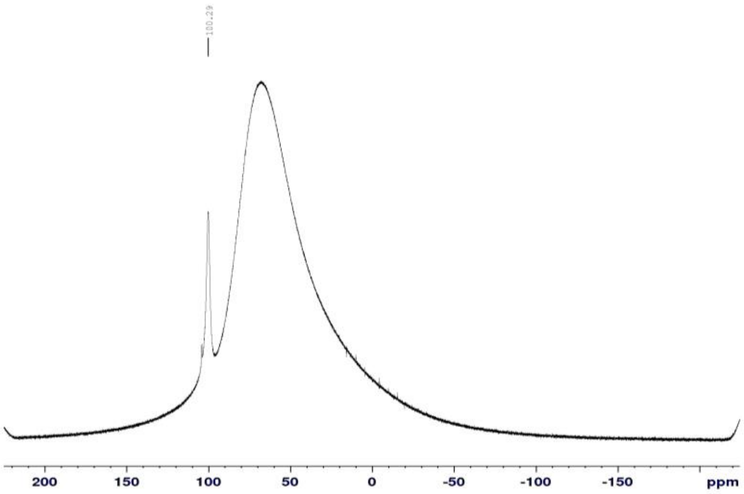


Figure S19: ^{27}Al NMR spectrum (104 MHz) of **IIf** in $CDCl_3$.

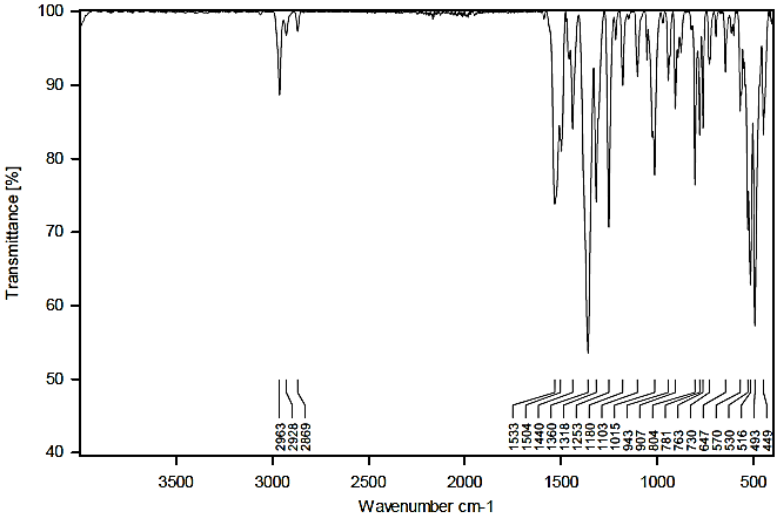


Figure S20: ATR-IR spectrum of **IIf**.

IIg

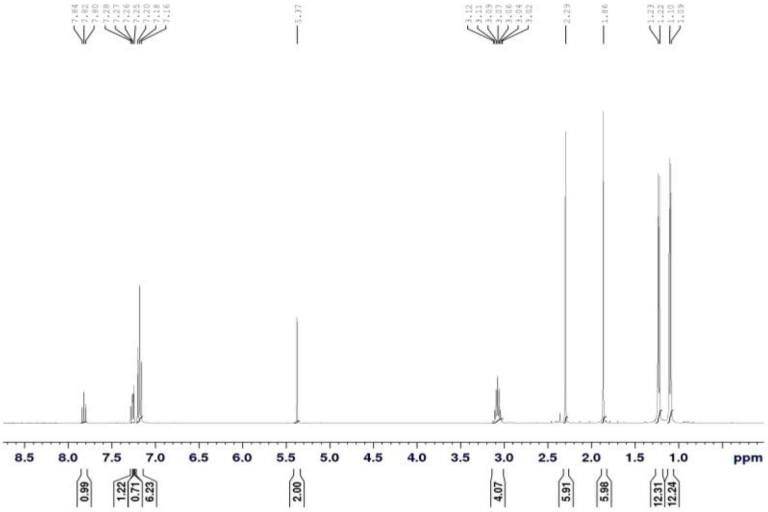


Figure S21: ^{1}H NMR spectrum (400 MHz) of **IIg** in CDCl$_3$.

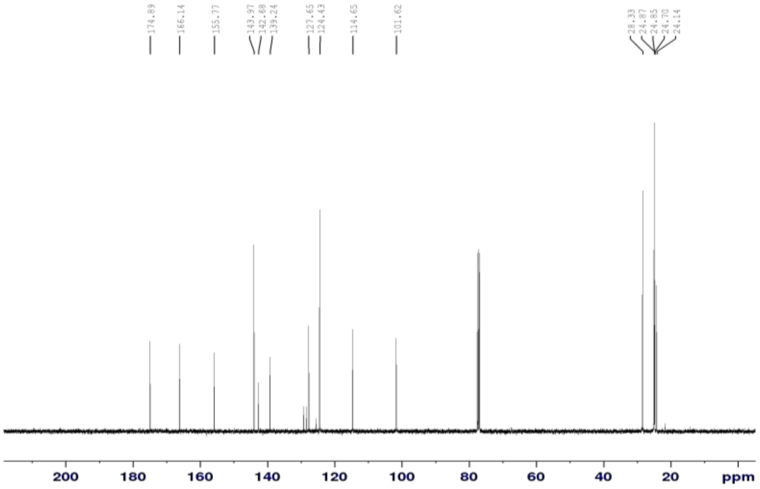


Figure S22: ^{13}C NMR spectrum (101 MHz) of **IIg** in CDCl$_3$.

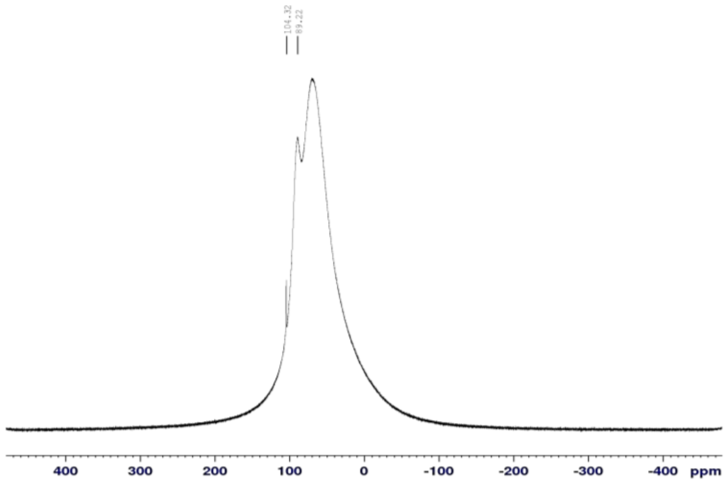


Figure S23: ^{27}Al NMR spectrum (104 MHz) of **IIg** in CDCl$_3$.

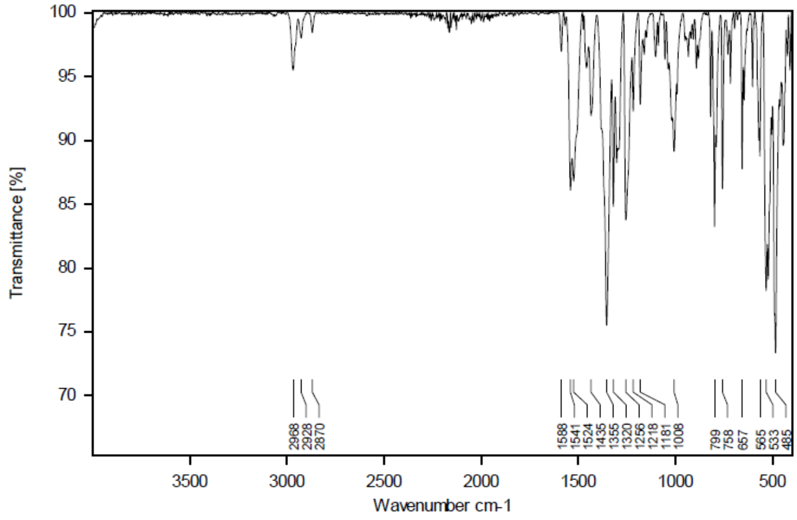


Figure S24: ATR-IR spectrum of **IIg**.

IIi

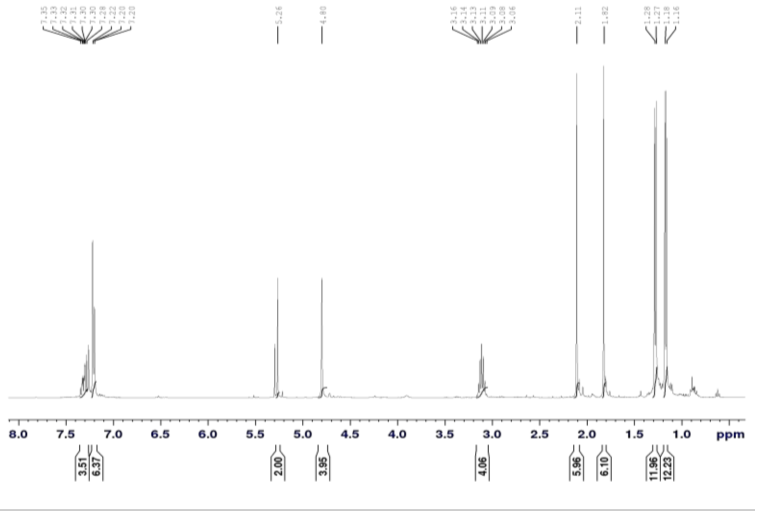


Figure S25: ^{1}H NMR spectrum (400 MHz) of **IIi** in CDCl$_3$.

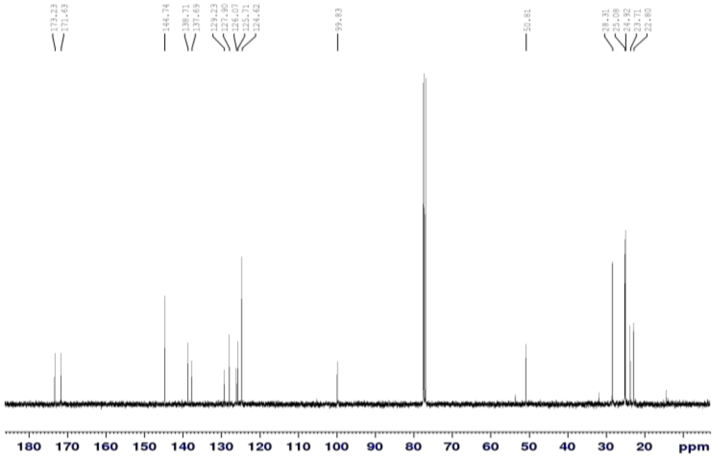


Figure S26: ^{13}C NMR spectrum (101 MHz) of **Ili** in $CDCl_3$.

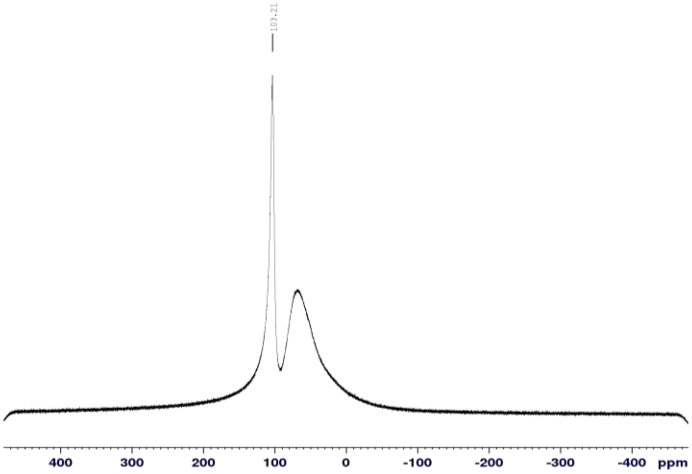


Figure S27: ^{27}Al NMR spectrum (104 MHz) of **Ili** in $CDCl_3$.

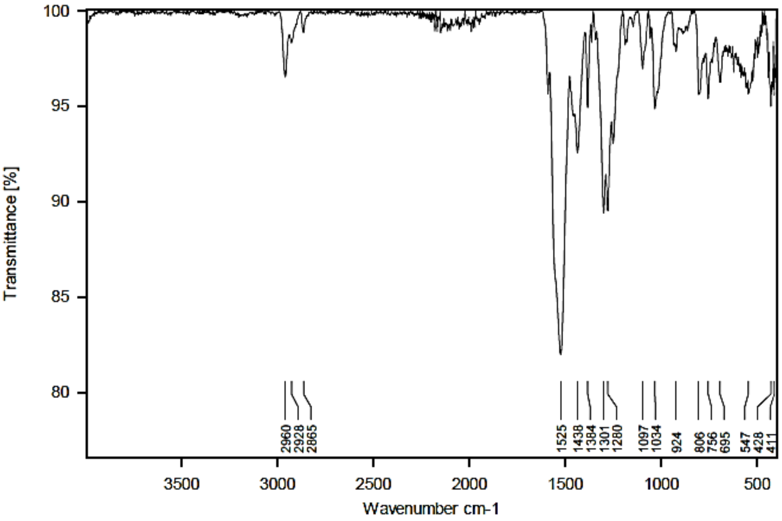


Figure S28: ATR-IR spectrum of **Ili**.

IIIa

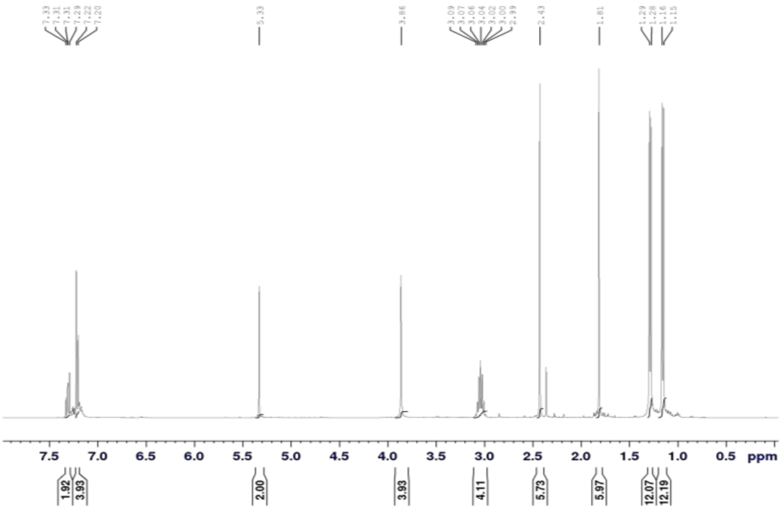


Figure S29: ^{1}H NMR spectrum (400 MHz) of **IIIa** in $CDCl_3$.

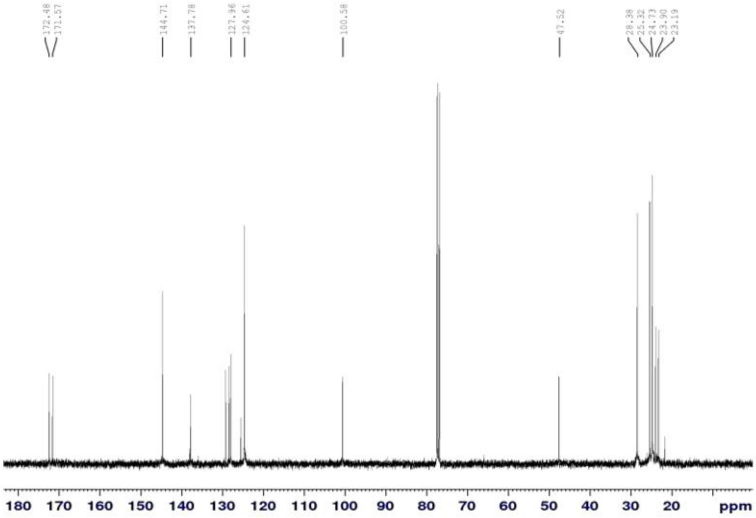


Figure S30: ^{13}C NMR spectrum (101 MHz) of **IIIa** in $CDCl_3$.

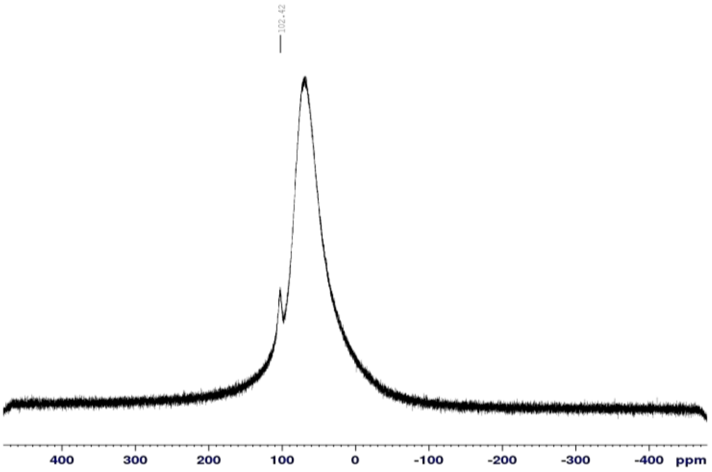


Figure S31: ^{27}Al NMR spectrum (104 MHz) of **IIIa** in $CDCl_3$.

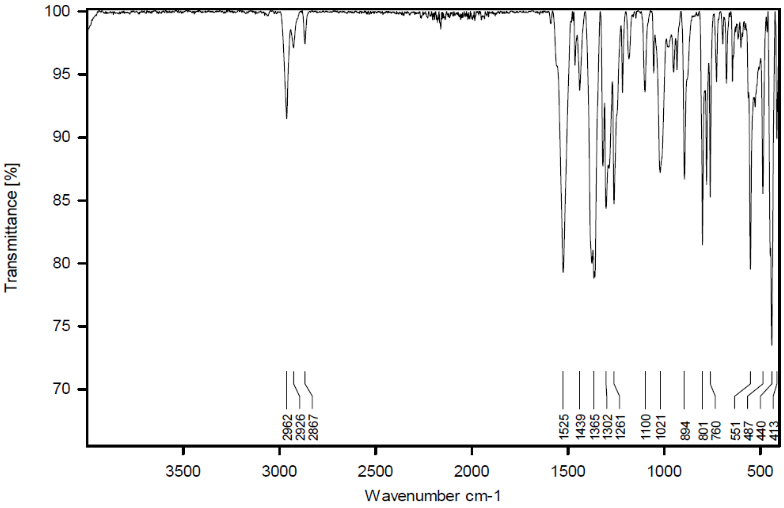


Figure S32: ATR-IR spectrum of **IIIa**.

IIIb

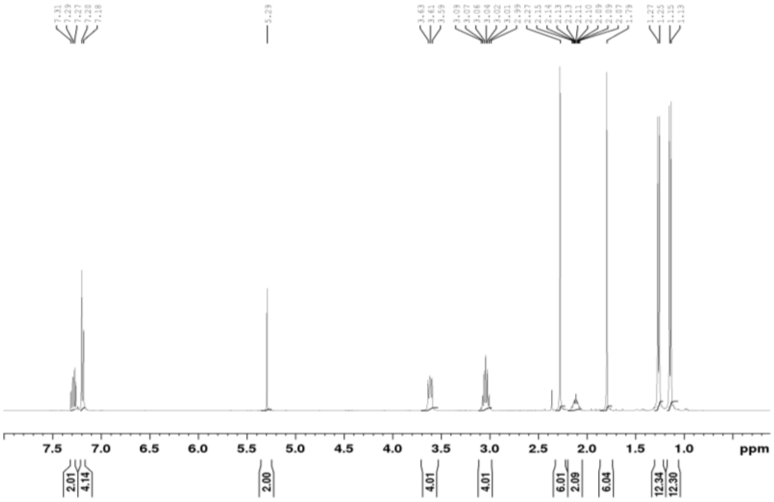


Figure S33: ^{1}H NMR spectrum (400 MHz) of **IIIb** in $CDCl_3$.

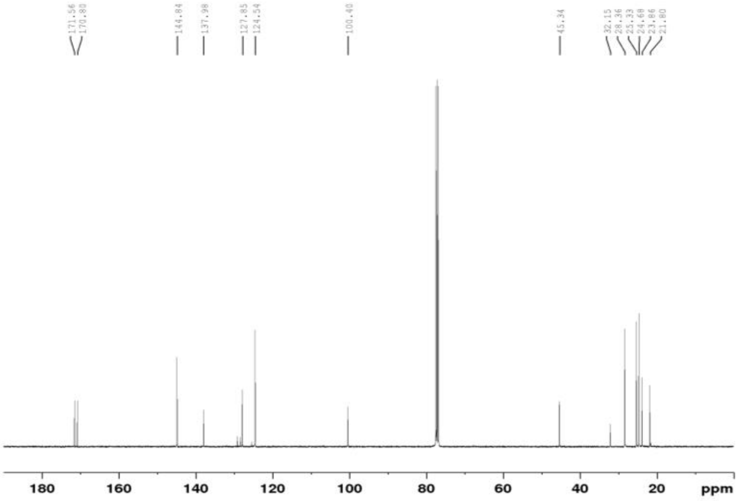


Figure S34: ^{13}C NMR spectrum (101 MHz) of **IIIb** in $CDCl_3$.

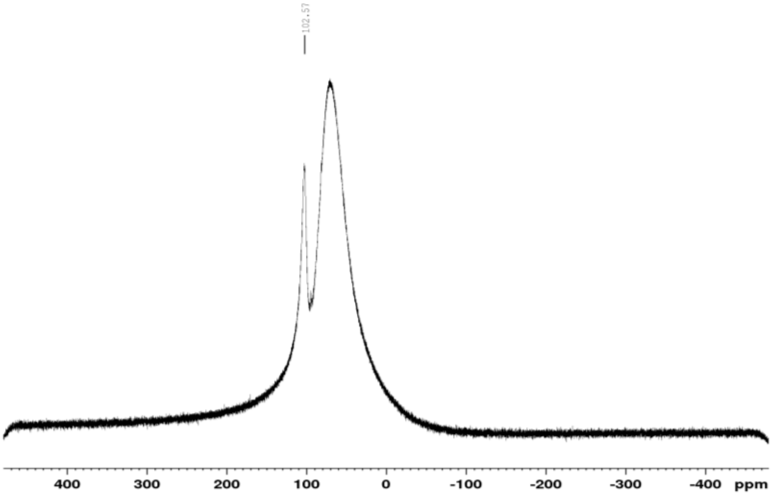


Figure S35: ^{27}Al NMR spectrum (104 MHz) of **IIIb** in CDCl$_3$.

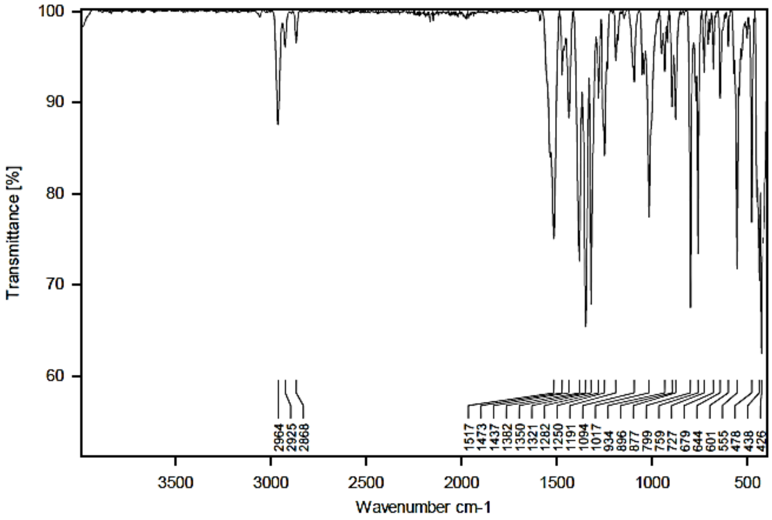


Figure S36: ATR-IR spectrum of **IIIb**.

IIId

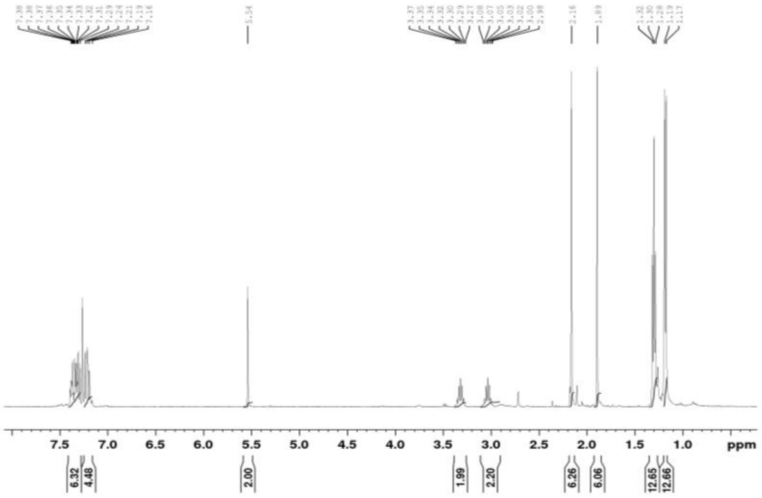


Figure S37: ^{1}H NMR spectrum (400 MHz) of **IIId** in CDCl$_3$.

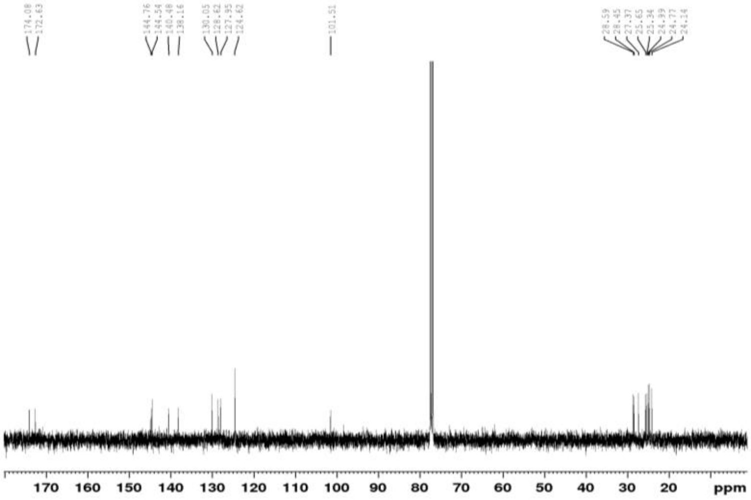


Figure S38: ^{13}C NMR spectrum (101 MHz) of **IIId** in CDCl$_3$.

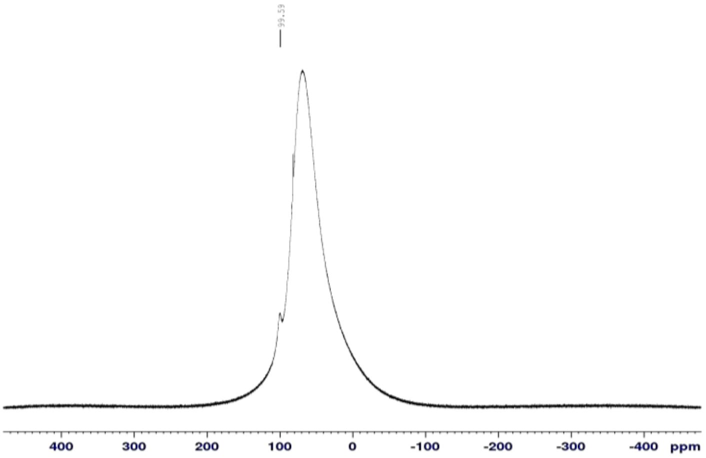


Figure S39: ^{27}Al NMR spectrum (104 MHz) of **IIId** in CDCl$_3$.

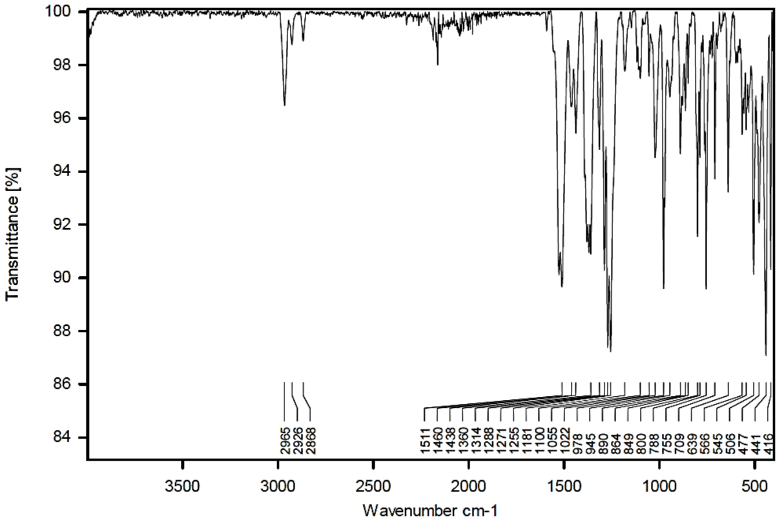


Figure S40: ATR-IR spectrum of **IIId**.

IIIe

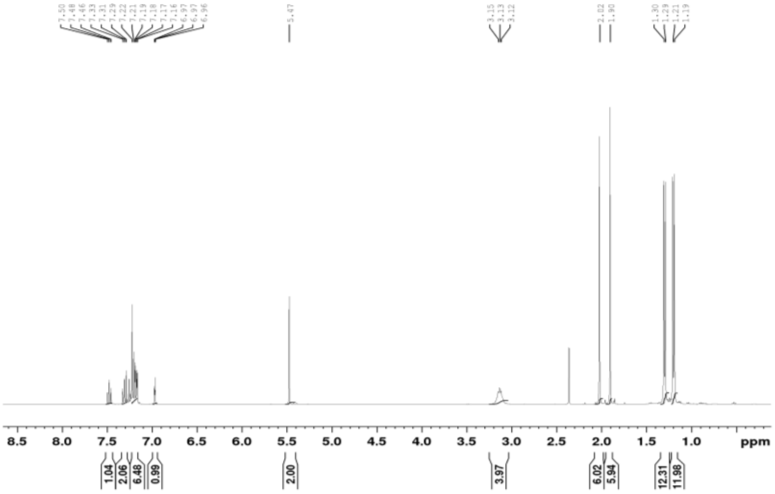


Figure S41: ^{1}H NMR spectrum (400 MHz) of **IIIe** in CDCl$_3$.

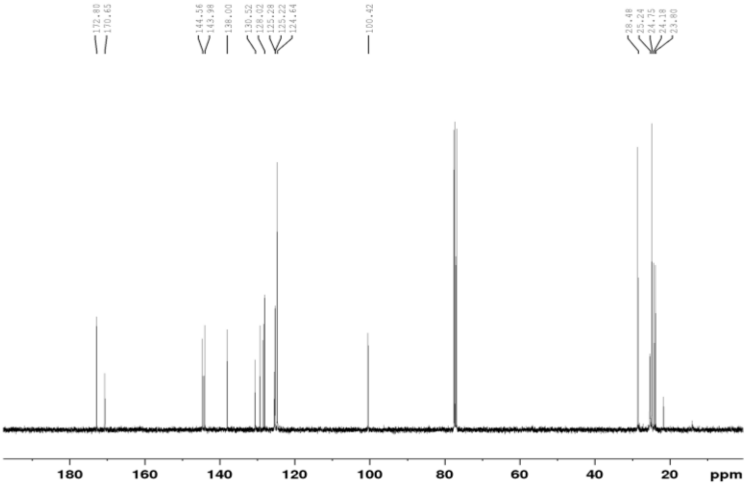


Figure S42: ^{13}C NMR spectrum (101 MHz) of **IIIe** in CDCl$_3$.

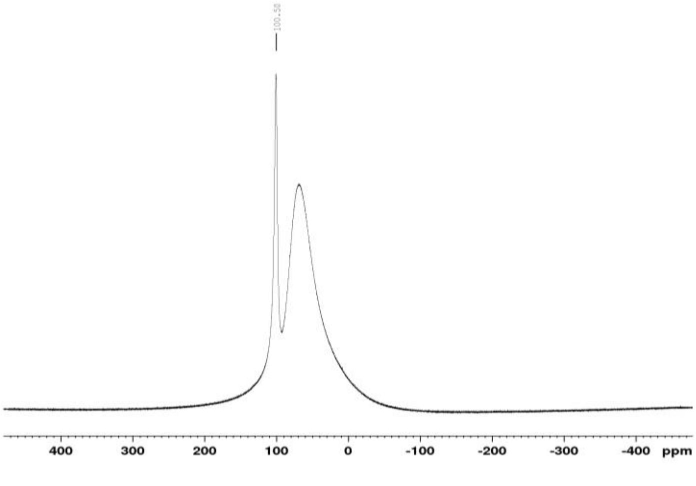


Figure S43: ^{27}Al NMR spectrum (104 MHz) of **IIIe** in CDCl$_3$.

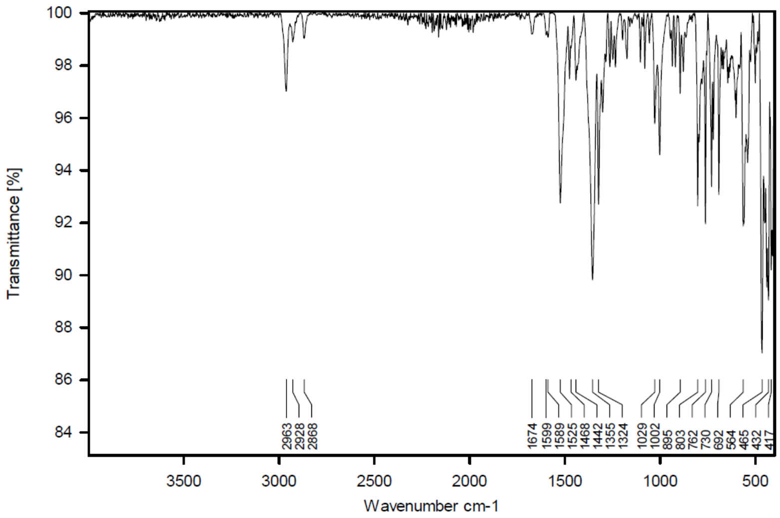


Figure S44: ATR-IR spectrum of **IIIe**.

IIIf

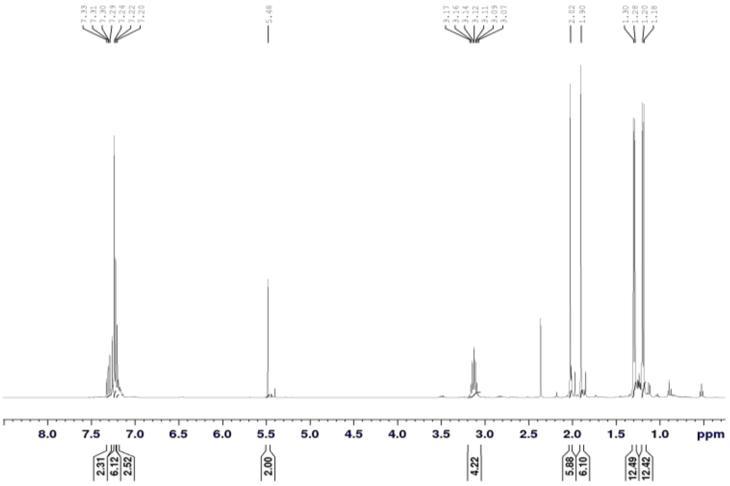


Figure S45: ^{1}H NMR spectrum (400 MHz) of **IIIf** in $CDCl_3$.

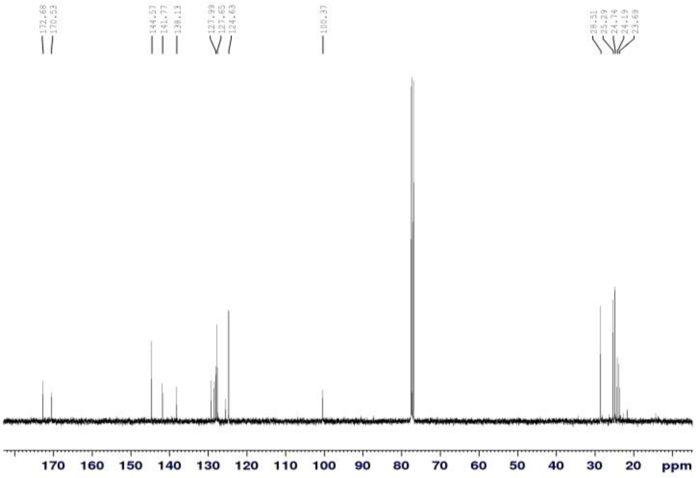


Figure S46: ^{13}C NMR spectrum (101 MHz) of **IIIf** in $CDCl_3$.

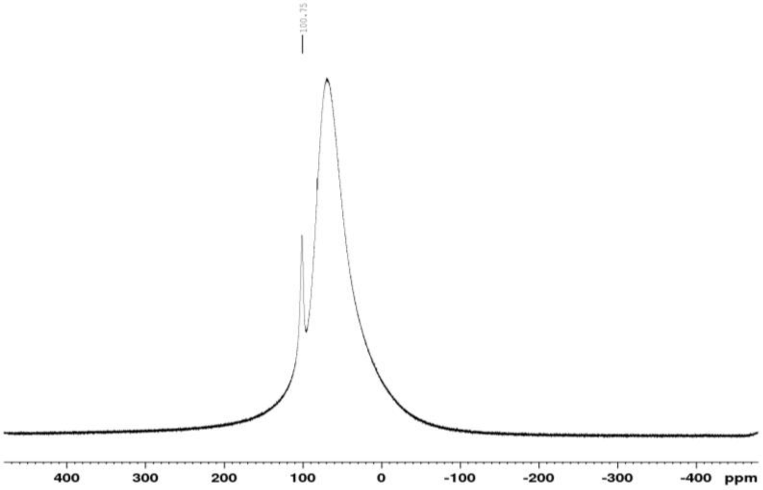


Figure S47: ^{27}Al NMR spectrum (104 MHz) of **IIIf** in $CDCl_3$.

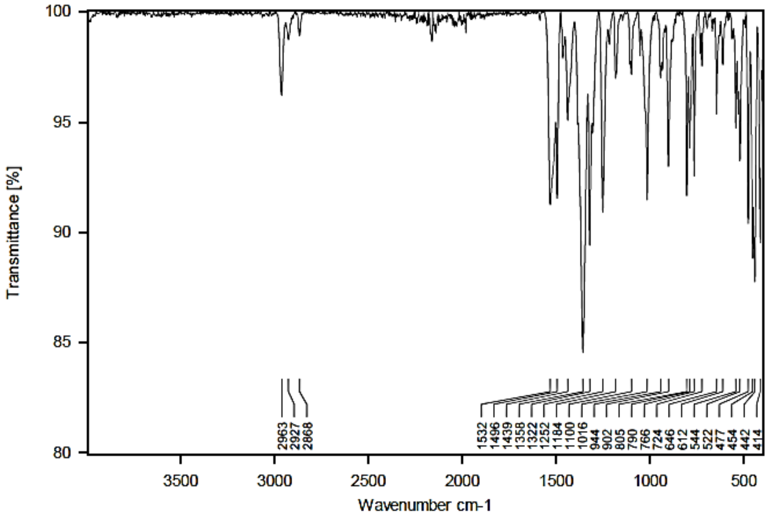


Figure S48: ATR-IR spectrum of **IIIf**.

IIIg

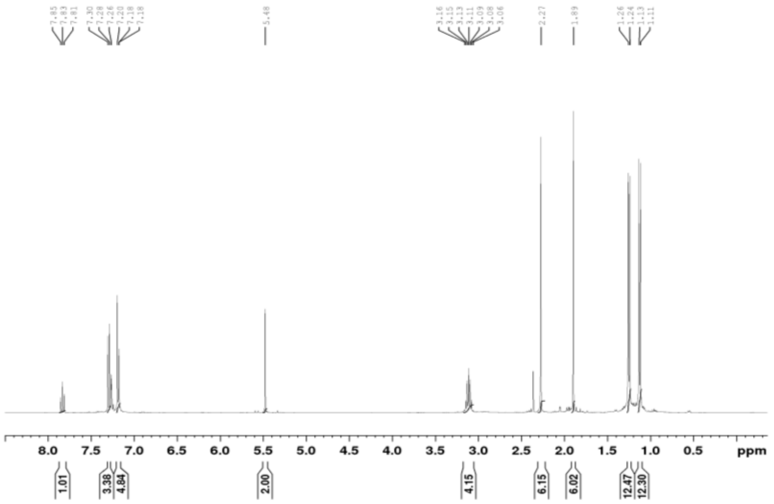


Figure S49: ^{1}H NMR spectrum (400 MHz) of **IIIg** in $CDCl_3$.

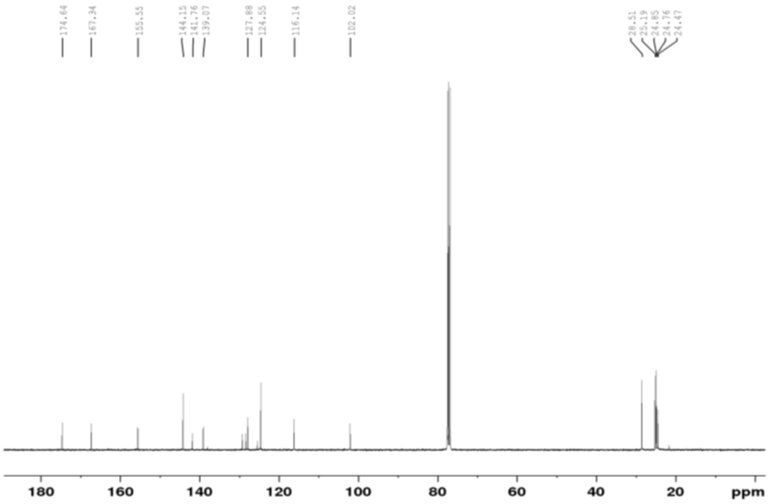


Figure S50: ^{13}C NMR spectrum (101 MHz) of **IIIg** in $CDCl_3$.

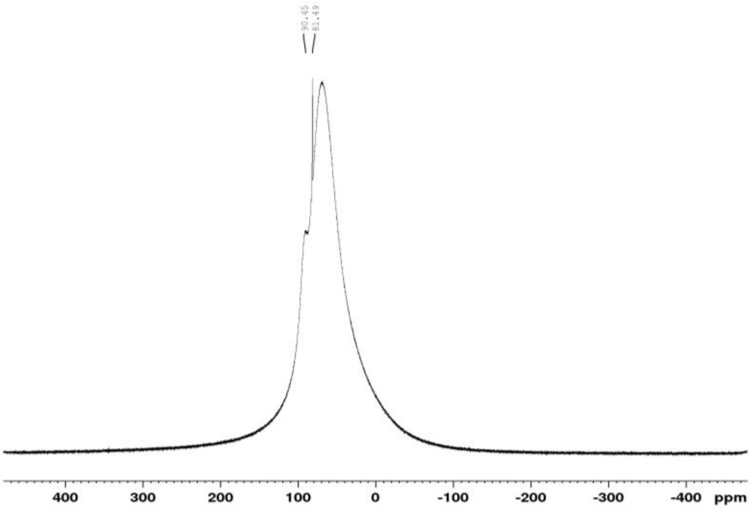


Figure S51: ^{27}Al NMR spectrum (104 MHz) of **IIIg** in $CDCl_3$.

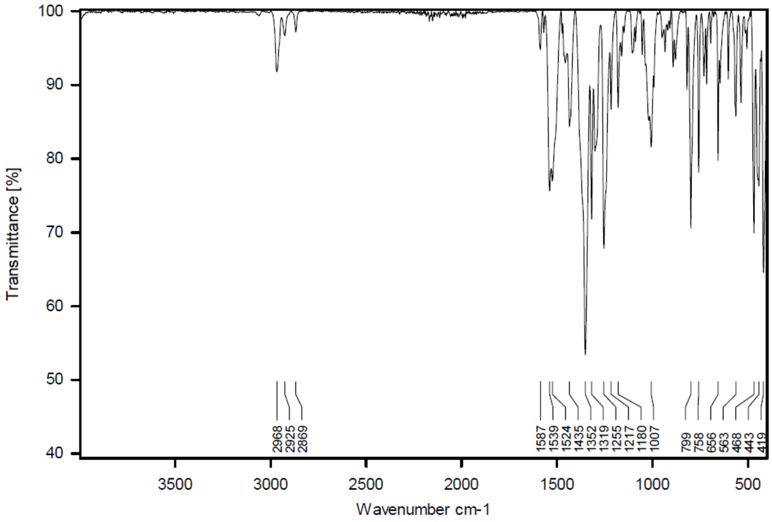


Figure S52: ATR-IR spectrum of **IIIg**.

IIIi

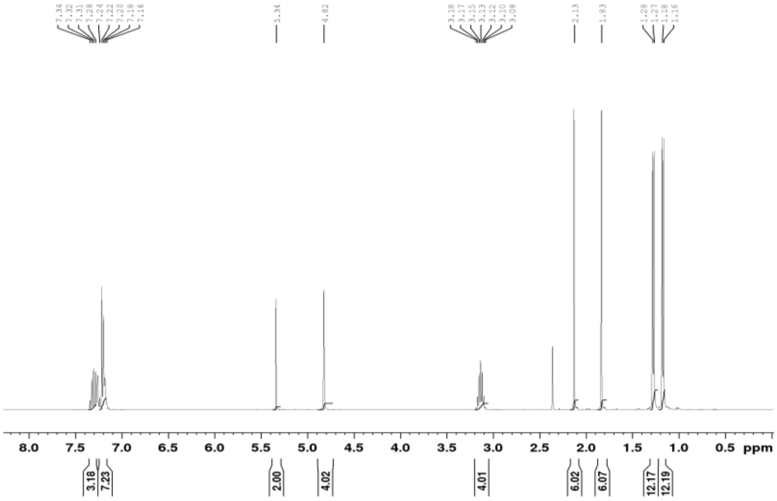


Figure S53: ^{1}H NMR spectrum (400 MHz) of **IIIi** in $CDCl_3$.

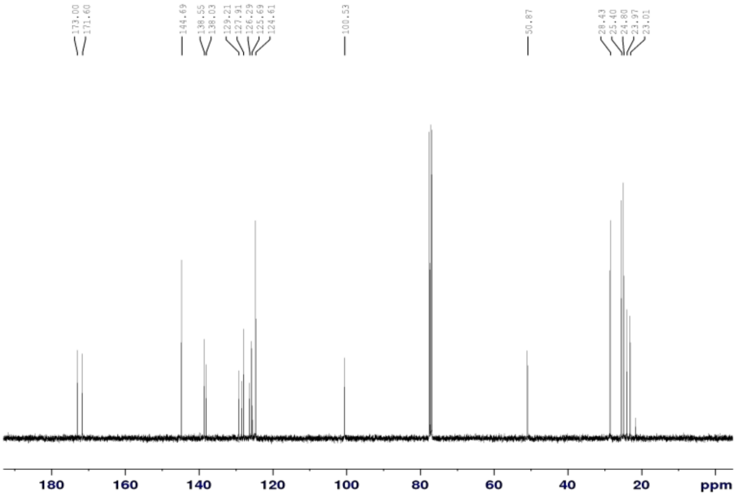


Figure S54: ^{13}C NMR spectrum (101 MHz) of **IIIi** in $CDCl_3$.

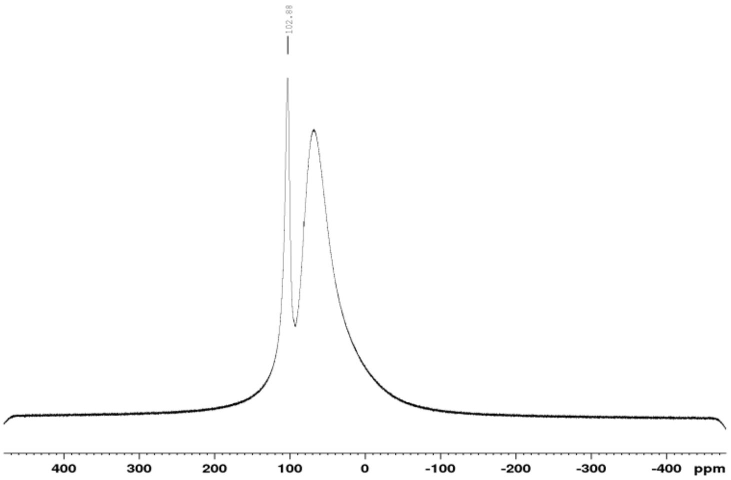


Figure S55: ^{27}Al NMR spectrum (104 MHz) of **IIIi** in $CDCl_3$.

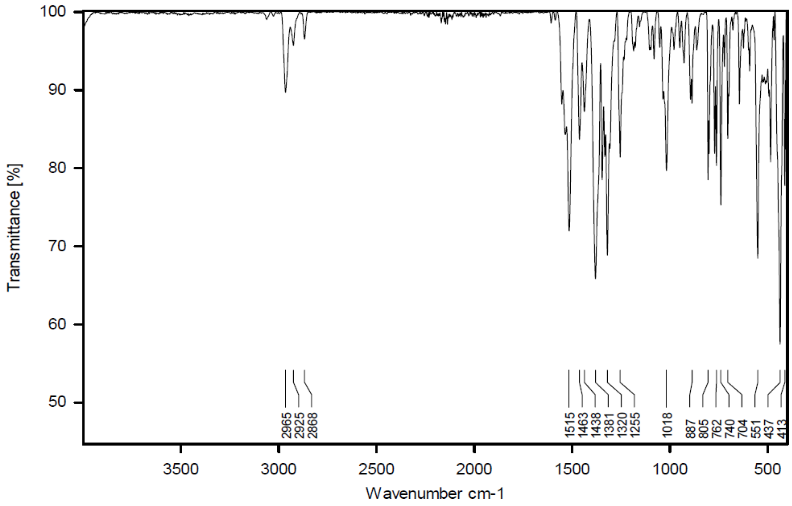


Figure S56: ATR-IR spectrum of **IIIi**.

IVa

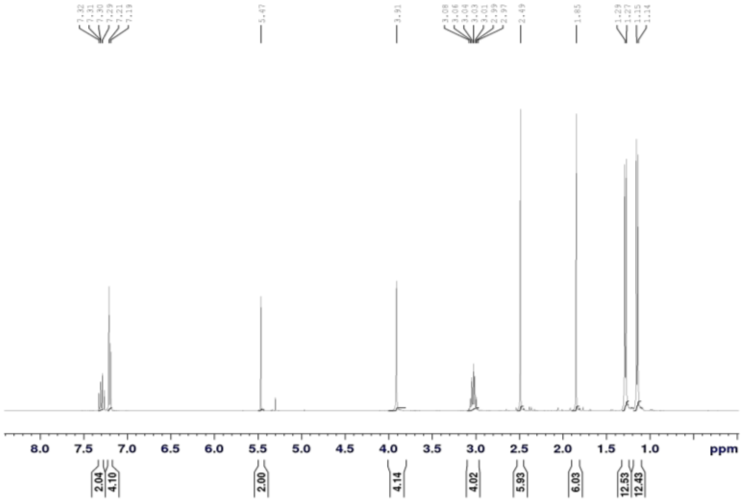


Figure S57: ^{1}H NMR spectrum (400 MHz) of **IVa** in $CDCl_3$.

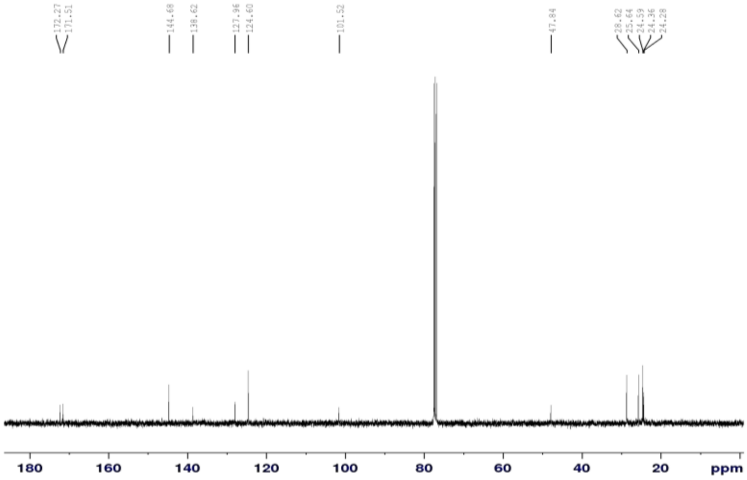


Figure S58: ^{13}C NMR spectrum (101 MHz) of **IVa** in $CDCl_3$.

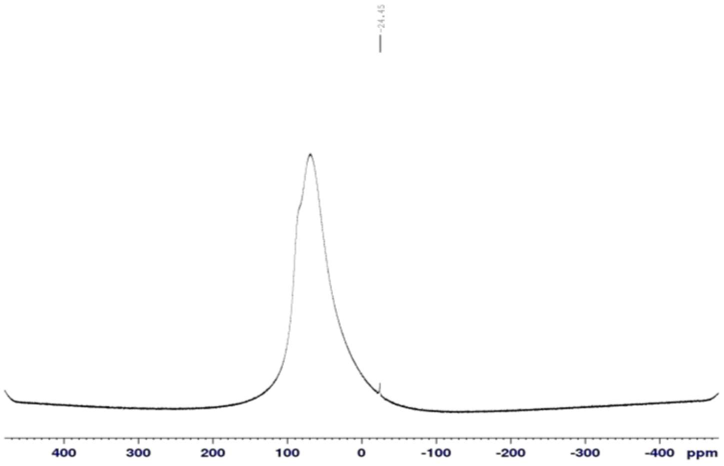


Figure S59: ^{27}Al NMR spectrum (104 MHz) of **IVa** in $CDCl_3$.

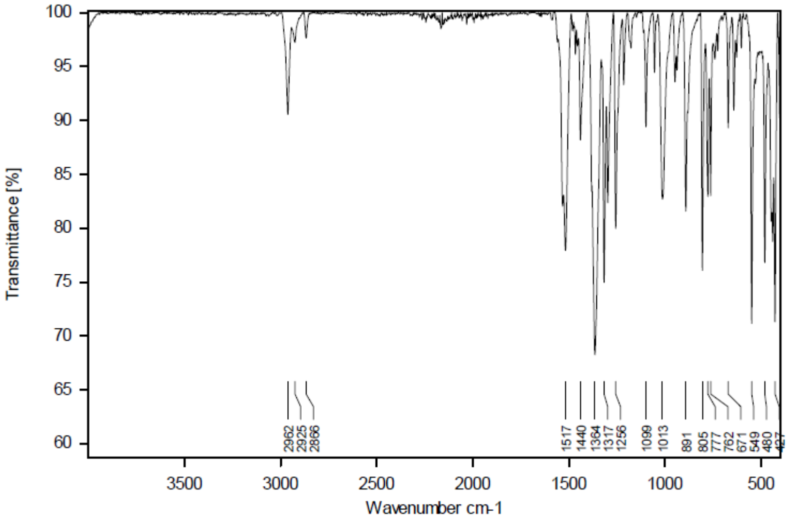


Figure S60: ATR-IR spectrum of **IVa**.

IVb

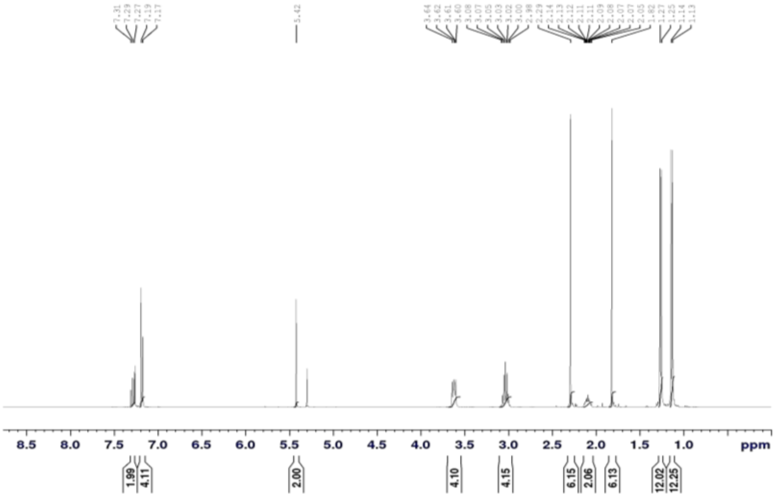


Figure S61: ^{1}H NMR spectrum (400 MHz) of **IVb** in $CDCl_3$.

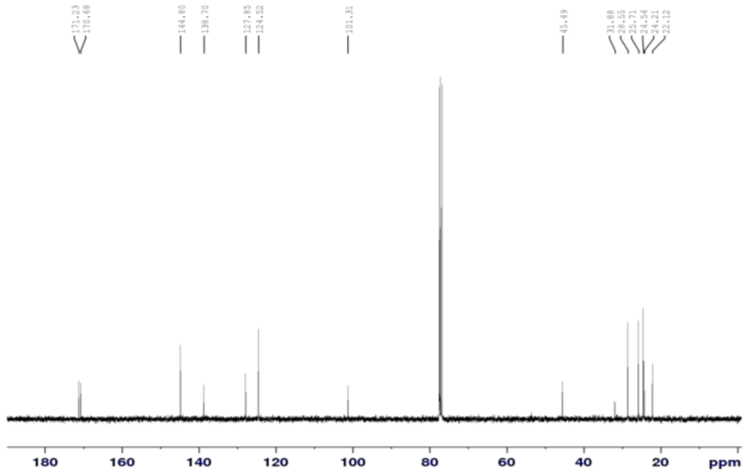


Figure S62: ^{13}C NMR spectrum (101 MHz) of **IVb** in $CDCl_3$.

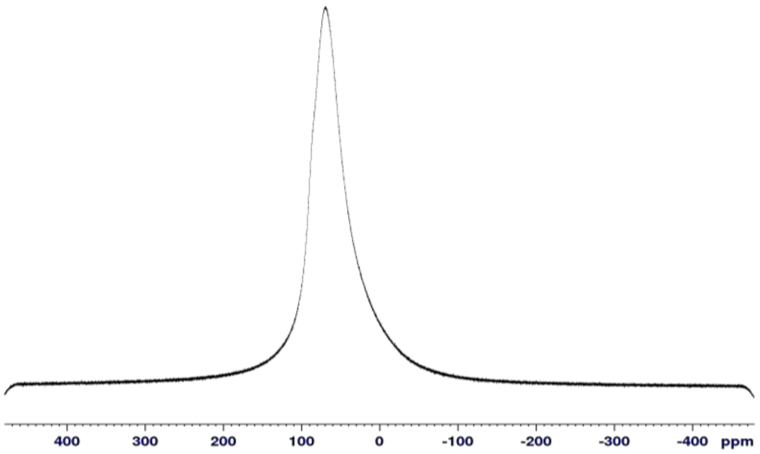


Figure S63: ^{27}Al NMR spectrum (104 MHz) of **IVb** in $CDCl_3$.

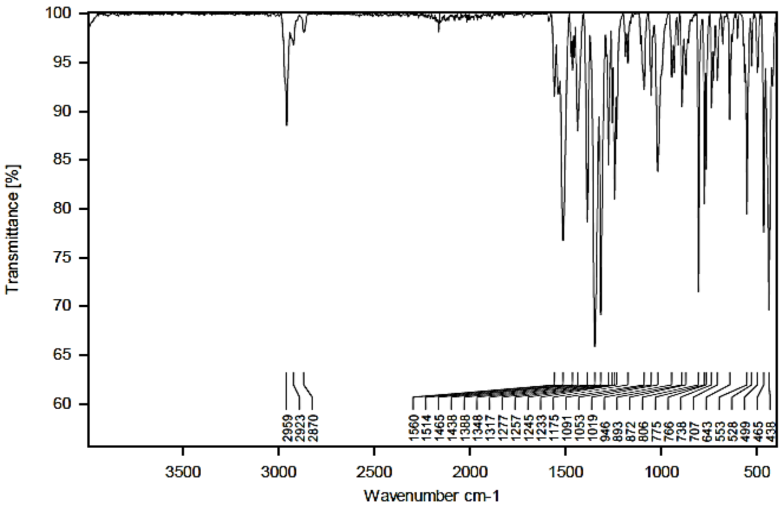


Figure S64: ATR-IR spectrum of **IVb**.

IVc

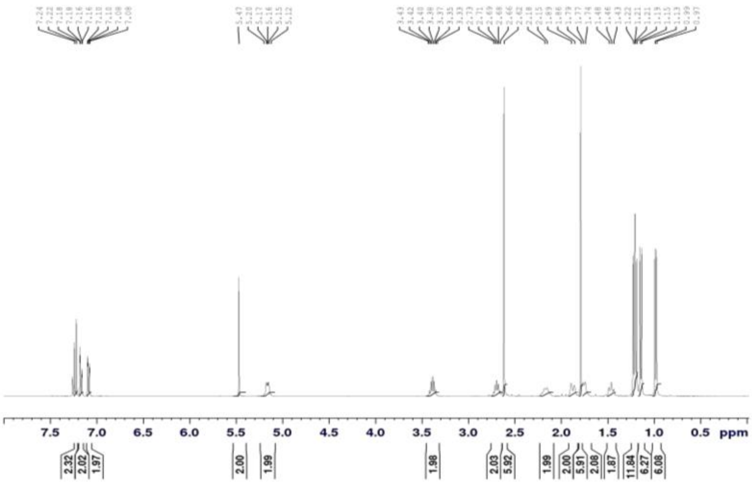


Figure S65: ^{1}H NMR spectrum (400 MHz) of **IVc** in $CDCl_3$.

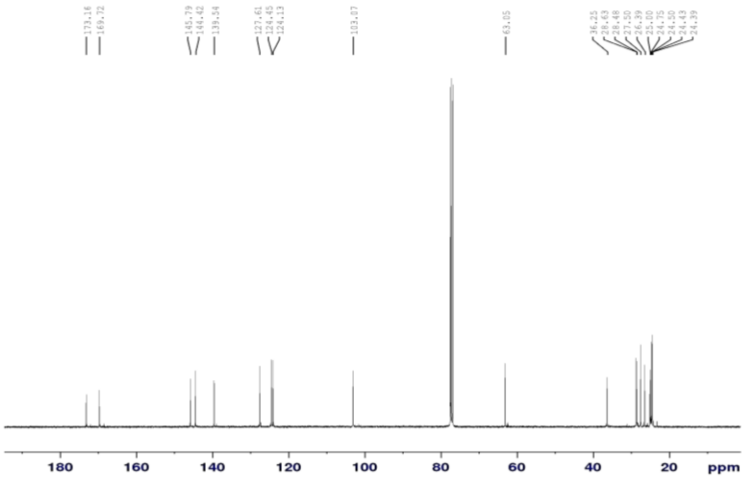


Figure S66: ^{13}C NMR spectrum (101 MHz) of **IVc** in $CDCl_3$.

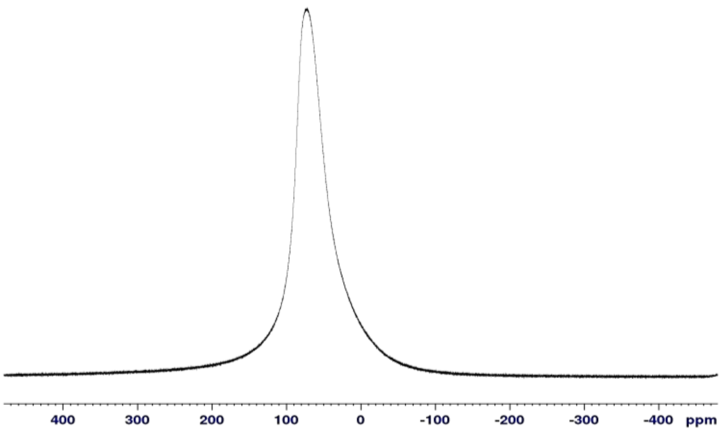


Figure S67: ^{27}Al NMR spectrum (104 MHz) of **IVc** in $CDCl_3$.

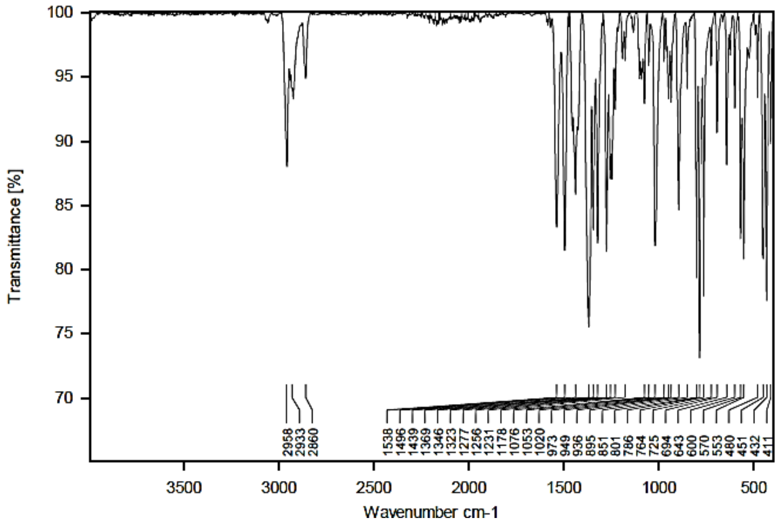


Figure S68: ATR-IR spectrum of **IVc**.

IVd

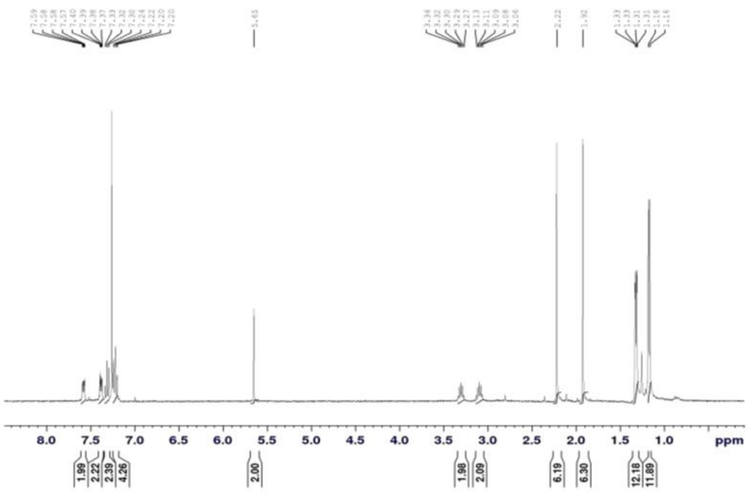


Figure S69: ^{1}H NMR spectrum (400 MHz) of **IVd** in $CDCl_3$.

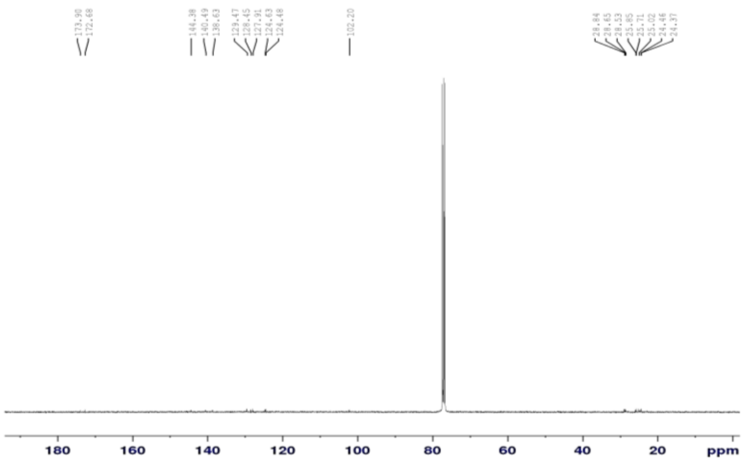


Figure S70: ^{13}C NMR spectrum (101 MHz) of **IVd** in $CDCl_3$.

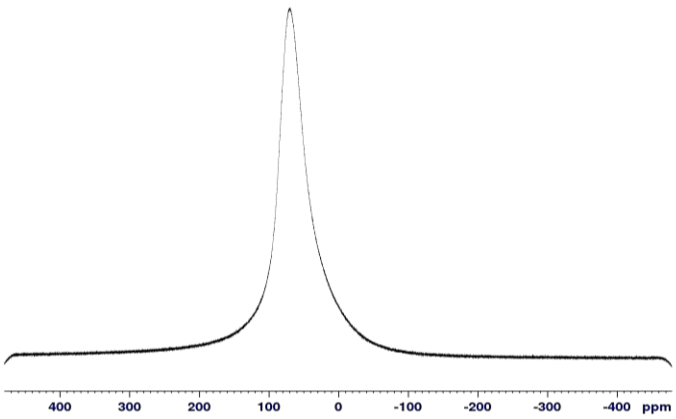


Figure S71: ^{27}Al NMR spectrum (104 MHz) of **IVd** in CDCl$_3$.

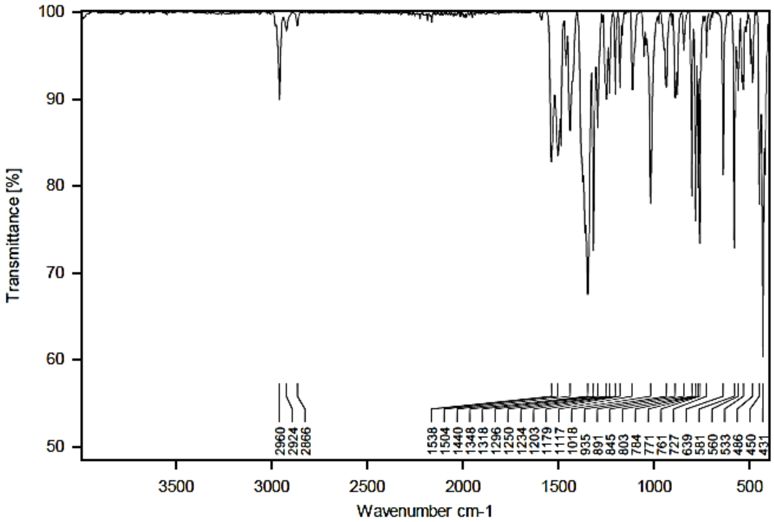


Figure S72: ATR-IR spectrum of **IVd**.

IVe

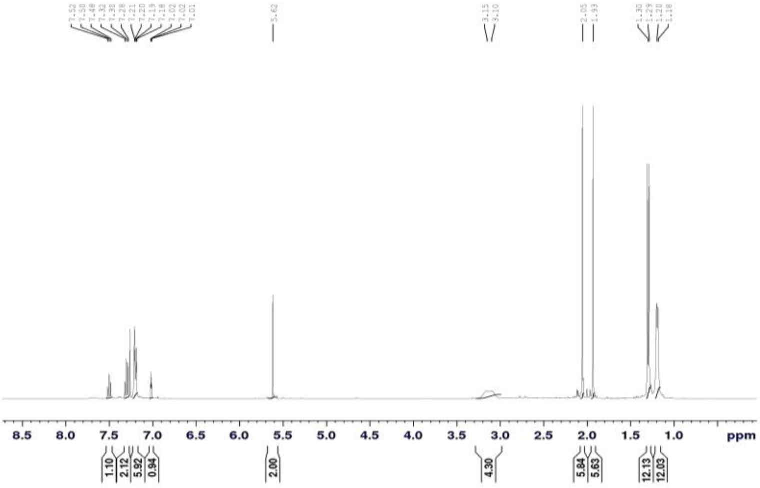


Figure S73: ^{1}H NMR spectrum (400 MHz) of **IVe** in CDCl$_3$.

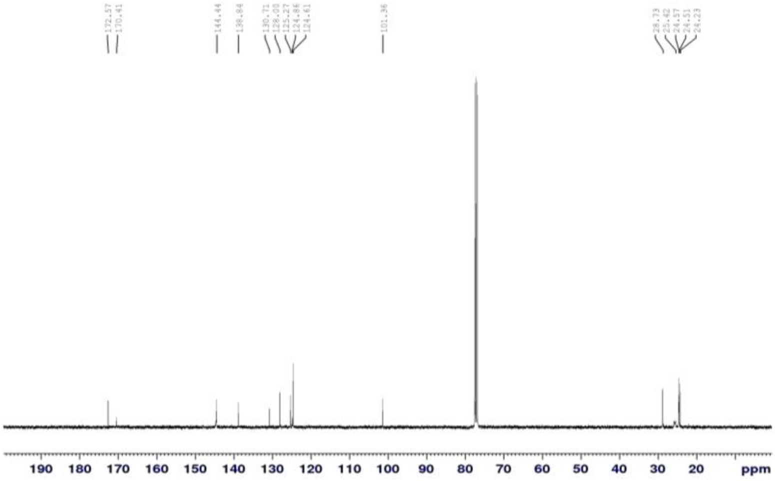


Figure S74: ^{13}C NMR spectrum (101 MHz) of **IVe** in $CDCl_3$.

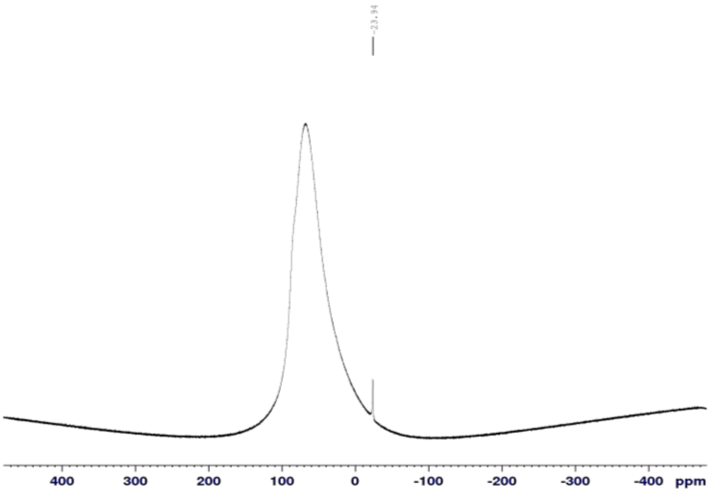


Figure S75: ^{27}Al NMR spectrum (104 MHz) of **IVe** in $CDCl_3$.

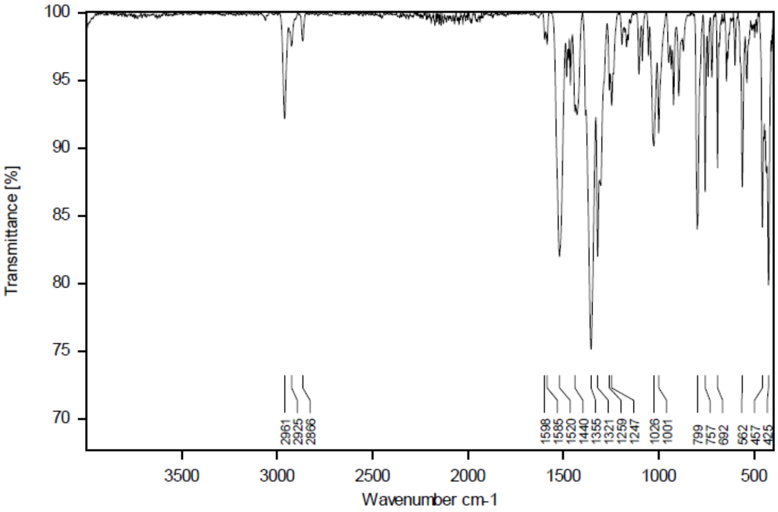


Figure S76: ATR-IR spectrum of **IVe**.

IVg

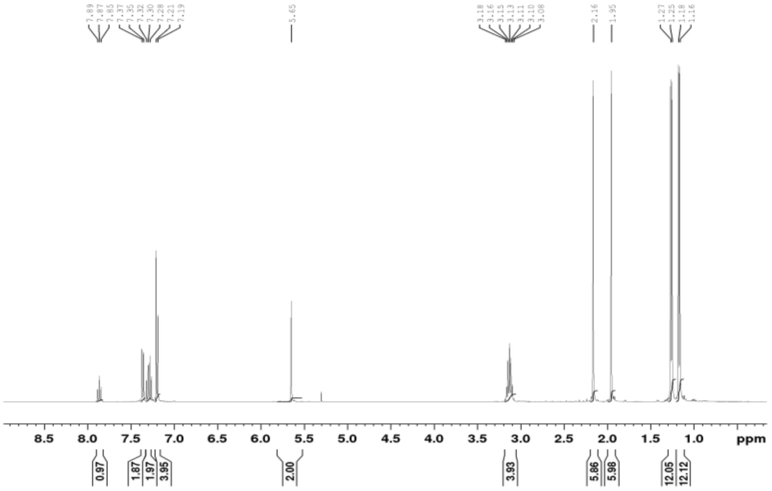


Figure S77: ^{1}H NMR spectrum (400 MHz) of **IVg** in $CDCl_3$.

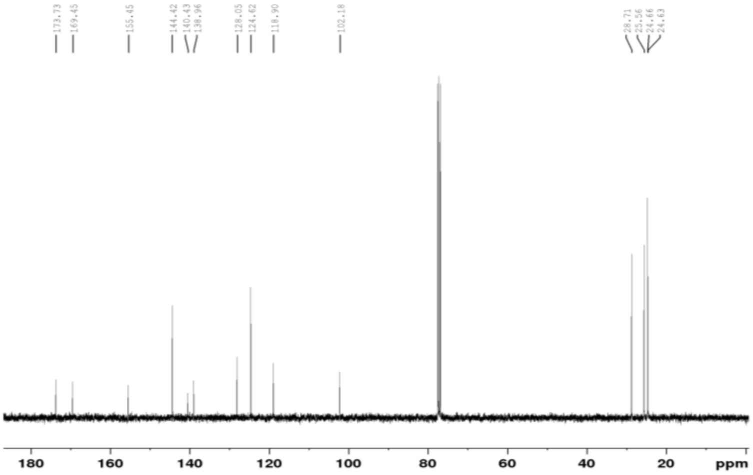


Figure S78: ^{13}C NMR spectrum (101 MHz) of **IVg** in $CDCl_3$.

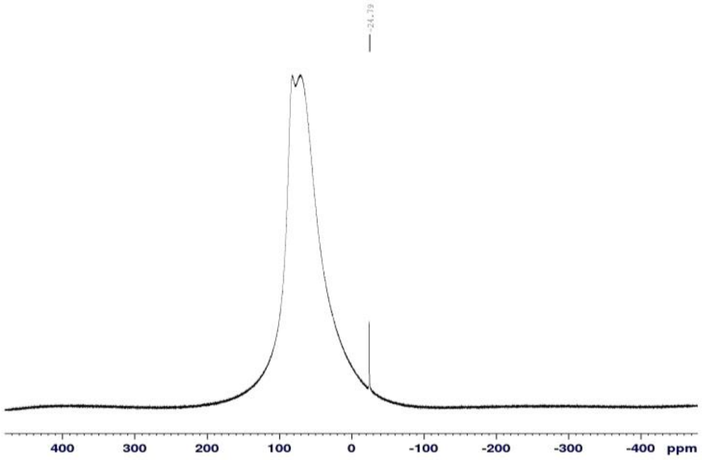


Figure S79: ^{27}Al NMR spectrum (104 MHz) of **IVg** in $CDCl_3$.

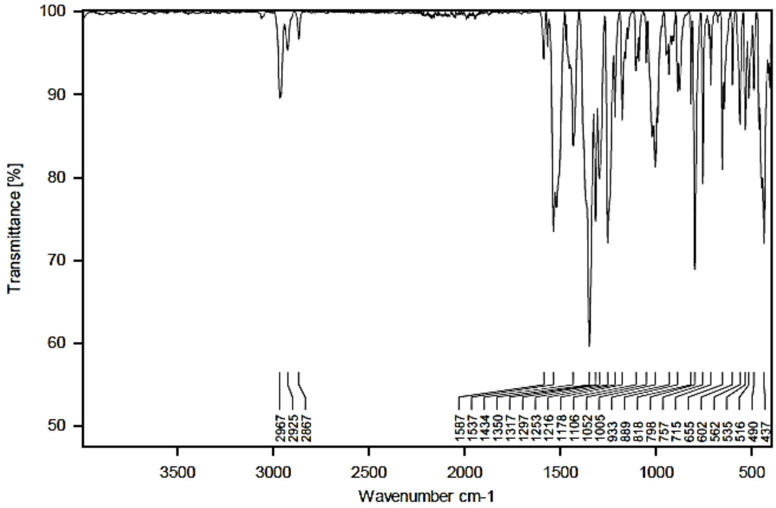


Figure S80: ATR-IR spectrum of **IVg**.

IVh

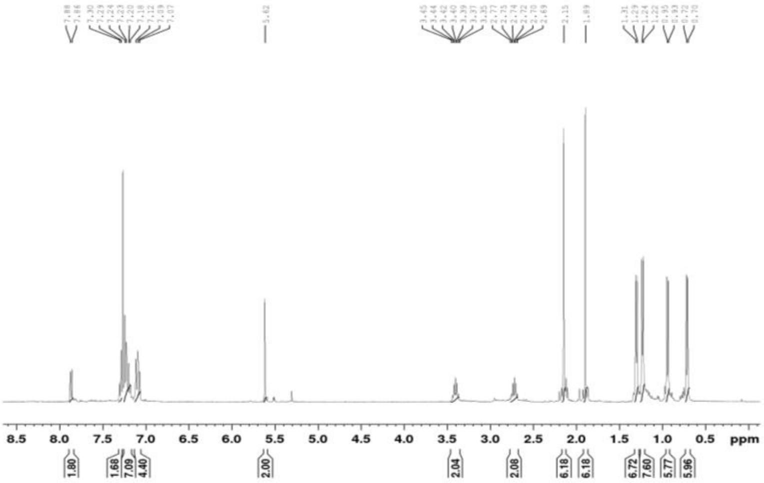


Figure S81: ^{1}H NMR spectrum (400 MHz) of **IVh** in CDCl$_3$.

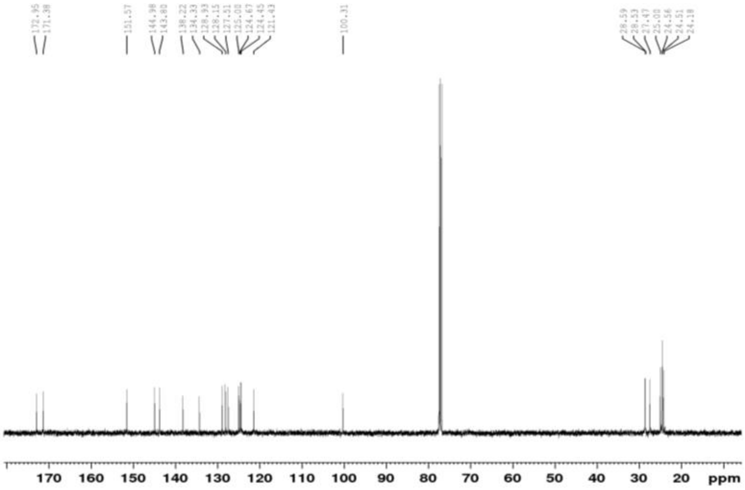


Figure S82: ^{13}C NMR spectrum (101 MHz) of **IVh** in CDCl$_3$.

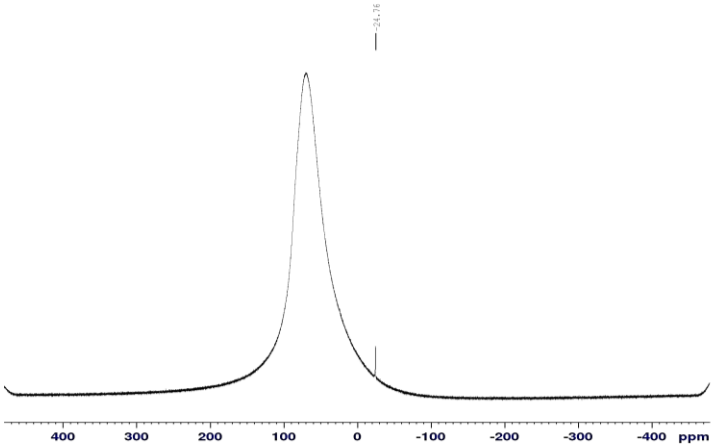


Figure S83: ^{27}Al NMR spectrum (104 MHz) of **IVh** in $CDCl_3$.

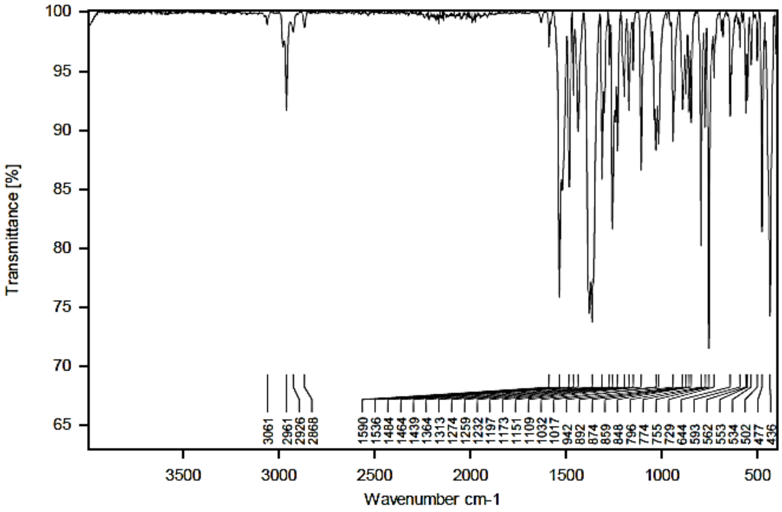


Figure S84: ATR-IR spectrum of **IVh**.

IVi

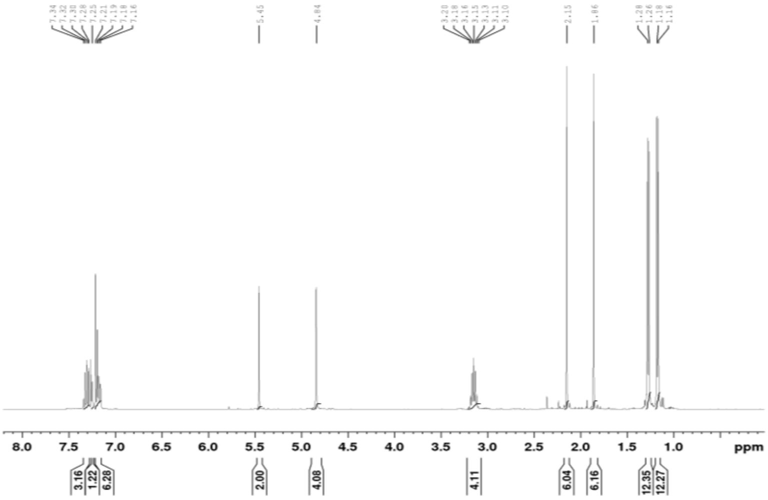


Figure S85: ^{1}H NMR spectrum (400 MHz) of **IVi** in $CDCl_3$.

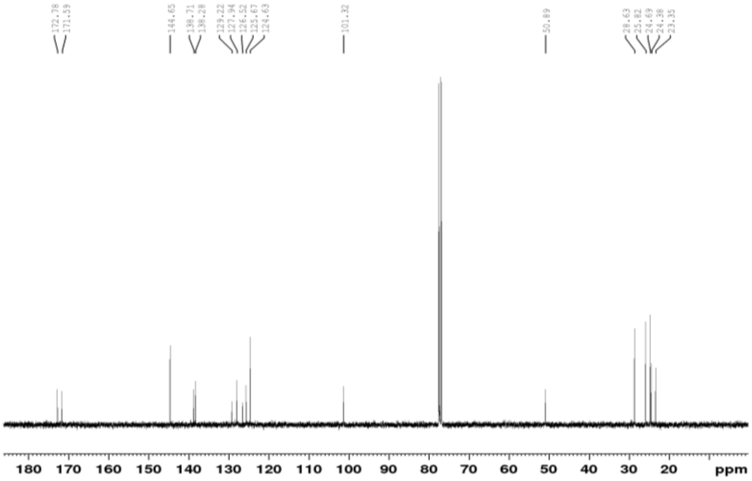


Figure S86: ^{13}C NMR spectrum (101 MHz) of **IVi** in CDCl$_3$.

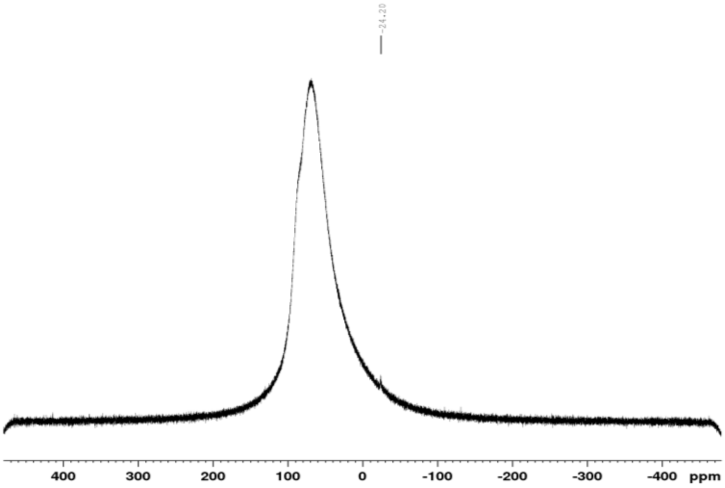


Figure S87: ^{27}Al NMR spectrum (104 MHz) of **IVi** in CDCl$_3$.

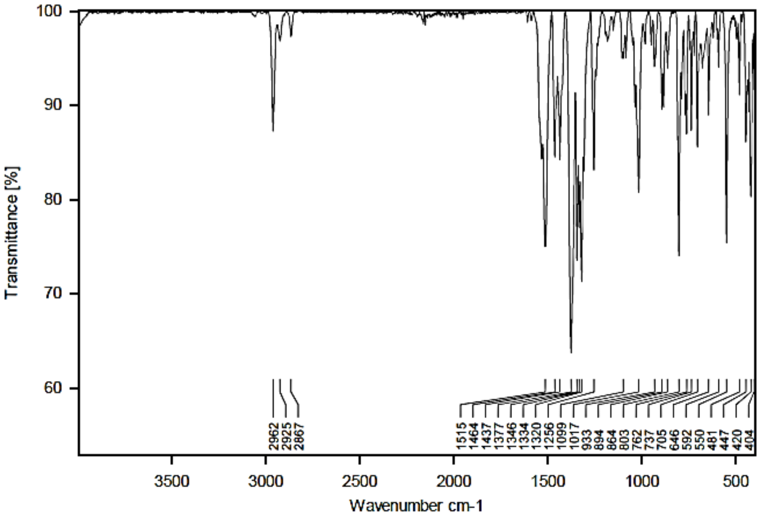


Figure S88: ATR-IR spectrum of **IVi**.

V

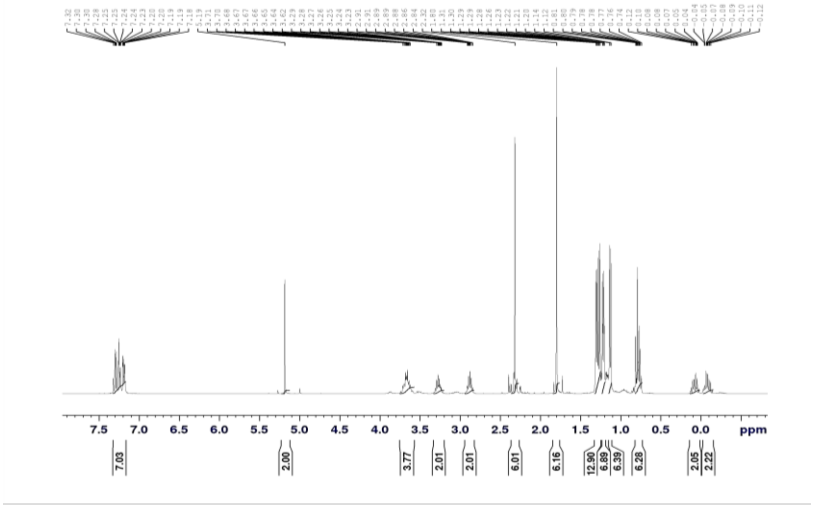


Figure S89: ^{1}H NMR spectrum (400 MHz) of **V** in $CDCl_3$.

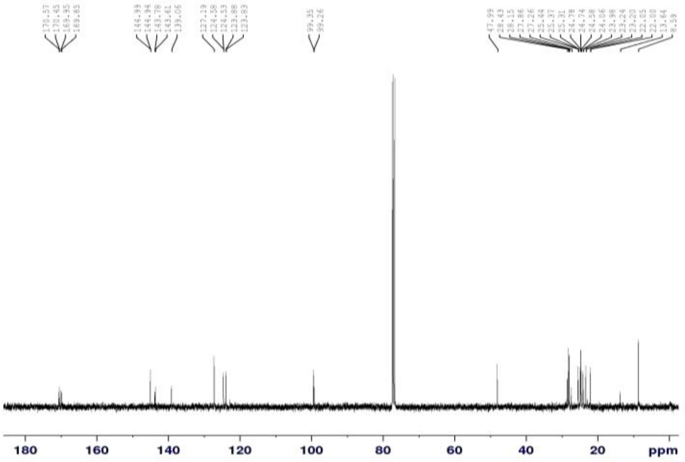


Figure S90: ^{13}C NMR spectrum (101 MHz) of **V** in $CDCl_3$.

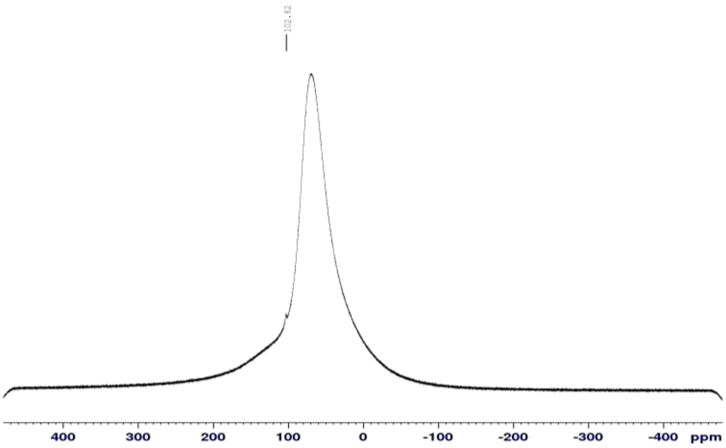


Figure S91: ^{27}Al NMR spectrum (104 MHz) of **V** in $CDCl_3$.

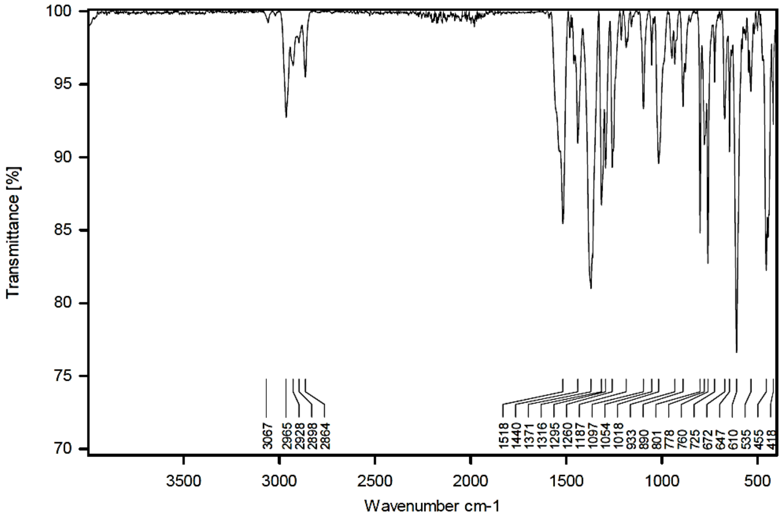


Figure S92: ATR-IR spectrum of **V**.

NMR reduction experiments

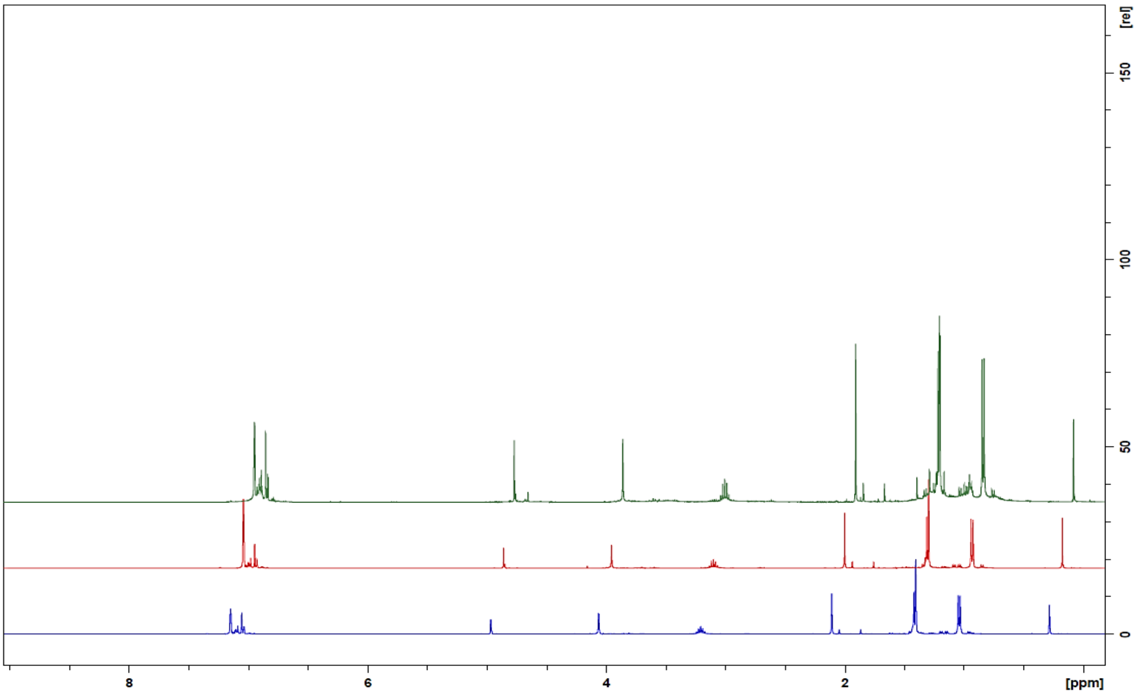


Figure S93: ^{1}H NMR spectrum (400MHz) of **IVa** (blue), **IVa**+KC_8 (red) and **IVa**+KC_8 after 1d at 65°C (green) in C_6D_6.

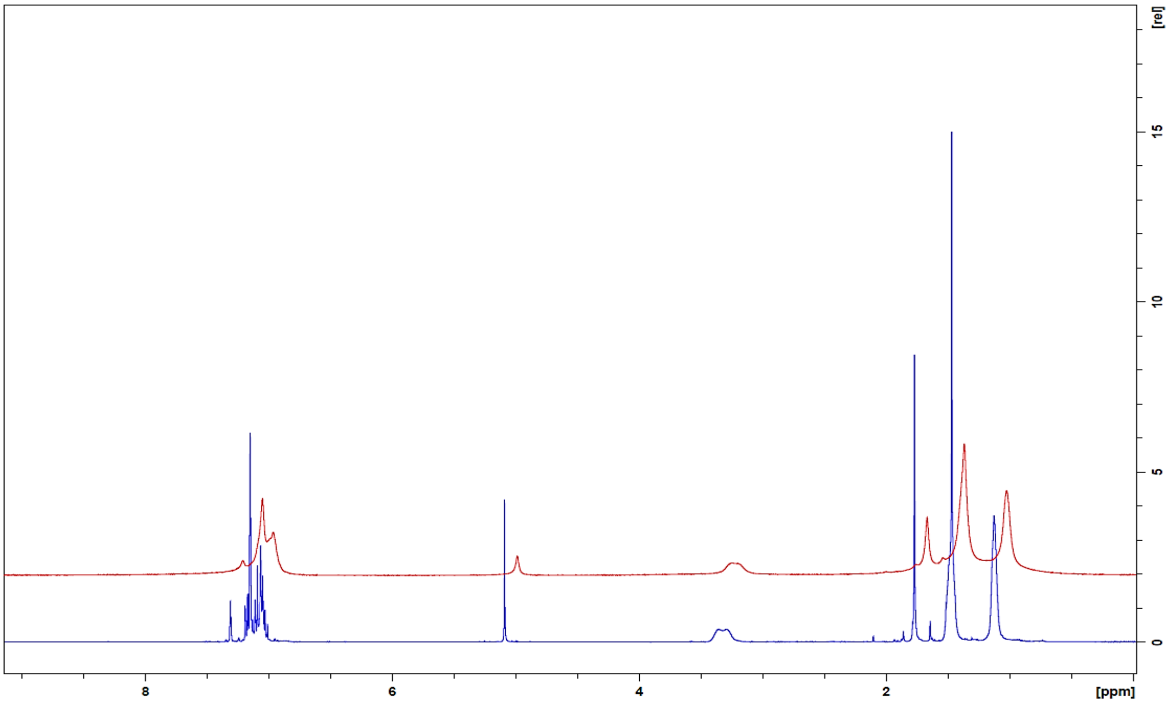


Figure S94: ^{1}H NMR spectrum (400MHz) of **IVe** (blue) and **IVe**+KC_8 (red) in C_6D_6.

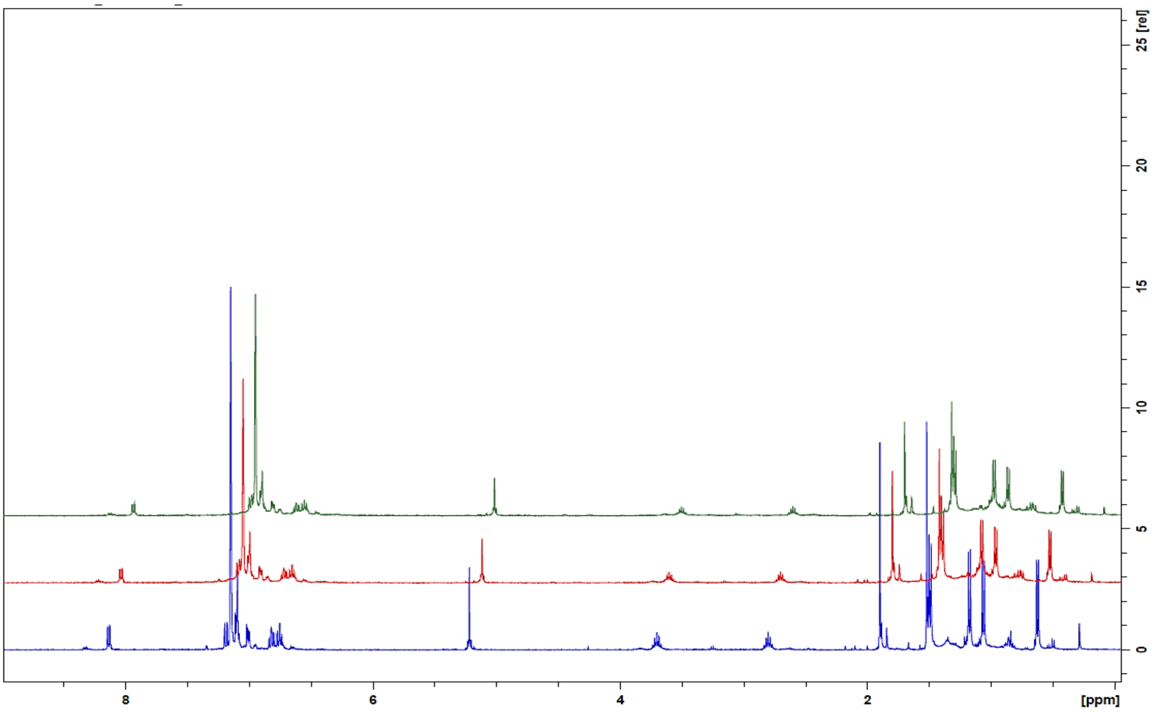


Figure S95: ^{1}H NMR spectrum (400MHz) of **IVh** (blue) **IVh**+KC_8 (red) and **IVh** after 1d (green) in C_6D_6.

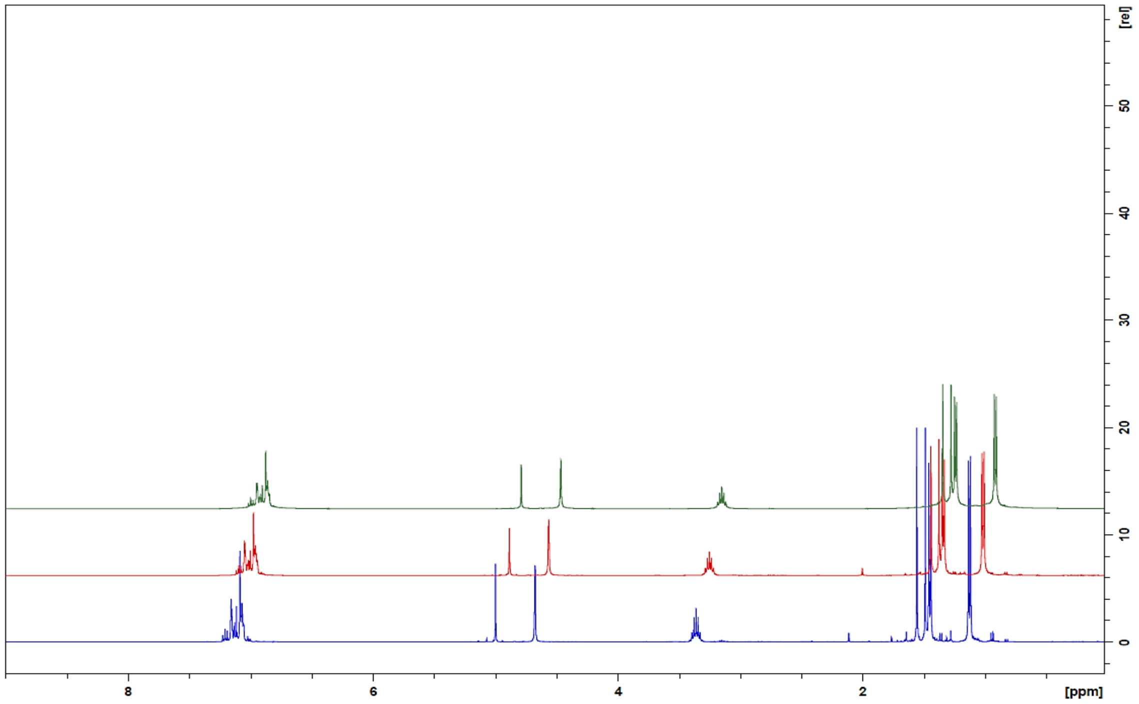


Figure S96: ^{1}H NMR spectrum (400MHz) of **IVi** (blue), **IVi**+KC_8 (red) and **IVi**+KC_8 after 1d at 65°C (green) in C_6D_6.

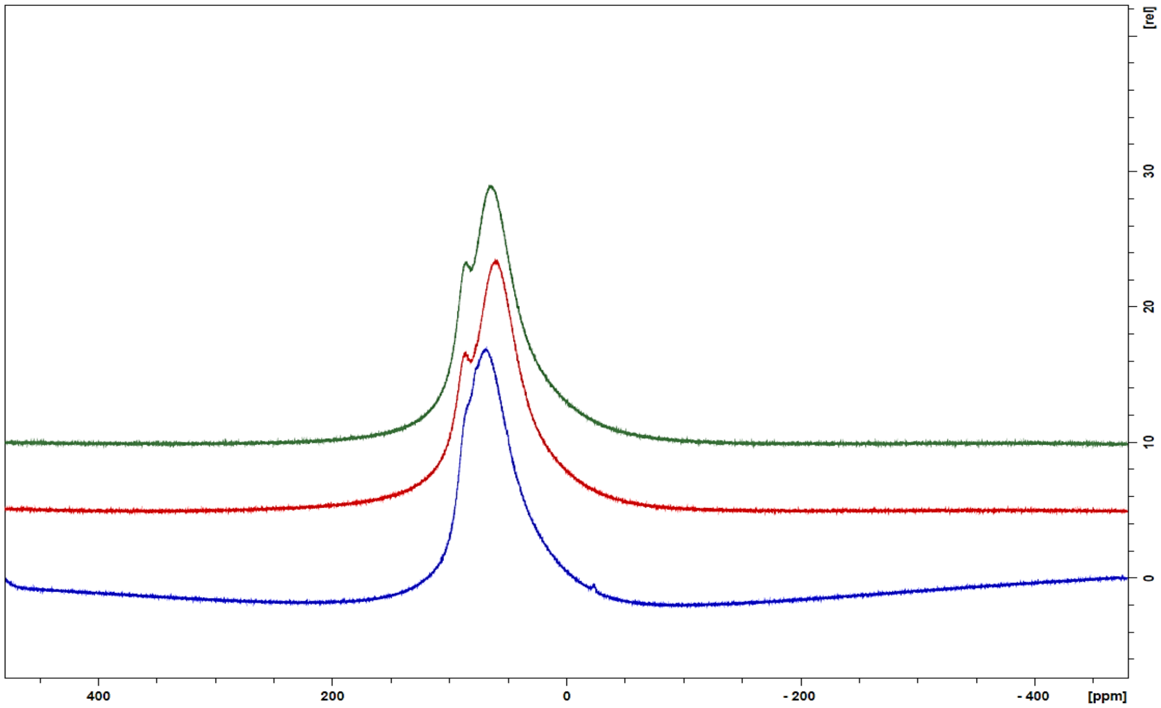


Figure S97: ^{27}Al NMR spectrum (104MHz) of **IVi** (blue), **IVi**+KC_8 (red) and **IVi**+KC_8 after 1d at 65°C (green) in C_6D_6.

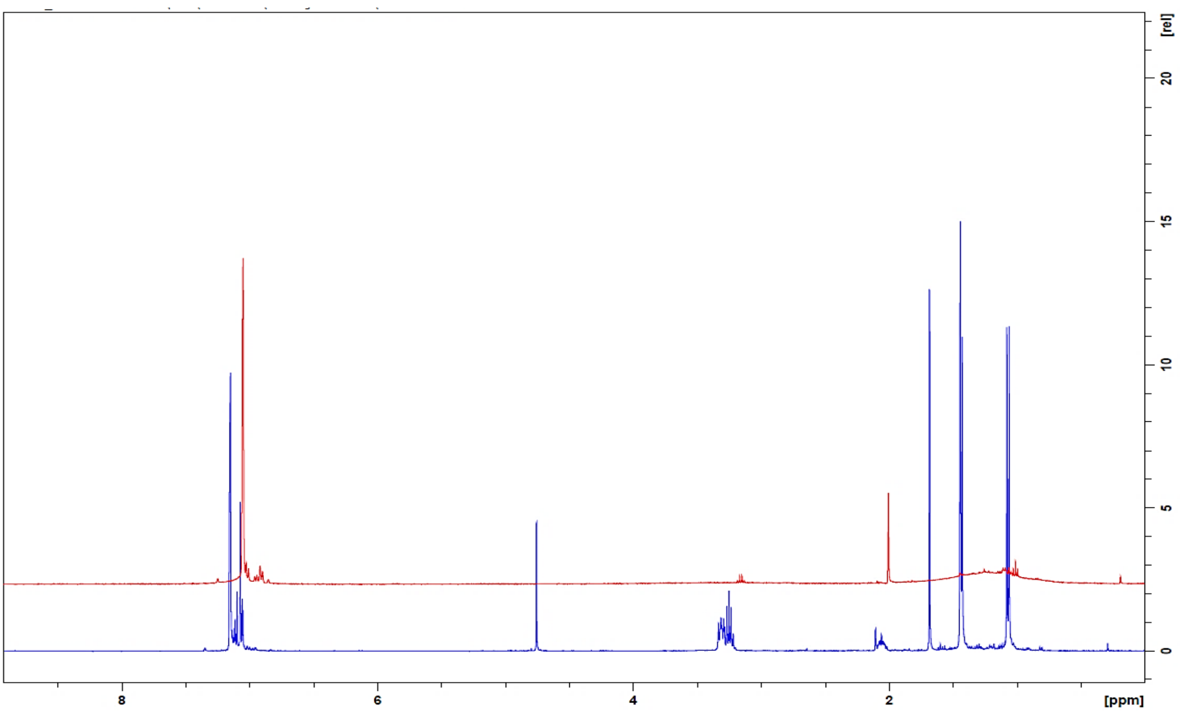


Figure S98: ^{1}H NMR spectrum (400MHz) of **IIb** (blue) and **IIb**+KC_8 (red) in C_6D_6.

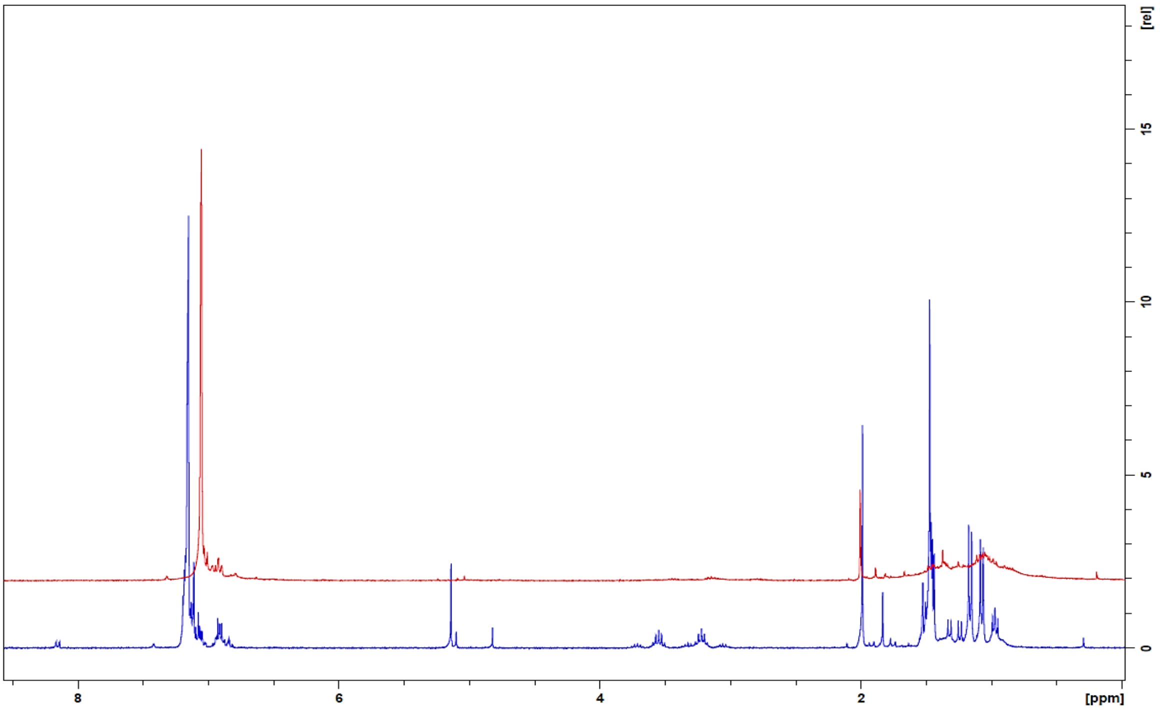


Figure S99: ^{1}H NMR spectrum (300MHz) of **IId** (blue) and **IId**+KC_8 (red) in C_6D_6.

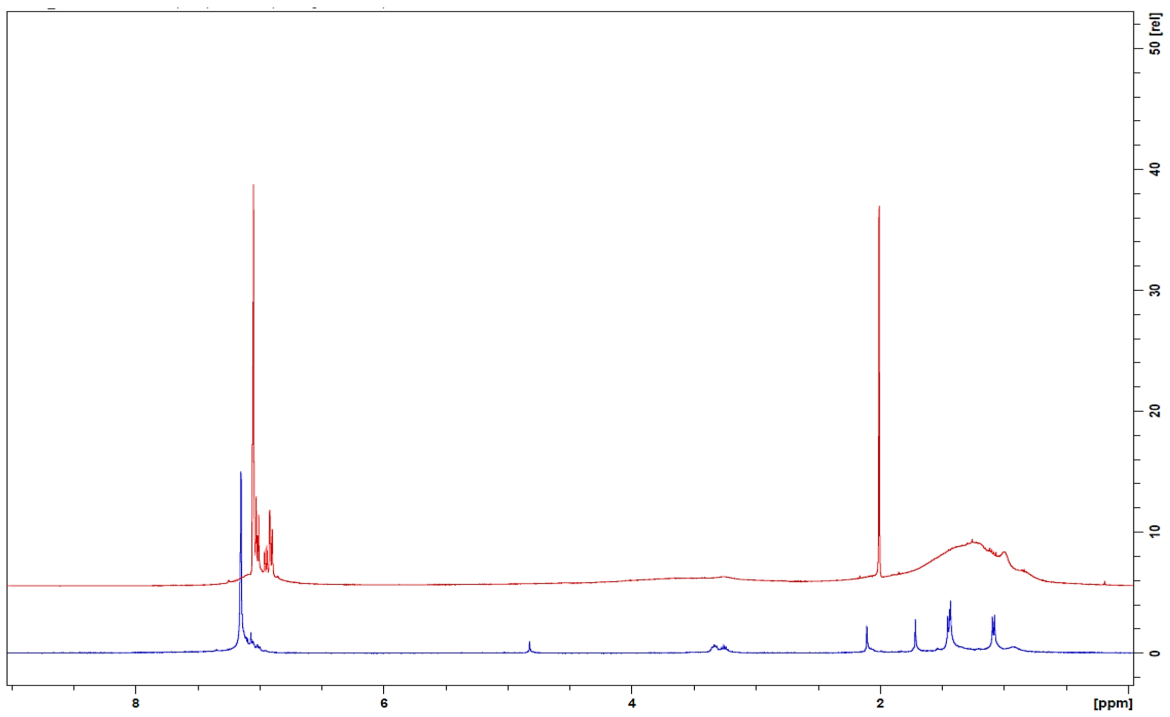


Figure S100: ^{1}H NMR spectrum (400MHz) of **IIIb** (blue) and **IIIb**+KC_8 (red) in C_6D_6.

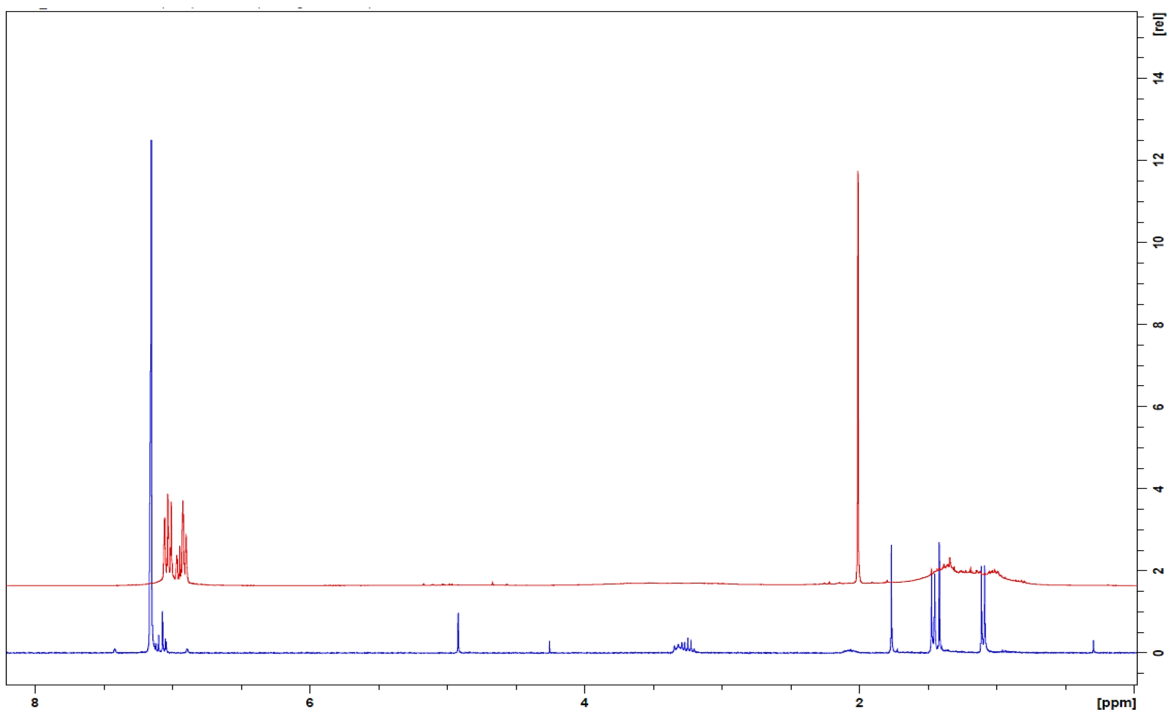


Figure S101: ^{1}H NMR spectrum (300MHz) of **IVb** (blue) and **IVb**+KC_8 (red) in C_6D_6.

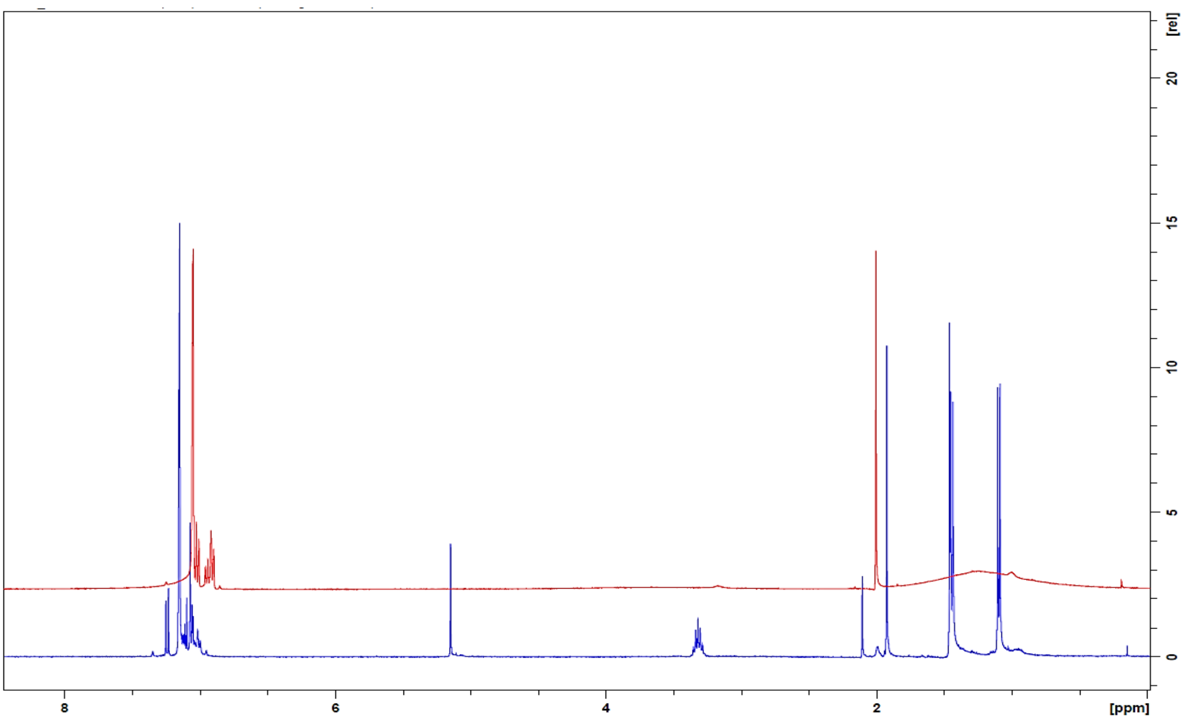


Figure S102: ^{1}H NMR spectrum (400MHz) of **IVg** (blue) and **IVg**+KC$_8$ (red) in C$_6$D$_6$.

Crystallographic Details

The single crystal X-ray diffraction data were recorded on either an Agilent Gemini R Ultra diffractometer with Cu K*α* radiation ($\lambda = 1.54184$ Å) **IIa**, a SuperNova diffractometer with microfocus Cu K*α* radiation ($\lambda = 1.54184$ Å) **IId, IIId** or a GV-50 diffractometer with Titan^{S2} detector from Rigaku Oxford Diffraction (formerly Agilent Technologies) applying Cu K*α* radiation ($\lambda = 1.54184$ Å) **IIIa**, **IIIi**, **IVa**, **IVe**, **IVi**, **Va**. Empirical multi-scan[S2] and analytical absorption corrections[S3] were applied to the data. Using Olex2,[S4] the structures were solved with SHELXT[S5] structure solution program using Intrinsic Phasing and least-square refinements on F^2 were carried out with SHELXL.[S6] For all single-crystals X-Ray structure determinations, the non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were located in idealized calculated positions and were refined isotropically according to the riding model.

IIa: The carbon and nitrogen atoms of the ethylene bridge unit are disordered over two positions and could be refined by using the disorder model.

IId: The aluminium and chloride atoms are disordered over two positions and could be refined by using the disorder model.

IIIa: In this compound, unresolved residual electron density around a center of inversion was present, which could be assigned one disordered solvent molecule of dichloromethane. The disorder could not be resolved completely, therefore the solvent mask of Olex2[S3] was applied and the presence of a solvent accessible void including 40 electrons was confirmed, which we assign one occupied dichloromethane molecules. In the subsequent refinement a modified reflection file without the contribution of the solvent was used.

IIIi: The data reduction was calculated as a twin structure with a BASF [0.5541(8)]. Additionally, the structure contains a toluene molecule around a center of inversion.

IVa: The iodide atoms are disordered over two positions and could be refined by using the disorder model.

IVe: In this compound, high residual electron density around the iodide atoms, which can't solve by using the disorder model. The high residual electron density is most likely due to the absorption effect of the crystal shape. Additionally, unresolved residual electron density around a center of inversion was present, which could be assigned two disordered solvent molecules of dichloromethane. The disorder could not be resolved completely, therefore the solvent mask of Olex2[S3] was applied and the presence of a solvent accessible void including 87 electrons was confirmed, which we assign two occupied dichloromethane molecules. In the subsequent refinement a modified reflection file without the contribution of the solvent was used.

IVi: The iodide atoms are disordered over two positions and could be refined by using the disorder model.

Va: Maxima in the Fourier difference maps of **Va** indicated the presence of a second species, which allowed for the refinement of a butylene group on the aluminum atoms. Additionally, the half of the nacnac backbone and the carbon atoms of the ethylene bridge unit are disordered over two positions and could be refined by using the disorder model.

CCDC 1942528-1942536 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data for $C_{36}H_{52}Al_2Cl_4N_4$ (**IIa**), $C_{40}H_{52}Al_2Cl_4N_4$ (**IId**), $C_{36}H_{52}Al_2Br_4N_4$ (**IIIa**).

	IIa	**IId**	**IIIa**
Empirical formula	$C_{36}H_{52}Al_2Cl_4N_4$	$C_{40}H_{52}Al_2Cl_4N_4$	$C_{36}H_{52}Al_2Br_4N_4$
CCDC No.	1942528	1942533	1942529
Formula weight	736.57	778.68	914.41
Temperature/K	123.1(4)	123.0(1)	123.0(1)
Crystal system	tetragonal	monoclinic	triclinic

Space group	$P\text{-}42_1m$	C2/c	P-1
a/Å	15.1997(2)	14.8213(3)	9.8779(6)
b/Å	15.1997(2)	17.1924(3)	10.4613(6)
c/Å	8.4998(2)	17.7670(4)	11.6094(7)
α/°	90	90	83.256(5)
β/°	90	114.032(3)	65.627(6)
γ/°	90	90	83.978(5)
Volume /Å^3	1963.72(7)	4134.8(2)	1083.1(1)
Z	2	4	1
ρ_{calc}g/cm^3	1.246	1.251	1.402
μ/mm^{-1}	3.398	3.161	5.134
F(000)	780.0	1645.0	462.0
Crystal size/mm^3	0.33 x 0.215 x 0.1	0.23 x 0.2 x 0.181	0.144 x 0.098 x 0.045
Radiation	Cu K**α** (λ = 1.54184)	Cu K**α** (λ = 1.54184)	Cu K**α** (λ = 1.54184)
2Θ range for data collection/°	8.226 to 133.346	8.314 to 147.16	8.39 to 147.128
Index ranges	-16≤h≤17, -18≤k≤18, -9≤l≤10	-18≤h≤12, -20≤k≤20, -20≤l≤21	-12≤h≤12, -12≤k≤13, -13≤l≤13
Reflections collected	11065	11295	14066
Independent reflections	1833 [R_{int}=0.0566, R_{sigma}=0.0316]	3962 [R_{int}=0.0200, R_{sigma}=0.0176]	4185 [R_{int}=0.0323, R_{sigma}=0.0282]
Data/restraints/parameters	1833/0/137	3962/24/269	4185/0/214
Goodness-of-fit on F^2	1.094	1.067	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0366, wR_2 = 0.0902	R_1 = 0.0426, wR_2 = 0.1034	R_1 = 0.0285, wR_2 = 0.0725
Final R indexes [all data]	R_1 = 0.0385, wR_2 = 0.0916	R_1 = 0.0446, wR_2 = 0.1047	R_1 = 0.0324, wR_2 = 0.0747
Largest diff. peak/hole / e Å^3	0.46/-0.26	0.74/-0.52	0.47/-0.61

Table S2. Crystallographic data for $C_{40}H_{52}Al_2Br_4N_4$ (**IIId**), $C_{46}H_{56}Al_2Br_4N_4$ (**IIIi**), $C_{36}H_{52}Al_2I_4N_4$ (**IVa**).

	IIId	**IIIi**	**IVa**
Empirical formula	$C_{40}H_{52}Al_2Br_4N_4$	$C_{46}H_{56}Al_2Br_4N_4$	$C_{36}H_{52}Al_2I_4N_4$
CCDC No.	1942534	1942531	1942530
Formula weight	962.45	1032.54	1102.37
Temperature/K	123.0(1)	123.0(1)	123.0(1)
Crystal system	monoclinic	triclinic	monoclinic
Space group	C2/c	P-1	C2/c
a/Å	14.6294(2)	10.3186(3)	14.3026(3)
b/Å	17.1475(2)	15.3369(3)	16.0773(4)
c/Å	18.3348(3)	16.8110(5)	19.0213(3)
α/°	90	65.970(2)	90
β/°	113.421(2)	80.143(2)	100.940(2)
γ/°	90	78.214(2)	90
Volume /Å^3	4220.5(1)	2367.1(1)	4294.4(2)

Z	4	2	4
ρ_{calc}g/cm^3	1.515	1.449	1.705
μ/mm^{-1}	5.304	4.770	23.398
F(000)	1944.0	1046.0	2136.0
Crystal size/mm^3	0.246 x 0.137 x 0.08	0.144 x 0.092 x 0.072	0.186 x 0.132 x 0.098
Radiation	Cu K**α** (λ = 1.54184)	Cu K**α** (λ = 1.54184)	Cu K**α** (λ = 1.54184)
2Θ range for data collection/°	8.364 to 147.036	6.382 to 147.158	8.36 to 148.976
Index ranges	-18≤h≤16, -20≤k≤20, -22≤l≤22	-12≤h≤12, -19≤k≤19, -19≤l≤20	-17≤h≤17, -13≤k≤19, -23≤l≤23
Reflections collected	14114	11445	11750
Independent reflections	4095 [R_{int}=0.0148, R_{sigma}=0.0119]	11445 [R_{int}=merged, R_{sigma}=0.0158]	4224 [R_{int}=0.0326, R_{sigma}=0.0283]
Data/restraints/parameters	4095/0/232	11445/36/527	4224/12/234
Goodness-of-fit on F^2	1.077	1.024	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0279, wR_2 = 0.0717	R_1 = 0.0327, wR_2 = 0.0920	R_1 = 0.0333, wR_2 = 0.0867
Final R indexes [all data]	R_1 = 0.0285, wR_2 = 0.0720	R_1 = 0.0362, wR_2 = 0.0938	R_1 = 0.0345, wR_2 = 0.0283
Largest diff. peak/hole / e Å^3	0.95/-0.71	0.55/-0.54	0.75/-1.15

Table S3. Crystallographic data for $C_{40}H_{52}Al_2I_4N_4$ (**IVe**), $C_{42}H_{56}Al_2I_4N_4$ (**IVi**), $C_{42}H_{64}Al_2Cl_2N_4$ (**Va**).

	IVe	**IVi**	**Va**
Empirical formula	$C_{40}H_{52}Al_2I_4N_4$	$C_{42}H_{56}Al_2I_4N_4$	$C_{42}H_{64}Al_2Cl_2N_4$
CCDC No.	1942536	1942532	1942535
Formula weight	1150.41	1178.46	738.45
Temperature/K	123.0(1)	123.0(2)	123.0(1)
Crystal system	triclinic	orthorhombic	monoclinic
Space group	P-1	Pbcn	I2/a
a/Å	10.6805(2)	15.1650(4)	14.7354(2)
b/Å	15.0278(4)	20.3470(6)	19.0556(3)
c/Å	16.5014(4)	30.398(1)	15.5377(2)
α/°	102.373(2)	90	90
β/°	101.912(2)	90	99.935(1)
γ/°	99.868(2)	90	90
Volume /Å^3	2466.1(1)	9379.7(5)	4297.4(1)
Z	2	8	4
ρ_{calc}g/cm^3	1.549	1.669	1.141
μ/mm^{-1}	20.402	21.471	1.987
F(000)	1116.0	4592.0	1593.0
Crystal size/mm^3	0.264 x 0.183 x 0.126	0.157 x 0.048 x 0.033	0.201 x 0.087 x 0.084
Radiation	Cu K**α** (λ = 1.54184)	Cu K**α** (λ = 1.54184)	Cu K**α** (λ = 1.54184)
2Θ range for data collection/°	7.224 to 148.51	5.814 to 148.88	7.408 to 147.672
Index ranges	-13≤h≤13, -18≤k≤18,	-16≤h≤18, -24≤k≤24,	-17≤h≤18, -19≤k≤23,

	-20≤l≤20	-37≤l≤37	-18≤l≤19
Reflections collected	52599	29805	14372
Independent reflections	9919 [R_{int}=0.0896, R_{sigma}=0.0451]	9215 [R_{int}=0.0802, R_{sigma}=0.0727]	4209 [R_{int}=0.0268, R_{sigma}=0.0182]
Data/restraints/parameters	9919/6/473	9215/12/500	4209/78/337
Goodness-of-fit on F^2	1.026	1.049	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0567, wR_2 = 0.1570	R_1 = 0.0649, wR_2 = 0.1503	R_1 = 0.0361, wR_2 = 0.1047
Final R indexes [all data]	R_1 = 0.0595, wR_2 = 0.1608	R_1 = 0.1032, wR_2 = 0.1745	R_1 = 0.0391, wR_2 = 0.1073
Largest diff. peak/hole / e Å^3	2.76/-1.63	1.75/-0.88	0.21/-0.21

Cyclic voltammetry

All cyclic voltammetry measurements were performed in THF at 295 K in a three electrode setup, with a platinum disc electrode (working electrode, 3 mm diameter), a non-aqueous Ag/Ag$^+$ electrode (pseudo-reference electrode) and a Pt-wire (auxiliary electrode), in combination with either a Potentiostat EmStat3+ by the company PalmSens, Compact Electrochemical Interfaces (**IIa**-**e**, **g**-**i**, **IIIa**-**e**, **g**-**i**, **IVa**-**c**, **e**-**g**, **i**, **Va**) or *CHI 600E* Potentiostat by the company CH Instruments, Inc. (**IIf**, **IIIf**, **IVd**, **IVh**). Bu$_4$NPF$_6$ (0.1 mol/L) was used as supporting electrolyte and all cyclic voltammograms are referenced against the Fc/Fc$^+$ redox couple.

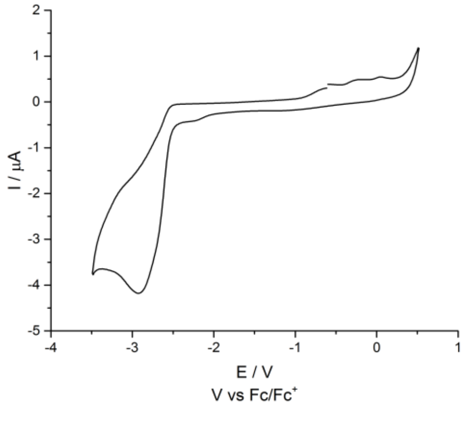


Figure S103. Cyclic voltammogram of **IIa** vs Fc/Fc$^+$.

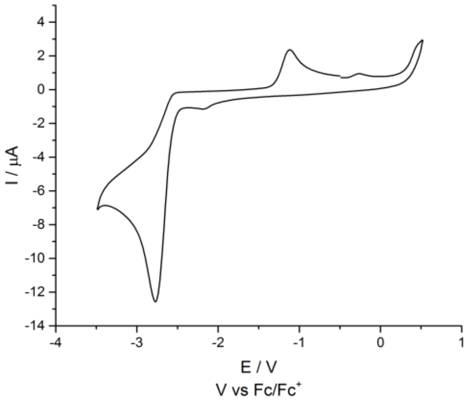


Figure S104. Cyclic voltammogram of **IIb** vs Fc/Fc$^+$.

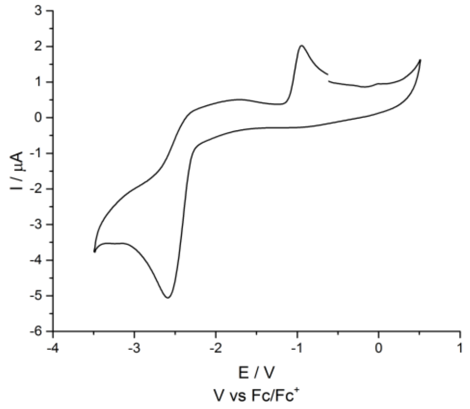


Figure S105: Cyclic voltammogram of **IId** vs Fc/Fc$^+$.

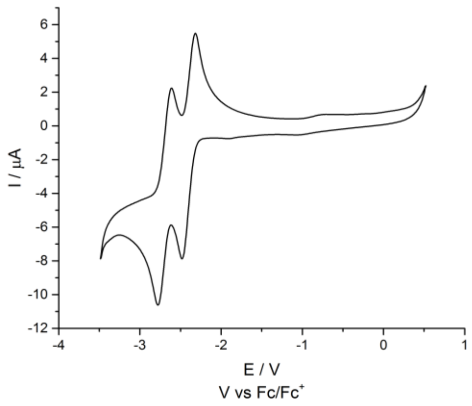


Figure S106: Cyclic voltammogram of **IIe** vs Fc/Fc$^+$.

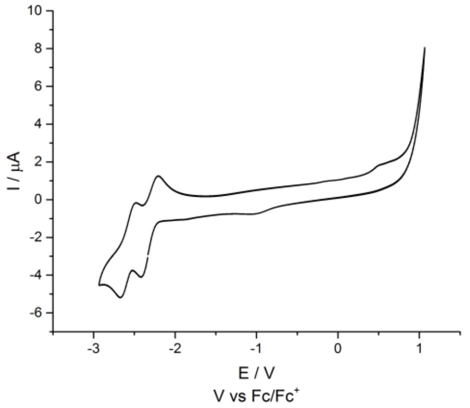


Figure S107: Cyclic voltammogram of **IIf** vs Fc/Fc$^+$.

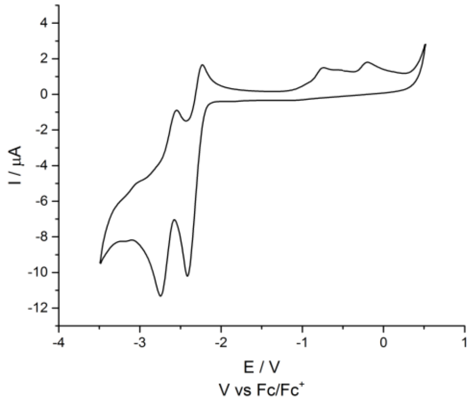


Figure S108: Cyclic voltammogram of **IIg** vs Fc/Fc$^+$.

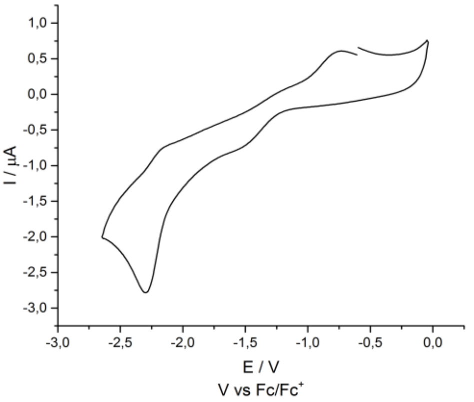


Figure S109: Cyclic voltammogram of **IIi** vs Fc/Fc$^+$.

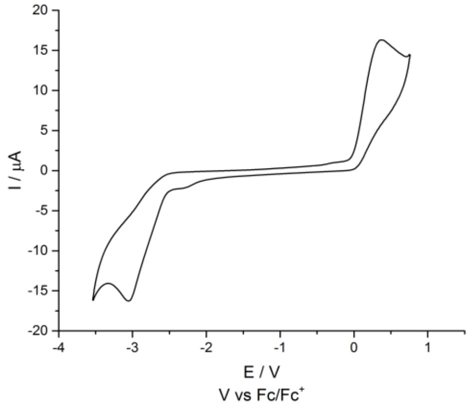


Figure S110: Cyclic voltammogram of **IIIa** vs Fc/Fc$^+$.

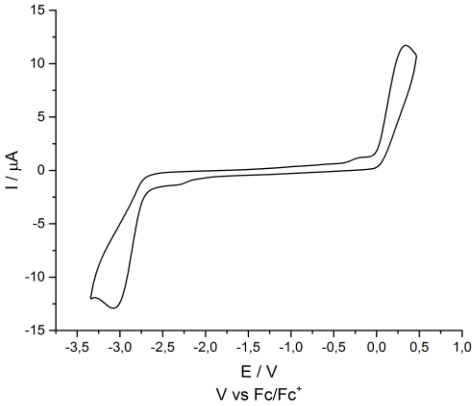
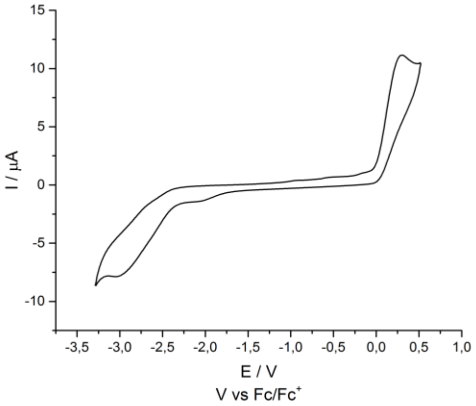


Figure S111: Cyclic voltammogram of **IIIb** vs Fc/Fc$^+$.



FigureS112: Cyclic voltammogram of **IIId** vs Fc/Fc$^+$.

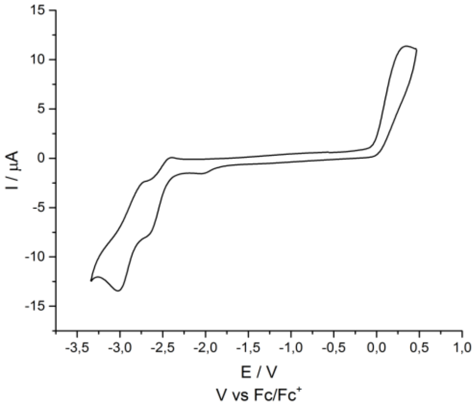


Figure S113: Cyclic voltammogram of **IIIe** vs Fc/Fc$^+$.

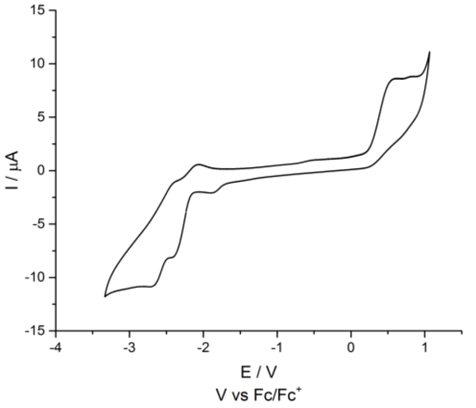


Figure S114: Cyclic voltammogram of **IIIf** vs Fc/Fc$^+$.

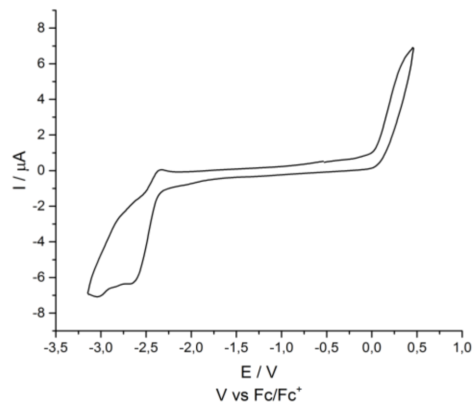


Figure S115: Cyclic voltammogram of **IIIg** vs Fc/Fc$^+$.

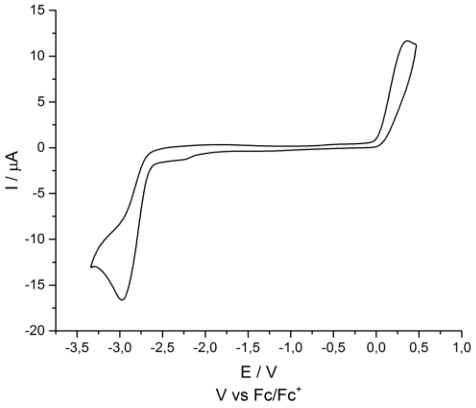


Figure S116: Cyclic voltammogram of **IIIi** vs Fc/Fc$^+$.

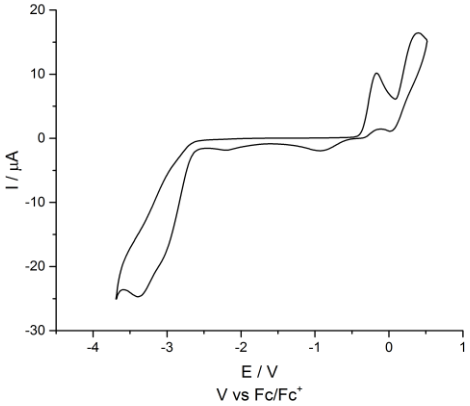


Figure117: Cyclic voltammogram of **IVa** vs Fc/Fc$^+$.

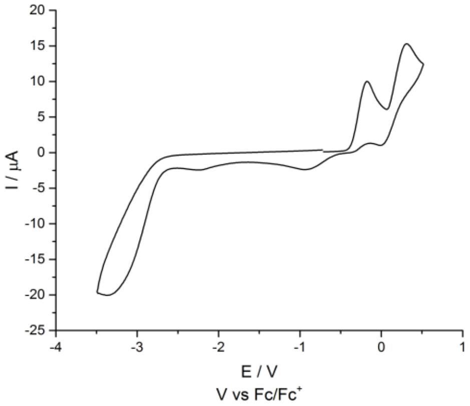


Figure S118: Cyclic voltammogram of **IVb** vs Fc/Fc$^+$.

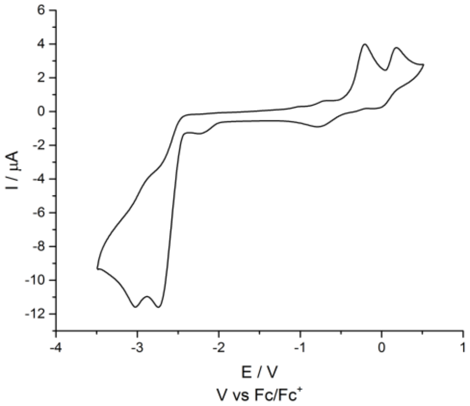


Figure S119: Cyclic voltammogram of **IVc** vs Fc/Fc$^+$.

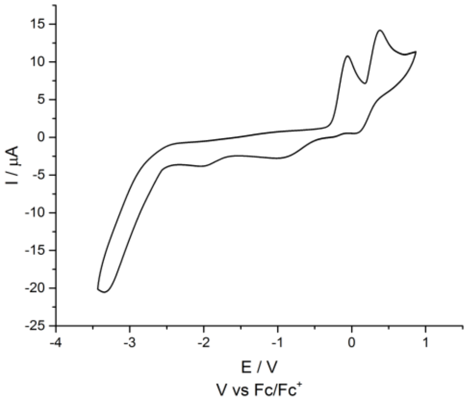


Figure S120: Cyclic voltammogram of **IVd** vs Fc/Fc$^+$.

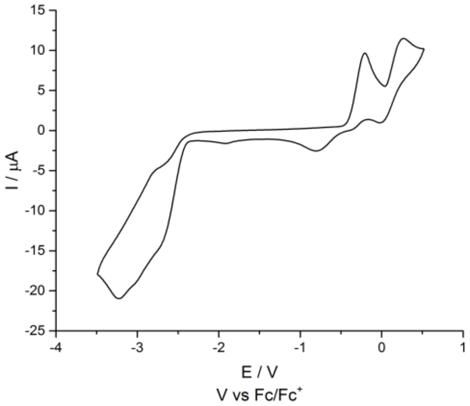


Figure S121: Cyclic voltammogram of **IVe** vs Fc/Fc$^+$

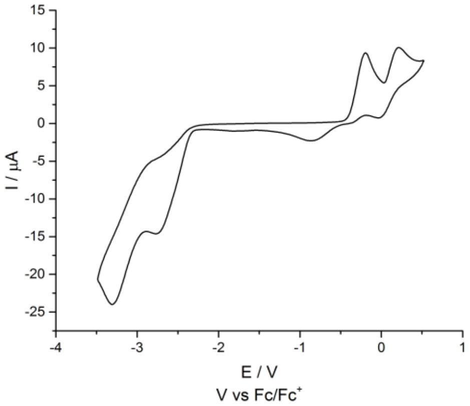


Figure S122: Cyclic voltammogram of **IVg** vs Fc/Fc$^+$.

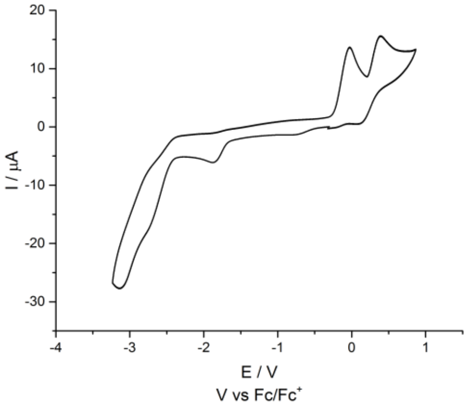


Figure S123: Cyclic voltammogram of **IVh** vs Fc/Fc$^+$.

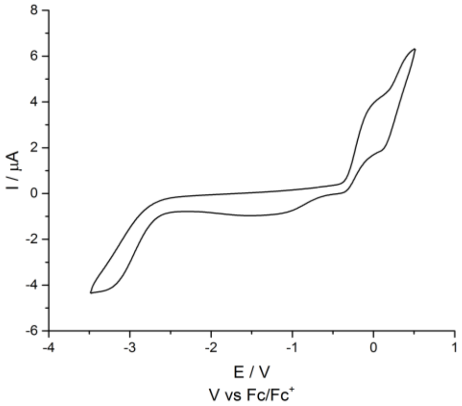


Figure S124: Cyclic voltammogram of **IVi** vs Fc/Fc$^+$.

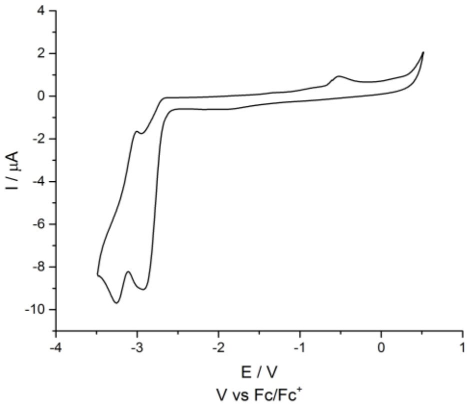


Figure S125: Cyclic voltammogram of **V** vs Fc/Fc$^+$.

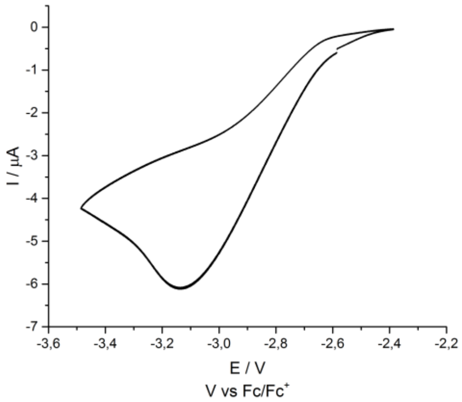


Figure S126: Cyclic voltammogram of **NacNacAl** vs Fc/Fc$^+$.

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8 Conclusion

This work gives a detailed insight into the stabilization of Group 13 element compounds in the oxidation state +1 and +3 based on bis(β-diketiminate) ligands. Of particular interest was the application of different linked bis(β-diketiminate)s and their influence on the molecular arrangement of the resulting metal compounds. The use of rigid, semi-rigid and flexible bridging scaffolds for connecting the NacNac ligands offers a new configuration of metal compounds, which allows or excludes a direct metal-metal interaction. Additionally, polynuclear compounds compared to their mononuclear congeners provide advantages in reactivity and selectivity and finally lead to the opportunities for cooperative and emergent effects.

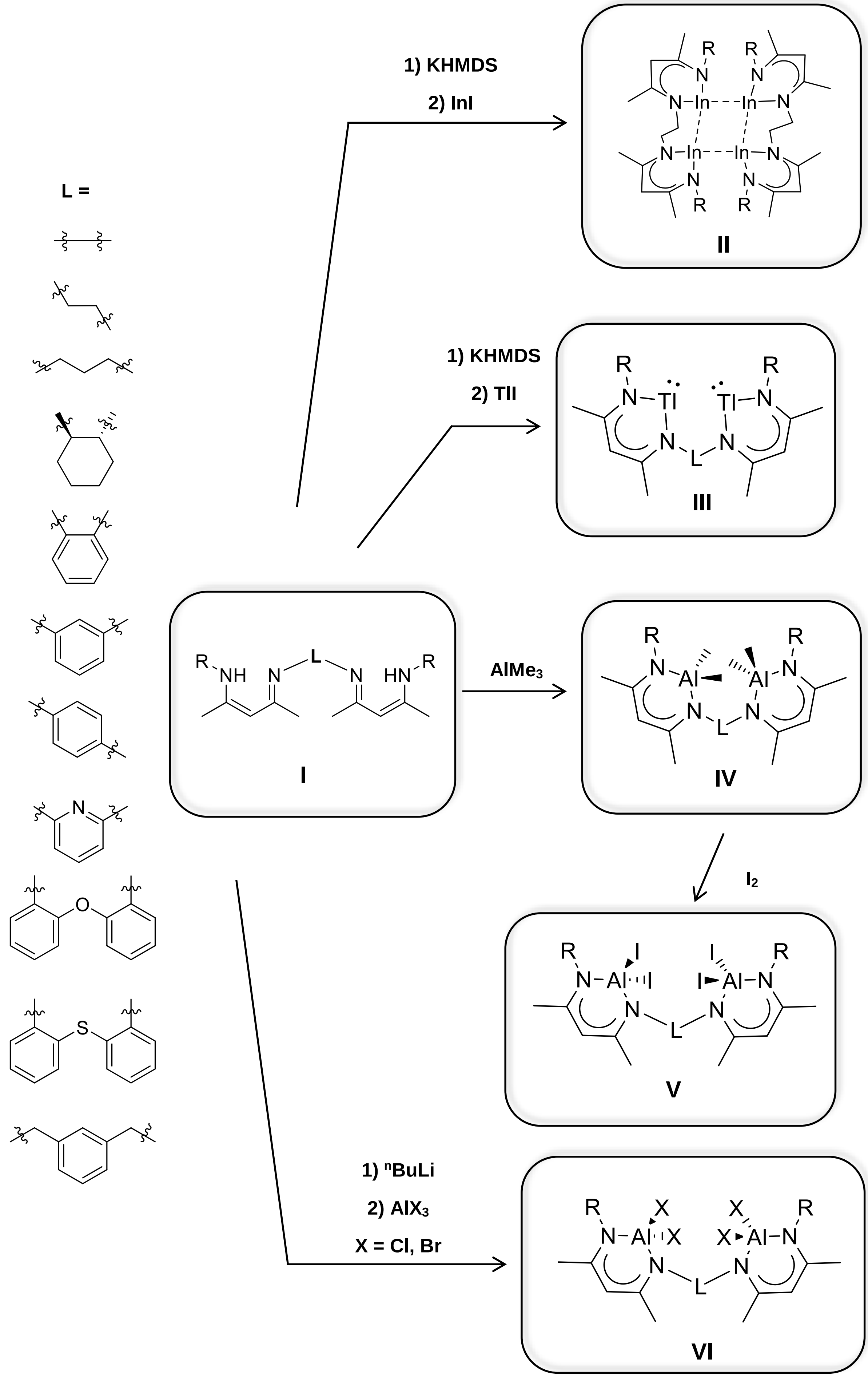
Therefore, a set of new and already known bis(β-diketimine) ligands **I** was introduced herein, exhibiting alkyl-, aryl- and N-N-bridged systems.[C1] The further transformations to polynuclear Group 13 compounds proceeded in different routes and an overview is depicted in Scheme1.

The synthesis of the indium and thallium biscarbenoids was achieved via an ‘one pot’ reaction of the respective ligand, potassium bis(trimethylsilyl) amide (KHMDS) and metal(I) iodide (M = In (**II**), Tl (**III**)) at -78 °C in the absence of light. After work up, yellow crystals could be obtained from a concentrated toluene solution as the products. By variation of the metal(I) precursor, and more specifically the counter ion, the impact on the synthetic access of the bis(carbene) analogues of indium and thallium could be investigated. Indium(I) chloride (InCl), indium(I) bromide (InBr), thallium(I) chloride (TlCl), thallium(I) bromide (TlBr) and thallium(I) tetrafluoroborate ($TlBF_4$) were selected as the metal(I) sources.

While no reaction was observed for InBr, using InCl lead to a mononuclear indium(III) compound bearing two chloride ions, where the indium atom was stabilized by the coordination of three nitrogen atoms of a bis(β-diketiminate) ligand.

The synthesis with TlBr allowed access to the related bis(carbene) analogue, which correspond to the same product as in the TlI reaction, whereas the yield is significantly lower. In contrast, no reaction has been observed with TlCl and $TlBF_4$.

The comparison of the reactions by using different metal(I) precursors obtained reveals that no explicit scheme can be applied. Only the metal(I) iodides and thallium(I) bromide lead to the bis(carbene) analogues of indium and thallium. In contrast, different results can be obtained by using other counter ions, which thus influence the product formation.



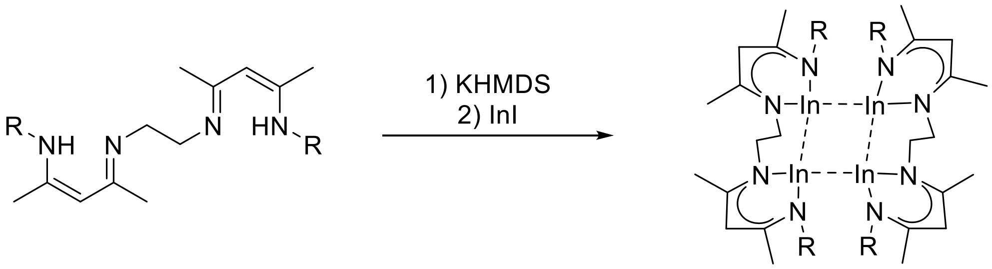
Scheme 1. Synthetic routes to the polynuclear Group 13 compounds originating from bis(β-diketimie)s. R = Dipp = 2,6-diisopropylphenyl.

The aluminium compounds were synthesized by another route. The respective dinuclear dimethyl aluminium complexes **III** were obtained by the reaction of the corresponding bis(β-diketimine) ligands with trimethyl aluminium and were isolated in good to quantitative yields. The further conversion of these compounds with iodide lead to the dinuclear aluminium iodide species **IV**. The derivatives of the dinuclear aluminium chloride and bromide complexes **VI** could be accessed by transmetalation of the corresponding lithium bis(β-diketiminate)s with aluminium(III) chloride ($AlCl_3$) and aluminium(III) bromide ($AlBr_3$), respectively.

Coordination behaviour of the heavier Group 13 bis(carbene) analogues

The interest of the research efforts was how the three-dimensional structure, and more specifically the metal-metal interaction, is affected by the bridging scaffold using bis(β-diketimine) ligands with different linker groups. The utilization of emergent effects by incorporating bis(β-diketimine)s resulted in the formation of new dinuclear Group 13 species, which were not accessible for monocarbenoids, because of the potential dimerization. Therefore, a polynuclear indium and a variety of dinuclear thallium diyls were synthesized, which serve as model compounds to investigate the metal-metal separation in the absence of co-coordinated molecules (additional ligands, solvent molecules).

As shown in Scheme 2, a novel four-membered indium metallacycle is formed by intramolecular and intermolecular In–In interactions in the solid state. The crystallographic study revealed that the In_4-ring is planar, the In–In bonds are coordinative to each other and the arrangement of the ditopic ligands are oppositely with respect to the ring plane. Within the centrosymmetric rhombus the intramolecular In1–In2 distances (3.1095(3) Å) are slightly shorter compared to the intermolecular In1–In2' bond length (3.1342(3) Å). Both distances exceed the value for an In–In single bond according to the covalent radii approach (2.84 Å).[C2] Thus, the In_4 cluster serves as the first example of a neutral and planar four-membered rhombic indacycle in the solid state. During the investigation of the compound in solution by NMR experiments, it was shown that the resonance pattern of 2,6-diisopropylphenyl groups in the ^{1}H NMR spectrum indicate a symmetric steric environment of the aryl substituents. This implies that the In_4 unit is only observed in the solid state, while in solution the structure is described best as the biscarbenoid. The driving force for the solid-state structure was obtained by dispersion stabilization, whereby the rather weak metal–metal interactions result from donation originating from diffuse s-type orbitals to unoccupied p-type orbitals. In solution, however, NMR spectroscopy and DFT calculations indicate labile metal–metal interactions, because the species behave as an unbound biscarbenoid.



I **II**

Scheme 2. Synthetic route to **II**. R = Dipp = 2,6-diisopropylphenyl.

The structures of a two-coordinated complex are obtained in all cases for the thallium bis(β-diketimine) species, because of the low energy and s-type character of the thallium lone pair. These compounds can serve as model to investigate the metal-metal interaction unperturbed by the electronics and steric of additional ligands.

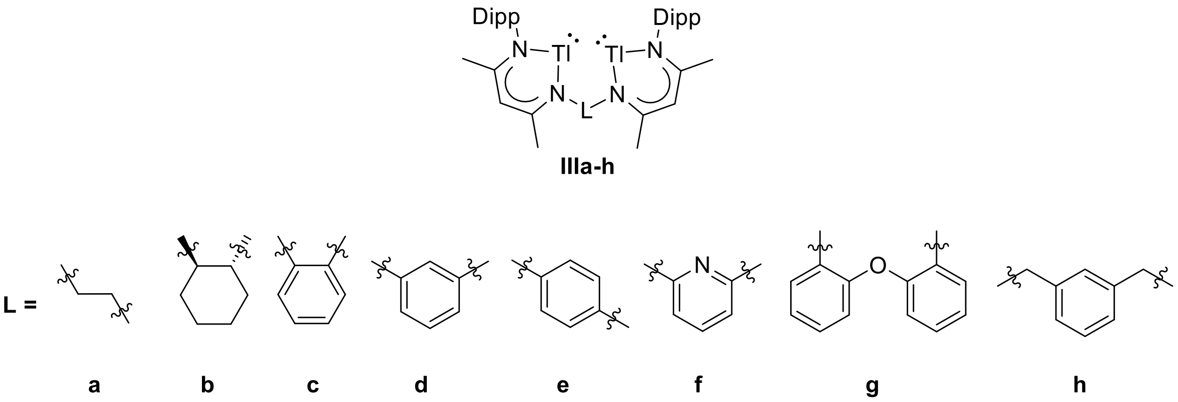


Figure 1. Bis(carbene) analogues of thallium.

Using the 1,2-ethylene bridged bis(β-diketimine) ligand for the stabilization of the thallium, an intramolecular Tl_2-dimer **IIIa** is observed with a Tl–Tl bond of 3.5059(3) Å, which are significantly longer than the predicted by using their single bond covalent radii 2.88 Å.[C2] The unusual orientation of both thallium atoms results by and large from the short ethylene linker, which also gives rise to a rather short contact of about 3 Å between thallium and the methine proton of the adjacent disordered iso-propyl group. Computational investigations revealed that the metal-metal interactions benefit distinctly from London dispersion forces, wherefore the Tl–Tl bond interactions are rather weak.

Using a 1,2-trans-cyclohexylene bridge (**IIIb**) where the rotation around the C–C bond is restricted, providing comparable electronic but different steric parameters, no Tl–Tl bond is formed in the solid state, resulting in separation of the thallium atoms of 4.294(8) Å. Free rotation along the C1-C2 axis cannot be obtained because the C_2 bridge is part of the cyclohexane ring, and thus both thallacycles are twisted away from each other. This may prohibit the cooperative effect despite the close proximity of both metal centres.

Changing the substitution pattern of the phenylene bridge from ortho (**IIIc**) to meta (**IIId**) and para (**IIIe**), the metal-metal separation is expected to be increased compared to the C_2-bridged species. While for the 1,3- and 1,4-phenylene based compounds accurate values for the Tl–Tl distance (7.51(1) Å, 8.4624(5) Å) can be obtained from the solid-state structure analysis, the 1,2 phenylene complex **IIIc** has a value of 4.82 Å, which was calculated by computational studies, because a single-crystal measurement was not possible. Again, in both solid-state structures (**IIId**, **IIIe**), an opposite orientation of the thallium centres is observed.

In case of the 2,6-pyridine bridged species (**IIIf**), for which, unfortunately, no crystals suitable for an X-ray analysis were obtained, the computational results, indicated that the energy-minimized structure corresponds to a heterobimetallic species with two different binding sites. While one thallium atom is ligated by three nitrogen atoms including the pyridine-based nitrogen atom, the second thallium atom behaves as a carbene analogue being only chelated by two nitrogen atoms, respectively, and the Tl–Tl distance amounts to 5.04 Å. The ^{1}H NMR spectrum of **IIIf**, however, only shows one set of doublets for the respective isopropyl methyl proton resonances of the 2,6-diisopropyl substituents, thus indicating magnetically equivalent binding sites in solution.

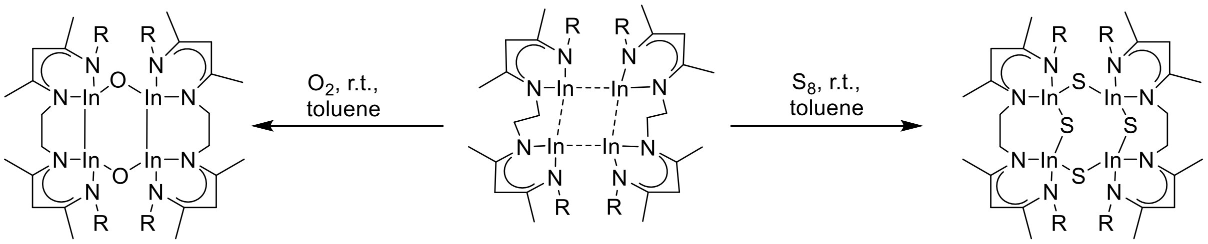
The 2,2'-oxydiphenyl-bridged (**IIIg**) compound shows in the solid-state structure, that both thallium centres are orthogonal directed, and the thallium-thallium separation adds up to 4.5266(1) Å. Remarkable, no direct bonding between the oxygen and the thallium atoms has been observed, although the Tl–O separation (3.156(3) Å) is below the sum of the van-der-Waals radii.

For the 1,3-xylylene-bridged derivate (**IIIh**), the Tl–Tl distance could only be calculated by computational studies and is in the range of 4.53 Å.

In summary, the different bridged bis(β-diketimine) compounds lead to the thallium-thallium distances range from 3.5059(3) Å to 8.4624(5) Å. Due to the absence of co-ligands, the dinuclear thallium diyls serve as model compounds for studying the intramolecular metal-metal separation without being perturbed by coordinated solvents or other ligands. This information is of crucial importance for the design of new bimetallic catalysts as the optimum of the metal-metal separation has been proposed to be within 3.5 and 6 Å.[C3]

Oxidative Addition of O_2 and S_8

The question arose if the indium bis(carbene) analogue can be used for oxidative additions, which are key to many important catalytic transformations. Therefore, reactions of In_4-species with oxygen and sulfur were performed. Thus, a freshly-prepared toluene solution of the four-membered indium metallacycle II was converted with a stream of dry oxygen or with sulfur, Scheme 3.



VII **II** **VIII**

Scheme 3. Reaction of the indium bis(carbenoid) **II** with oxygen and sulfur at room temperature. R = Dipp = 2,6-diisopropylphenyl.

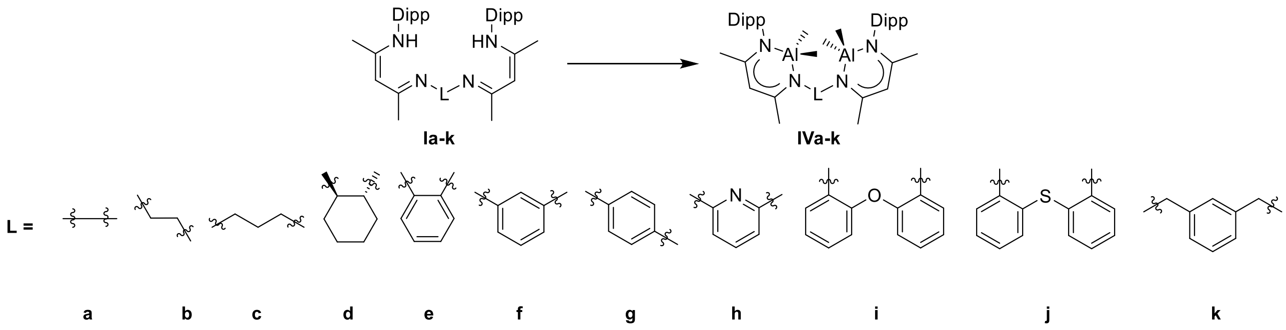
For **VII**, an almost planar In_4O_2 six-membered ring was obtained with indium in the formal oxidation state +II. This compound is an isovalence-electronic analogue of dioxane. The In–In bond lengths (2.7136(3) Å) of **VII** are significantly shortened compared to the intramolecular In–In bonds within **II** (3.1095(3) Å). The In–O bond lengths of 2.003(2) Å and 2.008(1) Å, respectively, are comparable to those observed in other In(III) oxo-species, such as the In_3O_3 ring stabilized by three NacNac ligands with In–O bond distances in the range of 1.972(5) to 2.006(5) Å[C4] or the acyclic In–O–In species reported by Uhl *et al.* (1.981(2) Å to 1.989(2) Å).[C5] In contrast, the weaker oxidant S_8 yields an In4S4 eight-membered ring in a 'deck-chair' conformation containing four indium atoms in the oxidation state +III and four sulfides in an alternating fashion, **VIII**. The indium sulfur bond distances of 2.3787(9) to 2.4156(8) Å in the ring match well with values obtained for neutral dinuclear indium(III) sulfides (2.3640(8) – 2.3691(8) Å)[C6] or indium sulfide cluster (2.395(4) to 2.437(5) Å for μ_2-sulfide bridges).[C7]

Therefore, these obtained compounds **VII** and **VIII** show, that the oxidative addition is possible by the reaction of an indium bis(carbenoid) with oxygen or sulfur.

Structure behaviours of dinuclear aluminium(III) complexes

As described in the introduction, one of the current topics in the industry is focused on the development of earth abundant and non (eco) toxic metal catalysts. Suitable for these are main group elements, which is why aluminium(III) compounds were investigated in part of this work.

With the preparation of aluminium alkyl compounds based on rigid, semirigid, and flexible bis(β-diketiminate) ligands, the steric constraints of the ligand were investigated on the element-element separation and the relative orientation of the two elemental centres, which are very relevant aspects in terms of cooperative catalysis. These aluminium alkyl complexes could be useful as catalyst for the ring-opening polymerization of cyclic esters. Therefore, a set of dinuclear aluminium alkyl compounds were synthesized and characterized, Scheme 4.



Scheme 4. Synthesis of dinuclear organoaluminium complexes **IVa-k**.

The molecular structures of five compounds (**IVa**, **IVb**, **IVc**, **IVe**, and **IVi**) has been elucidated by X-ray diffraction techniques. All structures feature two distorted tetrahedral aluminium centres that are projected out of the plane of each NacNac unit and the Al–Al separations increase in the order **IVa** (3.8866(6) Å) < **IVe** (6.4023(8) Å) < **IVb** (6.482(1) Å) < **IVc** (7.3823(4) Å) < **IVi** (7.396(1) Å) as a result of the length and the rigidity of the bridging unit. The molecular structures are consistent with the respective ^{1}H NMR resonance pattern observed in solution. A similar gradation of the metal-meta bond distances in dependence of the linker could be obtained with the thallium dimers **III**. The difference of the bond distance most likely arises from the increased steric demands of the Al(CH$_3$)$_2$ group in comparison with the “naked” Tl(I) centre bearing a diffuse s-type lone pair of electrons.

In future experiments, the impact of the metal-metal separation and the flexibility of the bridging unit on the catalytic performance in the ring-opening polymerization of cyclic esters will be investigated.

Nevertheless, aluminium(I) carbenoids could be more reactive than the aluminium(III) compounds. Therefore, a set of 22 dinuclear aluminium halide complexes based on bis(β-diketiminate) ligands has been synthesized.

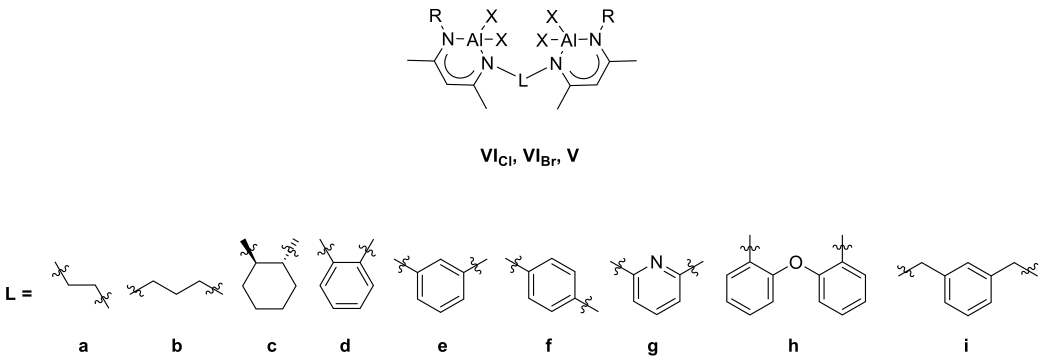


Figure 2. Dinuclear aluminium halide complexes. (**VI$_{\text{Cl}}$** for X = Cl, **VI$_{\text{Br}}$** for X = Br, **V** for X = I). R = Dipp = 2,6-diisopropylphenyl.

The characteristically studies showed an increase in the aluminium–aluminium separation as a result of the geometric constraints of the bridge in the following order: **VI$_{\text{Cl}}$a** (5.259(2) Å) < **VI$_{\text{Cl}}$d** (6.223(2) Å) < **VI$_{\text{Br}}$a** (6.273(2) Å) < **VI$_{\text{Br}}$d** (6.308(1) Å) < **Va** (6.393(2) Å) < **Ve** (6.747(2) Å) < **V$_{\text{Br}}$i** (7.119(1) Å) < **Vi** (7.479(4) Å). The dependence of the distances on the linkers was already observed within the aluminium alkyl compounds.

Due to the unique reactivity of the alane diyls and the interest in Group 13 bis(carbene) analogues, the reduction of the aluminium halide complexes using potassium graphite (C_8K) was attempted. NMR experiments of **Va**, **Ve**, **Vh** and **Vi** with potassium graphite in C_6D_6 shows no significant difference to the respective dinuclear aluminium(III) complexes and no colour change of the golden C_8K flakes was observed.

The reduction of **VI$_{\text{Cl}}$a**, **VI$_{\text{Cl}}$b**, **VI$_{\text{Cl}}$d**, **VI$_{\text{Cl}}$e**, **VI$_{\text{Cl}}$g**, **VI$_{\text{Br}}$a**, **VI$_{\text{Br}}$b**, **VI$_{\text{Br}}$d**, **Va**, **Vb**, **Ve**, and **Vg** in a 10:1 toluene diethyl ether mixture with an excess of potassium graphite were explored. In these cases, for the ^{1}H NMR spectra recorded in C_6D_6, only for **VI$_{\text{Cl}}$b**, **VI$_{\text{Cl}}$d**, **VI$_{\text{Br}}$b**, **Vb**, and **Vg**, weak and rather broad signals appeared in the aliphatic region. Unfortunately, the crystallisation of these compounds was unsuccessful, even after repeated attempts.

In order to rationalize the findings and evaluate whether the dinuclear aluminium halide **VI$_{\text{Cl}}$**, **VI$_{\text{Br}}$** and **V** are suitable precursors for aluminium(I) complexes, cyclic voltammetry of all compounds was measured. Summarized reduction potential strongly depends on the bridging group as well as on the halogen substituent and the reduction potentials are shifted to more negative values in the order Cl < Br < I. However, these results state that the reduction with potassium graphite is not possible for all dinuclear aluminium iodide complexes, but for the chloride and bromide species. The non-occurrence of any reduction event in case of the aluminium halide compounds in the NMR experiments reported above can be explained by solvent effects, which strongly impact the reduction potential. Based on these findings, the development of dinuclear aluminium complexes aiming to access dinuclear alane diyls is continued to explore.

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9 Appendix

9.1 Thematic List of Abbreviations

NMR Spectroscopy

NMR	Nuclear Magnetic Resonance
δ	chemical shift
ppm	part per million
Hz	Hertz, s^{-1}
J	coupling constant, Hz
s	singlet
d	doublet
t	triplet
s	septet with *J*
‘t’	pseudo triplet
m	multiplet
br	broad
VT	variable-temperature

tBu	*tert*-Butyl	$-C_4H_9$
Cp	cyclopentadienyl	η^5-C_5H_5
Cp*	η^5-C_5Me_5	
Cy	cyclohexyl	$-C_6H_{11}$
Dipp	2,6-diisopropylphenyl	
Dmp	2,6-dimethylphenyl	
Et	ethyl	$-C_2H_5$
Me	metyl	$-CH_3$
Mes	2,4,6 trimetylphenyl	
Ph	phenyl	$-C_6H_5$
Ar	Aryl	
Bn	Benzyl	-CH2C6H5
Pyr	pyridine	

Cyclic Voltammetry

CV	Cyclic Voltammetry
$E_{1/2}$	half potential
Fc/Fc^+	Ferrocene/Ferrocenium
µA	Mikroamper
V	Volt

Solvents

THF	tetrahydrofurane, C_4H_8O
Et_2O	diethylether, $C_4H_{10}O$
CH_2Cl_2	dichloromethane

T	temperature, K or °C
c	concentration, mol · L^{-1}
°	grad
r.t.	room temperature
d	die (lat.) = day
h	hora (lat.) = hour
v	wave number
ATR	attenuated total reflection
ROP	ring-opening polymerization
Å	Angstroem, $1\ \text{Å} = 1\cdot10^{-10}$ m

9.2 Acknowledgment

Finally, I want to thank…

- Prof. Dr. Robert Kretschmer for providing the interesting research topic and the supervision, for enabling my research stay in California. Additionally, for providing extraordinary and excellent working conditions.
- Prof. Dr. Manfred Scheer, Dr. Gábor Balázs, Barbara Bauer and all members of the working group of Prof. Scheer for the pleasant working atmosphere in the 3rd floor.
- Dr. Stefanie Gärtner for the valuable advice in X-ray structure refinements
- Prof. Dr. T. Don Tilley and Rosemary for giving me the opportunity to join this team in course of a research stay in California at UC Berkeley. Thanks to all group members for making it a pleasant stay, especially Maxinne, Felix and Yang-Jin.
- the staff of the Central Analytical Services of the University of Regensburg: X-ray, EA and NMR department. With special emphasis on Anette Schramm and Georgine Stühler for the countless ^{27}Al NMR measurements and Barbara Baumann for the EAs.
- the staff of the glass blowing, electronics and mechanics facilities of the University of Regensburg for their valuable work.
- the working group of Prof. Wolf for the possibility to measure CV experiments.
- all present and former members of the Kretschmer group for the pleasant working atmosphere and an unforgettable time: Andi, Alex, Maxi, Philipp, Tobi, Victor and Tyson
- especially my parents Christine and Gerhard, my sister Kathrin and my grand-parents Elfriede and Paul for their enduring support.

In memoriam to my granny Maria

✞ 28.05.2018