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Discipline / Spécialité: Chimie

Chimie de coordination de carbènes *N*-hétérocycliques substitués par des groupements alkylfluorényles:

interactions faibles, effets stériques, catalyse.

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List of abbreviations

#	
[cat]	catalyst
%*V*bur	percent buried volume
δ	chemical shift
2-Np	2-naphthyl

A	
Å	Ångström
AcO	acetate
AF	9-alkyl-9-fluorenyl
*a*NHC	abnormal *N*-heterocyclic carbene
Ar	Aryl
Arom.	Aromatic

B	
BDE	bond dissociation energy
Bn	benzyl
br	broad

C	
CM	cross-metathesis
conc.	concentrated
Cq	quaternary carbon
cyoct (or C8)	cyclo-octyl

D	
d	doublet
dba	dibenzylideneacetone
DFT	density functional theory
DMAc	*N,N'*-dimethylacetamide
DME	dimethoxyethane
DMSO	dimethylsulfoxide

E	
e-	electron

EF	9-ethyl-9-fluorenyl
equiv.	equivalent
eqn.	equation
Et	ethyl
eV	electron-volt

F

FT-IR	Fourier-transform infrared

H

h	hour
Hz	herz
HMDS	bis(trimethylsilyl)amide

I

i-Pr	*iso*-propyl

M

m	multiplet
M	any metal
M	mol/L
Me	methyl
Mes	2,4,6-trimethylphenyl
MIC	mesoionic carbene
min	minute
mp	melting point
M_r	relative molar mass

N

n-Bu	butyl
n-Pr	propyl
NHC	*N*-heterocyclic carbene
NMR	nuclear magnetic resonance
*n*NHC	normal *N*-heterocyclic carbene

P

PEPPSI	pyridine enhanced precatalyst: preparation, stabilisation, initiation
Ph	phenyl
ppm	parts per million
Py	pyridine

Q

q	quartet

R

RCM	ring closing metathesis
R_f	retardation factor
*r*NHC	remote *N*-heterocyclic carbene
ROCM	ring-opening cross-metathesis
ROESY	rotating frame nuclear overhauser effect spectroscopy
ROMP	ring-opening metathesis polymerisation
rt	room temperature

S

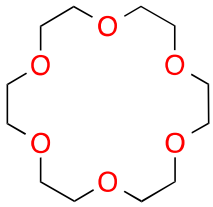
s	singlet

T

t	triplet
t-Bu	*tert*-butyl
TEP	Tolman electronic parameter
THF	tetrahydrofuran
THT	tetrahydrothiophene
TMEDA	tetramethylethylenediamine
TOF	turnover frequency
Tol	tolyl
TON	turnover number

V

vs.	versus



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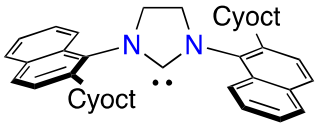

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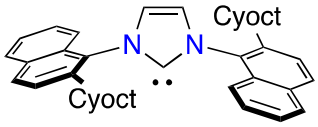

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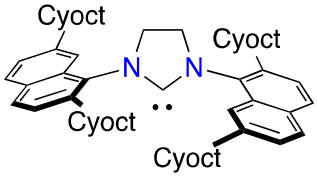

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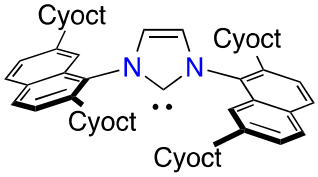

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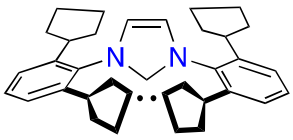

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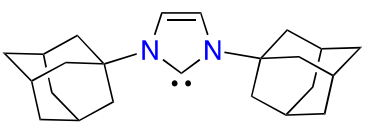

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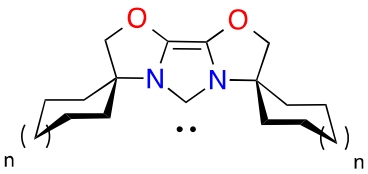

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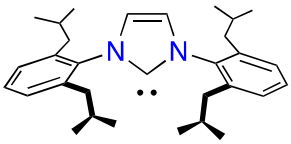

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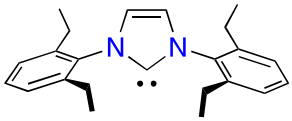

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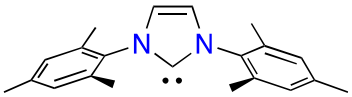

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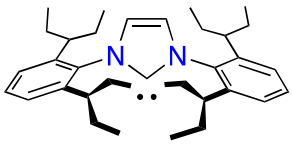

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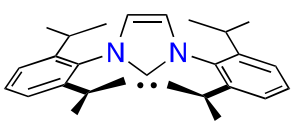
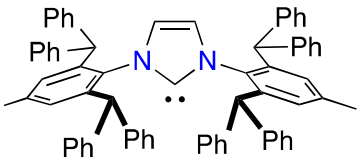
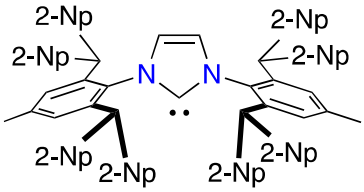


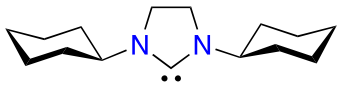
IPr



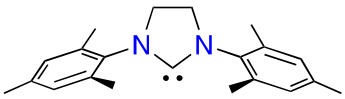
IPr*



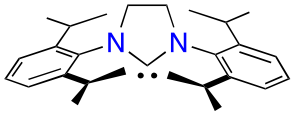
IPr*$^{(2\text{-Np})}$



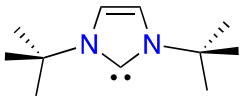
SICy



SIMes



SIPr



ItBu

Résumé de thèse

Cette thèse est consacrée à l'étude d'une série de ligands originaux appartenant à la famille des carbènes *N*-hétérocycliques (NHCs), tous caractérisés par la présence de substituants étendus de type alkylfluorényle (AF). Une attention particulière a été portée à l'étude des propriétés stériques de ces coordinats, ainsi qu'à l'influence de ces dernières sur des réactions catalysées par du palladium et du cuivre.

Le chapitre d'introduction commence par un rappel historique du développement de la chimie des NHCs. Il décrit également la nature des interactions métal-carbène dans les complexes contenant de tels ligands et montre comment il est possible de quantifier les propriétés stériques et électroniques des NHCs. Il précise l'intérêt des coordinats NHCs en chimie de coordination et en catalyse homogène en précisant leurs atouts par rapport à d'autres ligands donneurs de deux électrons.

Le chapitre I décrit la synthèse et la caractérisation d'une série de sels de *benzimidazolium* substitués par les groupements AF. Ces composés ont été préparés en trois étapes à partir d'*ortho*-phénylènediamine (Schéma 1).

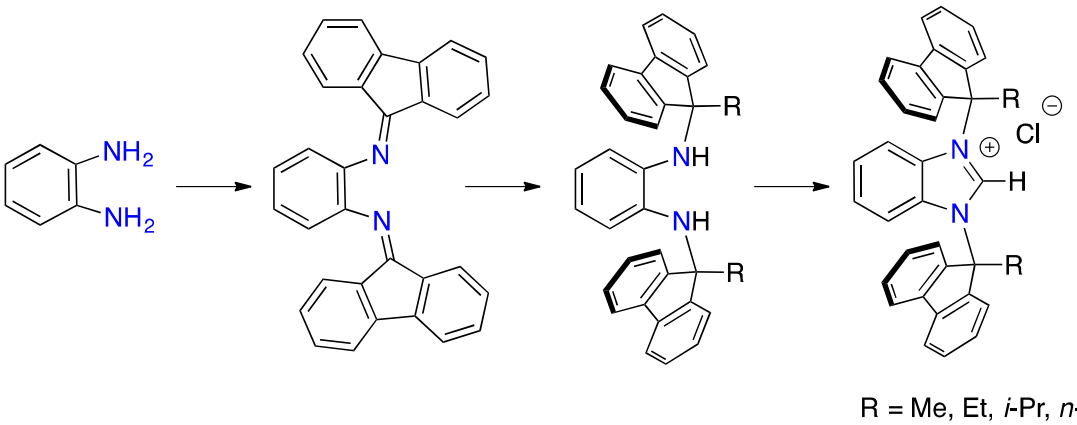


Schéma 1 : Synthèse des sels de benzimidazolium substitués par des groupements AF identiques.

Ces précurseurs carbéniques ont donné accès à des complexes de palladium de type Pd-PEPPSI-NHC (PEPPSI = *pyridine enhanced precatalyst, preparation, stabilisation and initiation*) (Schéma 2). Les complexes de cette famille sont réputés être d'excellents pré-catalyseurs de réactions de couplage croisé.

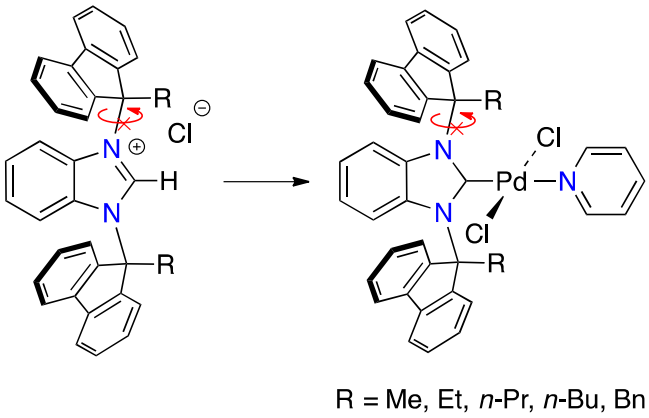


Schéma 2 : Synthèse des complexes (Pd-PEPPSI-NHC).

Des études par diffraction des rayons X et RMN ont révélé que dans tous les complexes formés la rotation du groupe AF autour de la liaison N-AF est bloquée en raison de la présence de l'unité benzimidazolylidène. Par ailleurs, le plan fluorénylidène, rabattu vers l'entité phénylène du benzimidazole, oriente son groupe alkyle vers l'axe dz^2 du plan métallique. Ainsi, l'encombrement stérique du palladium reste constant dans le temps (Figure 1). C'est là la caractéristique essentielle de ces NHCs.

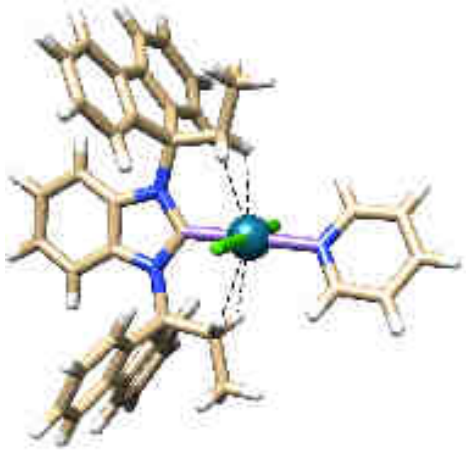


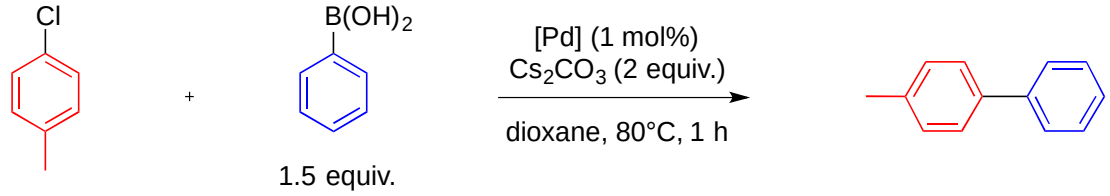
Figure 1 : Structure cristallographique d'un complexe Pd-PEPPSI-NHC obtenu à partir d'un NHC substitués par deux groupes AF (ici 9-éthyl-9-fluorényle).

Un examen approfondi des structures des complexes obtenus montre que, dans tous les cas, les protons du premier groupe méthylène de chacune des chaînes R forment avec le métal des liaisons C–H···Pd de type anagostique, dont la nature est principalement de type électrostatique. Ainsi, l'existence de ces interactions faibles, combinée à la forte liaison entre le carbone carbénique et le métal, permet de considérer ces NHCs comme des

tenailles monodentates (*monoligating clamps*); on peut également les voir comme des *pinces bimodales,* c'est-à-dire des coordinats tridentates produisant deux types distincts de liaisons, une liaison forte, la liaison de coordination, et deux liaisons faibles de type non covalentes.

Une étude catalytique réalisée avec ces précatalyseurs a révélé que le composé portant des substituants 9-éthyl-9-fluorényle (EF) (voir Figure 1) est particulièrement efficace en couplage de Suzuki-Miyaura (Tableau 1, entrée 3). Son activité est comparable, voire supérieure à celle des complexes Pd-PEPPSI-NHC les plus utilisés à ce jour, à savoir ceux formés contenants les coordinats carbéniques IPr, SIPr et IMes.

Tableau 1: Couplage de Suzuki-Miyaura entre l'acide phénylboronique et le *para*-chlorotoluène**.** La mention "9-alkyl-9-fluorényle" fait référence aux substituants des NHCs dans les complexes Pd-PEPPSI présentés dans le Schéma 2.



Entrée[a]	[Pd]	%*V*bur [%]	Rendement [%][b]
1	$Pd(OAc)_2$	-	0
2	**9-méthyl**-9-fluorényle	36.9	40
3	**9-éthyl**-9-fluorényle	37.2	70
4	**9-propyl**-9-fluorényle	38.1	60
5	**9-butyl**-9-fluorényle	38.0	21
6	**9-benzyl**-9-fluorényle	37.1	19
7	$[PdCl_2(ItBu)(Py)]$	36.2	20
8	$[PdCl_2(IMes)(Py)]$	31.6	63
9	$[PdCl_2(IPr)(Py)]$	35.7	38
10	$[PdCl_2(SIPr)(Py)]$	33.6	37

[a]*para*-chlorotoluène (1 mmol), acide phénylboronique (1.5 mmol), Cs_2CO_3 (2 mmol), dioxane (3 mL). [b]Rendements déterminés par RMN ^1H avec le 1,4-diméthoxybenzène comme talon interne. Moyenne sur deux expériences. Pas de produit d'homocouplage détecté.

Un des résultats les plus intéressants de cette étude a été de mettre en exergue une des limites du "percent buried volume" (%*V*bur), grandeur[1] fréquemment employée pour quantifier l'encombrement stérique d'un NHC. En effet, comme le montre l'étude au cours de laquelle les NHC synthétisés ont été comparés à des NHC de la littérature, deux NHCs ayant le même encombrement stérique peuvent conduire à des performances catalytiques complètement différentes. Cette observation montre que la seule connaissance du %*V*bur d'un NHC donné ne permet pas de prévoir les propriétés catalytiques des complexes correspondants et qu'il est indispensable d'identifier si le ligand considéré présente un encombrement stérique variable en solution (Tableau 1, entrées 2-6). Cette dernière donnée n'a, pour l'instant, pas été prise en compte dans la définition du %*V*bur.

L'étude a ensuite été étendue (Chapitre II) à des analogues portant deux groupements AF différents (R^1= Me, R^2 = Et, *n*-Pr, *n*-Bu, *i*-Pr, Bn, CH_2SMe) (Schéma 3). Leur synthèse a été réalisée à partir de la *N,N'*-bis(9H-fluorén-9-ylidène)benzène-1,2-diamine, par addition successive de deux nucléophiles distincts, puis cyclisation de la diamine correspondante.

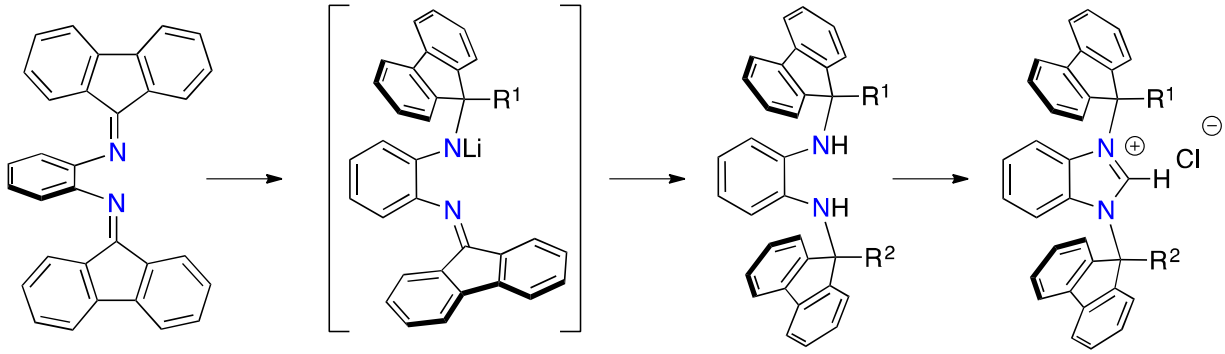


Schéma 3 : Synthèse des sels de benzimidazolium substitués par des groupements AF distincts.

Excepté pour le dérivé portant un groupement méthylthioether, tous les sels de benzimidazolium dissymétriques synthétisés ont permis de préparer des complexes de type Pd-PEPPSI-NHC (Schéma 4).

[1] Cette grandeur exprime la proportion d'espace occupée par le ligand à l'intérieur d'une sphère centrée sur le métal dont le rayon est arbitrairement fixé à 3.5 Å, rayon correspondant à env. 1.5 fois celui de la première sphère de coordination du métal.

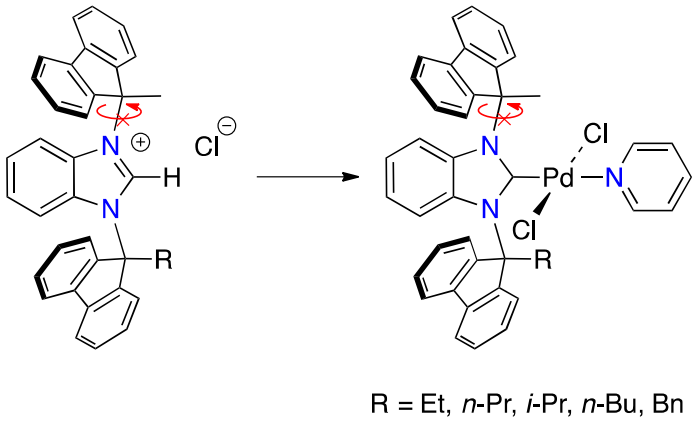


Schéma 4 : Synthèse des complexes (Pd-PEPPSI-NHC) dissymétriques.

Comme pour les complexes décrits plus haut dans lesquels les substituants AF sont identiques, des études par RMN et par diffraction des rayons X ont permis de mettre en évidence le confinement du centre métallique entre les deux chaînes alkyle des substituants AF. Autrement dit, ces ligands se comportent ici encore comme des *pinces bimodales*. Les diverses interactions anagostiques se traduisent, à l'état solide, par des séparations de l'ordre de 2.5 Å entre l'atome de palladium et les C*H* méthyléniques.

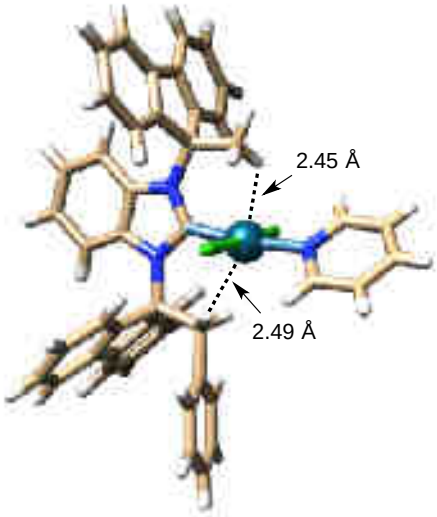


Figure 2 : Structure cristallographique d'un complexe Pd-PEPPSI-NHC portant deux groupements AF distincts.

Dans les mêmes conditions, le précurseur de NHC portant une chaîne méthylthioéther conduit à la formation quantitative d'un complexe pince contenant un exemple rare de coordinat tridentate hybride $S,C_{carbène},C_{alkyle}$, résultant d'une métallation du groupement méthylfluorényle (Schéma 5).

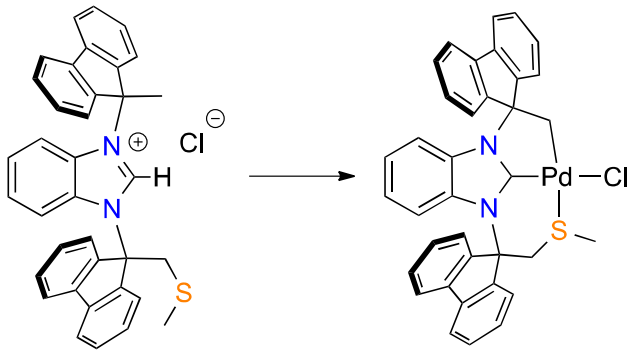


Schéma 5 : Synthèse d'un complexe de palladium contenant une pince *S,C,C.*

Vraisemblablement, la métallation observée implique la formation préalable d'un complexe chélate ($C_{carbène}$,S) qui positionne le groupement *méthyle* lié au fluorényle en *trans* de l'atome de soufre, facilitant ainsi l'activation d'une liaison CH du méthyle. On peut souligner que cette activation d'alkyle non usuelle se produit dans des conditions relativement douces.

Les complexes dissymétriques *non sulfurés* ont été testés en réaction de couplage de Suzuki-Miyaura. A l'instar de leurs analogues symétriques, ils sont tous actifs en couplage de l'acide phénylboronique et du *para*-chlorotoluène. Cependant, leurs performances restent inférieure à celle du composé symétrique Pd-PEPPSI-(benzimidazolylidene EF/EF) présenté plus haut (Figure 1).

Dans le chapitre III, nous exposons la préparation d'un sel d'imidazolium et d'un sel d'imidazolinium, chacun substitué par deux groupements EF identiques. L'intermédiaire-clé pour la synthèse des deux composés est une amine primaire inédite, la 9-éthyl-9-fluorénylamine qui a été préparée à partir de la fluorénone (Schéma 6).

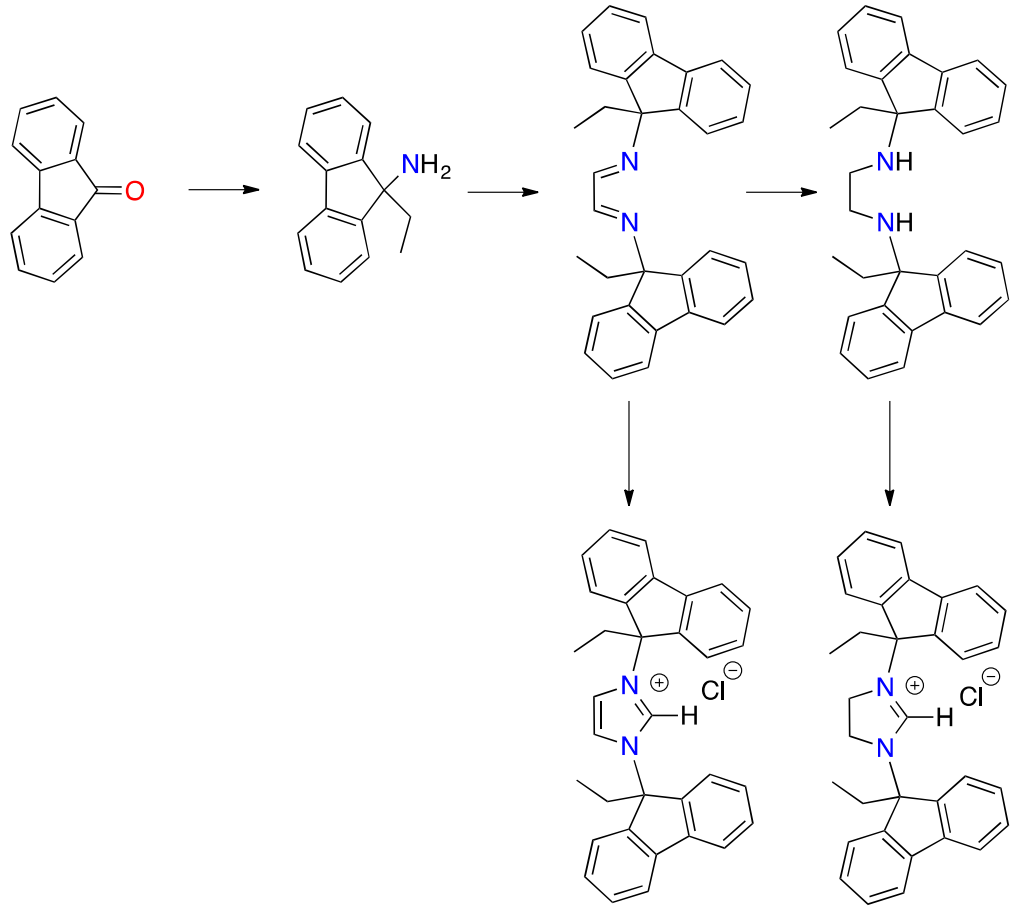


Schéma 6 : Synthèse des sels d'imidazolium et imidazolinium substitués par des groupements EF identiques.

Ces composés possèdent donc un hétérocycle plus petit que l'entité benzimidazole présente dans les composés des chapitres I et II. Ainsi, les groupements EF ne subissent pas de contraintes conformationnelles et peuvent tourner librement autour de la liaison N-C(EF).

Ces sels ont permis de synthétiser les deux complexes Pd-PEPPSI-NHC correspondants (Schéma 7).

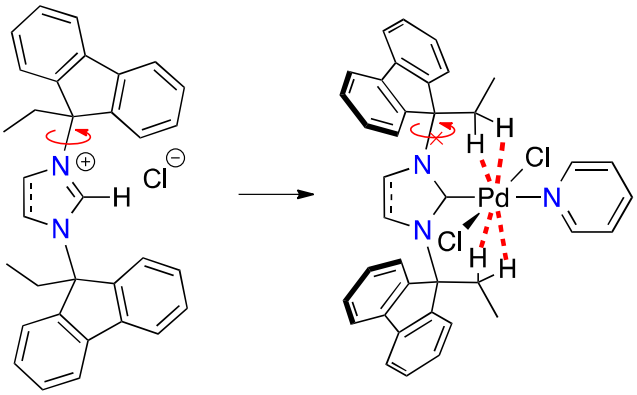


Schéma 7 : Synthèse des complexes Pd-PEPPSI-(imidazolinylidène EF/EF) et -(imidazolylidène EF/EF). Blocage de la liaison N-C(EF).

Malgré la libre rotation du groupement EF dans ces sels d'azolium, les ligands *N*-hétérocycliques correspondants se comportent là encore comme des pinces monodentes rigides dans leurs complexes de palladium. Cette conformation est visiblement imposée par les interactions anagostiques CH_2···Pd qui bloquent toute dynamique. Ces conclusions sont étayées par des études RMN en solution et par des études cristallographiques.

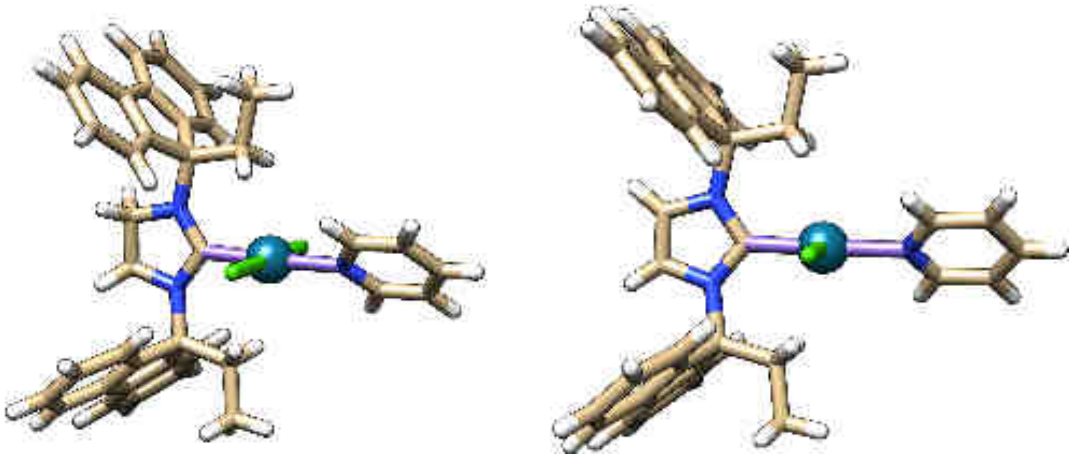


Figure 3 : Structure cristallographique des complexes Pd-PEPPSI-(imidazolinylidène EF/EF) (gauche) et Pd-PEPPSI-(imidazolylidène EF/EF) (droite).

Ces ligands possèdent donc, comme nous l'avons observé dans le cas des dérivés des benzimidazolylidènes décrits dans les chapitres I et II, un atome fortement coordinant (l'atome de carbone carbénique) et plusieurs donneurs additionnels (C*H*) capable d'interagir de manière non-covalente avec le métal complexé. Ces coordinats se comportent là encore en *pinces bimodales*.

Un complexe de l'argent, [AgCl(NHC)], a également pu être préparé (Schéma 8).

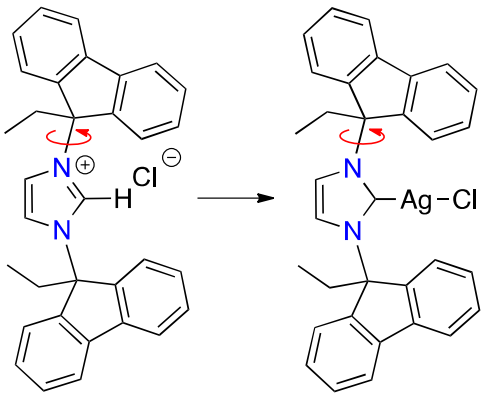


Schéma 8 : Préparation du complexe AgCl(imidazolylidène EF/EF).

Dans ce cas, contrairement aux deux complexes de palladium décrits plus haut, aucun indice spectroscopique en faveur d'interactions anagostiques CH_2···Ag n'a pu être détecté. A l'état solide, ce complexe adopte une structure de "sandwich ouvert", avec les deux entités fluorényle tournées vers l'atome d'argent (Figure 4). Les distances C-Ag les plus courtes (< 3 Å) sont typiques d'interactions π-métal-arène.

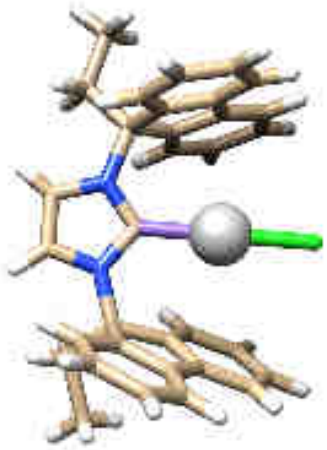


Figure 4 : Structure cristallographique du complexe AgCl(imidazolylidène EF/EF).

Cet autre mode de coordination du coordinat imidazolylidène EF-EF peut lui aussi être qualifié de type "pince bimodale", les interactions faibles impliquant la pince étant créées ici avec des unités aromatiques et non pas des CH aliphatiques. Les deux modes de coordination rencontrés pour ce NHC illustrent le caractère variable de l'encombrement stérique du ligand.

Le comportement catalytique des deux complexes Pd-PEPPSI-NHC a été évalué en réaction de couplage de Suzuki-Miyaura. Le complexe contenant l'imidazolylidène(EF-EF) a montré une aussi bonne activité que celle observée pour son analogue benzimidazolylidène(EF-EF) (Tableau 1, entrée 2). D'un point de vue pratique, ces systèmes pourront principalement être employés pour le couplage de chloroarènes peu encombrés.

Le chapitre IV décrit la synthèse d'un complexe de l'or(I), de formule [AuCl(NHC)], obtenu à partir du sel de benzimidazolium(EF-EF) décrit au chapitre I (Schéma 9). A l'heure actuelle, les complexes NHC de l'or (I) font partie des complexes NHC les moins étudiés. A l'état solide, ce complexe présente une structure singulière, puisque l'entité Au–Cl est située hors du plan carbénique. On observe donc d'une coordination imparfaite du

doublet du carbène (Figure 5), conférant au ligand la forme d'un colibri dont la tête est inclinée vers un nectar à extraire (l'atome d'or).

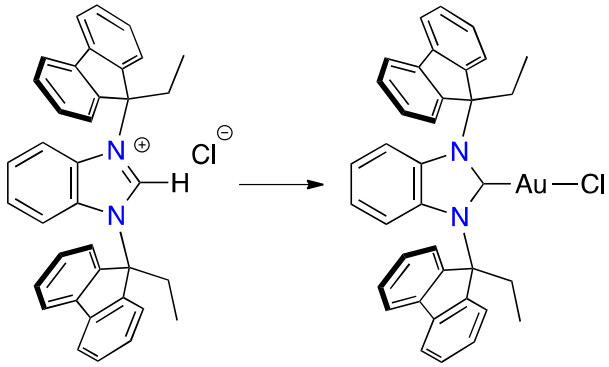
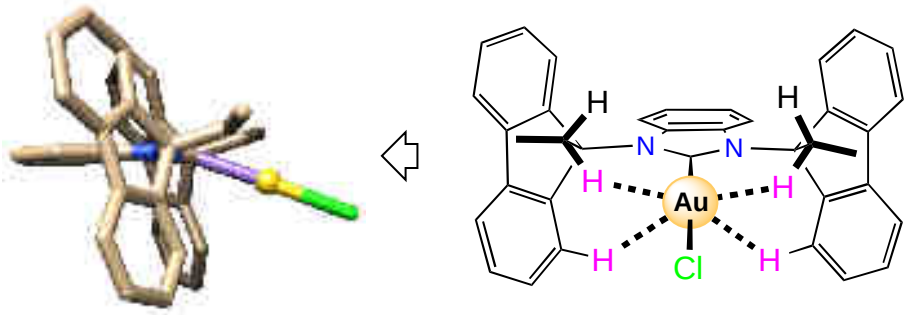


Schéma 9 : Synthèse du complexe d'or [AuCl(benzimidazolylidène EF/EF)].



(angle de pitch 21°)

Figure 5 : Structure cristallographique du complexe [AuCl(benzimidazolylidène EF/EF)] et représentation.

Des calculs théoriques DFT (réalisés par C. Gourlaouen) montrent que l'angle d'inclinaison de 21° formé à l'état solide entre l'entité Au-Cl et le plan carbénique, traduit d'une part un déplacement facile de l'ion or(I) hors de l'axe du doublet carbénique (ce déplacement nécessitant env. 3 kcal/mol), et d'autre part la stabilisation efficace de la position hors-axe par des interactions attractives CH···Au impliquant des atomes d'hydrogène aliphatiques (qui donnent lieu à des liaisons hydrogène) mais également, dans une moindre mesure, par des forces dispersives mettant en jeu des CH aromatiques. Dans la version BF (*n*-butylfluorényle)/BF du complexe étudié, l'atome d'or est situé cette fois, comme attendu, dans le plan. Globalement, on peut considérer que la localisation hors-axe observée pour le dérivé EF/EF, constitue une photo instantanée de l'oscillation naturelle de

l'atome d'or de part et d'autre de l'axe carbénique. Sa visualisation est rendue possible par la présence de substituants flexibles suffisamment étendus pour s'approcher du centre métallique désaxé et ainsi interagir avec celui-ci de façon liante. Bien entendu, aucune des études par RMN à température variable réalisées n'a permis de bloquer ce mouvement oscillatoire, les énergies mises en jeu étant trop faibles. Néanmoins, elles ont permis de mettre en évidence deux types de changement conformationnel au sein des groupes éthyle latéraux.

Une coordination de type "colibri" a également été observée dans le cas d'un complexe de cuivre (Figure 6).

Figure 6 : Structure cristallographique du complexe [CuCl(imidazolylidène EF/EF)].

On peut préciser ici que des coordinations imparfaites d'ions dans des complexes NHC avaient déjà été décrites dans la littérature, mais les distorsions observées étaient exclusivement induites par des répulsions stériques au sein des complexes considérés.

Le chapitre V concerne la préparation d'autres complexes de cuivre de type [CuCl(NHC)], complexes contenant également des carbènes *N*-hétérocycliques substitués par des groupements alkylfluorényle (Figure 7). Leur potentiel en hydrosilylation de dérivés carbonylés y a été évalué.

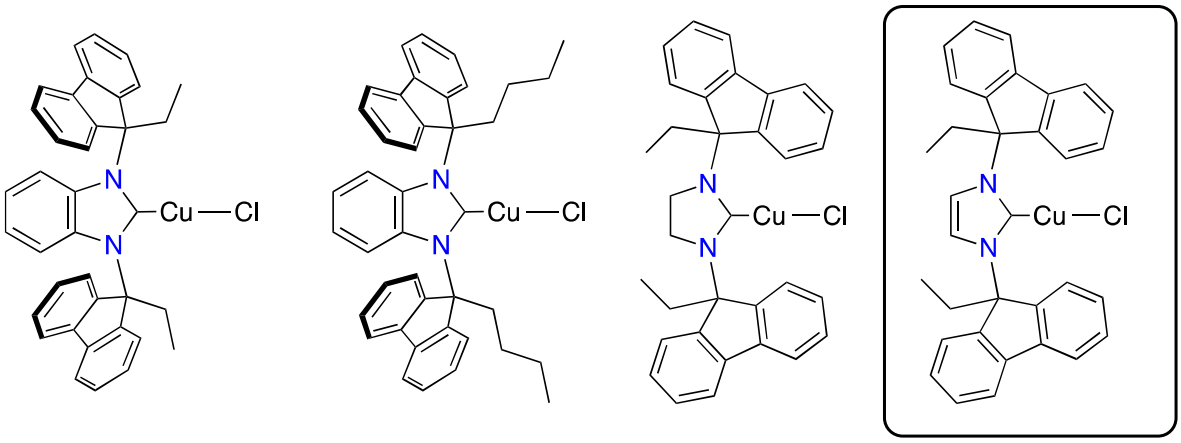
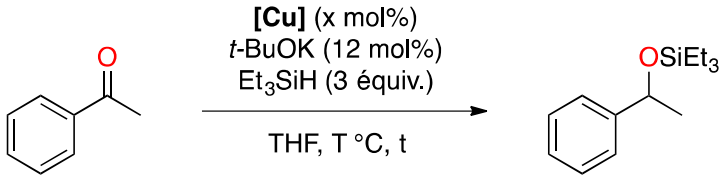


Figure 7 : Complexes de cuivre utilisés dans cette étude

L'un des complexes synthétisés, contenant un coordinat imidazolylidène (voir encadré, Figure 7), s'est avéré très efficace pour l'hydrosilylation de l'acétophénone avec du triéthylsilane comme source d'hydrure (Tableau 2). Le système correspondant est particulièrement stable.

Tableau 2: Tests préliminaires d'hydrosilylation de l'acétophénone[a]



Entrée	Complexe (charge)	Temp. [°C]	t (h)	Conv. [%][b]
1	–	65	24	0
2	**CuCl** (9 mol%)	65	24	0
3	**[CuCl(imidazolylidene EF/EF)]**(3 mol%)	25	3	**93**
4	[CuCl(IPr)] (3 mol%)	25	3	**97**
5	**[CuCl(imidazolylidene EF/EF)]** (0.25 mol%)	65	24	**97**
6	**[CuCl(imidazolylidene EF/EF)]** (0.1 mol%)	65	70	**<99**
7	[CuCl(IPr)] (0.25 mol%)	65	24	**35**

[a]Complexe (0.25 – 3 mol%), *t*-BuOK (12 mol%), Et_3SiH (6 mmol), THF (2 mL), acétophenone (2 mmol) ; [b] Conversions déterminées par RMN ^1H.

La stabilité remarquable de l'espèce active (Tableau 2, entrées 5, 6) résulte probablement de la capacité des plans fluorényle à protéger l'atome de cuivre durant le cycle catalytique

en formant un complexe de type sandwich (Schéma 10) analogue à celui observé au chapitre III pour un complexe d'argent(I). Une contribution additionnelle par des interactions CH···M mettant en jeu un comportement "colibri" du ligand tel que décrit au chapitre IV ne peut pas être exclue.

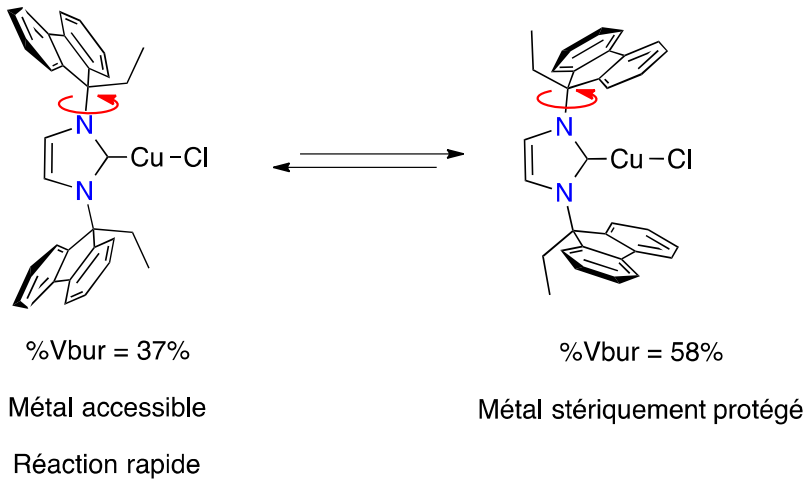


Schéma 10 : Encombrement stérique variable dans le complexe [CuCl(imidazolylidène Ef/EF)].

Alors qu'un comportement "sandwich" du ligand (correspondant à $\%V\text{bur}_{max}$ = 58%) assure une protection stérique efficace du centre métallique, l'adoption d'une conformation moins encombrée ($\%V\text{bur}_{min}$ = 37%), c'est-à-dire où les groupes éthyle pointent vers le métal, semble nécessaire pour permettre l'approche des substrats, surtout si ceux-ci sont de grande taille (Tableau 2).

Le caractère modulable de l'encombrement stérique de ce ligand (qui est donc une propriété susceptible d'assurer la stabilité d'espèces intermédiaires), nous a naturellement conduit à étendre le champ réactionnel des réactions d'hydrosylilation à des cétones plus encombrées ainsi qu'à des aldéhydes aromatiques. Dans tous ces cas, d'excellents rendements ont été obtenus, et ce avec de faibles charges de catalyseur (Schéma 11).

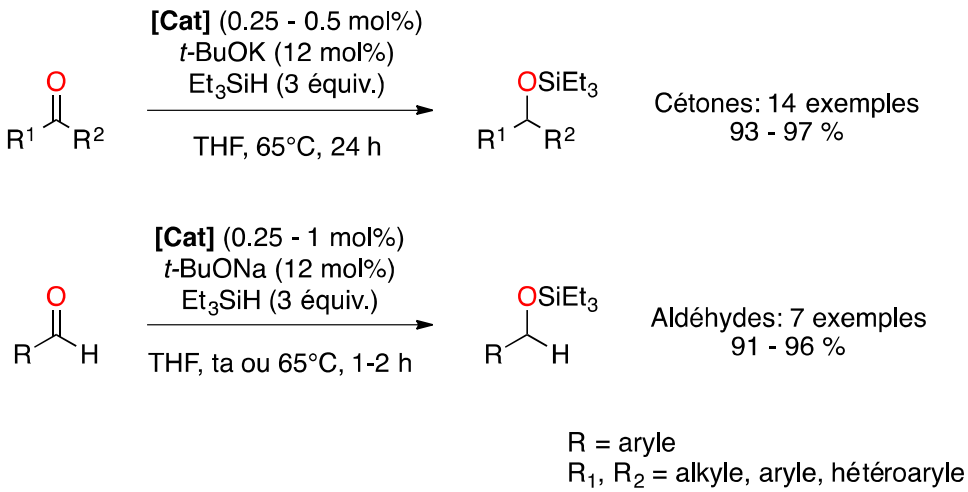


Schéma 11 : Conditions générales pour l'hydrosilylation de composés carbonylés

Cette étude a été entreprise dans le but de développer des catalyseurs d'hydrosilylation plus économiques que ceux généralement utilisés, à base de rhodium ou de ruthénium. Elle démontre le potentiel des systèmes étudiés.

Contents

General Introduction

General Introduction:

Abstract

This thesis deals with a series of new *N*-heterocyclic carbene (NHC) ligands substituted by expanded 9-alkyl-9-fluorenyl groups. Special focus has been put on the steric properties of these ligands and their influence on catalytic reactions involving palladium and copper centres.

Considering the large number of scientific papers and book chapters discussing all aspects of the *N*-heterocyclic carbene chemistry, the following introduction will only give a brief historical overview on carbene chemistry and carbene-metal bonds. The most common procedures for the synthesis of complexes containing NHC ligands will be presented and standard methods aimed at quantifying the steric and electronic properties of these species will be discussed. Finally, the beneficial impact resulting from the use of *sterically demanding* NHCs in some challenging metal-catalysed transformations will be highlighted.

I - Historical aspects of carbenes

Carbene compounds are defined as neutral organic species featuring a divalent carbon atom with two unshared electrons. They have been used as highly reactive synthetic tools for a century, especially in cyclopropanation reactions.[1-3] Methylidene (CH_2:) and dichlorocarbene (Cl_2C:) are the simplest members of this class of compounds, obtained respectively by from decomposition of diazomethane and deprotonation of chloroform.

Considered as highly unstable species, free carbenes could not be isolated easily, however, their metal complexes have been known for decades (Figure 1).

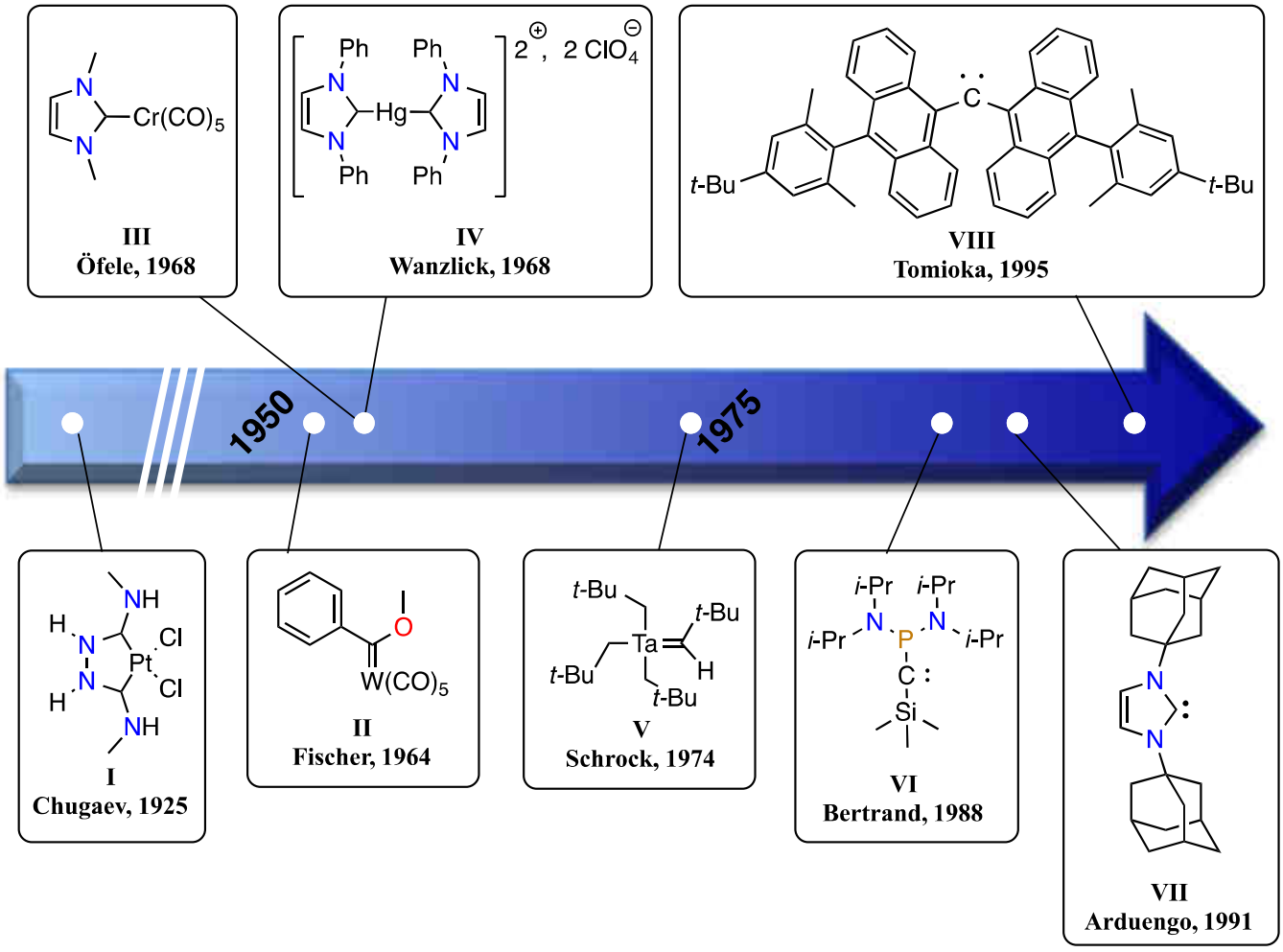
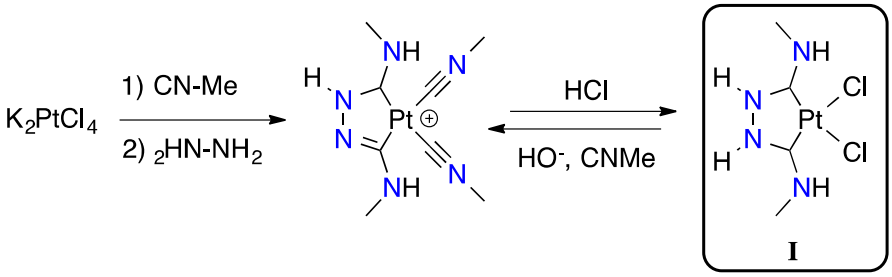


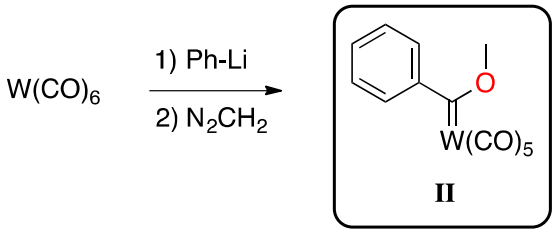
Figure 1: Important milestones in carbene chemistry

In 1925, Chugaev synthesised the first NHC complex.[4] Compound **I** was obtained from K_2PtCl_4 according to Scheme 1. However, this complex could not be unambiguously characterised before the early 70's.[5-7]



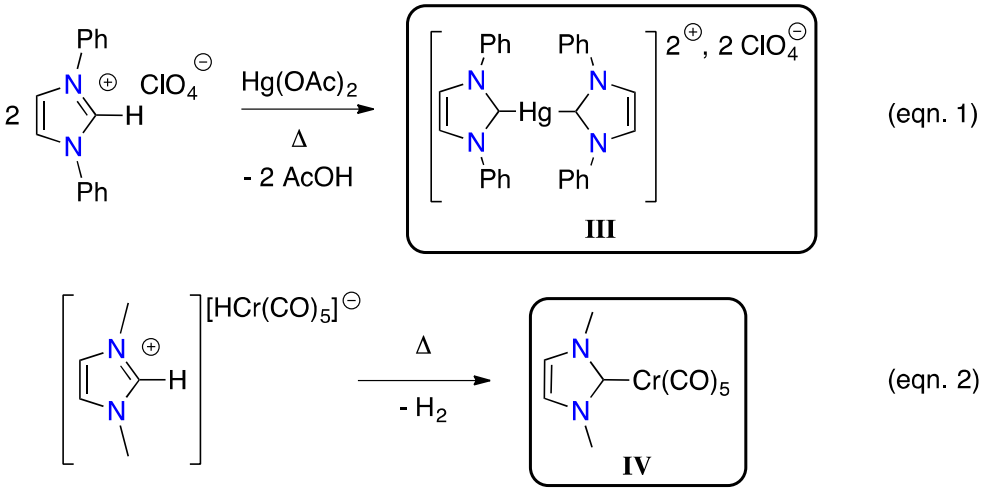
Scheme 1: Synthesis of Chugaev's carbene complex.

In 1964, Fischer *et al.* achieved the synthesis of carbene complex **II,** by successive addition of phenyl lithium and diazomethane to a tungsten hexacarbonyl complex (Scheme 2).[8]



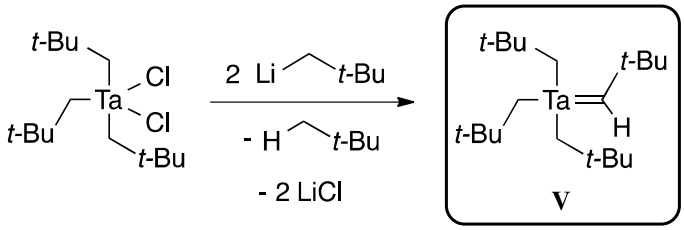
Scheme 2: Synthesis of the first Fischer-type carbene complex.

The first *N*-heterocyclic carbene complexes (**III** and **IV**), were reported in 1968 respectively by Wanzlick *et al.* (eqn. 1),[9] and Öfele (eqn. 2)[10] by mixing imidazolium salts with basic metal precursors (Scheme 3).



Scheme 3: Synthesis of the first *N*-heterocyclic carbene complexes.

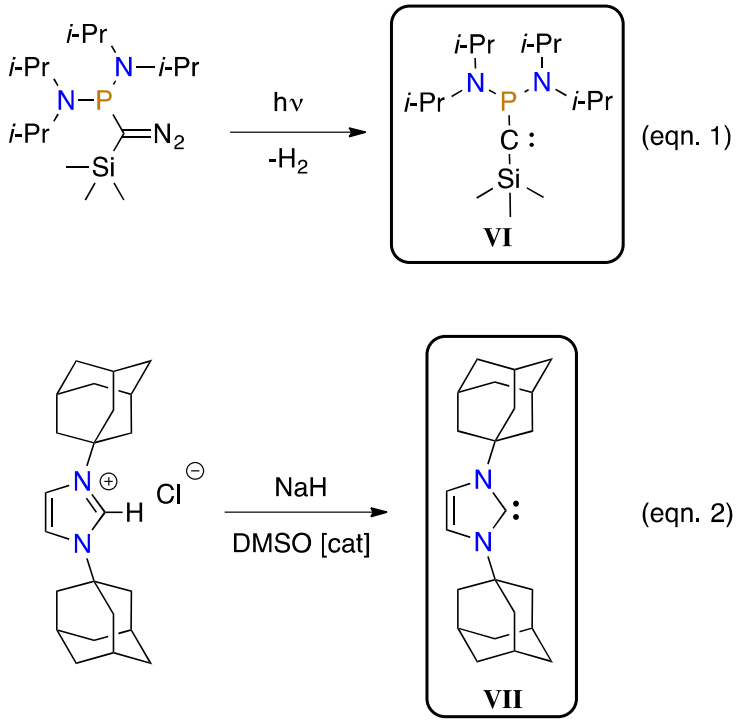
In 1974, Schrock *et al.* prepared the first triplet carbene complex (**V**).[11] It was obtained by α-hydrogen abstraction in a neopentyl tantalum(V) (Scheme 4).



Scheme 4: Synthesis of the first Schrock-type carbene complex.

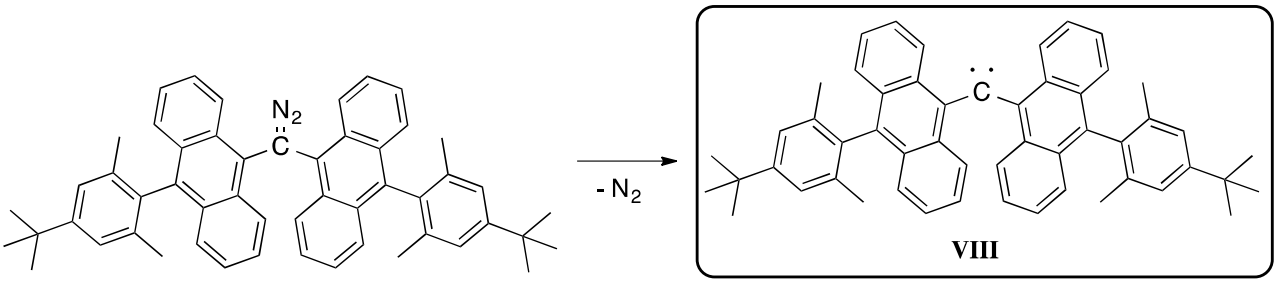
In 1988, Bertrand isolated the first stable free singlet carbene (**VI)** (Scheme 5, eqn. 1).[12] Favourable interactions with adjacent silicon and phosphorus atoms were responsible for the extended stability of in this linear species, which does not behave as a ligand. These investigations proved that free carbenes are not invariably transient species.

Three years later, Arduengo reported the relatively simple synthesis of the first "bottelable" free carbene (**VII)**, by deprotonation of an imidazolium precursor (Scheme 5, eqn. 2).[13] The structure of this carbene incorporated into a nitrogen heterocycle was unambiguously determined by X-ray diffraction studies.



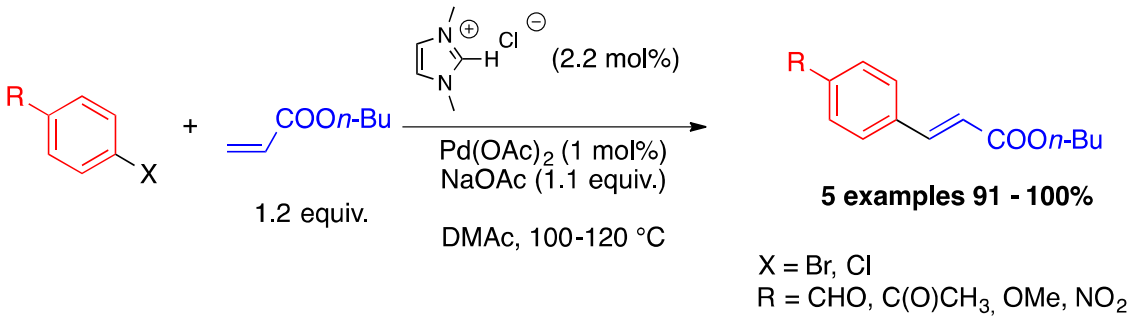
Scheme 5: Synthesis of the first stable free carbenes.

In 1995, Tomioka *et al.* synthesised the first stable triplet carbene. Compound **VIII** was obtained from the appropriate diazo precursor and benefited from a steric and electronic stabilisation by the substituents of the carbenic C atom (Scheme 6).



Scheme 6: First stable free triplet carbene.

Quickly after this discovery, Herrmann *et al.* reported the first catalytic systems using *in situ* generated NHC-Pd complexes (Scheme 7).[14]



Scheme 7: Example of a catalytic system using NHC ligands.

At this time, homogeneous catalysis was dominated by the use of phosphine ligands. With NHCs, the catalytic systems studied by Hermann displayed extended stability even at high temperature, thus enabling the use of low amounts of metal precursor (< 1 mol%). In addition, less reactive aryl chlorides could be activated under these conditions.

This early report pointed out the promising / superior role of NHCs as spectator ligands in this field of application.

The seminal reports of Arduengo and Herrmann led to an explosion of theoretical and expermiental studies, which precipitated the synthesis and analysis of a large variety of NHC derivatives. In the present work, the large range of applications of *N*-heterocyclic carbenes will be limited to NHC-transition metal complexes and their use in catalytic reactions.

II - Theoretical aspects

II - A) Ground state multiplicity

As defined above, carbenes are neutral organic species featuring a divalent carbon atom with two unshared electrons. In most cases, the two non-bonding orbitals are degenerate and are traditionally called p_π and σ. Two types of carbenes can be distinguished depending on the distribution of the valence electrons in p_π and σ (Figure 2): triplet carbenes, with unpaired electrons in separate orbitals ($\sigma^1\pi^1$) and singlet carbenes, with both electrons paired with antiparallel spin orientations ($\sigma^2\pi^0$).

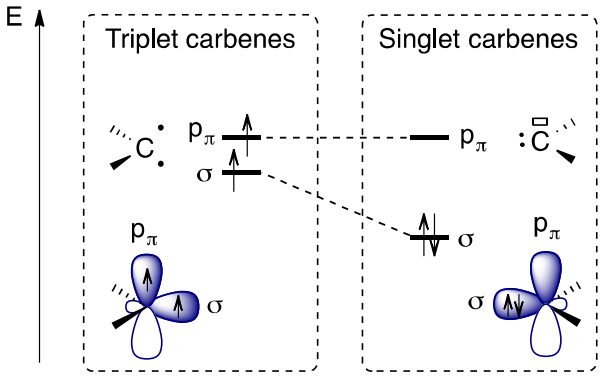


Figure 2: Triplet carbenes and singlet carbenes.

In 1968, Hoffmann *et al.* showed that the ground state multiplicity (triplet *vs.* singlet carbenes) is controlled by the p_π-σ energy gap.[15-17] Indeed, high energy gaps (more than 2 eV) favour singlet states, whereas low energy gaps (under 1.5 eV) favour triplet states. It is now well-established that adjacent σ-electron withdrawing[18-21] and π-electron-donating substituents[15, 22] increase this p_π-σ energy gap, thus favouring the singlet ground state (Figure 3). Notably, π interactions prevail over σ interactions.

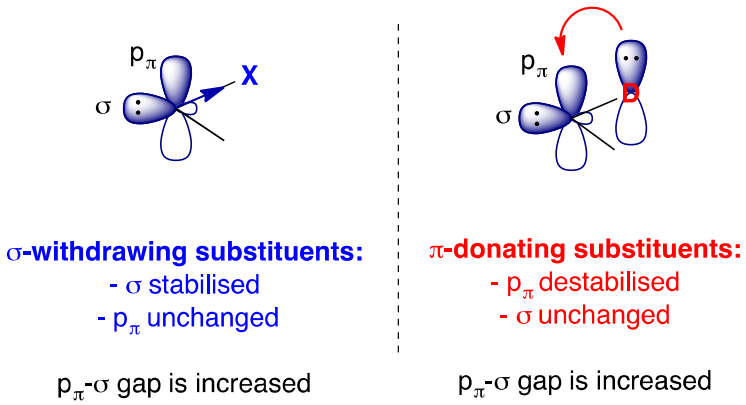


Figure 3: Influence of the electronic interactions on the stabilisation of singlet carbenes.

II - B) Schrock *vs.* Fischer-type carbenes

Schrock-type carbenes are triplet carbenes. They benefit from low electronic stabilisation by the α-substituents, resulting in a small p_π-σ energy gap and two singly occupied molecular orbitals. They are highly reactive and electrophilic carbenes.[23]

On the other hand, Fischer-type carbenes are singlet carbenes. In these species, the α-substituent is an heteroatom with σ-electron withdrawing and π-electron-donating properties. This increases the p_π-σ energy gap, resulting in paired valence electrons in the σ orbital. They are nucleophilic compounds.[23]

Although free Schrock and Fischer-type carbenes are difficult to isolate as such, their stabilisation through metal coordination has been observed decades ago (Figure 4).

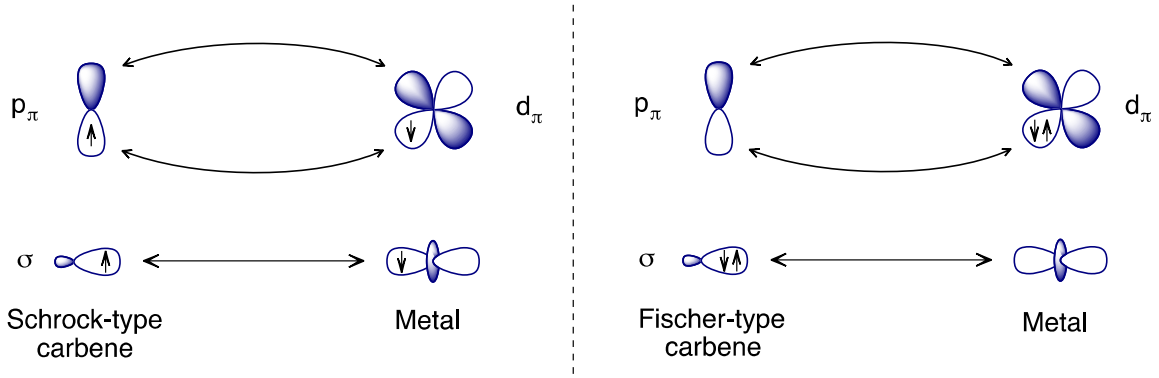


Figure 4: Orbital interactions in Schrock and Fischer-type carbene complexes

Schrock-type carbenes complexes are stabilised *via* interactions of the singly occupied σ and p_π orbitals with distinct singly occupied metal orbitals (d_σ and d_π), resulting in a carbene metal double bond (Figure 4, left). Therefore, Schrock-type carbenes do not freely rotate around the carbene-metal bond.

Fischer-type carbene complexes are stabilised by interaction of the filled σ orbital with a vacant metal orbital and additional π-back donation from a filled d_π metal orbital to the vacant p_π orbital (Figure 4, right). Overall, the metal-ligand bond acquires some multiple bond character and the rotation of Fischer type carbenes around the carbene-metal bond is prevented.

II - C) *N*-Heterocyclic carbenes

Structurally similar to Fischer-type carbenes, *N*-heterocyclic carbenes are persistent singlet carbenes incorporated in a heterocycle. They benefit from a superior heteroatom stabilising effect due to the presence one or two adjacent nitrogen atoms (Figure 5).

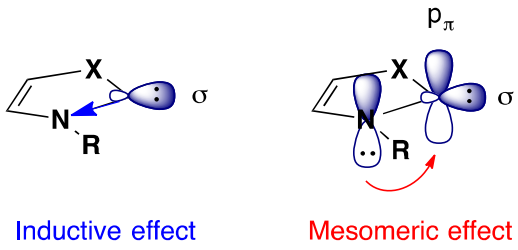
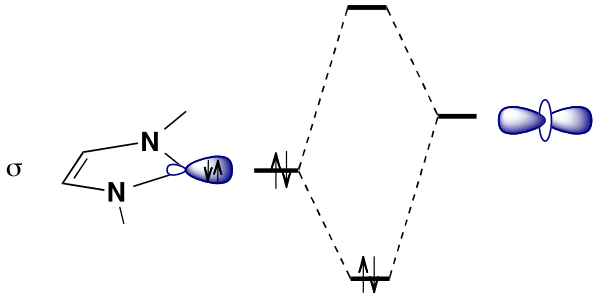


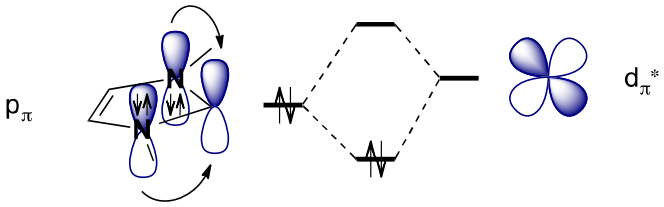
Figure 5: Electronic stabilisation in NHCs (X = NR, S, O, CR_2; R = alkyl, aryl, heteroaryl).

In order to characterise NHC-metal bonding, three different orbital interactions have to be considered (Figure 6).

a) NHC ➔ M σ-donation



b) NHC ➔ M π-donation



c) M ➔ NHC π-back donation

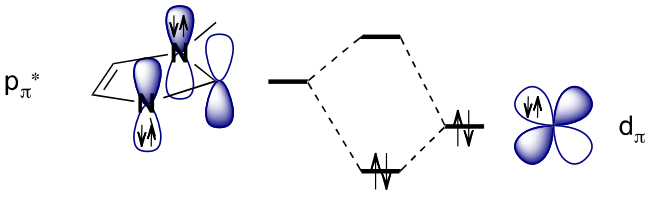
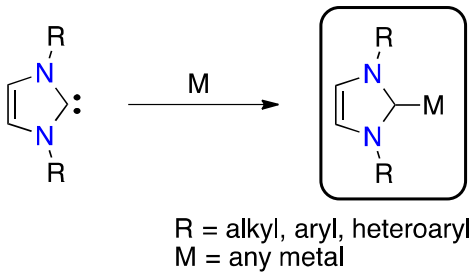


Figure 6: Orbital interactions in NHC-M complexes, partial diagram orbital.

Initially, the NHC-metal bond was assumed to result from pure σ interactions (Figure 6, (a)). However, recent studies showed that additional NHC-metal π-donation (Figure 6, (b)) and metal-NHC π-back donation (Figure 6, (c)) could be responsible for up to 20% of the total bond strength in extreme cases (with heavy metals, electron-rich or electron poor metal centres).[24] It is worth mentioning that these π interactions do not prevent NHCs from freely rotating around the ligand-metal bond, meaning that no multiple bond character is operative. Consequently, NHC complexes are traditionally drawn with a single ligand-metal bond.

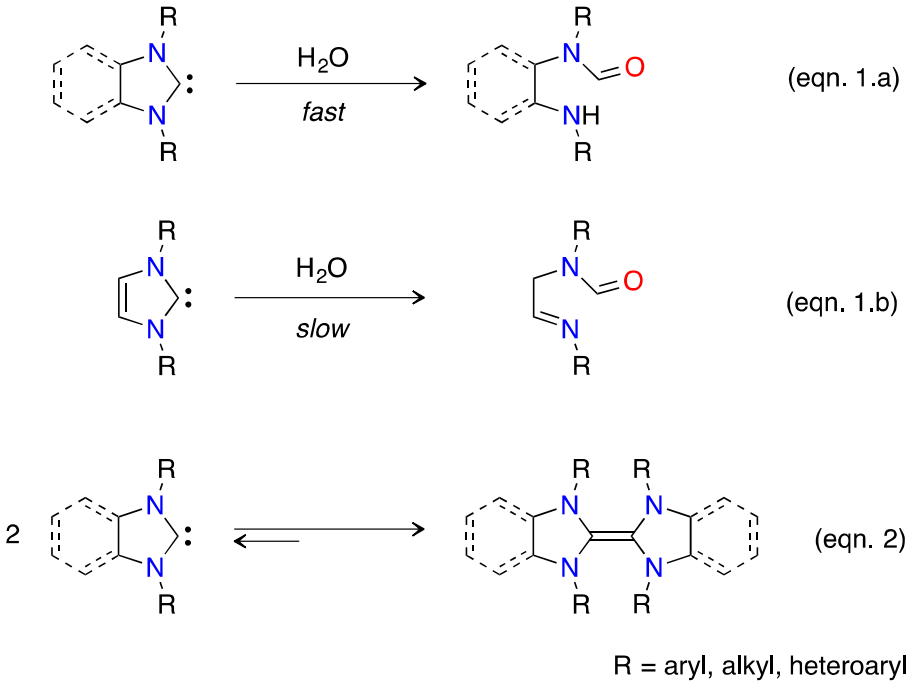
III - Synthesis of NHC-metal complexes

Free NHCs react with a broad range of organometallic precursors, either by direct coordination[25-33] or by displacement of a neutral 2e- ligand (pyridine, nitrile, phosphine, tetrahydrofuran (THF), carbon monoxide (CO), sulphide, sulfoxide, dinuclear complexes with bridging ligands, etc.).[34-46] The coordination sphere of the metal is not relevant in the following section and will therefore be omitted for clarity (Scheme 8).



Scheme 8: Synthesis of NHC complexes from free carbenes.

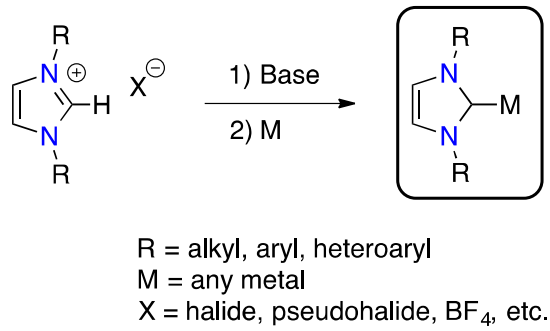
Although free NHCs are persistent in solution and in the solid state, they are still highly moisture-sensitive (Scheme 9, eqn. 1.a and 1.b)[47] and require handling under inert conditions. Their hydrolysis occurs *via* either insertion of the carbene into H_2O, or by nucleophilic addition of hydroxyde anion, leading to formamide degradation product. In addition, their propensity to dimerise has also been demonstrated (Scheme 9, eqn. 2).[48]



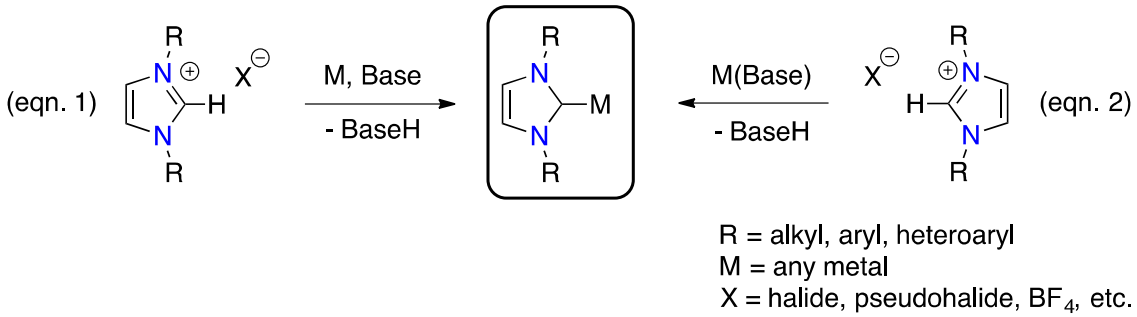
Scheme 9: Hydrolysis of diaminocarbenes (eqn. 1), dimerisation of carbenes (eqn. 2).

To limit this problem, free NHCs are either freshly prepared prior to use or *in situ* generated before metal coordination (Scheme 10).

Free *N*-heterocyclic carbenes are strong neutral bases (pKa (in water) ≈ 17-28),[49] meaning that they can be routinely obtained by treatment of suitable azolium cations with strong bases (NaH, *t*-BuOK, LiHMDS, KHMDS, BuLi, etc.) Straightforward *one-pot* reactions have also been developed (Scheme 11).



Scheme 10: *In situ* generation of free NHCs followed by metal coordination.

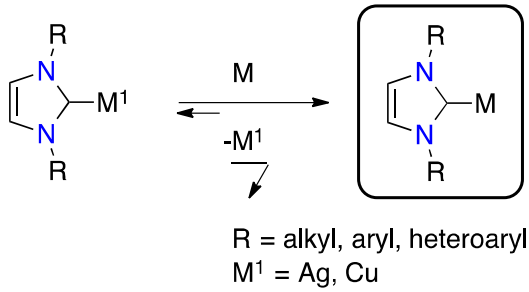


Scheme 11: *One-pot* synthesis of NHC complexes from azolium cations.

A first method consists in mixing the azolium salt and an external base in the presence of a metal precursor, resulting in the direct coordination of the *in situ* generated free carbene (Scheme 11, eqn. 1).[50-57]

A second strategy involves metal precursors containing a basic ligand (Scheme 11, eqn. 2). They readily react with azolium cations to yield the targeted complexes.[9, 10, 36, 39, 53, 57-78]

In some cases, assembling free NHCs and metal precursors can be problematic especially with *N*-heterocyclic carbenes having acidic functional groups such as enolisable protons.[79, 80] An alternative strategy makes use of transmetallation reagents to synthesise targeted NHC complexes (Scheme 12).



Scheme 12: Preparation of NHC-metal complexes by transmetallation

The most encountered transfer reagents are NHC-silver complexes.[36, 61, 63, 81-86] They are air-, moisture-stable and easily obtained by treatment of azolium salts with basic silver salt.[67, 70]

In the presence of a metal precursor displaying higher electronegativity, the NHC-Ag bond is broken and the ligand is transferred to the targeted metal centre with concomitant precipitation of silver salts.

Recently, Albrecht *et al.* reported that similar NHC-copper compounds were suitable transfer reagents for the synthesis of NHC-ruthenium complexes[87] and Cazin *et al.* extended this methodology to prepare gold and palladium complexes in high yields.[65]

IV - Diversity of NHCs

IV - A) Conventional NHCs

Traditionally, the term "conventional NHC" refers to any cyclic carbene with two adjacent heteroatoms, at least one of them being a nitrogen atom. This definitions includes fused and saturated derivatives and expanded NHCs (6-,7-, or 8-membered *N*-heterocyclic carbenes) (Figure 7).

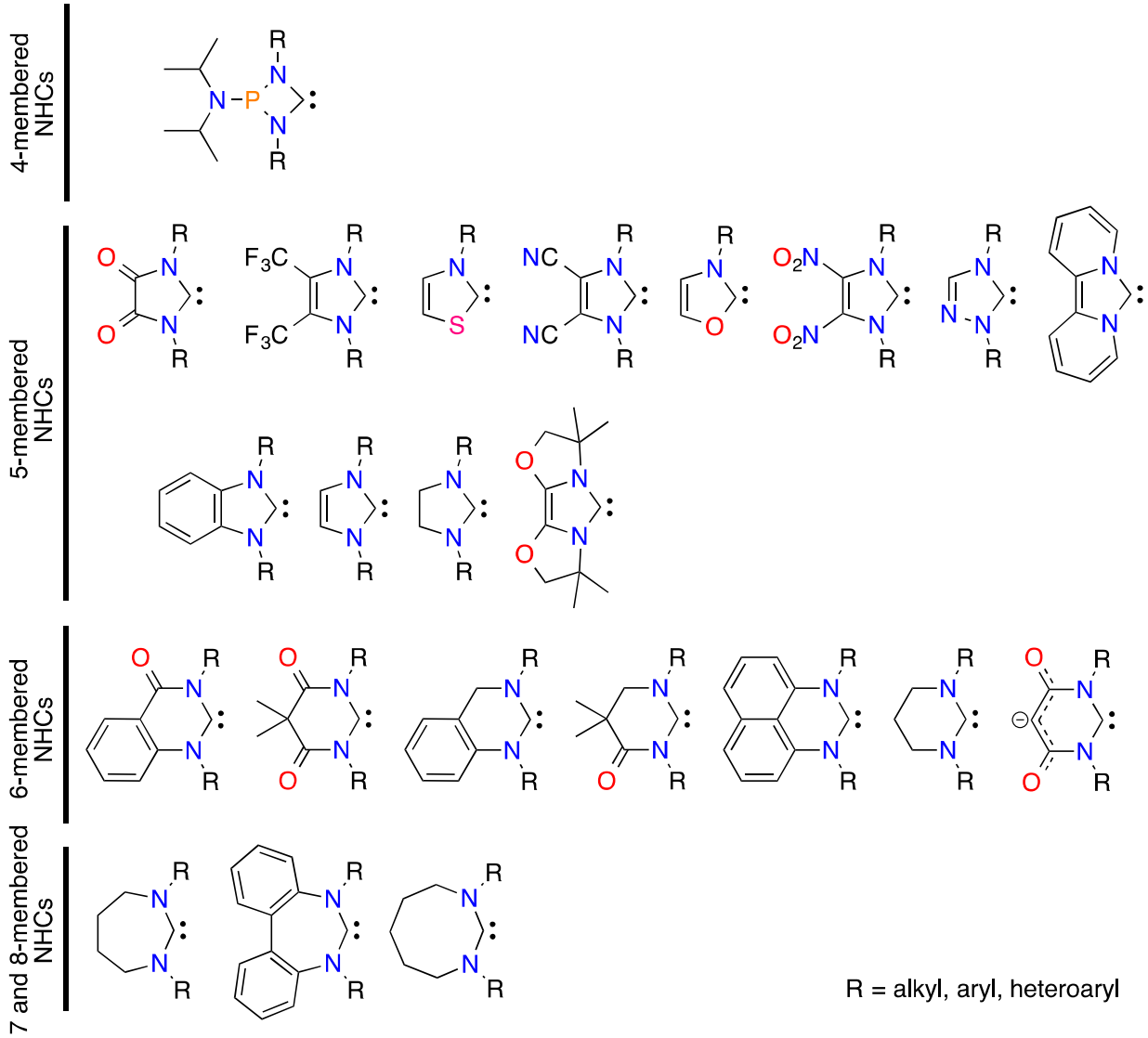


Figure 7: Conventional NHCs.

IV - B) Non-conventional NHCs

The term "non-conventional NHC" is used for designating non-cyclic diaminocarbenes, and cyclic / non-cyclic carbenes in which the carbenic C atom is bonded to less than two N atoms (Figure 8).

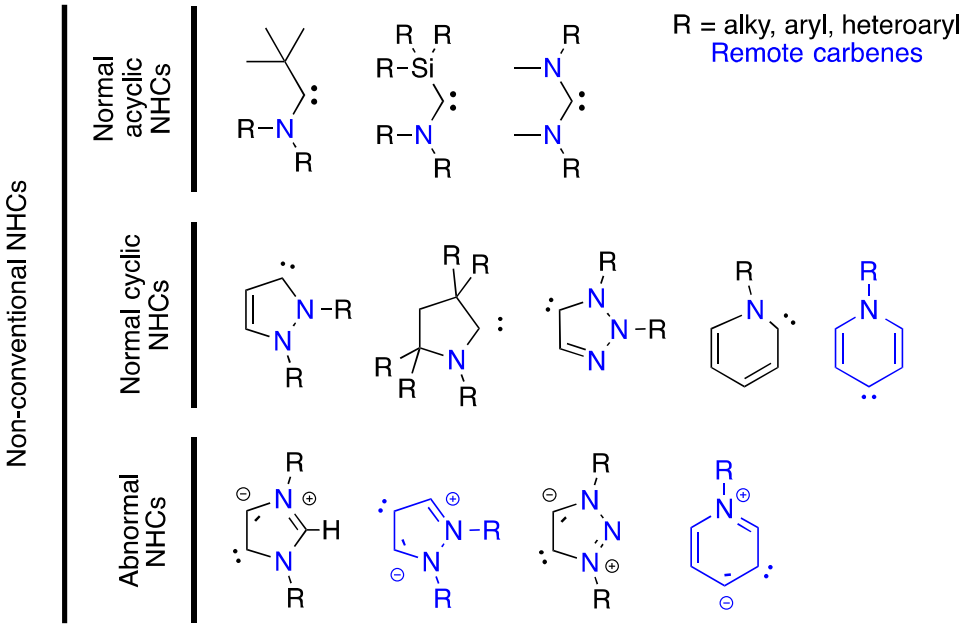


Figure 8: Non-conventional NHCs.

Some non-conventional NHCs are classified as normal carbenes (*n*NHCs), meaning that they can be represented by at least one neutral mesomeric form.

By essence, normal acyclic carbenes do not belong to the *N*-heterocyclic carbenes family even though they have two adjacent nitrogen atoms. The first acyclic diaminocarbene was reported almost 20 years ago by Orpen *et al.*[88] whereas Bertrand synthesised the first acyclic(alkyl)(amino)carbene in 2004.[89]

In contrary, abnormal NHCs (*a*NHCs) – also called mesoionic carbenes (MICs) – are compounds in which resonance structures cannot be drawn without adding formal charges to the molecule**.** The first example of a stable abnormal carbene was reported in 2009 by Bertrand *et al.*,[90] but *a*NHCs had already been observed in the early 2000's by Crabtree[91, 92] and Meyer[93, 94] with poly-NHCs.

Remote carbenes (*r*NHCs) have zero stabilising α-heteroatom and can be either normal or abnormal NHCs (Figure 8, in blue). The first example was reported in 2009 by Herrmann *et al.*[95]

Extending the diversity of *N*-Heterocyclic carbenes was mainly driven by the strong desire to investigate the structure-activity relationship in organometallic catalysis.

Among the large number of NHC derivatives described in the literature, 5-membered diaminocarbenes are most commonly used and imidazole-2-ylidene or imidazolin-2-ylidene derivatives have found widespread applications in homogeneous catalysis (Figure 9).[73, 96-105]

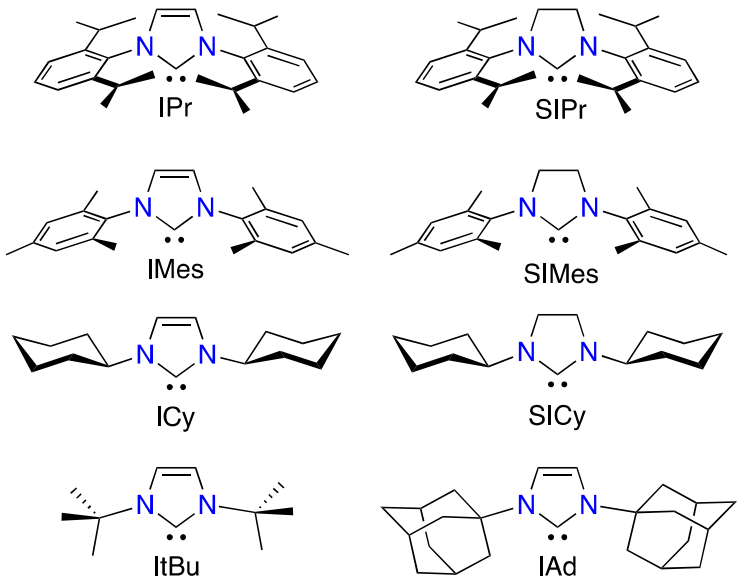


Figure 9: Most commonly used NHCs and their acronyms.

V - Electronic and steric properties of NHCs

Controlling the electronic and steric properties of a metal centre is crucial to rationalise or anticipate the catalytic behaviour of organometallic catalysts. As for phosphine ligands, spectroscopic and physico-chemical methods aimed at quantifying these parameters have been developed with NHCs.

First attempts to determine the intrinsic properties of *N*-heterocyclic carbenes were achieved by comparing bond dissociation energy values (BDEs) in their corresponding metal complexes.[106] As observed by Cavallo *et al.* for all NHCs tested in his study (except for the most sterically hindered adamantyl substituted imidazolylidene in which unfavourable steric interactions have to be considered), *N*-heterocyclic carbenes make stronger coordination bonds than even the most Lewis-basic phosphines (PCy_3). This feature was experimentally proven by Herrmann *et al.* with thermally and oxidatively more stable NHC-based catalysts compared to phosphine ones.[14]

V - A) Electronic parameters

V - A) 1) Tolman Electronic Parameter (TEP)

In 1977, Tolman *et al.* discussed the utility of R_3P-$M(CO)_x$ complexes to determine the electron-donating ability of phosphines.[107] Measuring the TEP allows quantification of these donating properties by measuring the IR frequency of other coordinated carbonyl ligands (Figure 10).

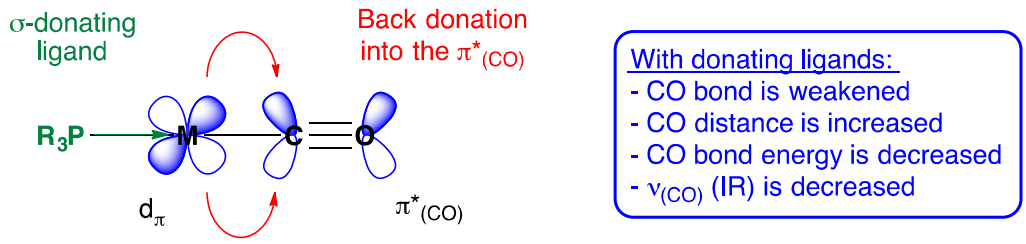


Figure 10: Orbital interactions in L-M-CO systems (L = Phosphine) (M = Ir, Ni, Ru, Rh, etc.), influence of the donating properties of phosphines on the $\nu_{(CO)}$.

In these systems, π-back donation from electron-rich metals into the empty $\pi^*_{(CO)}$ orbitals lowers C-O bond energies. Consequently, the more electron-donating the phosphine is, the lower the ν_{CO} and the TEP are. This method was successfully extended to NHC-$M(CO)_x$ complexes,[49, 108, 109] thus allowing direct comparison between the electronic properties of various phosphine and NHC ligands (Figure 11).

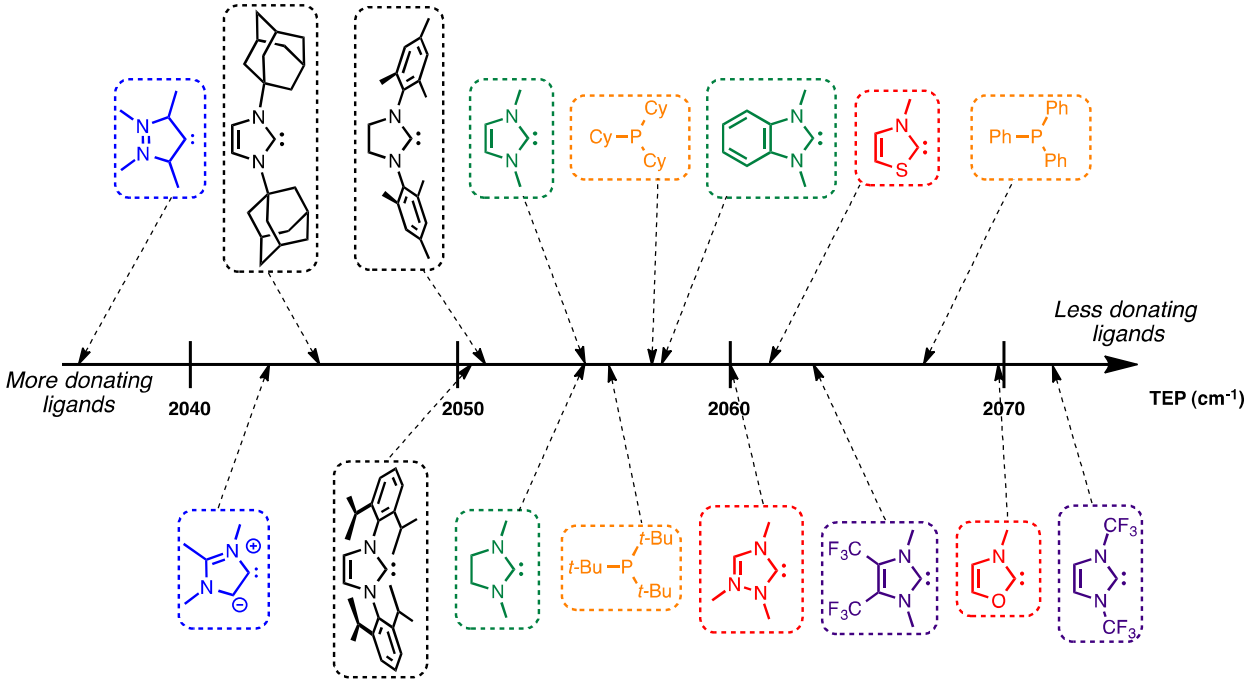


Figure 11: TEP values for various NHCs and phosphines (cm^{-1}).[109]

As depicted above, classically used NHC ligands (in black) are stronger donors than even the most basic phosphines (in orange). In addition, the number and the identity of the heteroatoms within the heterocycle (see red compounds), the nature of the heterocycle (see green compounds) and its substitution pattern (see purple compounds) strongly influence the donating properties of NHCs. Moreover, non-conventional carbenes (in blue) are more electron-rich than conventional NHCs. It is worth mentioning that the donating properties of *N*-heterocyclic carbenes also increase with the size of the heterocycle.[110]

V - A) 2) Other methods for assessing the donor strength of NHCs

Other methods based on ^{13}C NMR spectroscopy[111, 112] or pKa measurements[49] have also been developed, but are less employed.

V - B) Steric parameters

The conceptual percent buried volume (%*V*bur) was introduced in 2005 by Cavallo *et al*.[106] to measure the bulk of a ligand from its solid-state coordinates. It determines the proportion of space that is occupied by a ligand inside a hypothetical sphere centered on the metal atom (Figure 12) (most often, the metal-C separation (d) is fixed at 2.1 Å, that of the sphere radius (r) at 3.5 Å)

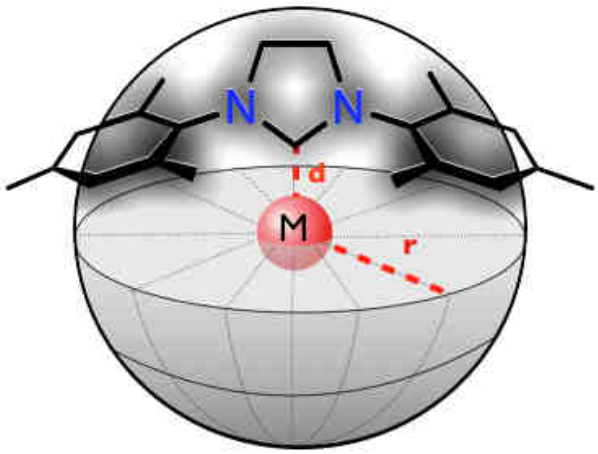


Figure 12: Representation of the conceptual percent buried volume (%*V*bur) (d = 2.1 Å, sphere radius (r) = 3.5 Å).

Interestingly, this method can be applied to phosphines, thus allowing direct comparison between ligands of both types (Figure 13).

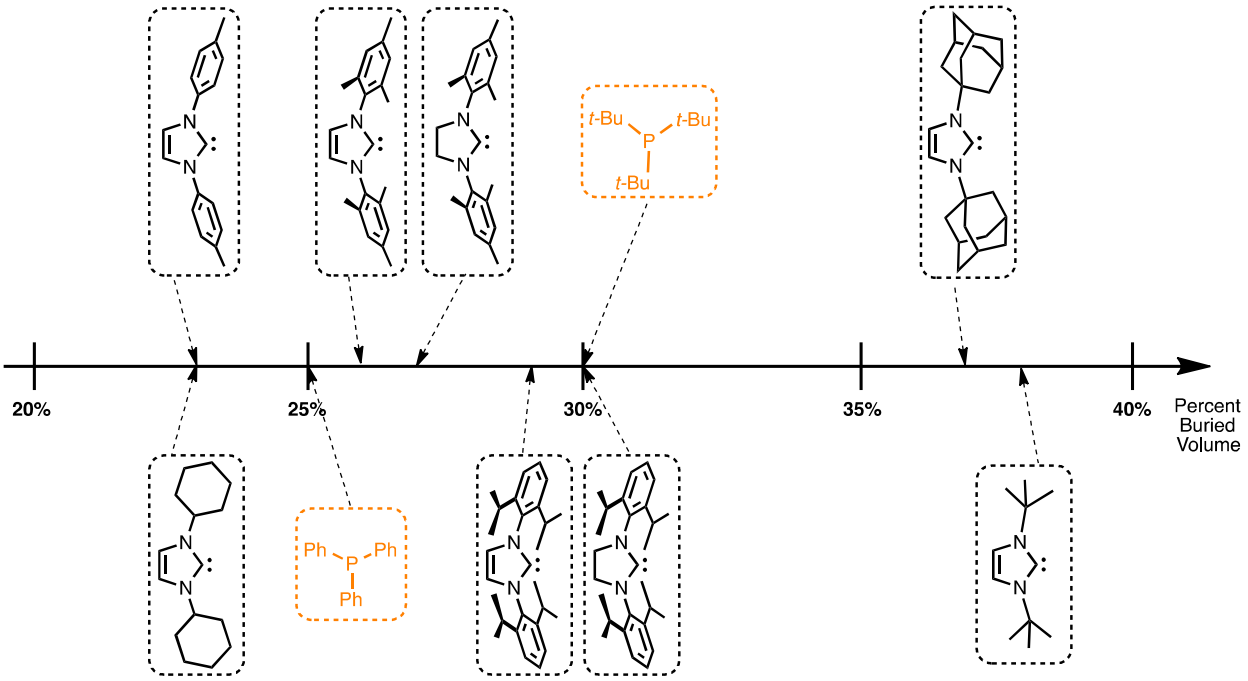


Figure 13: Percent buried volume of common NHCs and phosphines.[106]

As observed in Figure 13, the percent buried volume displayed by NHCs increases with the size of the *N*-substituents. For phosphine ligands, the very bulky P(*t*-Bu)$_3$ best compares with IPr (or SIPr), whereas the percent buried volume calculated for PPh_3 is similar to that of IMes (or ICy).

V - C) NHCs *vs.* phosphines

NHCs have been considered as phosphine mimics for a long time. However, the previous part showed significant differences between these classes of ligands in terms of electron-donating ability, steric and electronic properties.

Another disparity between these species involves their preparation. Indeed, large arrays of synthetic protocols have been reported for the synthesis of NHCs,[113-127] whereas the development of a phosphine is not always trivial. In addition, contrary to phosphines for which changing the substituents invariably affects both electronic and steric properties, the possibility to separately change the *N*-substituents, the backbone substitution pattern or the class of heterocycle allows modifications of each parameter more independently.

This feature is of major interest when synthesising ligands with finely tuned electronic and steric properties, thus ensuing the best possible control of their catalytic behaviour.

VI - Homogeneous catalysis

The particular properties of NHC complexes have led to a number of applications in homogeneous catalysis. For many reactions, NHC-metal complexes are nowadays preferred over phosphine-based systems.

VI - A) Definitions

The efficiency of a catalyst is a relative concept. It has been described as the combination of three parameters, namely the activity, the stability and the selectivity (Figure 14).[128]

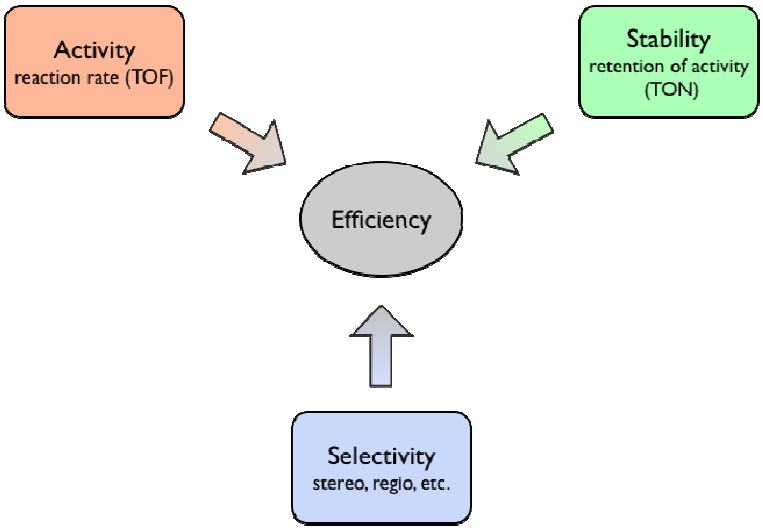


Figure 14: Three parameters defining the efficiency of a catalyst.

In organometallic catalysis, the activity of a catalyst refers to the reaction rate. It can be quantified by its turnover frequency (TOF), which measures the number of catalytic transformations realised by time unit.

The stability of a catalyst (or the retention of activity) is related to its lifetime. It is best described by the turnover number (TON), which measures the maximum number of substrate molecules converted to the product by a catalytic site before becoming inactive.

The selectivity of a catalyst can be divided in different classes with stereo-, chemo- and regioselectivity as examples. The stereoselectivity (enantio-, diastereo-) of a catalyst reflects its ability to induce chirality at a prochiral position. Chemoselectivity is the ability

for a catalyst to preferably react with specific chemical groups, whereas regioselectivity is the ability to discriminate similar reactive positions (the two sides of an olefin for instance).

In transition metal catalysis, fine-tuning of the steric and electronic environment of metal centres is mandatory to tailor the reactivity of the active species. In a laboratory, the ideal parameters are usually found *via* "ligand screening", meaning that various ligands with distinct properties are employed in a same model reaction and the optimal metal-ligand association is determined experimentally (better stability of the catalyst, higher activity or selectivity).

Regarding the abovementioned characteristics of organometallic complexes containing NHC ligands, the development of these species has led to the design of more active, stable and/or selective catalytic systems. Among transition metal catalysed reactions employing NHCs as ligands, ruthenium catalysed olefin metathesis and palladium catalysed cross-coupling reactions have largely benefited from the development of *N*-heterocyclic carbenes. For these reactions, the most challenging syntheses were successfully achieved by fine-tuning of ligand properties.

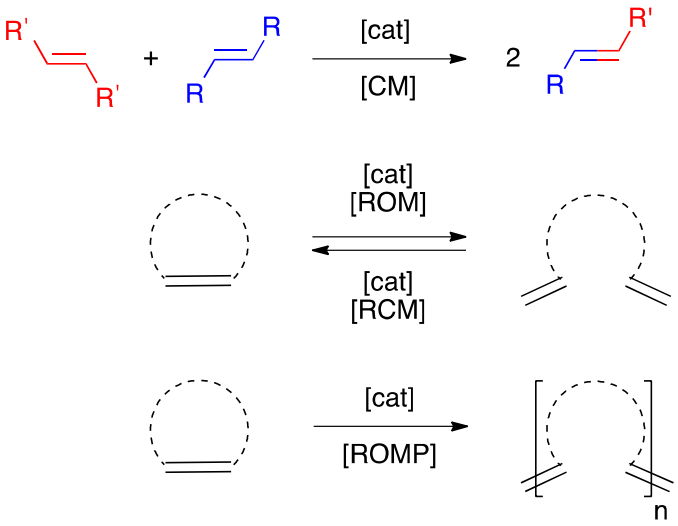
The following part will describe these "success stories" with a special emphasis on the role of the steric and electronic properties of the NHC ligand in catalysis.

VI - B) Ruthenium-catalysed olefin metathesis

VI - B) 1) Historical aspects

Among the large array of transition metal catalysed transformations, olefin metathesis is among the most famous. This reaction was initially applied in cross-metathesis (CM) reactions to form heavier olefins, but it has found further applications in organic synthesis, namely in ring-opening cross-metathesis (ROCM) and ring closing metathesis (RCM), as well as in polymer chemistry with ring-opening metathesis polymerisation reactions (ROMP) (Scheme 13).

In 2005, the Nobel prize in chemistry was jointly awarded to Robert H. Grubbs[129] and Richard R. Schrock[130] respectively for the development of ruthenium and molybdenum based olefin metathesis catalyst, and to Yves Chauvin for determining the mechanism of the reaction (Figure 15).[131, 132]



Scheme 13: Most important ruthenium-catalysed olefin metathesis reactions.

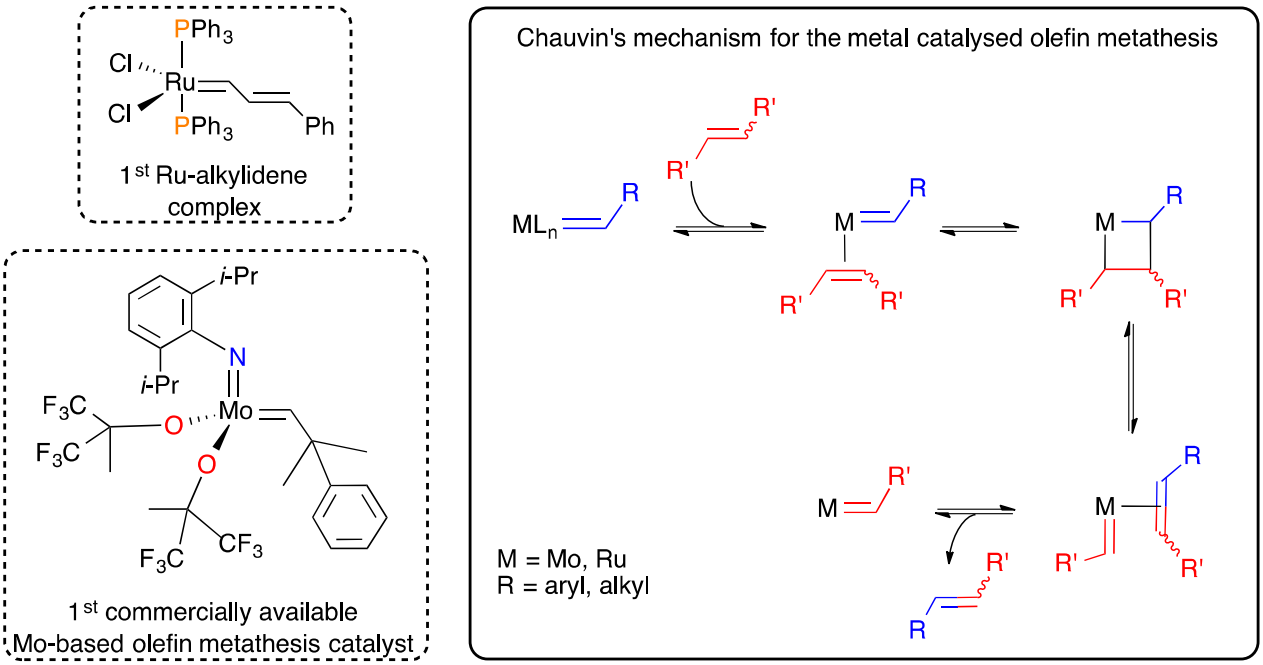


Figure 15: Mo and Ru based olefin metathesis catalysts and mechanism.

The first ruthenium alkylidene complex was synthesised in 1992 by Grubbs *et al.* (Figure 16). However, this ruthenium complex showed relatively low activity for the catalytic ring-opening cross-metathesis (ROCM), its scope being limited to highly strained cyclic olefins such as norbornene.[133]

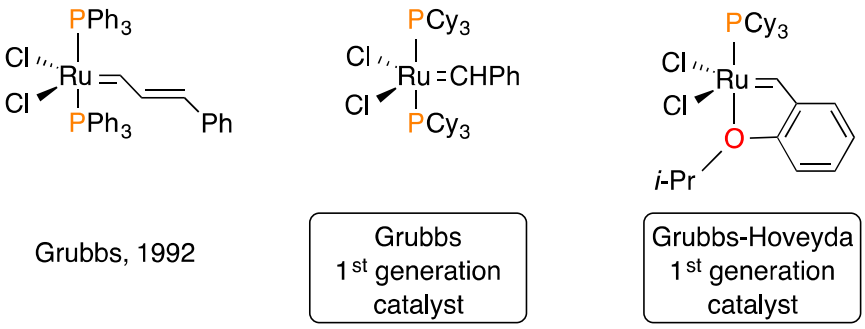
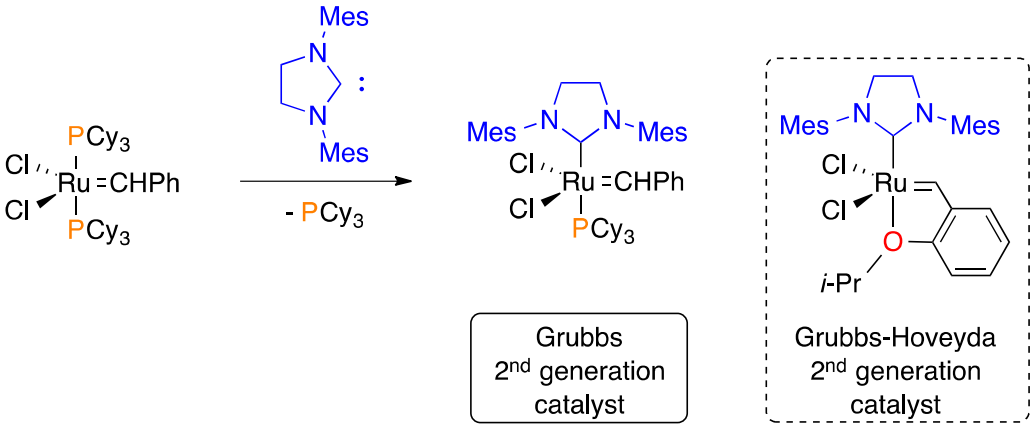


Figure 16: 1st Ru-alkylidene complex; 1st generation olefin metathesis catalysts.

The synthesis of an analogue in which the PPh_3 ligands had been replaced by PCy_3 resulted in a catalyst with higher activity, better thermal stability, and broader substrate range.[134-136] In 1999, the 1st generation Grubbs-Hoveyda catalyst bearing a chelating *iso*-propoxybenzylidene unit was reported.[137] The presence of the coordinating *iso*-propoxy group resulted in highly stable complexes, the used of decreased amounts of catalyst in metathesis reactions, and allowed recycling the ruthenium complex.

VI - B) 2) Beneficial impact of NHCs

The 2nd generation of olefin metathesis catalysts were obtained by replacement of one phosphine ligand by an *N*-heterocyclic carbene (Scheme 14).[42, 138-140]

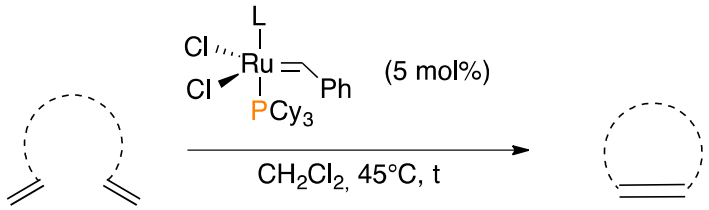


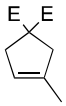
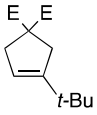
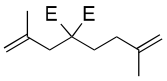
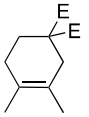
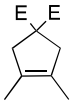
Scheme 14: Synthesis of 2nd generation olefin metathesis catalysts

This gave catalysts with significantly increased substrate range, higher TONs and TOFs. These complexes successfully performed in the challenging syntheses of tri- and tetrasubstituted olefins in moderate to high yields (Table 1), while remaining catalytically

active in CM, RCM and ROMP reactions employing much lower amounts of catalyst (not shown).

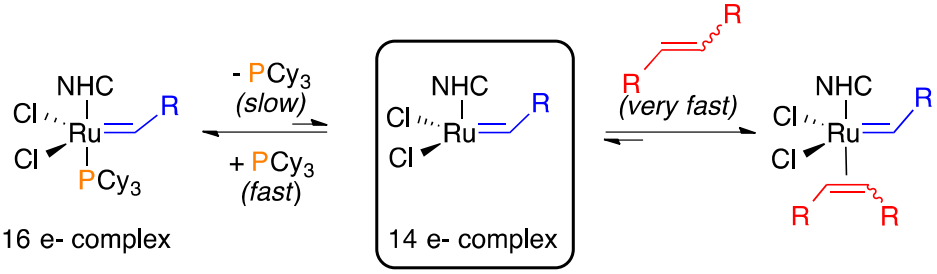
Table 1: Ruthenium-catalysed olefin metathesis, influence of the ligand (E = COOMe):



Entry	Substrate	Product	t	L		
				PCy_3[42]	IMes[42]	SIMes[141]
1			30 min	quant.	quant.	quant.
2			30 min	82 %	quant.	quant.
3			60 min	0 %	quant.	quant.
4			90 min	0 %	90 %	95 %
5			24 h	0 %	31 %	55 %

In order to explain the superior behaviour of NHC-Ru complexes, mechanistic studies and DFT calculations were performed on these systems.[142]

Initially, the stronger *trans* effect of *N*-heterocyclic ligands was mistakenly thought to promote the dissociation of the *trans*-coordinated phosphine ligand to explain higher reaction rates. Actually, dissociation of the phosphine ligand from the stable 16 e- complex appeared to be very slow, thus explaining the better stability of 2nd generation catalysts (Scheme 15).



Scheme 15: Dissociative substitution of phosphines in Ru-metathesis catalysts.

The higher activity of 2nd generation catalysts was explained by the much better affinity of 14e- NHC-Ru complexes for binding olefins in the presence of free phosphines. This feature is specific to NHC-Ru complexes and is not observed with diphosphino-Ru complexes.[143, 144] As a matter fact, the dissociative substitution of the phosphine by the olefin explains the higher activity encountered with NHC-based systems.

In 2006, Grubbs *et al*. reported standard systems of characterisation for olefin metathesis catlaysts.[128] This rigorous structure-activity relationship study based on a series of 2nd generation olefin metathesis catalysts tested in several model-reactions allowed head-to-head comparisons of the catalytic behaviour of various NHC-Ru complexes (Figure 17).

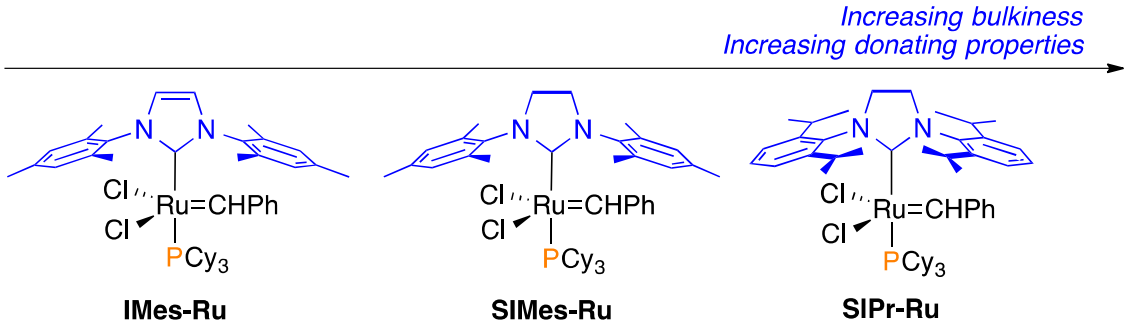


Figure 17: Catalysts used by Grubbs in the structure-activity relationship analysis.

Complexes **IMes-Ru**, **SIMes-Ru** and **SIPr-Ru** were tested in order to determine the influence of the electronic and steric properties of the NHCs on the efficiency of the corresponding catalysts in CM, RCM and ROMP.

The 1st generation Grubbs catalyst was used as a reference in this study. As a general trend, 2nd generation olefin metathesis catalysts displayed a better activity and stability.

Complex **IMes-Ru** was found to be the most stable (highest TONs) but least active catalyst (lowest TOFs). Indeed, the least bulky and least donating IMes ligand limits dissociation of the *trans*-coordinated phosphine, thus increasing the catalyst stability but slowing down the rate-determining dissociative substitution step.

On contrary, complex **SIPr-Ru** proved to be much more active (higher TOFs), but less stable (lower TONs) than **IMes-Ru** and **SIMes-Ru**. In this case, the most crowded and most donating SIPr favours dissociation of the *trans*-coordinated phosphine, which is likely to explain the improved reaction rates as well as the decreased stability of the active species.

It is worth mentioning that despite the higher activity of complex **SIPr-Ru**, and the higher stability of **IMes-Ru**, complex **SIMes-Ru** is actually most commonly used in routine syntheses. This feature illustrates a series of compromises that have to be made between the activity and the stability the active species**.**

Around 2010, only commercially available NHCs were commonly employed for performing catalytic olefin metathesis reactions. It is noteworthy that Grubbs- as well as Grubbs-Hoveyda- 2nd generation catalysts favour the formation of thermodynamic *E*-olefins, these catalysts being not suited for the synthesis of valuable *Z*-isomers present in natural products and biologically active compounds.

The last breakthrough arose in 2011 with the synthesis of a bulky, unsymmetrically substituted *N*-heterocyclic carbene based on a 2nd generation Grubbs-Hoveyda olefin metathesis catalyst scaffold (Figure 18).[145-147]

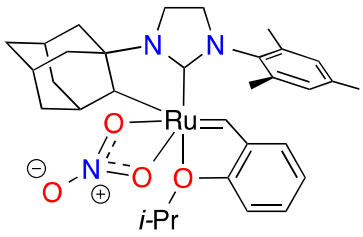
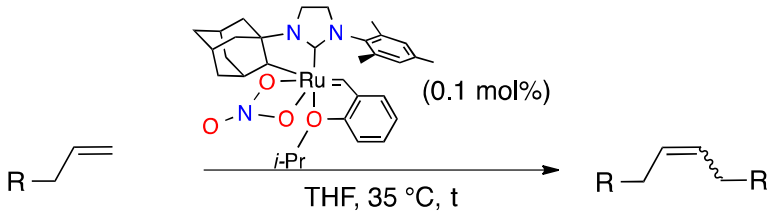


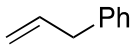
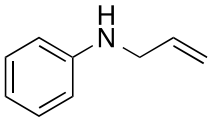
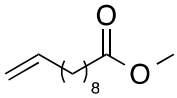
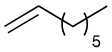
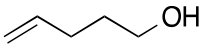
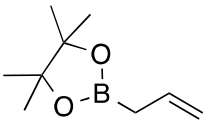
Figure 18: Grubbs *Z*-selective olefin metathesis catalyst.

This complex has a stereogenic ruthenium centre. It shows high stability (higher TON), thus allowing the use of only 0.1 mol% of catalyst to promote highly *Z*-selective cross-metathesis reactions in high yields (Table 2). It also proved to be active for the ROMP and RCM reactions (not shown).

The origin of the selectivity was mainly explained by the alkyl-M bond, which resulted from C-H metal insertion at the adamantyl substituent. This feature prevents the rotation of the ligand around the NHC-Ru bond, thus constantly holding the demanding mesityl substituent over the catalytically relevant alkylidene unit. Unfavourable steric interactions between these groups in the metallocyclobutane transition state are likely to explain the observed *Z*-selectivity.[148]

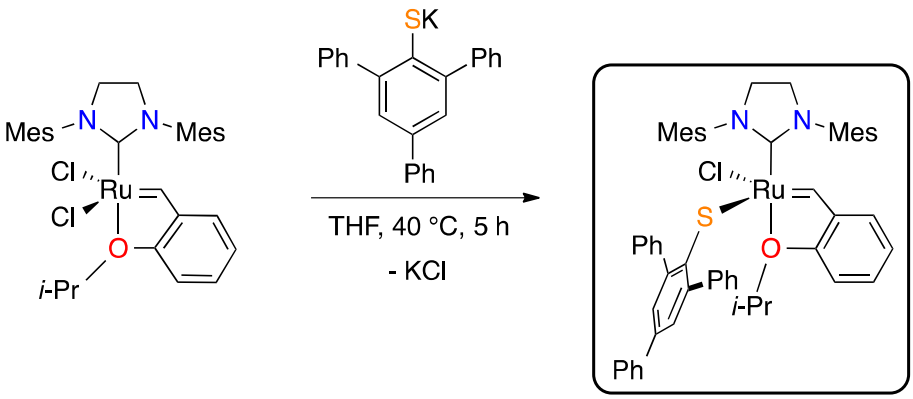
Table 2: Catalytic study on Grubbs *Z*-selective olefin metathesis catalyst:



Entry	Substrate	Time (h)	Yield	Z : E
1		3	91	92 : 8
2		12	12	90 : 10
3		12	85	91 : 9
4		12	83	92 : 8
5		12	67	81 : 19
6		3	36	95 : 5

The same year, Jensen *et al.* reported highly *Z*-selective olefin metathesis catalysts obtained by substitution of one chlorido atom by a bulky arylthiolato ligand in 2nd generation Grubbs-Hoveyda catalysts (Scheme 16).[149]

The steric hindrance generated by SIMes combined with the extremely demanding arylthiolato ligand resulted in highly *Z*-selective olefin metathesis reactions, however, only low yields were obtained using this compound.



Scheme 16: Synthesis of Jensen's highly *Z*-selective olefin metathesis catalyst

To conclude, kinetic, mechanistic, structure-activity relationship studies and the development of non-commercially available NHC ligands has led the development of ruthenium complexes with increased stability, activity, selectivity and substrate range. For these catalytic reactions, the superiority of NHCs *vs.* phosphines has been established. The importance of the electronic and steric parameters as well as their impact on the catalytic behaviour of ruthenium catalysts (TON, TOF, selectivity) has also been determined.

VI - C) Metal-catalysed cross-coupling reactions

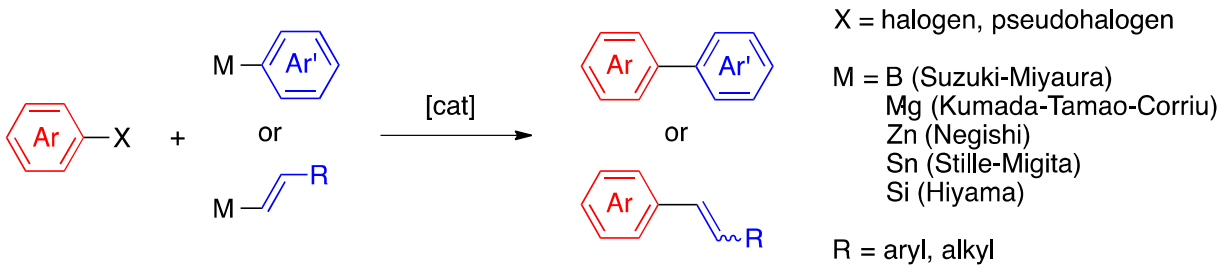
VI - C) 1) Historical aspects

Metal catalysed cross-coupling reactions are among the most commonly used reactions in routine synthesis. They represent efficient methods for the formation of carbon-carbon or carbon-heteroatom bonds.

This study started in 1941 when Kharasch and Fields described the first cross-coupling reaction by using cobalt salts and Grignard reagents,[150] and Tamura and Kochi successful extended this methodology to silver[151], copper[152] and iron[153] based catalysts. However, due to significant and unpredictable formation of homo-coupling products, the efficiency of these methods was limited in terms of yields.

This field of research culminated in 1972 when Tamao and Kumada[154] and Corriu[155] independently reported the use of nickel catalysts. In the meantime Heck and Mizoroki independently reported the coupling reaction of aryl iodides with olefins.[156, 157] Kumada was the first to introduce phosphine ligands in cross-coupling reactions.[154] In 1975, Murahashi extended cross-coupling reactions to palladium complexes.[158] Later on, many palladium catalysed reactions have been developed by varying the nucleophile, namely organomagnesium (Kumada-Tamao-Corriu), organozinc (Negishi),[159-161] organoboron (Suzuki-Miyaura),[162] organostannanes (Stille-Migita),[163-165] organocuprate (Sonogashira), organosilicates (Hiyama),[166, 167] amines (Buchwald-Hartwig-Yagupolskii)[168, 169] etc. In 2010, the Nobel Prize was awarded to Heck, Negishi and Suzuki for their collective contribution to the development of cross-coupling reactions.

A general overview of the most important cross-coupling reactions is given is in Schemes 17-20.



Scheme 17: Catalytic aryl-aryl or aryl-vinyl bond formation.

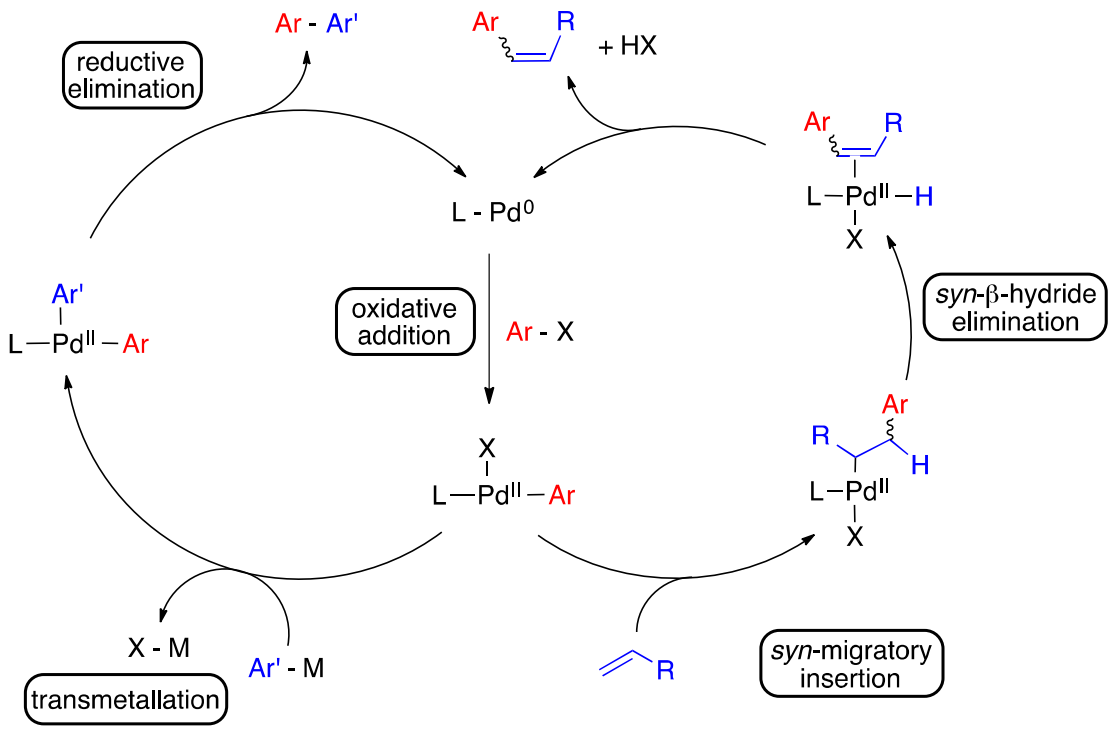
Scheme 18: Catalytic aryl-olefin bond formation (Mizoroki-Heck reaction).

Scheme 19: Catalytic aryl-alkyne bond formation (Sonogashira reaction).

Scheme 20: Catalytic aryl-nitrogen bond formation (Buchwald-Hartwig-Yagupolskii reaction).

VI - C) 2) Mechanism and challenges associated with cross-coupling reactions

The mechanism for each of these couplings is similar, and now well-established. The key-steps of these catalytic cycles are depicted in Scheme 21.



Scheme 21: Simplified mechanism describing the most important steps for aryl-aryl cross-coupling reactions and for the Mizoroki-Heck reaction. The fourth coordination site of some Pd(II) intermediates may be occupied by a solvent molecule.

From a mechanistic point of view, these reactions are mediated by two 2-electron redox cycles namely the oxidative addition and the reductive elimination (or *syn*-β-hydride elimination), and a transmetallation step (or a *syn*-migratory insertion). These key-steps are considered as rate determining.

The oxidative addition and transmetallation steps require a rather accessible metal centre to ensure the approach of the reagents, whereas the reductive elimination step should benefit from a more congested environment. This means that these rate-determining steps display different needs in terms of steric hindrance.

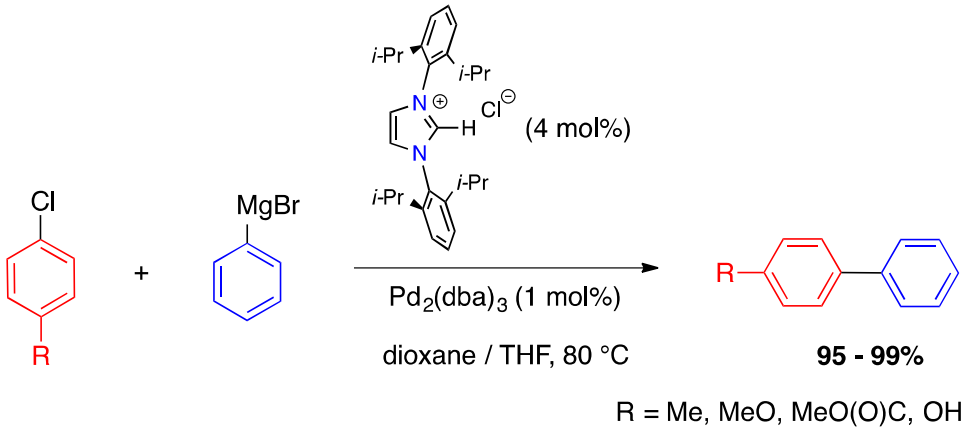
25 years ago, challenges associated with this type of reactions were 1) lowering the amount of catalyst, 2) activating aryl chlorides, 3) lowering reaction temperatures and 4) providing an easy access to the most challenging *ortho*-tetrasubstituted biphenyls.

VI - C) 3) Development of NHC-palladium catalysts in cross-coupling reactions

In 1995, Herrmann *et al.* reported the first catalytic system based on NHC-Pd complexes (Scheme 6).[14] In these systems, using NHC ligands prevented decomposition of the catalyst which remained catalytically active in solutions for extended reaction times, thus allowing the use of lower amounts of palladium precursors (< 1 mol%). In addition,

the Pd(0) atom was able to activate aryl chloride traditionally considered as resistant towards oxidative addition.

In the following year, Nolan *et al*. reported the first examples of NHC-Pd catalysed cross-coupling reactions with deactivated aryl chlorides (Scheme 22).[170]



Scheme 22: First NHC-Pd catalysed cross-coupling reactions with deactivated aryl chlorides.

Even if the *in situ* generation of the precatalyst promoted efficient cross-coupling reactions, the system described suffered from reproducibility, probably due to the excess of NHC precursor required to ensure quantitative formation of the active species.

To ensure fine control of ligand/palladium ratios, Herrmann *et al*. prepared the well-defined $(IAd)_2$-Pd(0) and IAd-Pd(0)-P(*ortho*-Tol)$_3$ complexes in 2002 (Figure 19).[171]

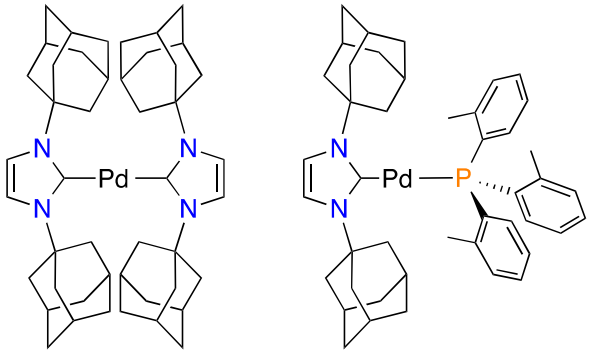


Figure 19: First well-defined NHC-Pd(0) complexes.

These complexes successfully performed cross-coupling reactions with aryl chlorides at room temperature. However, kinetic studies showed that the active species for the activation of aryl chlorides is a coordinatively unsaturated monoligated L-Pd(0) complex,[172] (where L is a 2e- donating ligand), suggesting decoordination of either a phosphine or NHC ligand.

Owing to the important steric hindrance displayed by NHCs and their strong coordination bonds with transition metals, these ligands are likely to favour the formation of the catalytically active NHC-Pd(0) complexes upon decoordination of other ligands.

Next efforts focused on the preparation of well-defined precatalysts with the general formula NHC-Pd(II)-L, where L is an ancillary ligand cleverly chosen in order to facilitate the activation of the catalysts (*e.g.* easy metal-L dissociation, reduction of the Pd(II) to Pd(0)) (Figure 20). These well-defined Pd(II) complexes are easily accessible and were preferred to Pd(0) precursors for practical reasons.

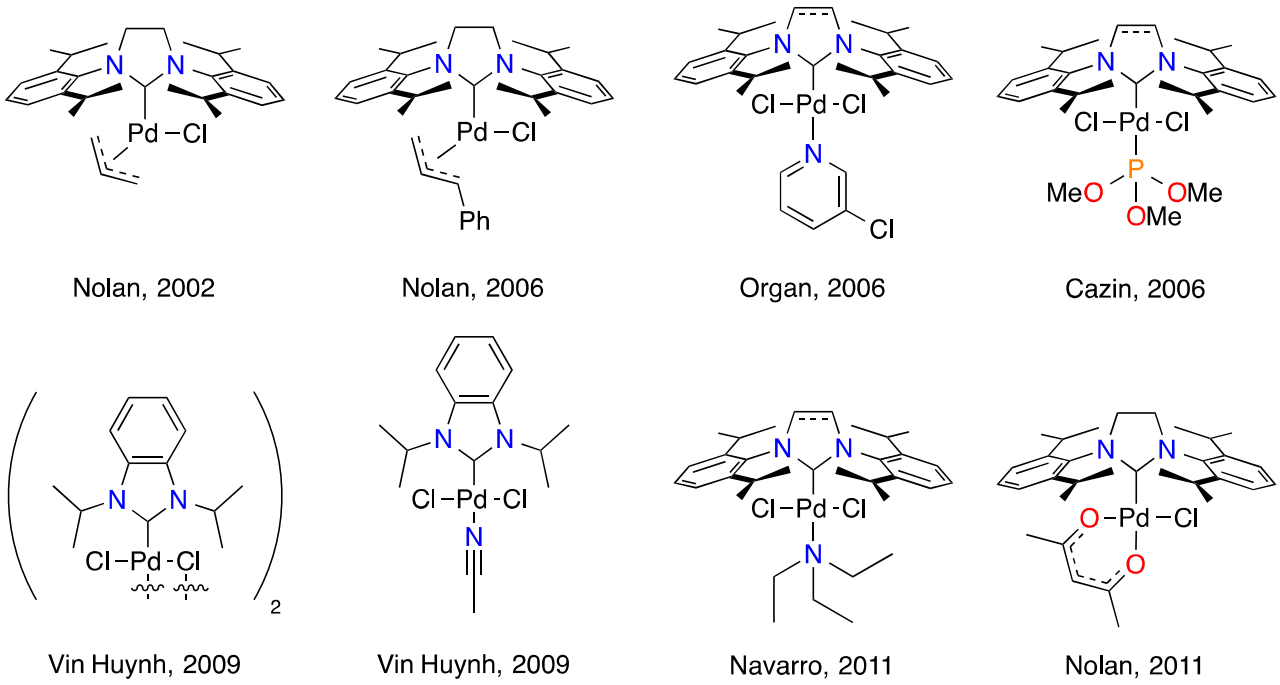
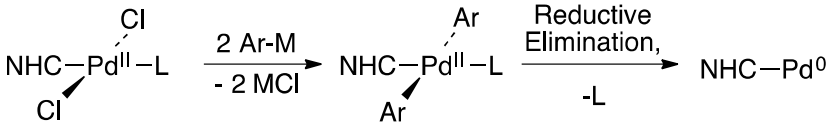


Figure 20: Typical NHC-Pd precatalysts

Among these complexes, [$PdCl_2$(NHC)(3-Cl-pyridine)],[52, 173] [$PdCl_2$(NHC)($P(OMe)_3$)][174] and [$PdCl_2$(NHC)(NEt_3)],[175] were reported as highly active precatalysts for cross-coupling reactions. The active species was readily obtained by reduction of the palladium atom and dissociation of the ancillary ligand (Scheme 23).

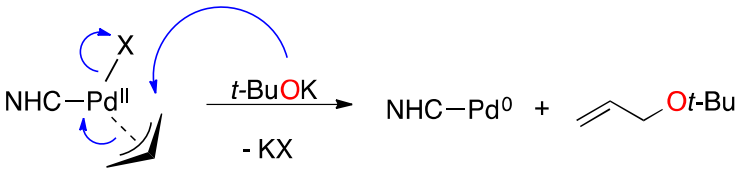


Scheme 23: General mechanism for the activation of [Pd(X_2)(NHC)L] precatalysts, where L is the ancillary ligand.

In these precatalysts, the easy dissociation of the ancillary ligand and its propensity to recoordinate to the [(NHC)-Pd(0)] complex when inactive resulted in the fast activation of the precatalyst and extended lifetime of the active species.

The Pd-PEPPSI-NHC system developed by Organ *et al*. has been extensively studied. Described as a universal precatalyst, it proved to successfully catalyse a large number of cross-coupling reactions including Kumada-Tamao-Corriu,[99] Negishi,[176] Suzuki-Miyaura,[52] Stille-Migita,[177] and Buchwald-Hartwig-Yagupolskii reactions.[98] To highlight the tremendous interest given to this field of application, it should be mentioned that each of these latter references were among the most downloaded and most cited reports in the year following their publication.

Nolan *et al*. used [PdCl(allyl)(NHC)][103] and [PdCl(cinnamyl)(NHC)],[44] precatalysts. In these complexes, the activation of the precatalyst occurred at room temperature upon addition of an alkoxide (Scheme 24).



Scheme 24: Activation of [PdX(allyl)(NHC)] complexes.

Interestingly, such a facile activation pathway allowed the use of as little as 50 ppm of precatalysts in room temperature Suzuki-Miyaura cross-coupling reactions,[44] but other catalytic applications were reported.[102, 178]

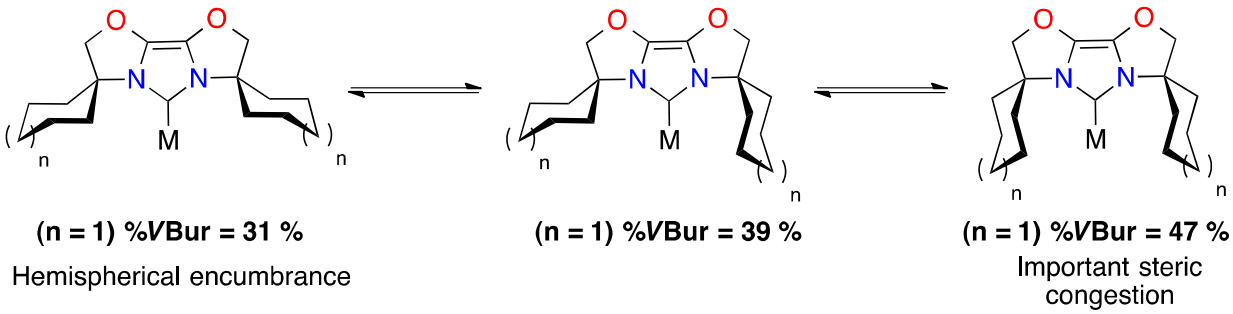
At this time, the most widely used NHC ligands were the commercially available SIPr, SIMes, IPr, and IMes, with a special preference for IPr which appeared to be more efficient for most types of cross-coupling reactions. Interestingly, all these ligands create a hemispherical encumbrance, resulting in protected metal centres that remain easily accessible. However, none of these NHCs allowed the routine synthesis of challenging

ortho-tetrasubstituted biphenyls, probably due to the variable steric requirements throughout the catalytic cycle.

As a result, next efforts focused on the development of new NHCs especially designed to promote these most challenging reactions.

VI - C) 4) Development finely tuned NHCs for the synthesis of tetra-*orthosubstituted biphenyl derivatives*

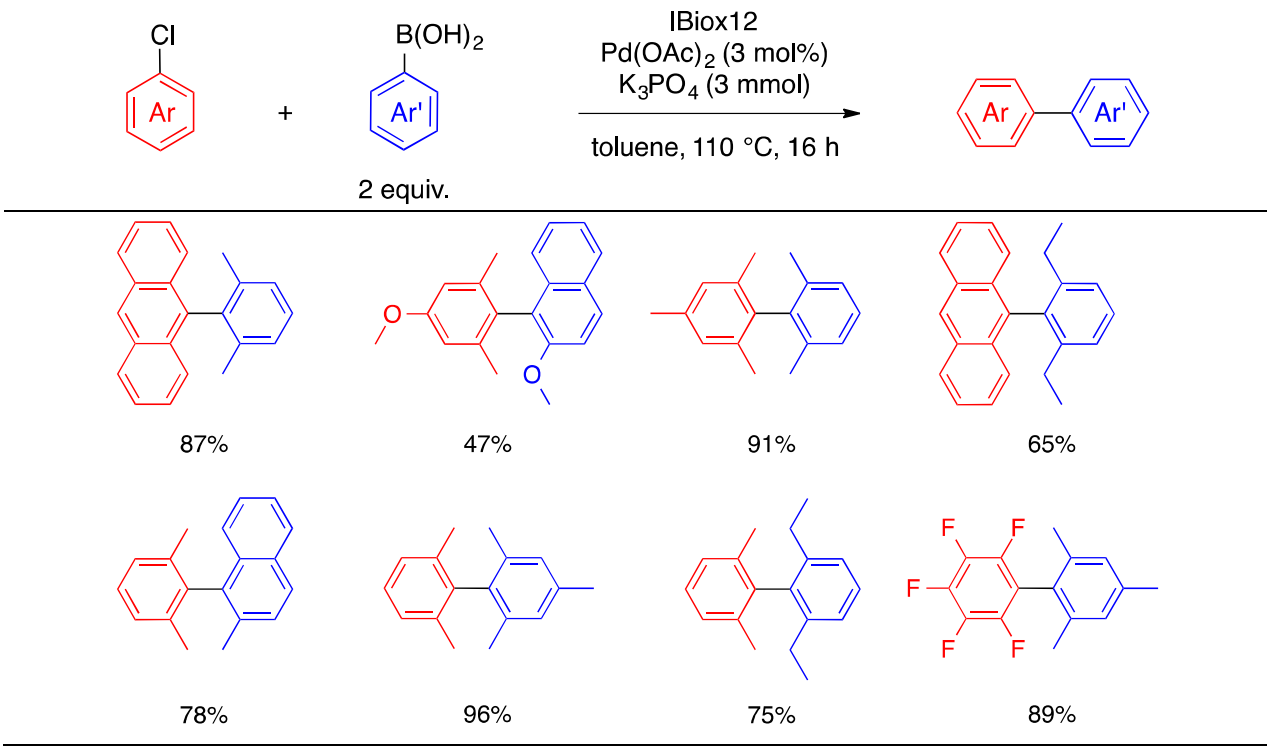
Glorius *et al.* introduced the concept of flexible bulk in 2003. NHC ligands based on a bis(spiro-oxazoline) skeleton called IBiox***N*** were developed, where ***N*** is the number of carbons in the cycloalkyl chain (Scheme 25).[179]



Scheme 25: Dynamic behaviour of IBiox6 complexes

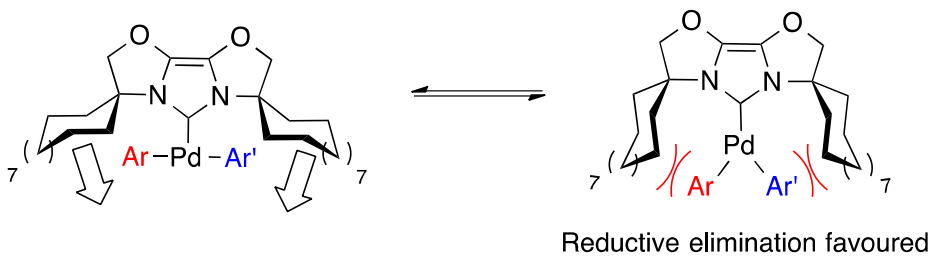
In a metal complex, the conformational flexibility of IBiox ligands allows folding-back of the cycloalkyl substituents (hemispherical encumbrance able to promote fast oxidative additions and fast transmetallations reactions) as well as surrounding the metal atom (important steric compression which promotes fast reductive eliminations). In other terms, the ligands can self-adapt to the changing needs of the catalytic cycle and should be able to provide the steric environment that is optimal for each rate-determining step.

Associated with Pd precursors, these ligands formed complexes *in situ* able to convert *ortho*-disubstituted aryl chlorides into their corresponding *ortho*-tri- or -tetra-substituted biphenyls.[180] Interestingly, the largest IBiox12 bearing cyclododecyl chains allowed medium to excellent yields in the most challenging cross-coupling products (Scheme 26).



Scheme 26: Pd-catalysed synthesis of biphenyl derivatives with IBiox12

The catalytic intermediate before the reductive elimination step is described as a monomeric three-coordinate L-Pd(II)(Ar)(Ar') complex with Ar and Ar' positioned *trans* to each other, resulting in a T-shaped geometry (Scheme 27, left).[181] In this situation, no coupling reaction can be expected. The steric interactions between the cyclododecyl chains and the aryl substituents (close to the 2nd coordination sphere of the metal centre) are able to distort this geometry to a trigonal-like one, more likely to perform the reductive elimination (Scheme 27, right).



Scheme 27: Influence of the ligand conformation on the geometry of the three coordinate Pd(II) intermediate.

In spite of these promising results, these systems still required high reaction temperatures, extended reaction times, and up to 3 mol% of palladium precursor.

In 2003, Andrus *et al.* reported catalytic systems based on NHCs with extended hemispherical encumbrance, using phenanthroline sidearms.[182] The flexible steric hindrance was introduced *via* cyclohexyl substituents cleverly positioned in the second coordination sphere of the metal centre (Figure 21). Initial studies for copper-free Sonogashira reactions showed that the bulkiest NHC most efficiently promotes cross-coupling reactions.[182]

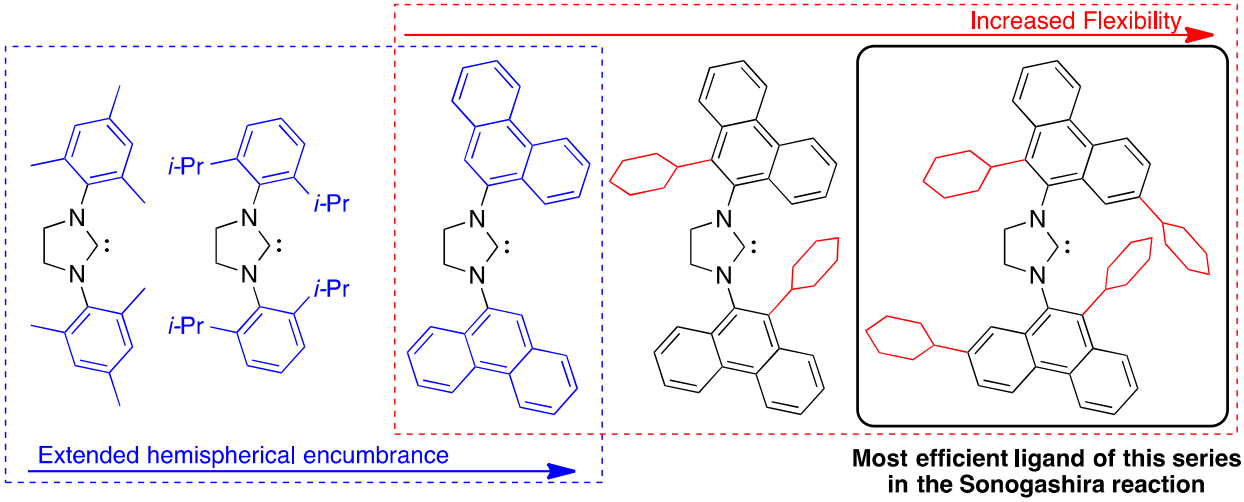
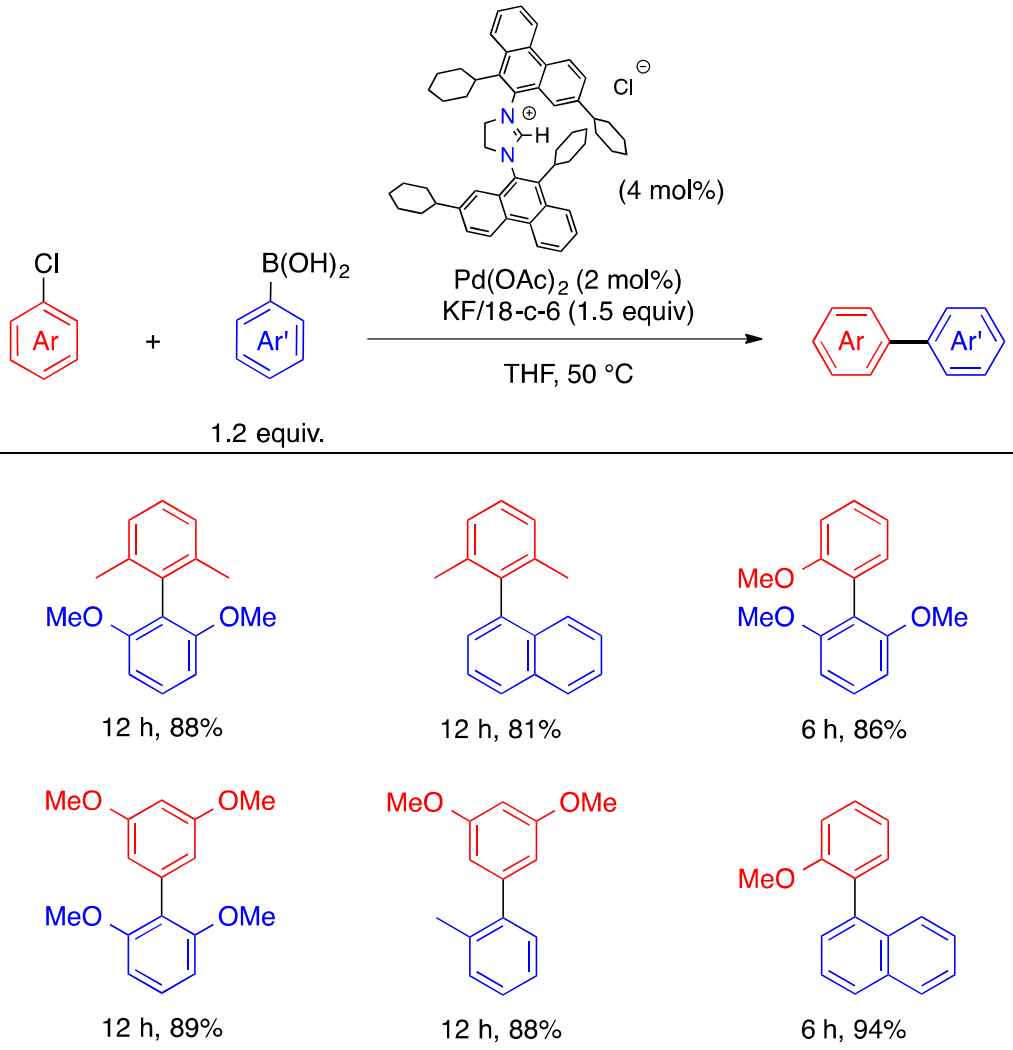


Figure 21: Ligands studied by Andrus *et al.*

Further catalytic tests for the Suzuki-Miyaura reaction were run with *in situ* generated palladium complexes.[183] The bulkiest NHC bearing 2,9-dicyclohexyl-10-phenanthroline substituents proved to be the most effective (Scheme 28).

However, the use of this ligand required 2 mol% of palladium precursor and did not allow syntheses at room temperature. In addition, examples of *ortho*-tetrasubstituted biaryl products remained rare.



Scheme 28: Pd-catalysed synthesis of biphenyl derivatives.

In 2012, Organ designed three Pd-PEPPSI-NHC complexes displaying an extended hemispherical encumbrance and a higher flexibility compared to the well-known IPr, IMes and IEt (Figure 22).[177] A systematic structure-activity relationship analysis was realised for these ligands.

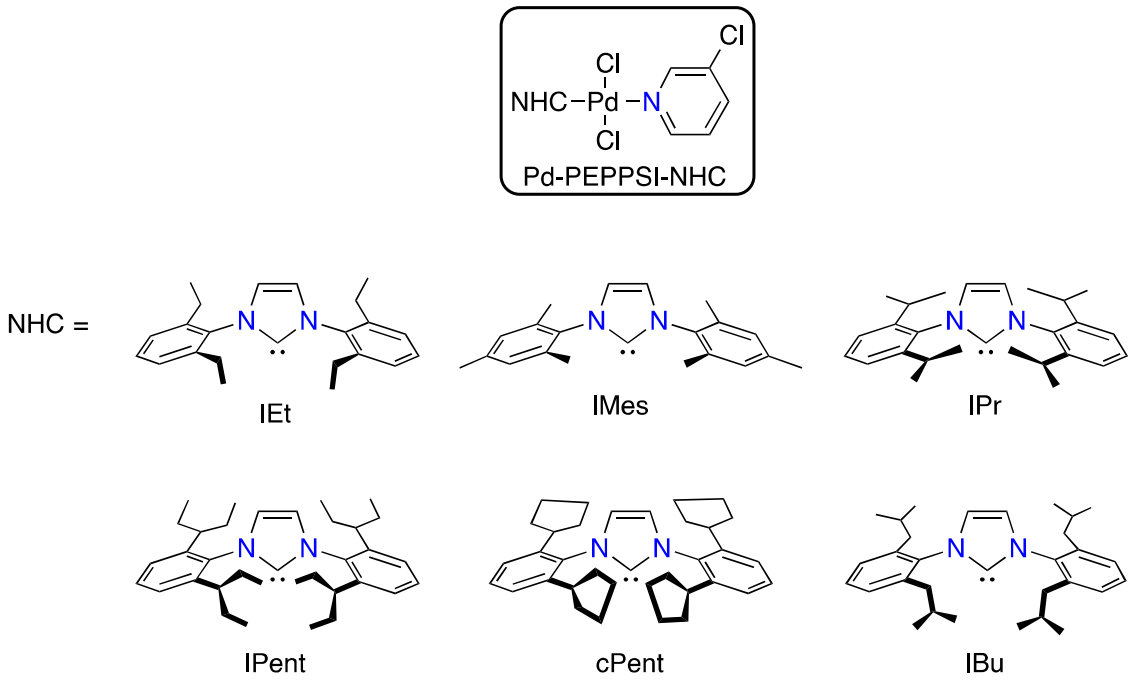


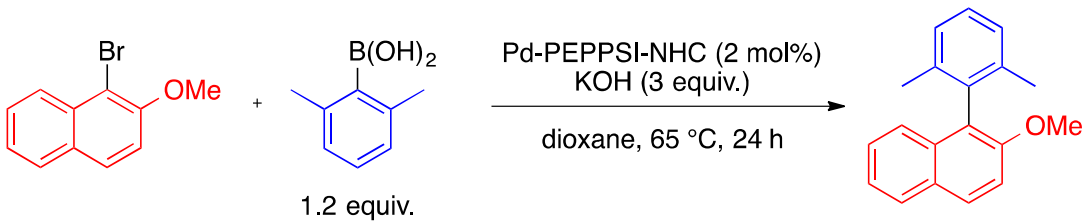
Figure 22: Pd-PEPPSI-NHC complexes used by Organ *et al.*

As reported in early work, IPr-Pd complexes have a superior catalytic behaviour compared to less bulky IMes and IEt compounds for steric reasons.[52]

Ipent, cPent as well as IBu have slightly longer wingtips compared to IPr, thus extending the hemispherical encumbrance. In addition, IPent is more flexible than cPent, whereas IBu appears to be less sterically hindered than IPent.

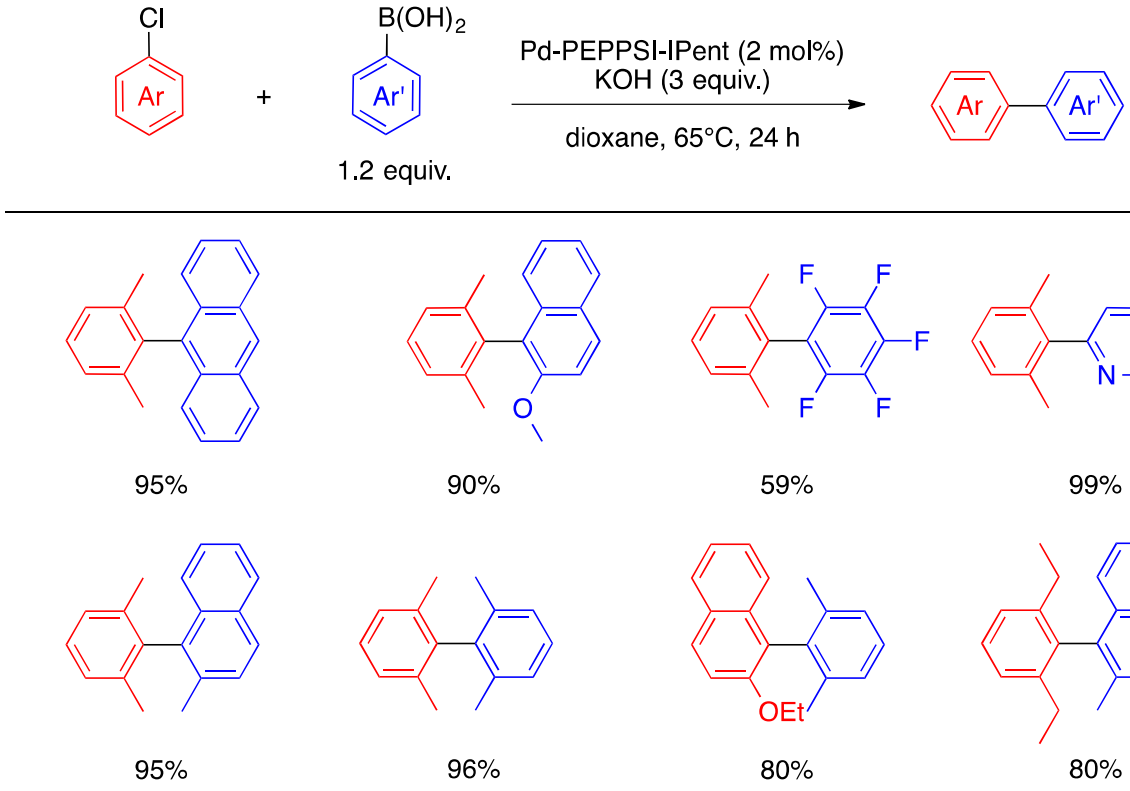
These complexes were tested for the synthesis of 1-(2,6-dimethylphenyl)-2-methoxynaphthalene *via* a Suzuki-Miyaura cross-coupling reaction (Table 3).

Table 3: Synthesis of 1-(2,6-dimethylphenyl)-2-methoxynaphthalene. Influence of the ligand.



Entry	NHC	Yield (%)
1	IPr	41
2	IPent	91
3	cPent	9
4	IBu	4

In this study, the bulkiest and most flexible IPent clearly outperformed the other ligands tested for this reaction with 91% of coupling product (Table 3, entry 2). These results highlighted the dramatic impact of the bulkiness and the topology of the ligand on the outcome of a catalytic reaction. The scope of application of IPent was successfully extended to the synthesis of other challenging compounds (Scheme 29).



Scheme 29: Pd-catalysed synthesis of challenging biphenyl derivatives with IPent

It is worth mentioning that the Pd-PEPPSI-IPent precatalyst also proved excellent in Sille-Migita, Negishi and Buchwald-Hartwig-Yagupol'skii cross-coupling reactions with aryl chlorides.[177]

Dorta *et al.* synthesised a series of well-defined [PdCl(cinnamyl)(NHC)] complexes with NHCs bearing naphthyl substitutents (Figure 23).[184]

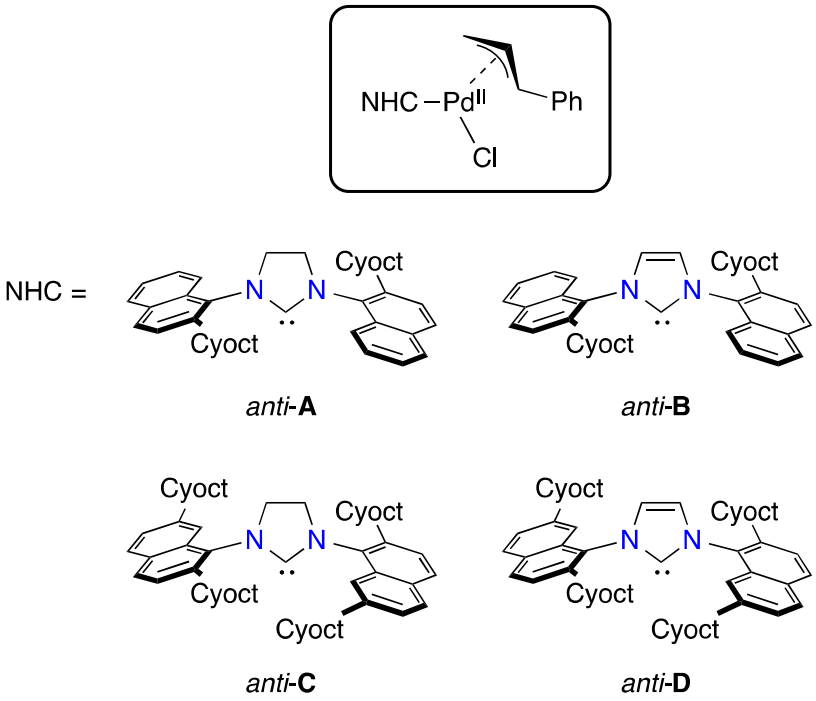


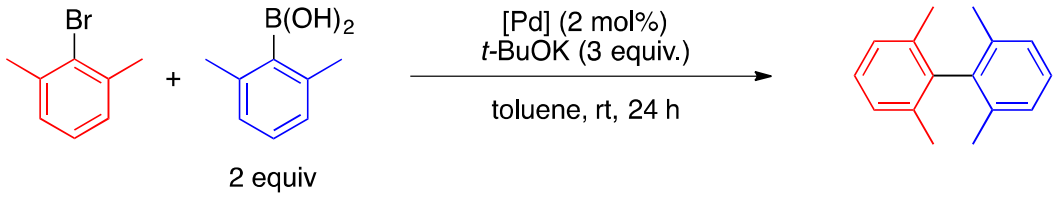
Figure 23: [PdCl(cinnamyl)(*anti*-C)] complexes developed by Dorta *et al.*

Smart functionalisation of the naphthyl moiety with flexible cyclooctyl chains ensured the variable occupancy of the 2nd coordination sphere of the metal atom. These complexes and other efficient Pd-based precatalysts were tested for the synthesis of 2,2',6,6'-tetramethyl-1,1'-biphenyl via a Suzuki-Miyaura cross-coupling reaction (Table 4).[185]

Dorta's four precatalysts (Table 4, entries 4-7) turned out to be more efficient than the corresponding SIPr- and IPr-based complexes (Table 4, entries 1-2). Pd-PEPPSI-IPent also proved to be less active (Table 4, entries 3) for this reaction even under the optimal conditions reported by Organ *et al* (not shown, ref [167]).

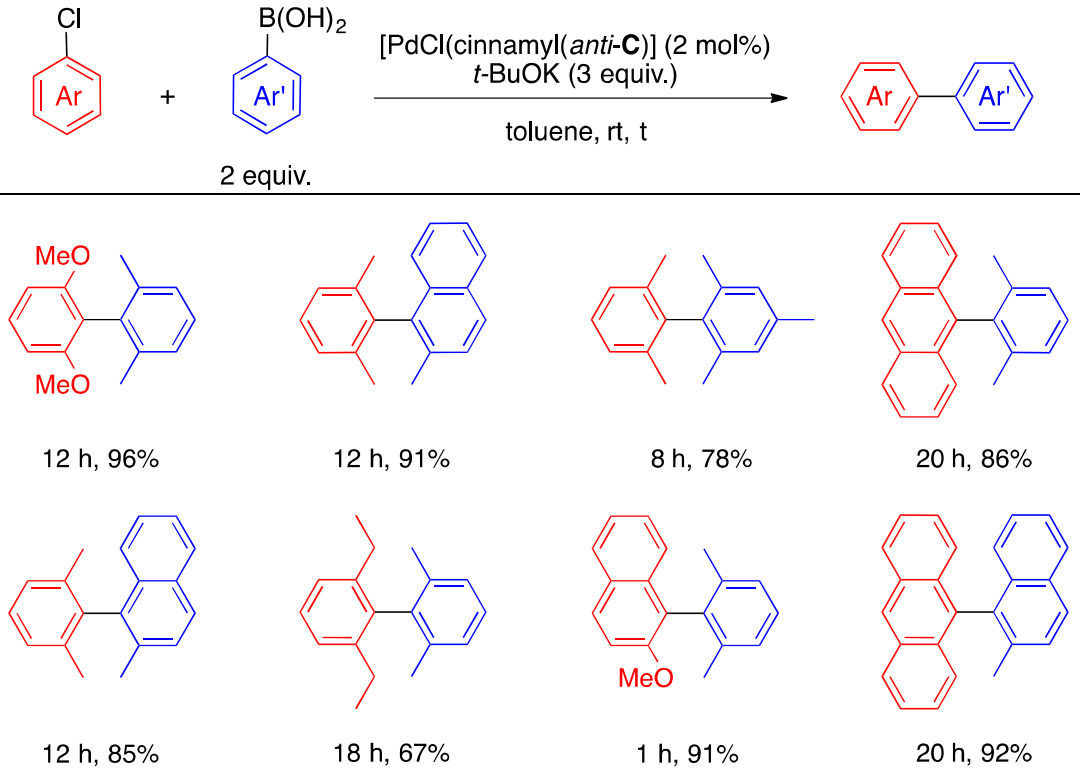
Among the complexes tested, [PdCl(cinnamyl)(*anti*-**C**)] led to the best results, the reaction being here achieved with 95% yield after 24h at room temperature. The same complex was also successfully employed at room temperature for the synthesis of other challenging biaryl derivatives (Scheme 30).

Table 4: Synthesis of 2,2',6,6'-tetramethyl-1,1'-biphenyl. Influence of the precatalyst.



Entry	Precatalyst	Conversion (%)
1	[PdCl(cinnamyl)(SIPr)]	39
2	[PdCl(cinnamyl)(IPr)]	40
3	Pd-PEPPSI-IPent	33
4	[PdCl(cinnamyl)(*anti*-**A**)]	45
5	[PdCl(cinnamyl)(*anti*-**B**)]	60
6	[PdCl(cinnamyl)(*anti*-**C**)]	95
7	[PdCl(cinnamyl)(*anti*-**D**)]	65

[a] Run realised in the optimal conditions:[177] KOH (3 equiv.) in dioxane.



Scheme 30: Pd-catalysed synthesis of biphenyl derivatives with *anti*-**C**

This excellent efficiency was mainly explained by steric factors. However, the flexible encumbrance and the overall percent buried volume (41% for *anti*-**C**) were not sufficient to rationalise such catalytic behaviour. Dorta proved that contrary to more symmetrical NHCs, the steric hindrance generated by *anti*-**C** was not equally distributed between the four quadrants of the metal centre (Figure 24).

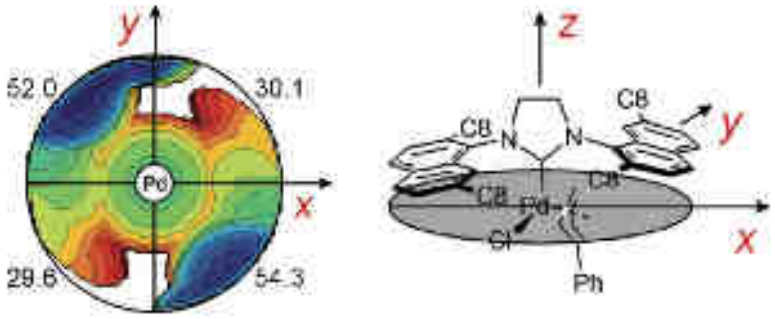
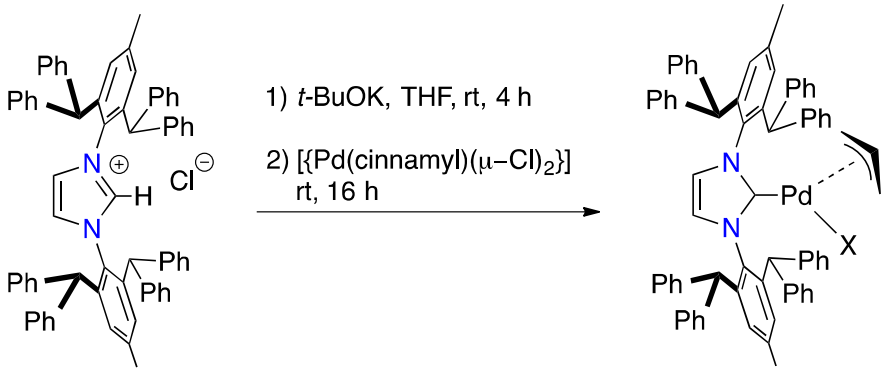


Figure 24: Steric hindrance generated by *anti*-**C** (ref. [155]) (C8 = cyclooctyl). (blue zones are sterically hindered, red zones are less sterically hindered)

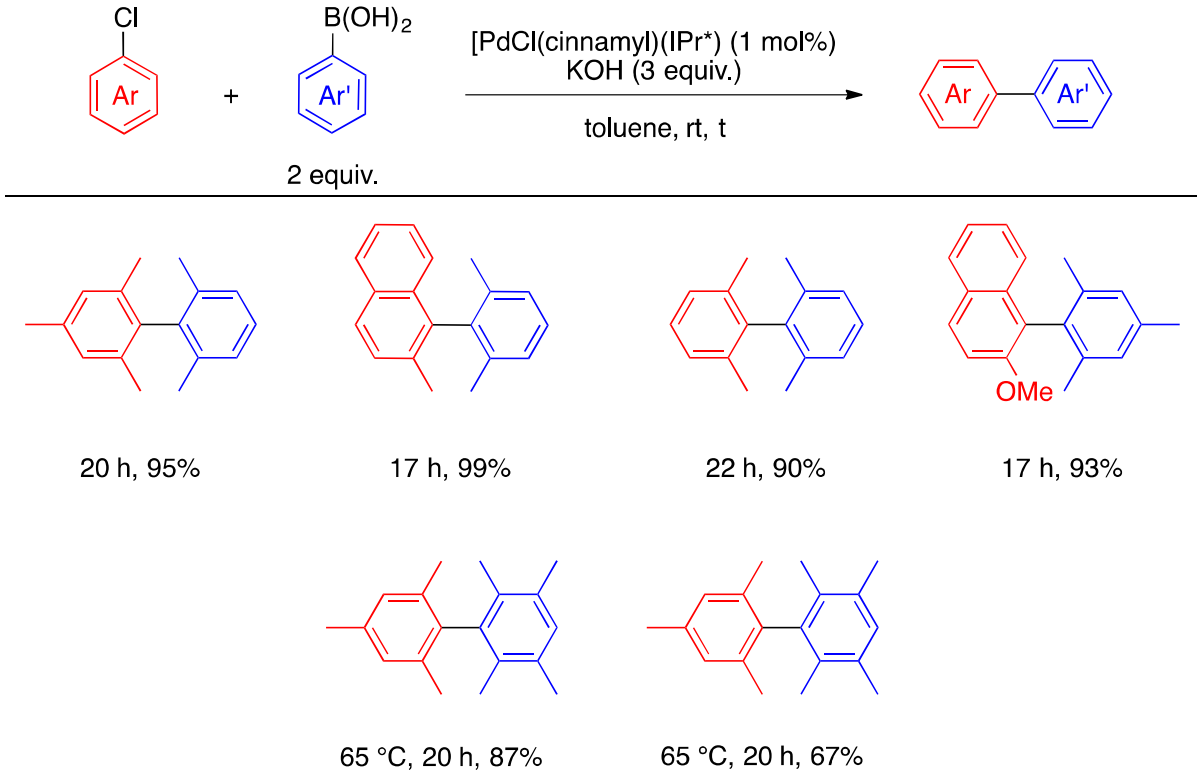
The unusual efficiency of the ligand was attributed to this unsymmetrical environment. *Anti*-**C** proved to provide simultaneously accessible areas able to accommodate the *ortho*-methyl groups of the aryl moieties, and highly crowded areas which favour fast reductive eliminations.

In 2010, Markò *et al.* synthesised a bulkier version of IPr called IPr* by replacement of the CH_3 groups by phenyl units.[46] Nolan *et al.* prepared the corresponding [PdCl(cinnamyl)(IPr*)] complex as a precatalyst for cross-coupling reactions (Scheme 31).[186] The percent buried volume was calculated and IPr* proved to be the most sterically demanding NHC ever reported at this time (44.6%*V*bur).



Scheme 31: Synthesis of the complex [Pd(cinnamyl)Cl(IPr*)].

This complex was successfully used for the synthesis of challenging biaryl compounds *via* a Suzuki-Miyaura cross-coupling reaction, at room temperature, using only 1 mol% of palladium precatalyst (Scheme 32).[186]



Scheme 32: Suzuki-Miyaura cross-coupling reactions catalysed by [PdCl(cinnamyl)(IPr*)].

Even though IPr* is a symmetrical ligand, its encumbrance is unequally distributed around the metal centre (Figure 25).

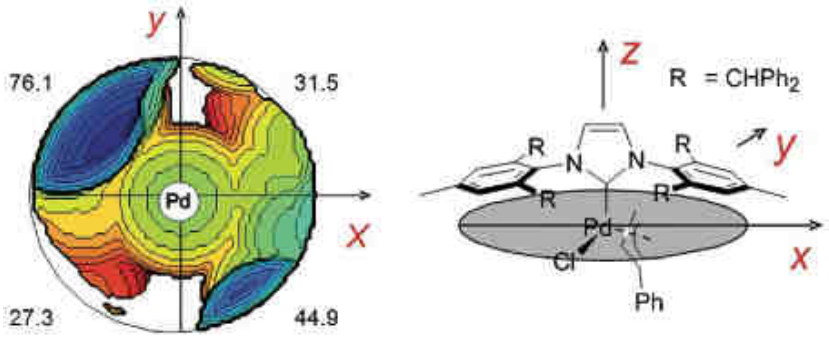


Figure 25: Steric hindrance generated by IPr* (ref. [156]).

As for *anti*-**C**, the efficiency of this system was mainly explained by the ability of IPr* to create accessible areas and an important steric congestion simultaneously.

Other catalytic systems using IPr* as ligand proved to be efficient in various cross-coupling reactions.[187-189]

Recently, Markò designed an even bulkier version of IPr* with 2-naphthly units instead of phenyl ones (Figure 26).[57]

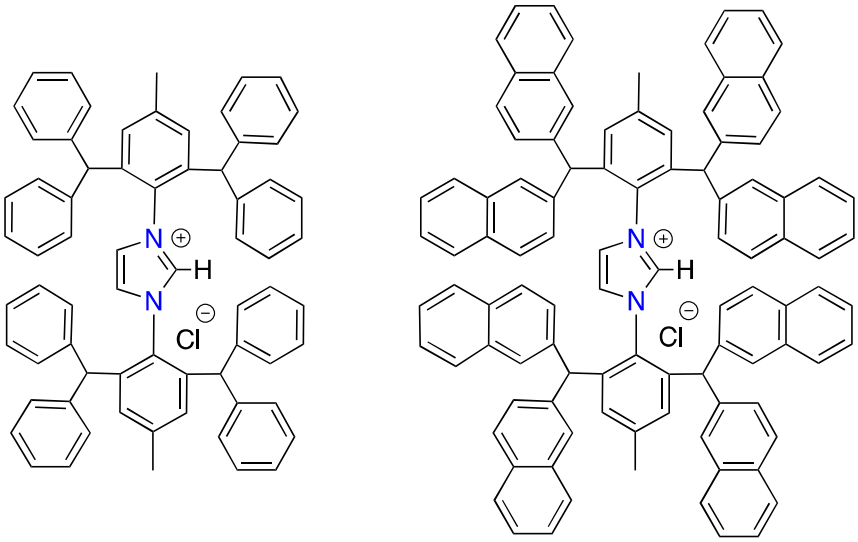


Figure 26: Structure of IPr* (left) *vs*. IPr*$^{(2\text{-Np})}$ (right).

The catalytic behaviour of this ligand has not been investigated yet. It may be anticipated that this ligand will display interesting properties regarding the efficiency displayed by IPr*.

VII - Notes and references

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Chapter I :

N-heterocyclic carbenes functioning as monoligating clamps

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Abstract

Benzimidazolium salts *N,N'*-disubstituted with 9-alkyl-9-fluorenyl (AF) groups (**3a-e**, alkyl = Me, Et, *n*-Pr, *n*-Bu, Bn) have been synthesized in three steps in high yields from *ortho*-phenylenediamine. This amine was reacted with fluorenone in the presence of $TiCl_4$ and tetraethylenediamine (TMEDA) resulting in *N,N'*-bis(9*H*-fluoren-9-ylidene)benzene-1,2-diamine (**1**) in 91%. Diamines **2a-e** were then obtained by reacting diimine **1** with the appropriate organolithium reagent in yields superior or equal to 77%. In the final step, diamines **2a-e** were treated with ethylorthoformate under acidic conditions to afford benzimidazolium salts **3a-e**. These were readily converted into the PEPPSI palladium complexes **4a-e**. NMR and X-ray diffraction studies revealed that the flat fluorenylidene moiety orientates the alkyl groups towards the metal and because of its restricted rotational freedom makes the ligand bulkiness time independent. Thus, the metal centre is permanently confined between the two alkyl groups, thereby forming with the carbenic centre a monoligating clamp. The CH_2 groups close to the palladium ion give rise to C–H···Pd anagostic interactions. Catalytic tests revealed that the palladium complexes **4a-e** are highly efficient in Suzuki-Miyaura cross-coupling reactions, their activity being equal or superior to the best commercially available PEPPSI catalysts reported to date.

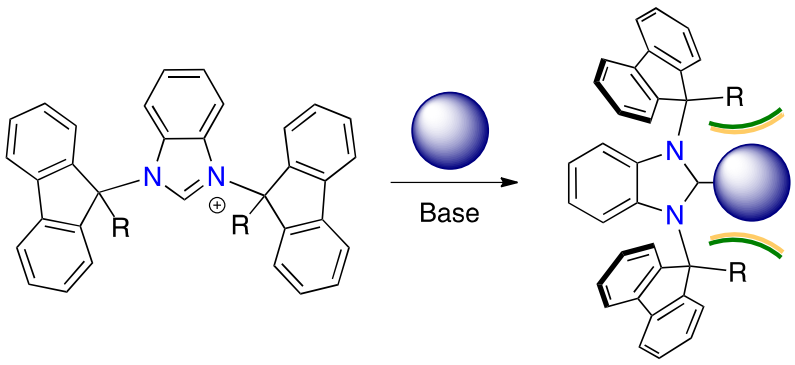
I - Introduction

N-heterocyclic carbenes (NHCs) have attracted considerable interest in transition metal chemistry since the isolation, in 1991, of the first stable compound of this family,[1] and the discovery of the catalytic activity of their complexes.[2-6] Palladium-mediated cross-couplings are among the catalytic reactions for which NHCs have been successfully applied.[3,7-13] In these transformations, electronic and steric ligand factors are crucial. While their strong σ-donor properties make the NHCs particularly efficient for promoting the oxidative addition step of the reaction, their steric encumbrance may facilitate the reductive elimination step as well as increase the stability of catalytic intermediates. As the carbenic centre of NHCs is part of a planar moiety, the steric properties of these ligands are

mainly determined by the bulk of the *N*-substituents that may form a pocket about the metal centre. These are remote from the heterocyclic moiety, and therefore any modification of the ligand encumbrance has essentially no significant effect on the electronic properties. Thus, steric fine-tuning of NHCs can be achieved straightforwardly without changing the ligand donor properties.

Many authors have attested to the pivotal role of steric parameters in Suzuki-Miyaura cross-coupling.[7,14,15] A general belief is that to be efficient, NHCs used in cross-coupling must create strong hemispherical encumbrance about the catalytic centre.

It has also been widely contended that high catalytic activity requires that the sterically demanding *N*-substituents (typically *o*-substituted aryls[8,16,17] or spiro-alkyl groups[7,18] possess sufficient structural flexibility to adapt to the steric requirements of the individual steps of the whole catalytic cycle. In the present study, we describe highly active Suzuki-Miyaura catalysts based on NHCs, which unlike the usual expanded NHCs, generate only "meridional" confinement in which encumbrance is created at two virtual, *trans*-located positions. These NHCs form complexes in which the metal centre is held within a clamp-like ligand characterised by its restricted conformational flexibility (Scheme 1). The new ligands, which were generated from benzimidazolium precursors, all have as *N*-substituents a AF group with such restricted rotational freedom that the steric congestion at the metal centre can undergo at most very minor fluctuations.

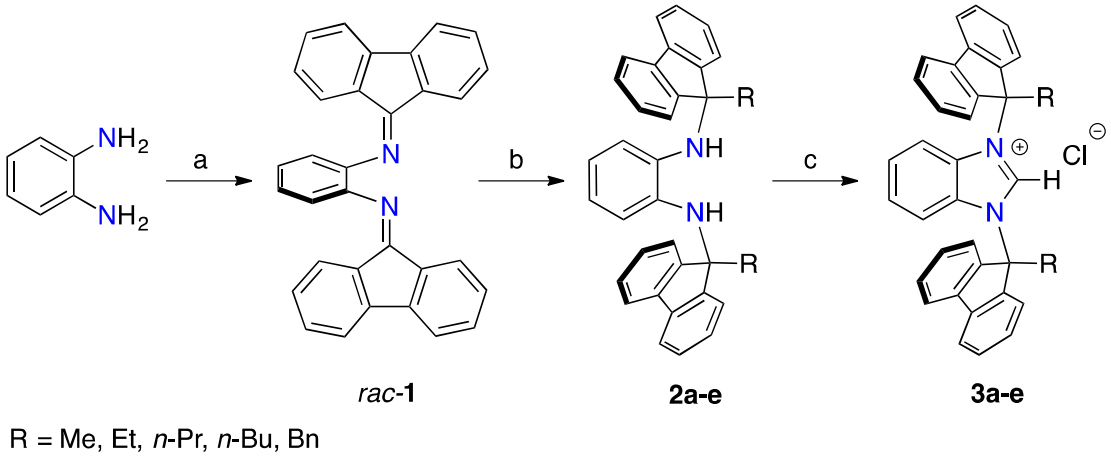


Scheme 1: Coordinating metal centres to clamp-like NHCs.

II - Results and Discussion

II - A) Syntheses of benzimidazolium salts

The AF-substituted benzimidazolium salts **3a-e** were obtained in three steps according to Scheme 2. Their syntheses began with that of **1**,[19] which was obtained by condensation of *ortho*-phenylenediamine with fluorenone in the presence of $TiCl_4$.



Scheme 2: Synthesis of benzimidazolium salts **3a-e.** Reagents and conditions: a) fluorenone, $TiCl_4$, TMEDA, toluene, reflux, 91%; b) R-Li, THF, -78°C to rt, 77-85%; c) $HC(OEt)_3$, HCl conc., 80°C, 75-95%. Compound **1** has a C_2-symmetric structure.

Diimine **1** was then reacted with five different organolithium reagents R-Li affording the corresponding diamines in high yields (**2a-e**). We observed that the use of Grignard reagents instead of alkyllithium compounds resulted in significantly lower yields (< 50%), the reactions leading in that case to azophilic addition products. In the final step, the amines were reacted with ethylorthoformate under acidic conditions resulting in the benzimidazolium chlorides **3a-e**.[20,21] In each of the corresponding ^1H NMR spectra, the C-2 proton of the imidazolium ring appears as a singlet at *ca.* 11.2 ppm. 2D-^1H NMR ROESY experiments established a strong proximity between this proton and the NCCH_2 atoms, but not with the aromatic H atoms of the benzimidazolium moiety, this being indicative of a folding back of the fluorenyl planes towards the central phenylene ring (see experimental section). This structural feature was confirmed by an X-ray diffraction study carried out for **3b** (Figure 1). Molecular modelling (SPARTAN[22]) further revealed that the AF groups cannot rotate about the C-N bond owing to the expanded structure of the fluorenylidene plane. Folding-back of these moieties was also found in diamine **2a** in the solid state (Figure 1).

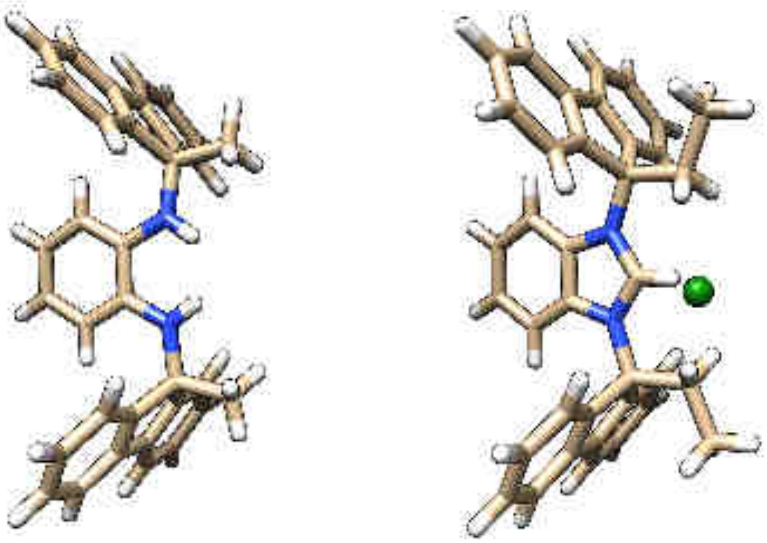
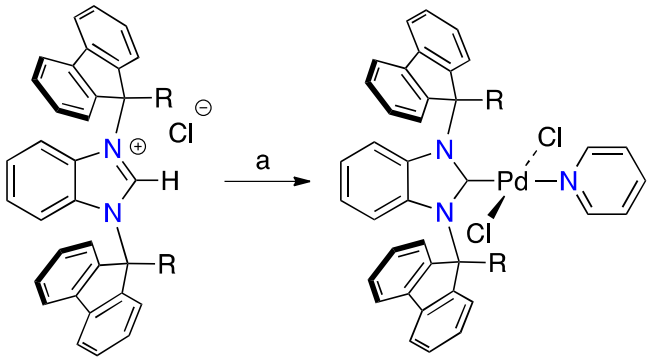


Figure 1: Solid-state structure of the diamine **2a** (left) and the benzimidazolium salt **3b** (right). Co-crystallising molecules of solvent are not shown.

II - B) Syntheses of Pd(II) complexes

The benzimidazolium salts **3a-e** were readily converted into the Pd-PEPPSI complexes **4a-e** by applying a standard procedure (Scheme 3).[23] These complexes are regarded as belonging to the most efficient cross-coupling catalysts.[15,16,23-25]



Scheme 3: Synthesis of palladium complexes **4a-e** (Conditions: $PdCl_2$, K_2CO_3, pyridine, 80°C, 22-85%).

The ^1H NMR spectra of complexes **4a-e** revealed the presence of a pyridine:NHC ratio of 1:1. The most remarkable feature of these spectra concerns the NCC*H*$_2$ signals, which are remarkably downfield shifted with respect to those of the corresponding diamines (δΔ = 2.26-3.38 ppm). X-ray diffraction studies carried out for **4a-c** (R = Me, Et, *n*-Pr) revealed that in the solid state the methylenic NCC*H*$_2$ atoms sit very close to the metal dz_2 axis, with the carbenic plane bisecting the two CH_2 groups. The methylenic C*H* atoms

being located at only *ca.* 2.55 Å from the metal centre, the NHC ligand can thus be viewed as a clamp that holds the metal meridionally confined (Figure 2).

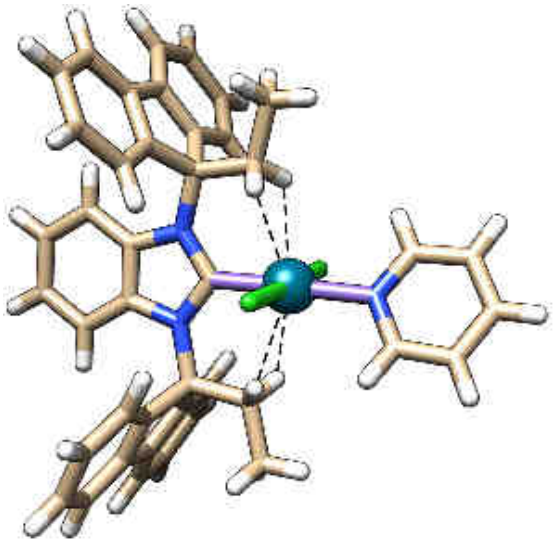


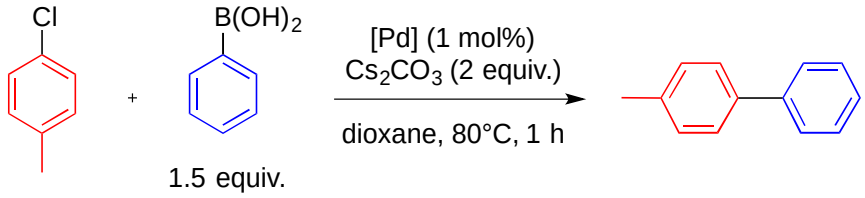
Figure 2: Solid-state structure of complex **4b**, bearing a NHC ligand behaving as a clamp.

This feature is obviously imposed by the directional properties of the fluorenyl planes that push the two methylenic NC*CH*$_2$ groups towards the dz$_2$ axis. As for **3a-e**, there is no indication of AF moieties freely rotating about the corresponding N–C(AF) bonds.[26] Thus, to the best of our knowledge, among the bulky NHCs reported to date,[27] the above ligands constitute the most confining NHCs with *time-independent* crowding. The downfield shift observed for the NCC*H*$_2$ protons as well as the $^1J(^{13}C,^1H)$ values (*ca.* 130 Hz) are typically those of anagostic C–H···Pd bonds in which the bonding interaction displays high electrostatic character.[28-30]

II - C) Catalysis

To assess their catalytic potential, complexes **4a-e** were used in a Suzuki-Miyaura test reaction, namely that between *para*-tolyl chloride and phenylboronic acid. The catalytic runs were carried out in dioxane at 80°C using 1 mol % of catalyst precursor in the presence of 2 equiv. of Cs_2CO_3. All complexes turned out to be active (Table 1).

Table 1: Suzuki-Miyaura cross-coupling of phenyl boronic acid with *para*-tolyl chloride using **4**-**8.**



Entry[a]	Complex	%*V*bur [%]	Yields [%][b]
1	$Pd(OAc)_2$	-	0
2	**4a**	36.9	40
3	**4b**	37.2	70
4	**4c**	38.1	60
5	**4d**	38.0	21
6	**4e**	37.1	19
7	$[PdCl_2(ItBu)(Py)]$ **5**	36.2[31-33]	20
8	$[PdCl_2(IMes)(Py)]$ **6**	31.6[31-33]	63
9	$[PdCl_2(IPr)(Py)]$ **7**	33.6[31-33]	38
10	$[PdCl_2(SIPr)(Py)]$ **8**	35.7[31-33]	37

[a]*para*-tolyl chloride (1 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (2 mmol), dioxane (3 mL). [b]Yields were determined by ^1H NMR using 1,4-dimethoxybenzene as internal standard. Averaged over two runs. No homocoupling products were detected.

Under the above conditions, the conversions ranged from 19% to 70% after 1 h, the highest reaction rates being observed with **4b** (R = Et). Interestingly, the activity of **4a** (R = Me) was twice that of $[PdCl_2(ItBu)(Py)]$ complex **5** (Figure 3), despite the fact that the corresponding NHCs have nearly the same buried volume (36.9% (**4a**); 36.6% (**5**)).[31-33]

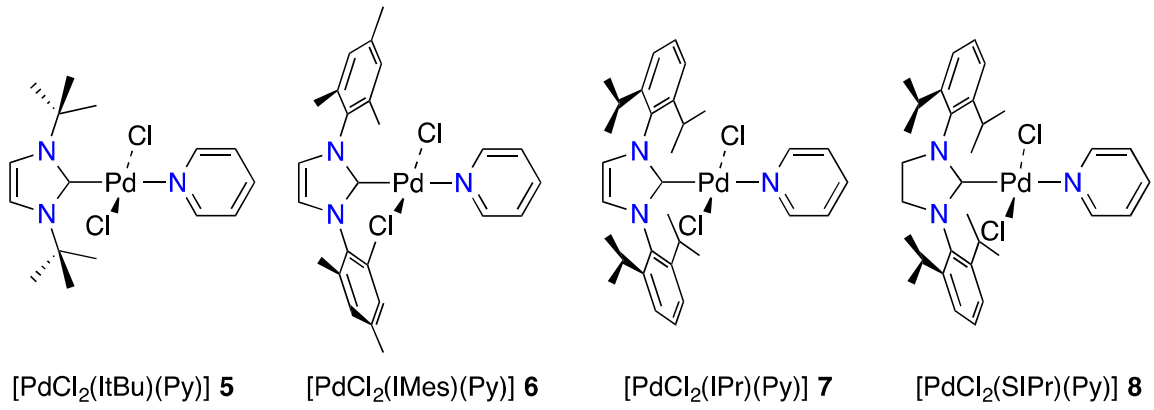


Figure 3: Palladium complexes with bulky NHC ligands used in cross-coupling reactions for comparison with **4a-e**.

This is likely to reflect the restricted rotational freedom of the *N*-subsituents of **4a**, which permanently holds the NC*Me* groups close to the metal centre and therefore increases the metal protection. In other terms, the time-averaged steric crowding about the metal centre is lower in **5**, as the *t*-Bu groups freely rotate around the corresponding N–C_{quat} bonds.

The significant activity increase observed on going from **4a** to the sterically more crowded complexes **4b** and **4c**, is possibly due to a lowering of the activation barrier of the reductive elimination step. However, increasing the bulk of the R groups using substituents larger than *n*-propyl (complexes **4d**, **4e**) led to somewhat lower activities, these groups probably restricting access of the substrate to the metal centre. The percent buried volume was calculated for this series of complexes (**4a-e**) and it turned out to lie in the range of 36.9%-38.1% despite the increasing size of R groups.

Clearly, these observations show that this parameter, although being useful in catalytic studies, does not take into account molecular dynamics that may result in a transient modification of the real bulk of a given ligand.

We also found that the activity of clamp complex **4b** surpasses that of the complexes **6**-**8** (Figure 3), containing the most commonly used NHCs in Suzuki-Miyaura cross-coupling reactions.[8,9,11,15,17,23]

Finally, preliminary tests showed that the above clamps can also efficiently be employed in more challenging cross-couplings. For example, in the reaction of 2,6-dimethoxyphenylboronic acid with 4-chlorotoluene, **4b** was twice as active than complex **6** (see experimental part).

III - Conclusions

In conclusion, we have shown that owing to its substituent-orienting properties, the fluorenylidene moiety constitutes a valuable tool for the creation of NHC-clamps with *time-independent* crowding. The palladium derivatives **4a-e**, that contain such monoligating NHCs, were shown to display activities superior or equal to those obtained with the fastest Pd-NHC Suzuki-Miyaura cross-coupling catalysts reported to date. Overall, the above results suggest that "meridional confinement"[34] may be an interesting alternative to hemispherical encumbrance. Ligands of this type will be assessed in other catalytic reactions.

IV - Experimental Section

IV - A) General information

All commercial reagents were used as supplied. The syntheses were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. Routine ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a FT Bruker AVANCE 300 (^{1}H: 300.1 MHz, ^{13}C: 75.5 MHz) instrument at 25°C. ^{1}H NMR spectral data were referenced to residual protonated solvents ($CHCl_3$, δ 7.26; [D_6] DMSO, δ 2.50), ^{13}C chemical shifts are reported relative to deuterated solvents ($CDCl_3$, δ 77.16; [D_6] DMSO, δ 39.52). Data are presented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (*J*) in Hertz (Hz), integration and assignment. In the NMR data given hereafter, Cq denotes a quaternary carbon atom. Flash chromatography was performed as described by Still et al.,[35] employing Geduran SI (E. Merck, 0.040-0.063 mm) silica. Routine thin-layer chromatography analyses were carried out by using plates coated with Merck Kieselgel 60 GF254. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie (CNRS), Strasbourg. Melting points were determined with a Büchi 535 capillary melting-point apparatus and are uncorrected. Precursor salts of complexes **5**,[20,36] **6**,[37,38] **7**,[37,38] and **8**,[37,38] were prepared following procedures described in the literature.

IV - B) General procedures

General procedure for palladium-catalysed Suzuki-Miyaura cross-coupling reactions

A mixture of the palladium complex (0.01 mmol), phenylboronic acid (0.183 g, 1.50 mmol), and base (2 mmol) was suspended in an appropriate solvent (3 mL). After addition of *para*-tolyl chloride (0.126 g, 1 mmol) the mixture was vigorously stirred at 80°C for a given period of time. The hot mixture was filtered through Celite. Then 1,4-dimethoxybenzene (0.069 g, 0.5 mmol; internal standard) was added to the filtrate. The solvent was removed under reduced pressure and the crude mixture analysed by ^{1}H NMR. The yields were determined by comparing the intensity of the methyl signal of the product (δ(Me) = 2.41 ppm) with that of the internal reference (δ(Me) = 3.78 ppm). In some experiments the product was isolated chromatographically. The isolated yield turned out to be very close (deviation less than 5%) to that determined using the internal reference.

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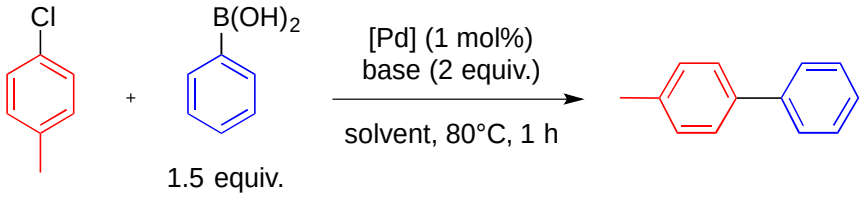
Base and solvent screening for the synthesis of 4-methylbiphenyl using palladium complex 4b[a]

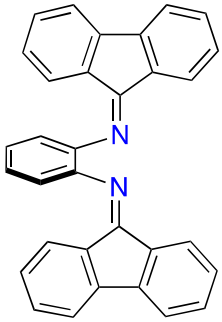


Entry	Solvent	Base	Yield (%)[b]
1	dioxane	NaOH	0
2	dioxane	NaOMe	50
3	dioxane	NaH	3
4	dioxane	Et_3N	0
5	dioxane	K_3PO_4	27
6	dioxane	K_2CO_3	12
7	dioxane	*t*-BuOK	13
8	dioxane	CsF	43
9	dioxane	Cs_2CO_3	70
10	toluene	Cs_2CO_3	0
11	THF	Cs_2CO_3	0[c]
12	DME	Cs_2CO_3	35
13	H_2O	Cs_2CO_3	7
14	EtOH	Cs_2CO_3	0
15	EtOH	NaOH	3
16	*i*-PrOH	NaOMe	6
17	*i*-PrOH	*t*-BuOK	12

[a]*para*-tolyl chloride (1 mmol), phenylboronic acid (1.5 mmol), base (2 mmol), solvent (3 mL). [b]Yields shown are determined by 1H NMR using 1,4-dimethoxybenzene as internal standard. Averaged over two runs. [c] The reaction was conducted at 65°C.

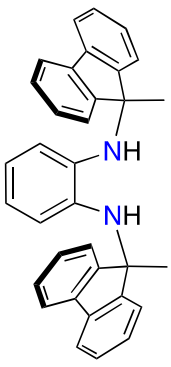
IV - C) Syntheses of amines

***N,N'*-bis(9*H*-fluoren-9-ylidene)benzene-1,2-diimine (1):** A solution of *ortho*-



phenylenediamine (2.160 g, 20 mmol), fluorenone (7.630 g, 42.3 mmol) and TMEDA (36 mL, 240 mmol) in toluene (200 mL) was heated at 80°C. $TiCl_4$ (6.7 mL, 60 mmol) was then added dropwise over 20 min before raising the temperature to 110°C. After 5 h, the reaction mixture was cooled to room temperature and filtered through Celite to remove insoluble materials. These were washed with AcOEt (100 mL) and the filtrate concentrated to dryness. The residue was dissolved in AcOEt (*ca.* 20 mL) and the resulting solution was passed through a short pad of silica gel, eluting with AcOEt until the product was completely recovered. The dark orange filtrate was concentrated to afford a red solid, which was purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether 60:40). Diimine **1** was obtained as an orange solid (7.85 g, 91%): mp > 250°C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.72 (d, ^3J = 7.5 Hz, 2H, ArH), 7.50-7.41 (m, 4H, ArH), 7.35-7.10 (m, 12H, ArH), 7.00 (ddd, ^3J = $^3J'$ = 7.5 Hz ^4J = 0.9 Hz, 2H, ArH); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 162.9 (C=N), 143.6 (arom. Cq), 141.7 (arom. Cq), 140.9 (2×, arom. Cq), 137.6 (arom. Cq), 131.8 (arom. CH), 131.6 (arom. CH), 128.3 (arom. CH), 127.7 (arom. CH), 127.0 (arom. CH), 125.0 (arom. CH), 123.5 (arom. CH), 120.1 (arom. CH), 119.8 (arom. CH), 119.4 (arom. CH). The spectroscopic data are in full agreement with those of the literature.[19]

***N,N'*-bis(9-methyl-9*H*-fluoren-9-yl)benzene-1,2-diamine (2a):** To a stirred solution of



diimine **1** (1.150 g, 2.67 mmol) in THF (10 mL) cooled to -78°C, was added dropwise MeLi (1.6 *M* in Et_2O, 4 mL, 6.40 mmol). The red solution quickly turned black. The reaction mixture was allowed to reach room temperature and was stirred for 30 min. After slow addition of water (30 mL), the mixture was extracted with AcOEt (3 × 40 mL), the combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether 0.5:99.5) to afford **2a** as a pale brown solid (1.030 g, 83%): mp 178°C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.51 (d, ^3J = 7.1 Hz, 4H, ArH), 7.41-7.35 (m, 8H, ArH), 7.30-7.25 (m, 4H, ArH), 6.10 (m, 2H, ArH), 5.63 (m, 2H, ArH), 4.38 (br s, 2H, NH), 1.76 (s, 6H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 150.0 (arom. Cq), 139.1 (arom. Cq), 135.8 (arom.

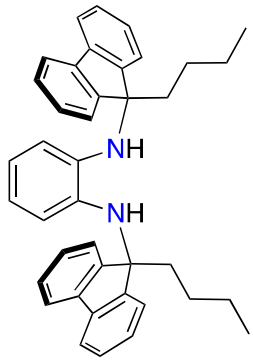
Cq), 128.1 (arom. CH), 127.8 (arom. CH), 123.2 (arom. CH), 120.4 (arom. CH), 119.8 (arom. CH), 117.2 (arom. CH), 65.4 (*C*qCH$_3$), 30.8 (CH$_3$). Found: C, 87.68; H, 6.14; N, 5.85. Calc. for $C_{34}H_{28}N_2$ (M_r = 464.60): C, 87.90; H, 6.07; N, 6.03%.

***N,N'*-bis(9-ethyl-9*H*-fluoren-9-yl)benzene-1,2-diamine (2b):** A solution of ethyl bromide (1.850 g, 17 mmol) in pentane (15 mL) was added to a suspension of lithium powder (25 wt% in mineral oil, 0.940 g, 34 mmol) in pentane (15 mL), at a rate to maintain a steady reflux (about 1 h). Refluxing was maintained for 3 h and the solution was allowed to reach room temperature. After decantation, the clear supernatant (25 mL, C ≈ 0.5 mol/L,[39] 12.5 mmol) was removed and added dropwise *via* syringe to a stirred solution of **1** (2.17 g, 5 mmol) in THF (17 mL), at -78°C. The dark solution was then allowed to reach room temperature. After stirring for 1 h, water (40 mL) was slowly added, then the product was extracted with AcOEt (3 × 40 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether 0.5:99.5) to afford **2b** as a pale brown solid (2.010 g, 82%): mp 130 °C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.76 (d, ^3J = 7.4 Hz, 4H, ArH), 7.42-7.35 (m, 8H, ArH), 7.31-7.26 (m, 4H, ArH), 6.10-6.07 (m, 2H, ArH), 5,66-5.63 (m, 2H, ArH), 4.43 (br s, 2H, NH), 2.22 (q, ^3J = 7.4 Hz, 4H, CH_2), 0.61 (t, ^3J = 7.4 Hz, 6H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 148.3 (arom. Cq), 140.2 (arom. Cq), 135.8 (arom. Cq), 128.1 (arom. CH), 127.6 (arom. CH), 123.5 (arom. CH), 120.2 (arom. CH), 119.6 (arom. CH), 117.0 (arom. CH), 69.0 (*C*qCH_2), 36.4 (CH_2), 8.4 (CH_3). Found: C, 87.63; H, 6.56; N, 5.49. Calc. for $C_{36}H_{32}N_2$ (M_r = 492.65): C, 87.77; H, 6.55; N, 5.69%.

***N,N'*-bis(9-propyl-9*H*-fluoren-9-yl)benzene-1,2-diamine (2c):** Propyl bromide (0.516 g, 4.20 mmol) dissolved in pentane (7 mL) was added to a suspension of lithium powder (25 wt% in mineral oil, 0.234 g, 8.4 mmol) in pentane (7 mL) at a rate to maintain a steady reflux (about 1 h). Refluxing conditions were maintained for 3 h. After decantation at room temperature, the clear supernatant (6.7 mL, C ≈ 0.5 mol/L,[6] 3.30 mmol) was removed and added dropwise *via* syringe to a stirred solution of **1** (0.562 g, 1.30 mmol) in THF (6 mL), at -78°C under nitrogen. The dark solution was allowed to reach room temperature. After stirring for a further 1 h, water (20

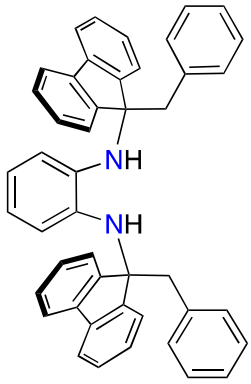
mL) was slowly added and the reaction mixture extracted with AcOEt (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether 0.5:99.5) to afford **2c** as a pale brown solid (0.521 g, 77%): mp 80°C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.77 (d, ^3J = 7.4 Hz, 4H, ArH), 7.43-7.37 (m, 8H, ArH), 7.31-7.27 (m, 4H, ArH), 6.12-6.09 (m, 2H, ArH), 5,68-5.65 (m, 2H, ArH), 4.44 (br s, 2H, NH), 2.18-2.13 (m, 4H, CqCH_2), 1.01-0.90 (m, 4H, CH_2CH$_3$), 0.86 (t, ^3J = 7.4 Hz, 6H, CH$_3$), ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 148.7 (arom. Cq), 140.0 (arom. Cq), 135.8 (arom. Cq), 128.0 (arom. CH), 127.6 (arom. CH), 123.5 (arom. CH), 120.1 (arom. CH), 119.6 (arom. CH), 117.1 (arom. CH), 68.7 (*C*qCH$_2$), 45.8 (Cq*C*H$_2$), 17.2 (*C*H$_2$CH$_3$), 14.4 (CH$_3$). Found: C, 87.53; H, 6.93; N, 5.28. Calc. for $C_{38}H_{36}N_2$ (M_r = 520.71): C, 87.65; H, 6.97; N, 5.38%.

***N*,*N*′-bis(9-butyl-9*H*-fluoren-9-yl)benzene-1,2-diamine (2d):** To a stirred solution of



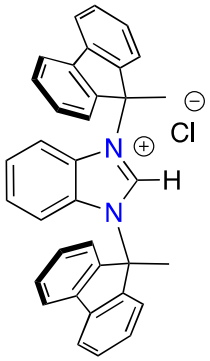
diimine **1** (1.020 g, 2.35 mmol) in THF (10 mL) cooled to -78°C was added BuLi (1.6 *M* in hexanes, 4.4 mL, 7.04 mmol). The red solution quickly turned black. The reaction mixture was allowed to reach room temperature and stirred for 30 min. After slow addition of water (30 mL), the reaction mixture was extracted with AcOEt (3 × 40 mL), the combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether 0.5:99.5) to afford **2d** as a pale brown solid (1.010 g, 78%): mp 79°C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.77 (d, ^3J = 7.4 Hz, 4H, ArH), 7.43-7.36 (m, 8H, ArH), 7.32-7.27 (m, 4H, ArH), 6.14-6.11 (m, 2H, ArH), 5.67-5.66 (m, 2H, ArH), 4.43 (br s, 2H, NH), 2.19-2.14 (m, 4H, CqCH_2), 1.26 (tq, ^3J = $^3J'$ = 7.3 Hz, 4H, CH_2CH$_3$), 1.03-0.92 (m, 4H, CqCH$_2$CH_2), 0.84 (t, ^3J = 7.3 Hz, 6H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 148.8 (arom. Cq), 140.1 (arom. Cq), 135.8 (arom. Cq), 128.0 (arom. CH), 127.6 (arom. CH), 123.5 (arom. CH), 120.2 (arom. CH), 119.6 (arom. CH), 117.2 (arom. CH), 68.6 (*C*qCH$_2$), 43.3 (Cq*C*H$_2$), 26.0 (CqCH$_2$*C*H$_2$), 23.0 (*C*H$_2$CH$_3$), 14.1 (CH$_3$). Found: C, 87.21; H, 7.39; N, 5.39. Calc. for $C_{40}H_{40}N_2$ (M_r = 548.76): C, 87.55; H, 7.35; N, 5.10%.

***N,N'*-bis(9-benzyl-9*H*-fluoren-9-yl)benzene-1,2-diamine (2e):** To a mixture of *t*BuOK



(0.151 g, 1.34 mmol) and toluene (143 mL, 1.31 mmol) in THF (10 mL) cooled to -78°C, was added BuLi (1,6 *M* in hexanes, 760 mL, 1,22 mmol). The suspension quickly turned red. After 20 min at -78°C, diimine **1** (0.200 g, 0.46 mmol) was added portionwise and the mixture quickly turned black. The reaction mixture was allowed to reach room temperature and was stirred for 30 min. After slow addition of water (20 mL), the reaction mixture was extracted with AcOEt (3 × 20 mL), the combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether 0.5:99.5) to afford **2e** as a pale brown solid (0.241 g, 85%): mp 103 °C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.64 (d, ^3J = 7.5 Hz, 4H, ArH), 7.39-7.33 (m, 4H, ArH), 7.28 (m, 8H, ArH), 7.23-7.14 (m, 6H, ArH), 6.89 (dd, ^3J = 7.7 Hz ^4J = 1.5 Hz, 4H, ArH), 6.04-6.00 (m, 2H, ArH), 5.58-5.55 (m, 2H, ArH), 4.68 (br s, 2H, NH), 3.42 (s, 4H, CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 147.9 (arom. Cq), 139.9 (arom. Cq), 135.7 (arom. Cq), 135.5 (arom. Cq), 130.9 (arom. CH), 128.2 (arom. CH), 127.6 (arom. CH), 127.3 (arom. CH), 126.8 (arom. CH), 124.1 (arom. CH), 120.2 (arom. CH), 119.5 (arom. CH), 116.5 (arom. CH), 69.0 (CqCH$_2$), 50.1 (CH_2). Found: C, 89.09; H, 6.10; N, 4.52. Calc. for $C_{46}H_{36}N_2$ (M_r = 616.79): C, 89.58; H, 5.88; N, 4.54%. Despite several recrystallizations the carbon content remained below the expected value.

1,3-bis(9-methyl-9*H*-fluoren-9-yl)benzimidazolium chloride (3a). Diamine **2a** (0.502

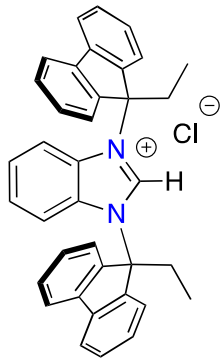


g, 1.08mmol) was dissolved under magnetic stirring in $HC(OEt)_3$ (3 mL). Then HCl 12 *M* (120 mL, 1.40 mmol) was added and the mixture was heated at 80°C for 15 h. After cooling to room temperature, petroleum ether was added (*ca.* 20 mL). The precipitate was filtered off and washed with petroleum ether (3 × 15 mL). **3a** (0.553 sg, 86%) was obtained as a white solid: mp 210°C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 11.24 (s, 1H, NCHN), 7.89 (d, ^3J = 7.5 Hz, 4H, ArH), 7.85 (d, ^3J = 7.5 Hz, 4H, ArH), 7.50 (ddd, ^3J = $^3J'$ = 7.6 Hz ^4J = 0.9 Hz, 4H, ArH), 7.35 (ddd, ^3J = $^3J'$ = 7.6 Hz ^4J = 0.9 Hz, 4H, ArH), 6.82-6.78 (m, 2H, ArH), 6.25-6.21 (m, 2H, ArH), 2.96 (s, 6H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 145.1 (arom. Cq), 142.6 (NCHN), 139.0 (arom. Cq), 130.9 (arom. Cq), 130.3 (arom. CH), 129.4 (arom. CH), 126.3 (arom. CH), 124.9 (arom. CH), 120.8 (arom. CH), 114.8 (arom. CH),

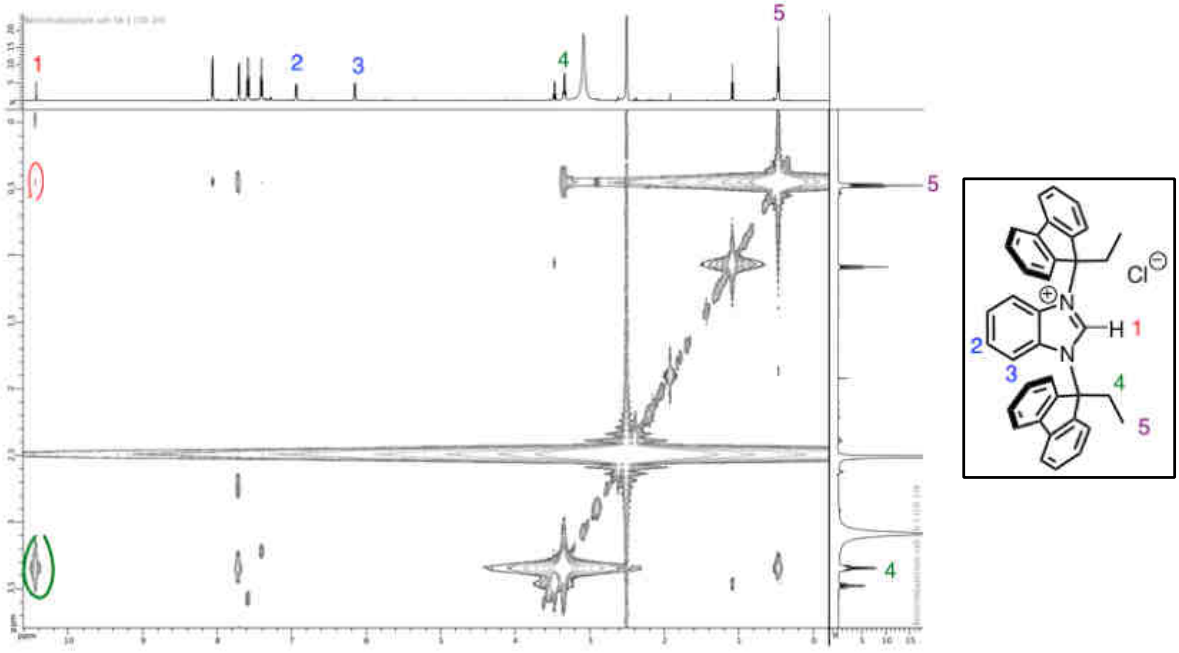
71.4 (*C*qCH$_3$), 27.3 (CH$_3$). Found: C, 78.61; H, 5.55; N, 4.98. Calc. for $C_{35}H_{27}ClN_2 \cdot 1.4\ H_2O$ (M_r = 511.06 + 25.22): C, 78.39; H, 5.60; N, 5.22%.

IV - D) Syntheses of benzimidazolium salts

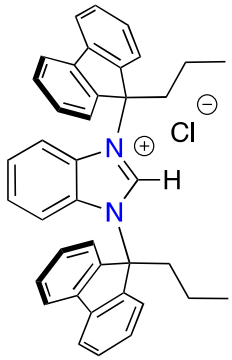
1,3-bis(9-ethyl-9*H*-fluoren-9-yl)benzimidazolium chloride (3b). Diamine **2b** (0.400 g, 0.81 mmol) was dissolved under magnetic stirring in HC(OEt)$_3$ (3 mL). After addition of HCl 12 *M* (89 mL, 1.07 mmol), the mixture was heated at 80°C for 15 h. After cooling to room temperature, petroleum ether was added (*ca.* 20 mL). The precipitate was filtered and washed with petroleum ether (3 × 15 mL). Compound **3b** (0.414 g, 95%) was obtained as a white solid: mp 205°C; ^{1}H NMR (CDCl$_3$, 300 MHz), δ 11.11 (s, 1H, NCHN), 7.81 (d, ^3J = 7.5 Hz, 4H, ArH), 7.79 (d, ^3J = 7.5 Hz, 4H, ArH), 7.48 (ddd, ^3J = $^3J'$ = 7.5 Hz ^4J = 0.9 Hz, 4H, ArH), 7.34 (ddd, ^3J = $^3J'$ = 7.5 Hz ^4J = 0.9 Hz, 4H, ArH), 6.76-6.73 (m, 2H, ArH), 6.25-6.21 (m, 2H, ArH), 3.68 (q, ^3J = 7.0 Hz, 4H, CH$_2$), 0.51 (t, ^3J = 7.0 Hz, 6H, CH$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz), δ 143.2 (arom. Cq), 142.2 (NCHN), 140.6 (arom. Cq), 131.6 (arom. Cq), 130.4 (arom. CH), 129.6 (arom. CH), 126.3 (arom. CH), 125.1 (arom. CH), 120.6 (arom. CH), 115.0 (arom. CH), 75.4 (*C*qCH$_2$), 31.7 (CH$_2$), 7.6 (CH$_3$). Found: C, 79.94; H, 6.20; N, 4.80. Calc. for $C_{37}H_{31}ClN_2 \cdot H_2O$ (M_r = 539.11 + 18.02): C, 79.77; H, 5.97; N, 5.03%.



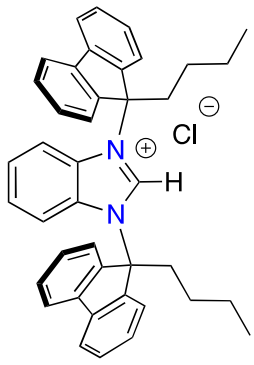
2D-^{1}H NMR ROESY spectrum ([D$_6$] DMSO, 600 MHz, 80°C):



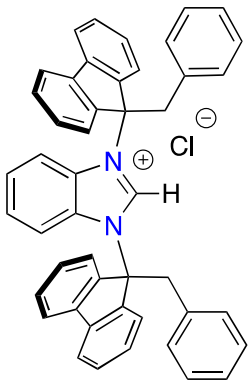
1,3-bis(9-propyl-9*H*-fluoren-9-yl)benzimidazolium chloride (3c). Diamine **2c** (0.422 g, 0.81 mmol) was dissolved under magnetic stirring in $HC(OEt)_3$ (3 mL). After addidtion of HCl 12 *M* (89 mL, 1.07 mmol) the mixture was heated at 80°C for 15 h. The solution was cooled to room temperature, and petroleum ether was added (*ca.* 20 mL). The resulting precipitate was filtered off and washed with petroleum ether (3 × 15 mL). **3c** (0.358 g, 78%) was obtained as a white solid: mp 195°C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 11.03 (s, 1H, NCHN), 7.82 (d, ^3J = 7.5 Hz, 4H, ArH), 7.80 (d, ^3J = 7.5 Hz, 4H, ArH), 7.47 (ddd, $^3J = {}^3J' = 7.5$ Hz $^4J = 0.9$ Hz, 4H, ArH), 7.34 (ddd, $^3J = {}^3J' = 7.5$ Hz $^4J = 0.9$ Hz, 4H, ArH), 6.74-6.71 (m, 2H, ArH), 6.23-6.19 (m, 2H, ArH), 3.62-3.57 (m, 4H, CqCH_2), 0.92 (t, ^3J = 7.1 Hz, 6H, CH_3), 0.85-0.72 (m, 4H, CH_2CH$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 143.6 (arom. Cq), 141.9 (NCHN), 140.3 (arom. Cq), 131.0 (arom. Cq), 130.3 (arom. CH), 129.5 (arom. CH), 126.1 (arom. CH), 125.1 (arom. CH), 120.5 (arom. CH), 114.9 (arom. CH), 74.8 (*C*qCH$_2$), 39.9 (Cq*C*H$_2$), 16.6 (*C*H$_2$CH$_3$), 14.1 (CH$_3$), Found: C, 80.91; H, 6.27; N, 4.77. Calc. for $C_{39}H_{35}ClN_2 \cdot 0.7\ H_2O$ (M_r = 567.16 + 12.61): C, 80.79; H, 6.33; N, 4.83%.



1,3-bis(9-butyl-9*H*-fluoren-9-yl)benzimidazolium chloride (3d). Diamine **2d** (0.912 g, 1.66 mmol) was dissolved under magnetic stirring in $HC(OEt)_3$ (5 mL). After addidtion of HCl 12 *M* (183 mL, 2.19 mmol) the mixture was heated at 80°C for 15 h. The solution was then cooled to room temperature and petroleum ether was added (*ca.* 20 mL). The precipitate was filtered off, then washed with petroleum ether (3 × 15 mL) and dried in vacuo. **3d** (0.878 g, 89%) was obtained as a white solid: mp 170°C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 11.10 (s, 1H, NCHN), 7.83 (d, ^3J = 7.5 Hz, 4H, ArH), 7.82 (d, ^3J = 7.5 Hz, 4H, ArH), 7.49 (dd, $^3J = {}^3J' = 7.5$ Hz, 4H, ArH), 7.35 (dd, $^3J = {}^3J' = 7.5$ Hz, 4H, ArH), 6.75-6.70 (m, 2H, ArH), 6.23-6.19 (m, 2H, ArH), 3.67-3.62 (m, 4H, CqCH_2), 1.40 (tq, $^3J = {}^3J' = 7.3$ Hz, 4H, CH_2CH$_3$), 0.77-0.67 (m, 10H, CqCH$_2$CH_2 and CH$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 143.7 (arom. Cq), 142.1 (N*C*HN), 140.4 (arom. Cq), 131.0 (arom. Cq), 130.3 (arom. CH), 129.5 (arom. CH), 126.1 (arom. CH), 125.1 (arom. CH), 120.5 (arom. CH), 114.9 (arom. CH), 74.8 (*C*qCH$_2$), 37.7 (Cq*C*H$_2$), 25.34 (CqCH$_2$*C*H$_2$), 22.59 (*C*H$_2$CH$_3$), 14.28 (CH$_3$), Found: C, 80.59; H, 6.62; N, 4.71. Calc. for $C_{41}H_{39}ClN_2 \cdot 0.8\ H_2O$ (M_r = 595.21 + 14.41): C, 80.78; H, 6.71; N, 4.60%.

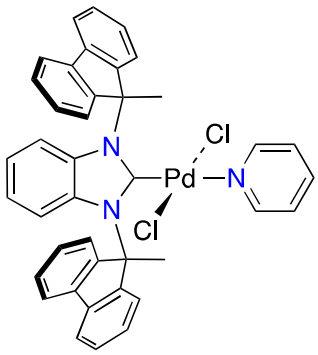


1,3-bis(9-benzyl-9*H*-fluoren-9-yl)benzimidazolium chloride (3e). Diamine **2e** (0.450 g, 0.73 mmol) was dissolved under magnetic stirring in $HC(OEt)_3$ (3 mL), then HCl 12 *M* (81 mL, 0.97 mmol) was added. The mixture was heated at 80°C for 15 h. After cooling to room temperature, petroleum ether was added (*ca.* 20 mL) and the resulting precipitate was filtered off and washed with petroleum ether (3 × 15 mL). **3e** (0.362 g, 75%) was obtained as a white solid: mp 225°C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 11.49 (s, 1H, NCHN), 8.01-8.07 (m, 4H, ArH), 7.52-7.50 (m, 4H, ArH), 7.42-7.35 (m, 8H, ArH), 6.93 (t, ^3J = 7.5 Hz, 2H, ArH), 6.83-6.76 (m, 6H, ArH), 6.61 (d, ^3J = 7.5 Hz, 4H, ArH), 6.25-6.22 (m, 2H, ArH), 5.06 (s, 4H, CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 143.9 (arom. Cq), 142.9 (NCHN), 142.2 (arom. Cq), 132.0 (arom. Cq), 131.1 (arom. Cq), 131.0 (arom. CH), 130.3 (arom. CH), 128.9 (arom. CH), 127.0 (arom. CH), 126.6 (arom. CH), 126.3 (arom. CH), 125.6 (arom. CH), 120.4 (arom. CH), 115.2 (arom. CH), 75.1 (*C*qCH_2), 44.2 (CH_2); Found: C, 80.43; H, 5.34; N, 4.11. Calc. for $C_{47}H_{35}ClN_2 \cdot 2\ H_2O$ (M_r = 663.25 + 36.03): C, 80.73; H, 5.62; N, 4.01%.



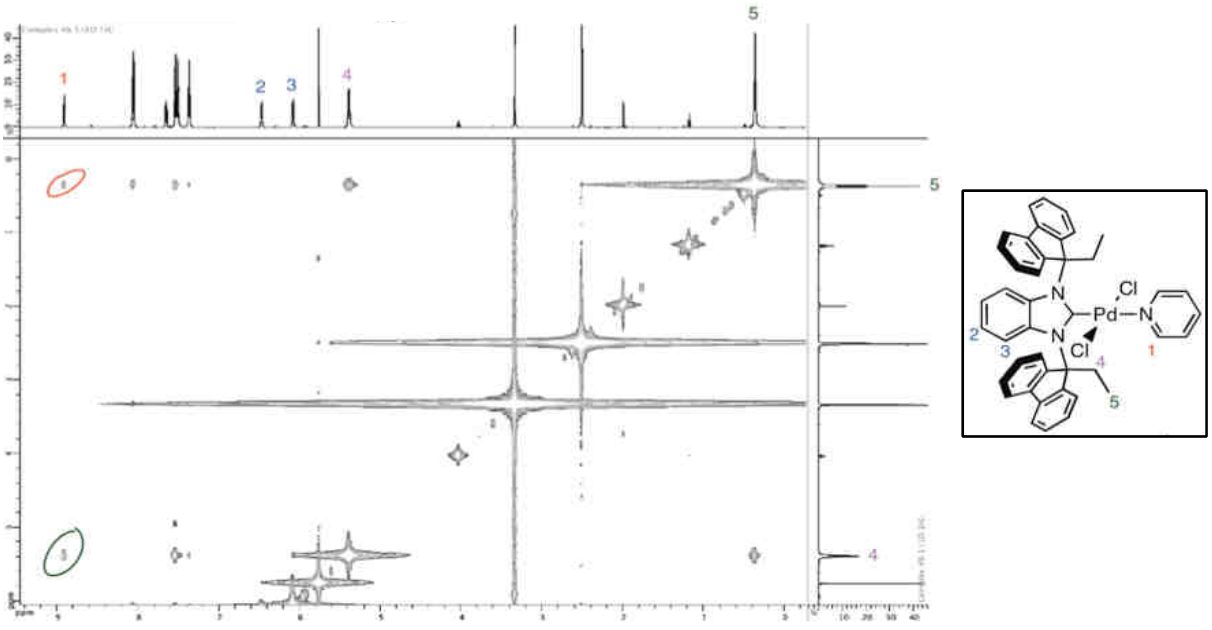
IV - E) Syntheses of palladium complexes

***trans*-[1,3-bis(9-methyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene](pyridine) palladium(II) dichloride (4a):** Nitrogen was passed (2 min) through a suspension of benzimidazolium salt **3a** (0.260 g, 0.51 mmol), K_2CO_3 (0.356 g, 2.58 mmol) and $PdCl_2$ (0.110 g, 0.62 mmol) in pyridine (3 mL). The suspension was then heated at 80°C for 15 h under vigorous stirring. After cooling to room temperature, the mixture was filtered through Celite and the solid washed with CH_2Cl_2 (*ca.* 20 mL). The solvent was removed in vacuo, and the residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether 50:50) to afford **4a** as a yellow solid (0.316 g, 85%): mp > 240°C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 9.19-9.12 (m, 2H, *ortho*-NC_5H_5), 7.85-7.78 (m, 9H, 8H ArH and 1H *para*-NC_5H_5), 7.47-7.37 (m, 6H, 4H ArH and 2H *meta*-NC_5H_5), 7.29 (dd, ^3J = $^3J'$ = 7.5 Hz, 4H, ArH), 6.40-6.37 (m, 2H, ArH), 6.08-6.05 (m, 2H, ArH), 4.02 (s, 6H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 161.5 (NCN), 151.8 (arom. CH), 149.2 (arom. Cq), 138.4 (arom. Cq), 138.2 (arom. CH), 134.4 (arom. Cq), 129.1 (2×, arom. CH), 124.9 (arom. CH), 124.7 (arom. CH), 122.5 (arom. CH), 120.7 (arom. CH), 113.1 (arom. CH), 72.2 (*C*qCH_3), 33.8 (CH_3); Found: C, 64.39; H, 4.31; N, 5.56. Calc. for $C_{40}H_{31}Cl_2N_3Pd \cdot 0.2\ CH_2Cl_2$ (M_r = 731.02 + 16.99): C, 64.55; H, 4.23; N, 5.62%.



***trans*-[1,3-bis(9-ethyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene](pyridine) palladium(II) dichloride (4b):** Nitrogen was passed (2 min) through a stirred suspension of benzimidazolium salt **3b** (0.103 g, 0.19 mmol), K_2CO_3 (0.132 g, 0.96 mmol) and $PdCl_2$ (0.041 g, 0.23 mmol) in pyridine (2.5 mL). The suspension was then heated at 80°C for 15 h under vigorous stirring. After cooling to room temperature, the mixture was filtered through Celite and the solid washed with CH_2Cl_2 (*ca.* 20 mL). The filtrate was concentrated under vacuum and purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether 50:50) to afford **4b** as a yellow solid (0.113 g, 78%): mp > 240°C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 9.13-9.10 (m, 2H, *ortho*-NC_5H_5), 7.84-7.76 (m, 5H, 4H ArH and 1H *para*-NC_5H_5), 7.72 (d, ^3J = 7.5 Hz, 4H, ArH), 7.45-7.35 (m, 6H, 4H ArH and 2H *meta*-NC_5H_5), 7.28 (ddd, $^3J = {}^3J' = 7.5$ Hz $^4J = 0.9$ Hz, 4H, ArH), 6.37-6.34 (m, 2H, ArH), 6.18-6.15 (m, 2H, ArH), 5.45 (q, $^3J = 7.3$ Hz, 4H, CH_2), 0.42 (t, $^3J = 7.3$ Hz, 6H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 160.4 (NCN), 151.8 (arom. CH), 146.4 (arom. Cq), 140.3 (arom. Cq), 138.2 (arom. CH), 134.6 (arom. Cq), 129.1 (2×, arom. CH), 125.0 (arom. CH), 124.8 (arom. CH), 122.1 (arom. CH), 120.0 (arom. CH), 113.5 (arom. CH), 76.7 (*C*qCH_2), 36.8 (CH_2), 8.7 (CH_3). Found: C, 66.73; H, 4.99; N, 5.16. Calc. for $C_{42}H_{35}Cl_2N_3Pd$ (M_r = 759.07): C, 66.46; H, 4.65; N, 5.54%.

2D-^{1}H NMR ROESY spectrum ([D_6] DMSO, 600 MHz, 80°C):



***trans*-[1,3-bis(9-propyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene](pyridine) palladium(II) dichloride (4c):** Nitrogen was passed (2 min) through a suspension of benzimidazolium salt **3c** (0.352 g, 0.62 mmol), K_2CO_3 (0.427 g, 3.09 mmol) and $PdCl_2$ (0.132 g, 0.74 mmol) in pyridine (3 mL). The suspension was then heated at 80°C for 24 h under vigorous stirring. After cooling to room temperature, the mixture was filtered through Celite and the filtered solid washed with CH_2Cl_2 (*ca.* 20 mL). The solvent was removed in vacuo and the residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether 50:50) affording **4c** as a yellow solid (0.108 g, 22%): mp > 240°C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 9.16-9.14 (m, 2H, *ortho*-NC_5H_5), 7.87-7.72 (m, 9H, 8H ArH and 1H *para*-NC_5H_5), 7.43-7.38 (m, 6H, 4H ArH and 2H *meta*-NC_5H_5), 7.30-7.26 (m, 4H, ArH), 6.35-6.32 (m, 2H, ArH), 6.15-6.11 (m, 2H, ArH), 5.46-5.41(m, 4H, CqCH_2), 0.92 (t, ^3J = 7.2 Hz, 6H, CH_3), 0.62 (tq, ^3J = $^3J'$ = 7.2 Hz, 4H, CH_2CH$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 160.7 (NCN), 151.9 (arom. CH), 147.0 (arom. Cq), 140.0 (arom. Cq), 138.2 (arom. CH), 134.5 (arom. Cq), 129.1 (arom. CH), 129.1 (arom. CH), 124.9 (arom. CH), 124.8 (arom. CH), 122.4 (arom. CH), 120.0 (arom. CH), 113.4 (arom. CH), 76.0 (*C*qCH$_2$), 46.0 (Cq*C*H$_2$), 17.6 (*C*H$_2$CH$_3$), 14.5 (CH_3). Found: C, 66.06; H, 4.96; N, 5.14. Calc. for $C_{44}H_{39}Cl_2N_3Pd$·0.2 CH_2Cl_2 (M_r = 787.13 + 16.99): C, 66.02; H, 4.94; N, 5.23%.

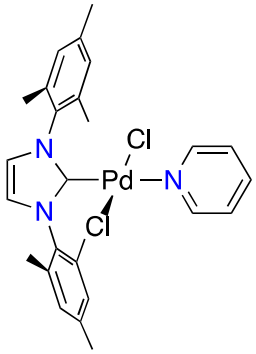
***trans*-[1,3-bis(9-butyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene](pyridine) palladium(II) dichloride (4d):** Nitrogen was passed (2 min) through a suspension of benzimidazolium salt **3d** (0.503 g, 0.84 mmol), K_2CO_3 (0.590 g, 4.27 mmol) and $PdCl_2$ (0.179 g, 1.01 mmol) in pyridine (3 mL). The mixture was then heated at 80°C for 15 h under vigorous stirring. After cooling to room temperature, the mixture was filtered through Celite and the filtered solid washed with CH_2Cl_2 (*ca.* 20 mL). The solvent was removed in vacuo and the residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether 50:50) to afford **4d** as a yellow solid (0.279 g, 41%): mp > 240°C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 9.19-9.17 (m, 2H, *ortho*-NC_5H_5), 7.83-7.72 (m, 9H, 8H ArH and 1H *para*-NC_5H_5), 7.43-7.38 (m, 6H, 4H ArH and 2H *meta*-NC_5H_5), 7.30-7.25 (m, 4H, ArH), 6.34-6.31 (m, 2H, ArH), 6.15-6.11 (m, 2H, ArH), 5.47-5.41 (m, 4H, CqCH_2), 1.34 (tq ^3J = $^3J'$ = 7.3 Hz, 4H, CH_2CH$_3$), 0.69 (t, ^3J = 7.3 Hz, 6H, CH_3), 0.55 (tt, ^3J = $^3J'$ = 7.3 Hz, 4H, CqCH$_2$CH_2);

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 160.5 (NCN), 151.9 (arom. CH), 147.0 (arom. Cq), 140.1 (arom. Cq), 138.2 (arom. CH), 134.6 (arom. Cq), 129.1 (arom. CH), 129.0 (arom. CH), 124.9 (arom. CH), 124.7 (arom. CH), 122.3 (arom. CH), 120.0 (arom. CH), 113.4 (arom. CH), 76.1 (*C*qCH$_2$), 43.6 (Cq*C*H$_2$), 26.1 (CqCH$_2$*C*H$_2$), 23.0 (*C*H$_2$CH$_3$), 14.1 (CH$_3$). Found: C, 67.37; H, 5.39; N, 4.99. Calc. for $C_{46}H_{43}Cl_2N_3Pd \cdot 0.1\ CH_2Cl_2$ (M_r = 815.18 + 8.49): C, 67.22; H, 5.29; N, 5.10%.

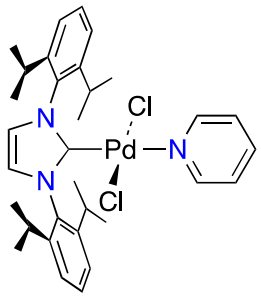
***trans*-[1,3-bis(9-benzyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene](pyridine) palladium(II) dichloride (4e):** Nitrogen was passed (2 min) through a suspension of benzimidazolium salt **3e** (0.200 g, 0.30 mmol), K_2CO_3 (0.207 g, 1.5 mmol) and $PdCl_2$ (0.065 g, 0.36 mmol) in pyridine (3 mL). The suspension was then heated at 80°C for 15 h under vigorous stirring. After cooling to room temperature, the mixture was filtered through Celite and the filtered solid washed with CH_2Cl_2 (*ca.* 20 mL). The solvent was removed in vacuo and the residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether 50:50) to afford **4e** as a yellow solid (0.177 g, 67%): mp > 240°C; ^1H NMR ($CDCl_3$, 300 MHz), δ 9.01-8.98 (m, 2H, *ortho*-NC$_5H_5$), 8.02-7.97 (m, 4H, ArH), 7.66 (tt, ^3J = 7.7 Hz ^4J = 1.7 Hz, 1H, *para*-NC$_5H_5$), 7.44-7.22 (m, 14H, 12H ArH and 2H *meta*-NC$_5H_5$), 6.94 (tt, ^3J = 7.4 Hz ^4J = 1.1 Hz, 2H, ArH), 6.83-6.74 (m, 8H, 4H ArH and 4H CH$_2$), 6.41 (d, ^3J = 7.4 Hz, 4H, ArH), 6.38-6.35 (m, 2H, ArH), 6.16-6.12 (m, 2H, ArH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 161.3 (NCN), 151.6 (arom. CH), 146.2 (arom. Cq), 140.1 (arom. Cq), 138.0 (arom. CH), 134.6 (arom. Cq), 134.5 (arom. Cq), 131.2 (arom. CH) 129.2 (arom. CH), 128.6 (arom. CH), 126.6 (arom. CH), 125.9 (arom. CH), 125.4 (arom. CH), 125.0 (arom. CH) 122.5 (arom. CH), 119.9 (arom. CH), 113.8 (arom. CH), 76.3 (*C*qCH$_2$), 50.0 (Cq*C*H$_2$). Found: C, 70.72; H, 4.56; N, 4.82. Calc. for $C_{52}H_{39}Cl_2N_3Pd$ (M_r = 883.21): C, 70.71; H, 4.45; N, 4.76%.

***trans*-[1,3-bis(tert-butyl)benzimidazol-2-ylidene](pyridine)palladium(II)dichloride (5):** Nitrogen was passed (2 min) through a suspension of 1,3-bis(tert-butyl)benzimidazolium chloride (0.630 g, 2.36 mmol), K_2CO_3 (1.63 g, 11.8 mmol) and $PdCl_2$ (0.415 g, 2.34 mmol) in pyridine (5 mL). The suspension was then heated at 80°C for 15 h under vigorous stirring. After cooling to room temperature, the mixture was filtered through Celite and the filtered solid

washed with CH_2Cl_2 (*ca.* 20 mL). The combined washings and the filtrate were evaporated to dryness. The residue was then purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether 50:50) to afford **5** as a yellow solid (0.921 g, 80%): mp 229°C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 9.03-8.98 (m, 2H, *ortho*-NC_5H_5), 7.83-7.79 (m, 2H, ArH), 7.78 (tt, ^3J = 7.6 Hz ^4J = 1.6 Hz, 1H, *para*-NC_5H_5), 7.38-7.33 (m, 2H, *meta*-NC_5H_5), 7.24-7.18 (m, 2H ArH), 2.52 (s, 18H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 157.2 (NCN), 151.6 (arom. CH), 137.9 (arom. CH), 135.1 (arom. Cq), 124.7 (arom. CH), 121.6 (arom. CH), 115.3 (arom. CH), 61.3 (CqCH$_3$), 31.9 (CH_3). Found: C, 48.81; H, 5.64; N 8.43. Calc. for $C_{20}H_{27}Cl_2N_3Pd$ (M_r = 486.77): C, 49.35; H, 5.59; N, 8.63%.

***trans*-[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene](pyridine)palladium(II) dichloride (6):** 

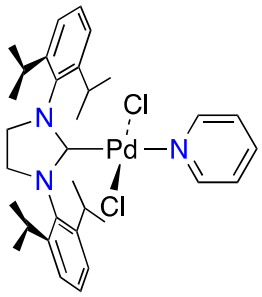
Nitrogen was passed (2 min) through a suspension of bis(2,4,6-trimethylphenyl) imidazolium chloride (0.511 g, 1.50 mmol), K_2CO_3 (1.04 g, 7.50 mmol) and $PdCl_2$ (0.320 g, 1.80 mmol) in pyridine (5 mL). The suspension was then heated at 80°C for 15 h under vigorous stirring. After cooling to room temperature, the mixture was filtered through Celite and the collected solid washed with CH_2Cl_2 (*ca.* 20 mL). The filtrate was evaporated to dryness and the resulting residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether 50:50) to afford **6** as a yellow solid (0.689 g, 82%): mp > 240°C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 8.54-8.48 (m, 2H, *ortho*-NC_5H_5), 7.54 (tt, ^3J = 7.6 Hz ^4J = 1.5 Hz, 1H, *para*-NC_5H_5), 7.12-7.07 (m, 2H, *meta*-NC_5H_5), 7.06 (s, 2H, ArH), 7.05 (s, 4H, ArH), 2.37 (s, 6H, *para*-CH_3); 2.36 (s, 12H, *ortho*-CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 152.9 (NCN), 151.6 (arom. CH), 139.2 (arom. Cq), 137.5 (arom. CH), 136.4 (arom. Cq), 135.2 (arom. Cq), 129.3 (arom. CH), 124.2 (arom. CH), 124.0 (arom. CH), 21.3 (*para*-CH_3) 19.2 (*ortho*-CH_3). Found: C, 55.68; H, 5.51; N 7.23. Calc. for $C_{26}H_{29}Cl_2N_3Pd$ (M_r = 560.85): C, 55.68; H, 5.21; N, 7.49%.

***trans*-[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](pyridine)palladium(II) dichloride (7):** 

Nitrogen was passed (2 min) through a suspension of bis(2,6-diisopropylphenyl)imidazolium chloride (0.301 g, 0.71 mmol), K_2CO_3 (0.493 g, 3.55 mmol) and $PdCl_2$ (0.151 g, 0.85 mmol) in pyridine (5 mL). The suspension was then heated at 80°C for 15 h under vigorous stirring. After cooling to room temperature, the mixture was filtered through Celite and the collected solid washed

with CH_2Cl_2 (*ca.* 20 mL). The filtrate and the washings were evaporated to dryness and the resulting residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether 50:50) to afford **7** as a yellow solid (0.322 g, 70%): mp 235°C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 8.58-8.51 (m, 2H, *ortho*-NC_5H_5), 7.57-7.44 (m, 3H, 2H ArH and 1H *para*-NC_5H_5), 7.35 (d, ^3J = 7.6 Hz, 4H, ArH), 7.14-7.05 (m, 4H, 2H ArH and 2H, *meta*-NC_5H_5), 3.18 (qq, ^3J = $^3J'$ = 6.7 Hz, 4H, C*H*Me$_2$), 1.49 (d, ^3J = 6.7 Hz, 12H, CHC*H*$_3$), 1.12 (d, ^3J = 6.7 Hz, 12H, CHC*H*$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 155.0 (NCN), 151.5 (arom. CH), 146.7 (arom. Cq), 137.5 (arom. CH), 135.2 (arom. Cq), 130.3 (arom. CH), 125.1 (arom. CH), 124.1 (2×, arom. CH), 28.8 (*C*HMe$_2$) 26.4 (CH_3) 23.4 (CH_3). Found: C, 59.53; H, 6.63; N 6.29. Calc. for $C_{32}H_{41}Cl_2N_3Pd$ (M_r = 645.01): C, 59.59; H, 6.41; N, 6.51%. The spectroscopic data are in full agreement with those of the literature.[203]

***trans*-[1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene](pyridine)palladium(II) dichloride (8):** Nitrogen was passed (2 min) through a suspension of bis(2,6-diisopropylphenyl)imidazolinium chloride (0.303 g, 0.71 mmol), K_2CO_3 (0.496 g, 3.55 mmol) and $PdCl_2$ (0.152 g, 0.85 mmol) in pyridine (5 mL). The suspension was then heated at 80°C for 15 h under vigorous stirring. After cooling to room temperature, the mixture was filtered through Celite and the collected solid washed with CH_2Cl_2 (*ca.* 20 mL). The filtrate was evaporated to dryness and the resulting residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether 50:50) to afford **8** as a yellow solid (270 mg, 58%): mp 227°C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ 8.54-8.47 (m, 2H, *ortho*-NC_5H_5), 7.52 (tt, ^3J = 7.6 Hz ^4J = 1.6 Hz, 1H, *para*-NC_5H_5), 7.44-7.37 (m, 2H, ArH), 7.32-7.27 (m, 4H, ArH), 7.10-7.04 (m, 2H, *meta*-NC_5H_5), 4.06 (s, 4H, CH_2), 3.60 (qq, ^3J = $^3J'$ = 6.7 Hz, 4H, C*H*Me$_2$), 1.57 (d, ^3J = 6.7 Hz, 12H, CHC*H*$_3$), 1.27 (d, ^3J = 6.7 Hz, 12H, CHC*H*$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 186.2 (NCN), 151.3 (arom. CH), 147.6 (arom. Cq), 137.4 (arom. CH), 135.5 (arom. Cq), 129.5 (arom. CH), 125.5 (arom. CH), 124.0 (arom. CH), 58.9 (CH_2), 28.8 (*C*HMe$_2$) 26.9 (CH_3) 24.3 (CH_3). Found: C, 59.15; H, 6.98; N 6.01. Calc. for $C_{32}H_{43}Cl_2N_3Pd$ (M_r = 647,03): C, 59.40; H, 6.70; N, 6.49%.



IV - F) Crystal data

Crystal data for diamine 2a

Crystals suitable for X-ray diffraction were obtained by slow evaporation of a deuterated chloroform solution of the diamine: $C_{35}H_{28}ClN_2$, M_r = 512.04, triclinic, space

group *P*-1, *a* = 6.8781(3), *b* = 12.9897(6), *c* = 16.6410(9) Å, □□= 86.149(4), *V* = 1366.00(11) Å^3, *Z* = 2, □□= 0.166 mm^{-1}, *F*(000) = 538. Crystals of the compound were mounted on a Oxford Diffraction CCD Safire 3 Xcalibur diffractometer. Data collection with Mo-*K*□□radiation (□□= 0.71073 Å) was carried out at 150 K. 18667 reflections were collected (2.57 < □ < 27.00°), 5960 were found to be unique and 2581 were observed (merging *R* = 0.0651). The structure was solved with SHELXS-97.[40] Final results: *R*2, *R*1, *wR*2, *wR*1, Goof; 0.1558, 0.0626, 0.1701, 0.1539, 0.967. Residual electron density minimum/maximum = −0.413/0.855 e Å^{-3}. The diffraction study revealed the presence of a highly disordered CH2Cl2 molecule. CCDC 811569 contains the supplementary crystallographic data for this structure. Crystallographic data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB 11EZ, UK; ax: (internat.) 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. An ORTEP representation given in the main text.

Crystal data for benzimidazolium salt 3b•MeOH

Crystals suitable for X-ray diffraction were obtained by slow evaporation of a deuterated chloroform solution of the complex: $C_{38}H_{35}ClN_2O$, M_r = 571.13 monoclinic, space group $P2_1/c$, *a* = 13.2006(3), *b* = 16.0741(4), *c* = 14.5915(4) Å, □□ = 102.141(3), *V* = 3026.89(13) Å^3, *Z* = 4, □ = 0.160 mm^{-1}, *F*(000) = 1208. Crystals of the compound were mounted on a Oxford Diffraction CCD Safire 3 Xcalibur diffractometer. Data collection with Mo-$K_□$ radiation (□ = 0.71073 Å) was carried out at 140 K. 23233 reflections were collected (2.66 < □□□< 27.00°), 6590 were found to be unique and 3594 were observed (merging *R* = 0.0549). The structure was solved with SHELXS-97.[40] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.0957, 0.0394, 0.0889, 0.0811, 0.819. Residual electron density minimum/maximum = –0.237/0.254 e Å^{-3}. CCDC 811568 contains the supplementary crystallographic data for this structure. Crystallographic data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB 11EZ, UK; ax: (internat.) 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. An ORTEP representation given in the main text.

Crystal data for complex 4b

Crystals suitable for X-ray diffraction were obtained by slow diffusion of thf into a deuterated chloroform solution of the complex: $C_{42}H_{35}Cl_2N_3Pd$, M_r = 759.03, monoclinic,

space group $P2_1/n$, a = 11.27110(10), b = 22.3694(3), c = 17.3400(2) Å, □□ = 93.3090(10), V = 4364.61(9) Å^3, Z = 4, □ = 0.576 mm^{-1}, F(000) = 1552. Crystals of the compound were mounted on a Oxford Diffraction CCD Safire 3 Xcalibur diffractometer. Data collection with Mo-K□ radiation (□ = 0.71073 Å) was carried out at 150 K. 61105 reflections were collected (2.78 <□□< 27.00°), 9522 were found to be unique and 6814 were observed (merging R = 0.0462). The structure was solved with SHELXS-97.[40] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.0579, 0.0341, 0.1380, 0.1203, 0.559. Residual electron density minimum/maximum = –0.324/0.365 e Å^{-3}. CCDC 811477 contains the supplementary crystallographic data for this structure. Crystallographic data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB 11EZ, UK; ax: (internat.) 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. An ORTEP representation given in the main text.

V - Notes and references

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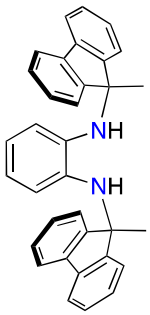

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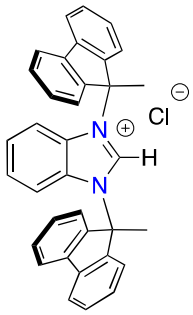

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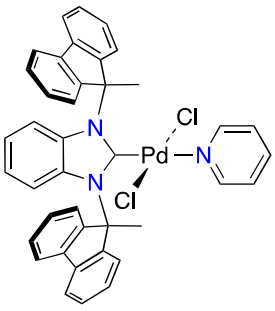

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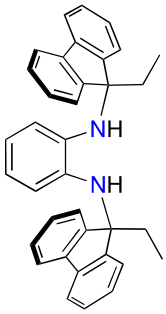

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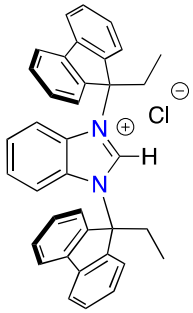

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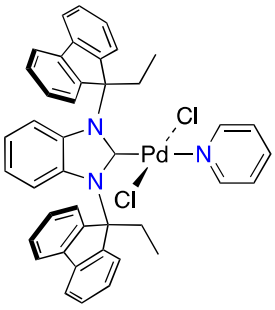

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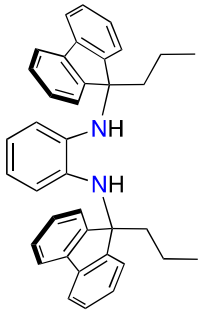

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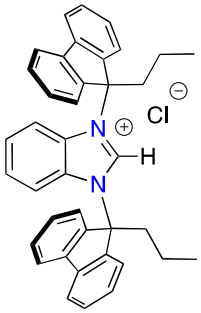

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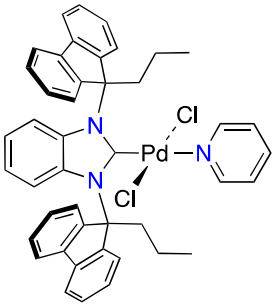

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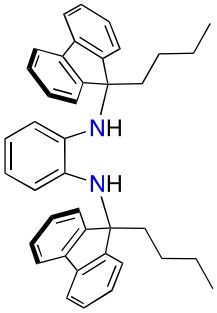

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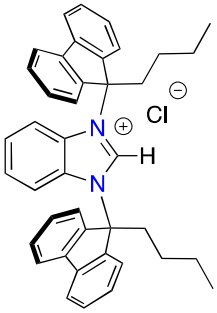

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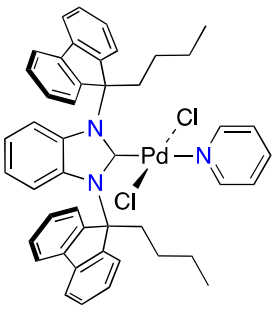

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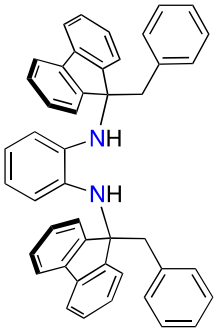

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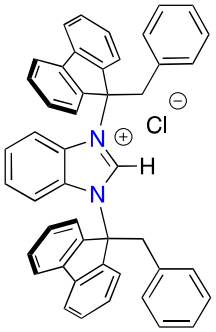

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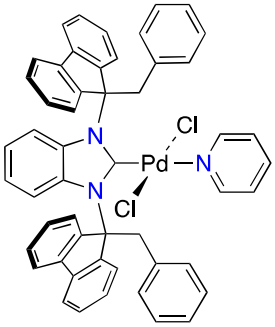

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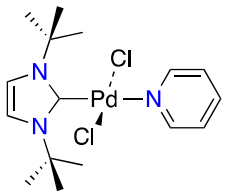
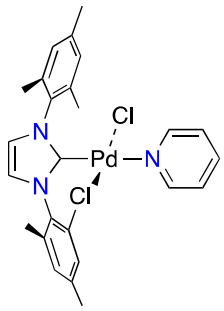


[$PdCl_2$(ItBu)(Py)] **5**



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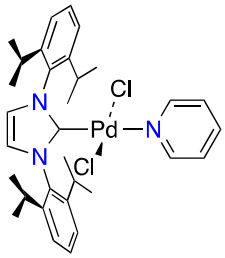
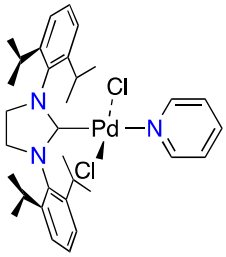


[$PdCl_2$(IPr)(Py)] **7**



[$PdCl_2$(SIPr)(Py)] **8**

Chapter II :

Directional properties of fluorenylidene moieties in unsymmetrically substituted *N*-heterocyclic carbenes. Unexpected CH activation of a methylfluorenyl group with palladium. Use in palladium catalysed Suzuki-Miyaura cross-coupling of aryl chlorides.

Chapter II:

Directional properties of fluorenylidene moieties in unsymmetrically substituted *N*-heterocyclic carbenes. Unexpected CH activation of a methylfluorenyl group with palladium. Use in palladium catalysed Suzuki-Miyaura cross-coupling of aryl chlorides.

Abstract

Benzimidazolium salts having their two nitrogen atoms substituted by different 9-alkyl-9-fluorenyl (AF) groups (**4a-e** and **4g**, alkyl[1]/alkyl[2] = Me/Et, Me/*n*-Pr, Me/*i*-Pr, Me/*n*-Bu, Me/Bn, Me/CH_2SMe have been synthesised in high yields in two or three steps from *N,N'*-bis(9*H*-fluoren-9-ylidene)benzene-1,2-diamine (**1**). The imidazolium salts **4a-e** were converted readily into the corresponding PEPPSI-type palladium complexes (PEPPSI = pyridine-enhanced precatalyst, preparation stabilisation and initiation), while reaction of the methylthioether-substituted salt **4g** with $PdCl_2/K_2CO_3$/pyridine afforded the palladacycle **5g** resulting from metallation of the methyl group attached to the fluorenylidene moiety. NMR and X-ray diffraction studies revealed that the carbene ligands of **4a**-**4e** behave as clamp-like ligands, the resulting metal confinement arising from a combination of the orientational properties of the fluorenylidene moieties that push the alkyl groups towards the metal centre and attractive anagostic interactions involving CH_2(fluorenyl) groups. Complexes **4a-e** were assessed in Suzuki-Miyaura cross-coupling reactions. Like their symmetrical analogues they displayed high activity in the coupling of phenyl boronic acid with *para*-tolyl chloride but their performance remained slightly inferior to that of the related, symmetrical Et/Et complex **5h**.

I - Introduction

A number of palladium complexes with a single *N*-heterocyclic carbene (NHC) ligand have proven to be useful catalysts in cross-coupling reactions of aryl halides (Figure 1).[1-27] Among the most popular catalysts for such reactions are palladium complexes of the type $[PdX_2(NHC)L]$ (X = halide), in which L is an ancillary ligand that readily dissociates.[28-37] Several authors have identified pertinent criteria that may increase the effectiveness of the NHC ligand. Thus, optimised NHCs should contain *N*-substituents that are both bulky and

flexible, bulkiness favouring the reductive elimination step and stabilisation of catalytic intermediates, the flexibility enabling an entering substrate to approach the metal centre after release of the product in the last step of the catalytic cycle.

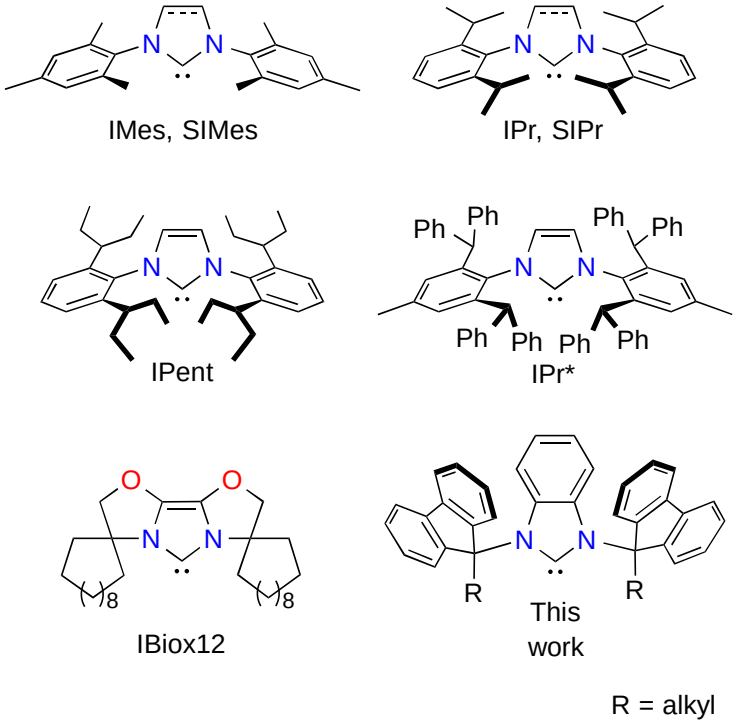


Figure 1: Effective NHCs used as ligands in palladium-catalysed cross-coupling reactions

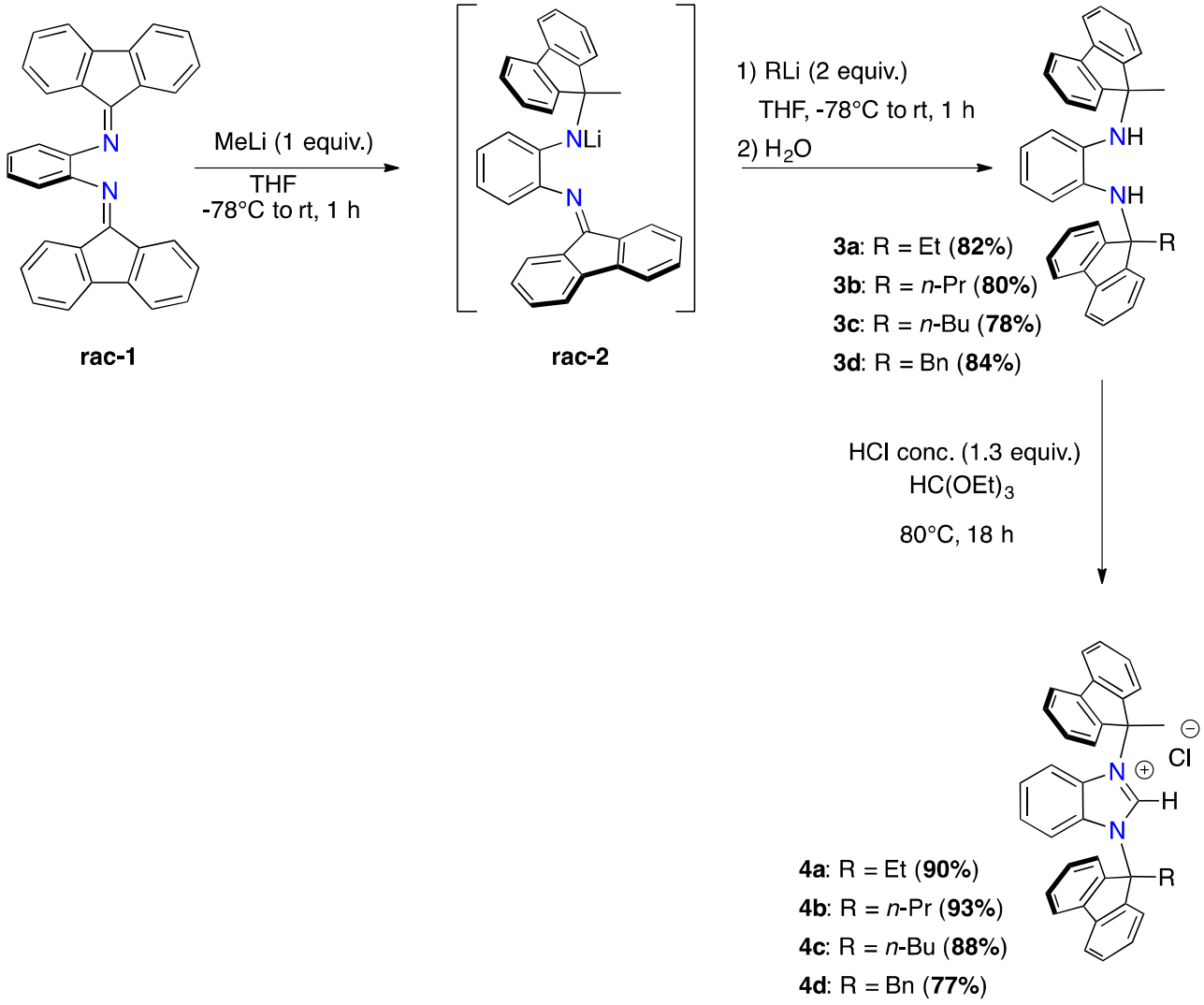
We have recently reported a series of NHC-Pd complexes in which the two nitrogen atoms are substituted by (identical) AF substituents.[27] The large fluorenylidene moiety was shown to orientate the alkyl groups towards the palladium centre while its restricted rotational freedom made the ligand bulkiness time independent. It is worthy of note that these ligands (Figure 1) do not display hemispherical encumbrance such as do, e.g., IPr, IPr*, or SIPr. Instead, the ligands give rise to meridional encumbrance, with two small, apically localised CH_2 (or CH_3) groups coming in close contact to the palladium centre. Despite their rather inflexible form, these NHCs resulted in fast Suzuki-Miyaura cross-coupling catalysts.

As an extension of these studies, we now report the synthesis and catalytic performance in Suzuki-Miyaura coupling of related Pd-complexes containing unsymmetrically substituted NHCs. One of the NHCs contains a potentially coordinating -CH_2SMe side group.

II - Results and discussion

II - A) Syntheses of benzimidazolium salts

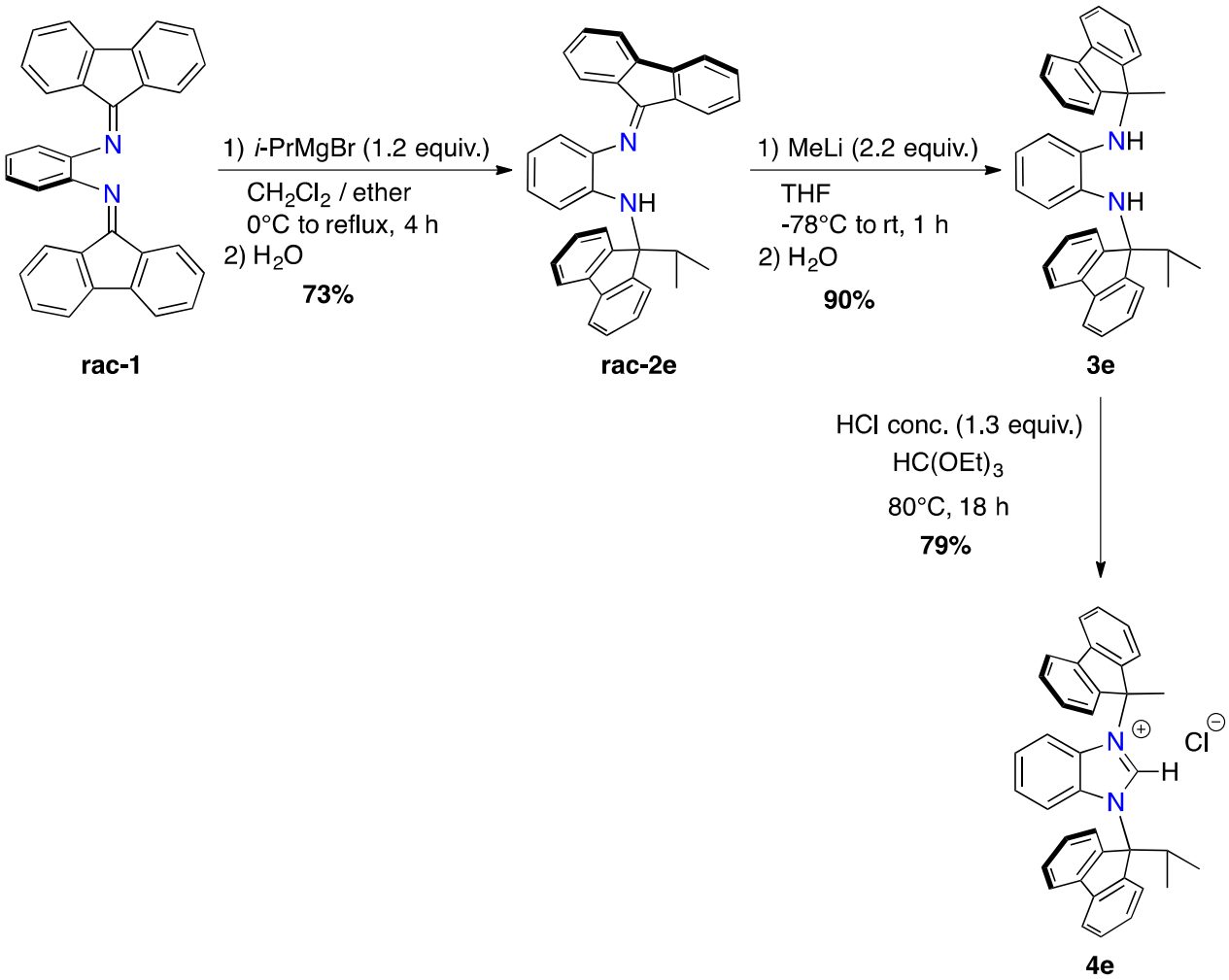
The synthesis of the palladium complexes used for this study began with that of unsymmetrically substituted imidazolium ligand-precursors (**4a-d**).



Scheme 1: Synthesis of benzimidazolium salts **4a-d**

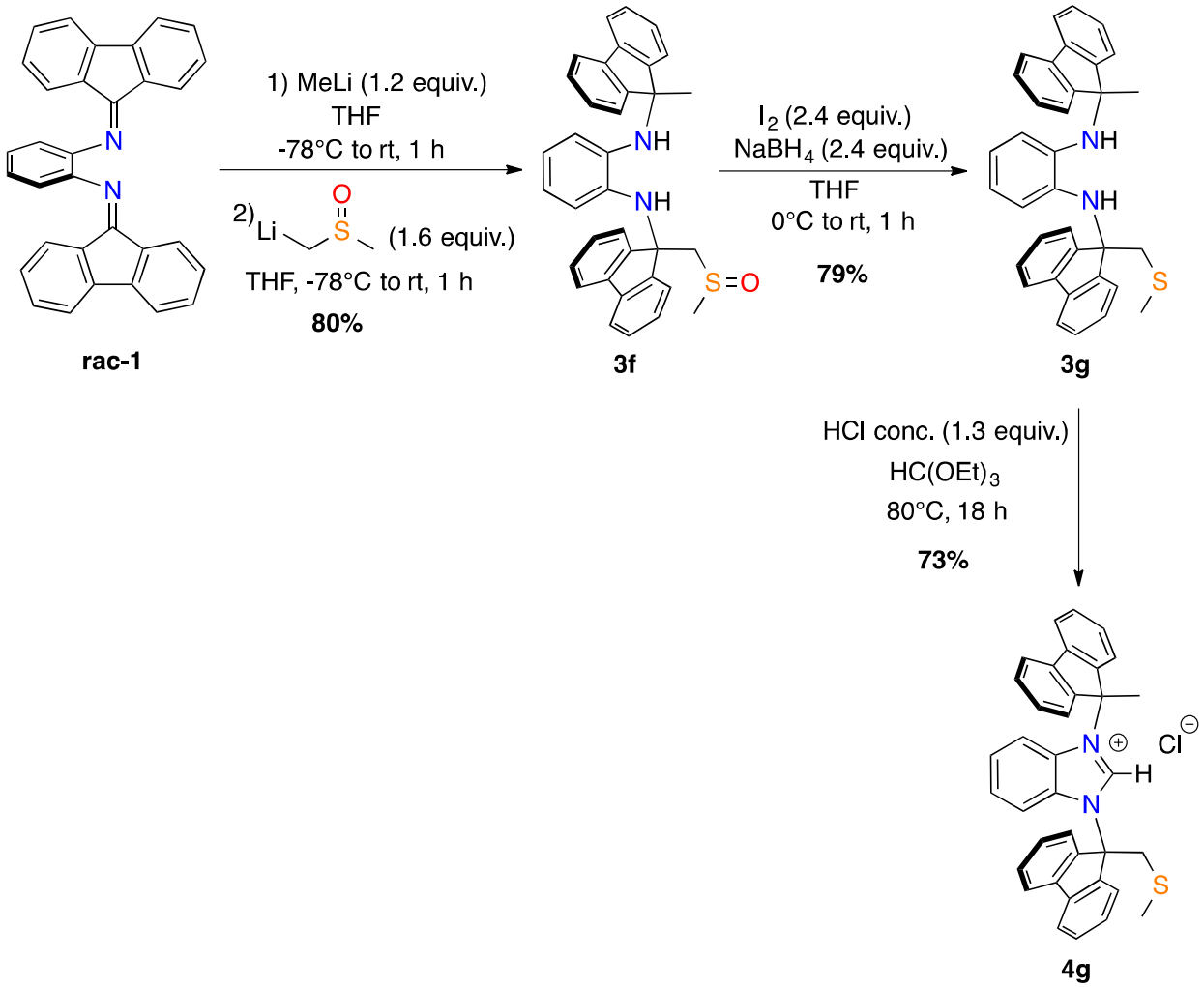
The one-pot synthesis of **4a-4d** was achieved by treatment of **rac-1** with one equiv. of MeLi and subsequent addition of a second, distinct alkyllithium reagent (2 equiv.). Workup resulted in the corresponding diamines (**3a-3d**) in over 78% yield. Ring closure to the imidazolium salts **4a-4d** was then performed with triethylorthoformate and HCl. Attempts to prepare an Et/*n*-Pr analogue of **3b** in a pure form (using EtLi and *n*-PrLi as reagents) were unsuccessful, as this product could not be separated from the Et/Et and *n*-Pr/*n*-Pr side products that formed during its synthesis.

For the preparation of **4e**, the first alkylation was arbitrarily performed with a Grignard reagent, namely *i*-PrMgBr, this leading after hydrolysis to the mixed imine-amine **2e** in 73% yield (Scheme 2). Alkylation of **2e** with MeLi and subsequent hydrolysis gave **3e** in 90% yield. Finally, diamine **3e** was reacted with $HC(OEt)_3$/HCl to yield the imidazolium salt **4e** in 79%.



Scheme 2: Synthesis of benzimidazolium salt **4e**

The preparation of thioether-imidazolium salt **4g**, which we considered as a potential precursor (*vide infra*) of a chelating *carbene-thioether* ligand is basically similar to that of **4a**-**4d**, although this synthesis required an additional step to generate the thioether function (Scheme 3).



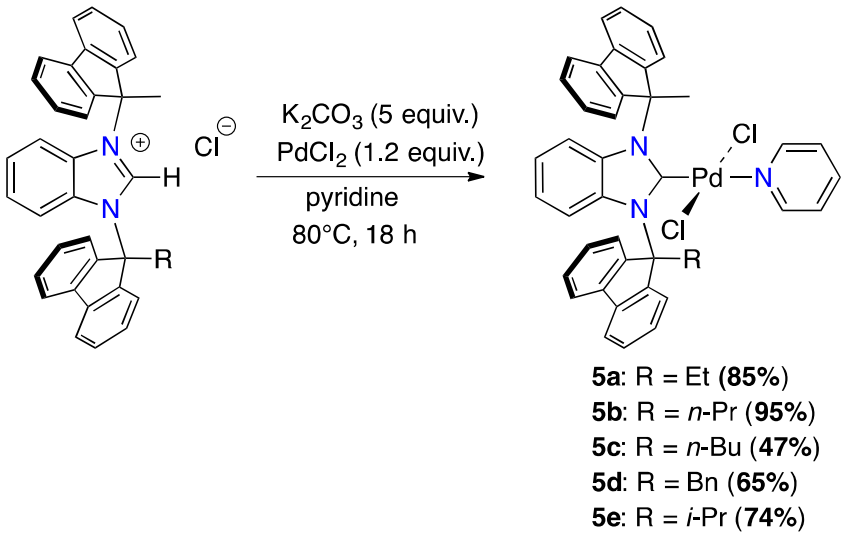
Scheme 3: Synthesis of benzimidazolium salt **4g**

Thus, after sequential addition of MeLi (1.2 equiv.) and $LiCH_2S(O)Me$ (1.6 equiv.), diamine-sulfoxide **3f** was obtained in 80% yield. Reduction of the sulfoxide was carried out with $NaBH_4$ in the presence of iodine, leading to thioether **3g** in 79% yield. In the last step imidazolium salt **4g** was readily synthesised applying the above $HC(OEt)_3$/HCl procedure.

All imidazolium salts **4a-g** are characterised by a methine signal in their ^1H NMR spectrum lying in the range 11.15-11.70 ppm.

II - B) Syntheses of palladium complexes

The PEPPSI-type[28-31] palladium complexes **5a-e** were obtained in medium-to-good yields using the standard procedure initially developed by Organ (Scheme 4).



Scheme 4: Synthesis of palladium complexes 5a-e

As already observed for related palladium complexes having two (identical) AF substituents, *e.g.* **5h** (Figure 2), all the NCC*H* signals are markedly downfield shifted when compared to their analogues in the corresponding imidazolium precursor (δΔ= 1.0-1.7 ppm). This reflects anagostic CH interactions between these protons and the palladium centre, and means that the alkyl groups attached to the fluorenylidene moiety are pushed towards the metal d_z^2 orbital, while the fluorenylidene plane itself is bent towards the NHC-fused aromatic ring.

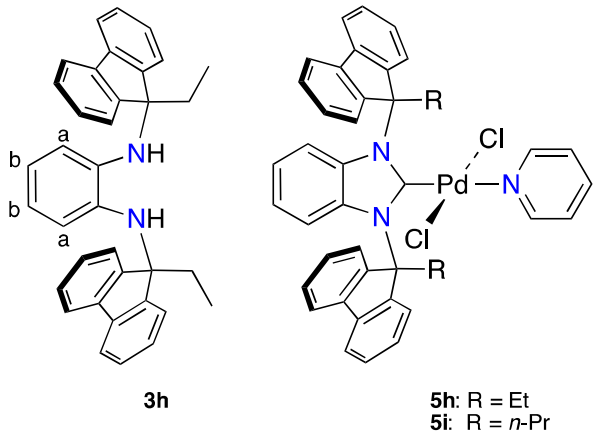


Figure 2: Diamine **3h** and palladium complexes **5h** and **5i**

The particular orientation of the fluorenyl group is seemingly persistent in solution, as the only ROESY correlations involving the benzimidazolium unit are seen with aromatic protons of the fluorenylidene moieties, but with none of the alkyl groups.[38] A single crystal X-ray diffraction study carried out for **5d** confirmed the orientation of the methyl and benzyl moieties towards the metal d_z^2 orbital, which results in a double apical encumbrance of the metal centre (Figure 3).

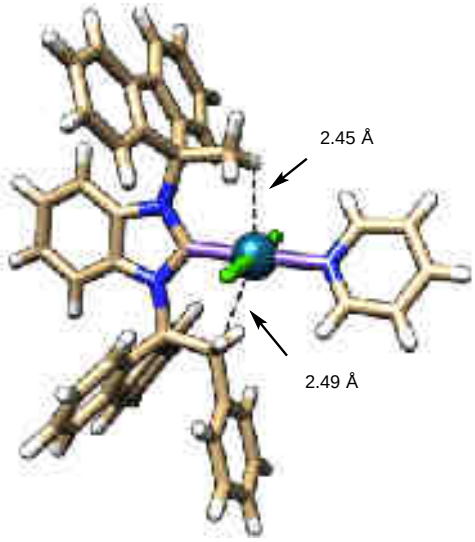


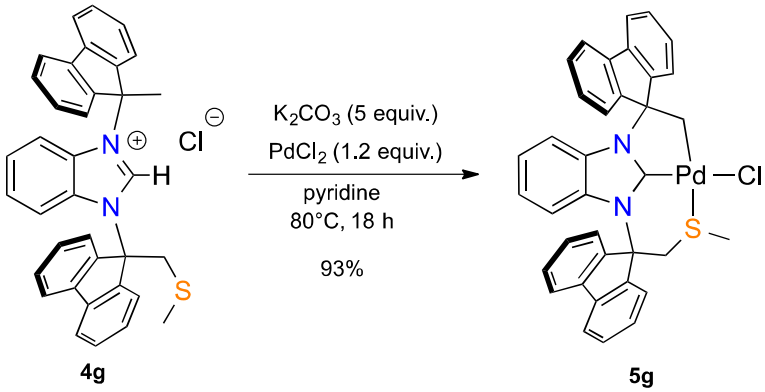
Figure 3: Solid state structure of complex **5d** (only one of the two similar molecules in the unit cell is shown)

The unit cell of this structure contains two nearly identical molecules. Short CH···Pd separations consistent with anagostic interactions between CH atoms of the methyl and benzyl groups were found in both of them, the shortest CH···Pd distances being 2.457 Å (in molecule 1) and 2.455 Å (in molecule 2). The X-ray study further allowed evaluation of the percent buried volume of the carbene ligand of **5d** as 36.7% (using a M-$C_{carbene}$ bond fixed at 2.10 Å for the calculation), which actually is close to that of IMes (31.6%).[39-40] It is worthy of mention here that, as inferred from 2D-^{1}H NMR ROESY experiments, a "folded-back" orientation of the fluorenylidene planes as in **5a-5e** (as well as **5h**, taken as reference compound), can also be seen in the corresponding amine and imidazolium precursors. This conclusion was corroborated by the observation that the H^a protons belonging to the C_6H_4-ring have significantly higher-field shifts (*ca.* 0.8 ppm) with respect to their analogues in *ortho*-phenylenediamine. This is a consequence of the fact that the H^a protons lie in the shielding region of the neighbouring fluorenylidene.

Preliminary DFT calculations carried out on the reference complex **5h,** which has two ethyl substituents oriented towards the d_z^2 orbital, indicate a rotational barrier of *ca.* 30 kcal mol^{-1} for a 180° rotation of the AF groups about its C-N bond. In the following, an alkyl orientation as in **5h** will be termed an exo-orientation, while the opposite one will be called an endo-orientation. The theoretical study revealed that **5h** is more stable by about 16.4 kcal mol^{-1} than a hypothetical endo/endo rotamer, that is the one with the fluorenylidene plane inclined towards the metal ion. Interestingly, the calculated rotational barrier for an endo-exo alkyl orientational change was found to be lower by *ca.* 15 kcal mol^{-1} than the exo-endo conversion discussed above. This obviously reflects the

presence of anagostic interactions in the exo/exo conformer, which significantly increase the stability of this rotamer vs. the opposite one. Overall these calculations lead us to refine somewhat our previous description of the clamp-like behaviour of the carbene ligand of complex **5h** and related ones. Clearly, the encumbrance of the d_z^2 orbital in all the PEPPSI complexes discussed in this study is due to a combination of the orientational propeties of the pre-oriented fluorenylidene plane and the attractive anagostic interactions that contribute to maintain the steric encumbrance on both sides of the coordination plane.

Attempts to form an analogue of **5a**-**5e** starting from the thioether imidazolium salt **4g** failed. Instead, the cyclometallated pincer-type complex **5g** formed quantitatively (Scheme 5), the structure of which was determined by a single crystal X-ray diffraction study (Figure 4).



Scheme 5: High yield synthesis of the cyclometalated complex **5g.**

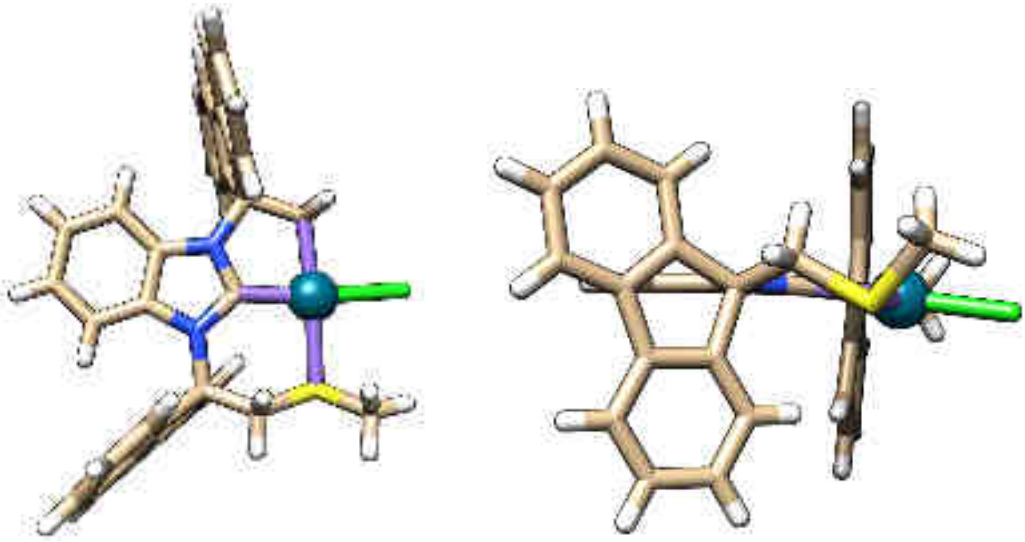


Figure 4: Molecular structure of **5g** (top view (left), side view (right)).

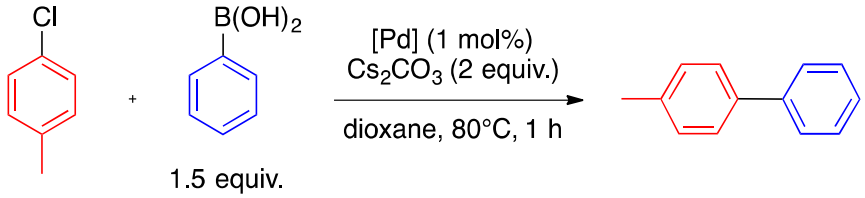
In the ^{1}H NMR spectrum, the metalated CH_2 group appears as a sharp singlet at 3.70 ppm (cf. 2.31 ppm for the methyl group of precursor **4g**). In contrast, the CH_2S signal is broad, this reflecting some dynamics within the puckered *Pd,*$C_{carbene}$*,S* ring. Complex **5g** is the only known example of a palladium-NHC complex containing a metallated alkyl side group (It is noteworthy that CH activation of propane with NHC-Pd complexes has been reported recently).[41] As K_2CO_3 and pyridine are both relatively weak bases, metalation probably occurred through CH activation by the palladium centre after coordination of the thioether group. Molecular models clearly show that owing to the orientational properties of the fluorenyl moieties, *C,S*-chelation of an hypothetical thioether-carbene ligand positions the Me group of the 9-methyl-9-fluorenyl substituent trans to the sulfur atom, thereby strongly facilitating a CH activation process.

II - C) Catalysis

In our previous publication on clamp-like carbene ligands, we had assessed symmetrically substituted analogues of the above complexes in Suzuki-Miyaura cross-coupling reactions. Thus for example, the meridionally encumbered complexes **5h** and **5i** were found to behave as fast catalytic systems in the coupling of phenylboronic acid with *para*-tolyl chloride, their activities being equal or superior to those of the fastest commercially available PEPPSI systems reported to date (Pd-PEPPSI-IMes, Pd-PEPPSI-IPr).[27] To answer the question whether an unsymmetrical ligand structure in a related complex would modify the catalytic outcome, tests were performed with **5a**-**5e** under conditions identical to those previously applied for **5h** and **5i**, namely by operating with 1 mol% of palladium complex and 2 equivalents of Cs_2CO_3 in dioxane at 80°C. The reaction rates observed for the unsymmetrical complexes were of the same order of magnitude as those of **5h** and **5i**, although slightly inferior (Figure 6). As for symmetrically substituted benzimidazolylidene ligands, the calculated buried volumes in **5a-e** (36.1%-40%) did not allow any rationalisation of the catalytic behaviour of these species.

The sole complex leading to a somewhat disappointing performance was the Me/Bn complex **5d**, this probably reflecting the bulkiness of the benzyl group that hinders substrate approach. A similar effect had previously been observed for the corresponding Bn/Bn complex.

Table 1: Suzuki-Miyaura cross-coupling of $PhB(OH)_2$ with *para*-tolyl chloride using palladium complexes **5a-e** and **5h,i**[a]



Entry	[Pd]	Yield [%][b]
1	**5a**	54
2	**5b**	42
3	**5c**	51
4	**5d**	13
5	**5e**	57
6	**5h**	70
7	**5i**	60
8	$[PdCl_2(IMes)(Py)]$	63
9	$[PdCl_2(IPr)(Py)]$	38
10	$[PdCl_2(SIPr)(Py)]$	37

[a]*para*-tolyl chloride (1 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (2 mmol), [Pd] (1 mol%). [b]Yields were determined by ^1H NMR.

III - Conclusion

We have described synthetic methodology that enables preparation in three or four steps of benzimidazolium salts having their two nitrogen atoms substituted by different AF groups. With the exception of the thioether derivative **4g**, these salts readily form PEPPSI-type palladium complexes in which both fluorenylidene moieties orientate the corresponding alkyl group towards the d_z^2 orbital of the palladium ion. Owing to a high rotational barrier about the N-C(AF) bond, time independent crowding is created about the metal in the most stable conformer, in which anagostic interactions significantly contribute to maintain the observed apical encumbrance. With imidazolium salt **4g**, and by applying conditions that normally lead to Pd-PEPPSI complexes, the cyclometallated pincer complex **5g** was obtained quantitatively. Its formation is likely to involve CH activation by the palladium centre after formation of a carbene ligand and binding of the thioether group. Like their symmetrical analogues, the complexes displayed high activities in the cross-

coupling of phenyl boronic acid with *para*-tolyl chloride, but their performance did not surpass that of the symmetrical complex **5h**.

IV - Experimental section

IV - A) General information

All commercial reagents were used as supplied. The syntheses were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. Routine ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a FT Bruker AVANCE 300 (^{1}H: 300.1 MHz, ^{13}C: 75.5 MHz) instrument at 25°C. ^{1}H NMR spectral data were referenced to residual protonated solvents ($CHCl_3$, δ 7.26; [D_6] DMSO, δ 2.50), ^{13}C chemical shifts are reported relative to deuterated solvents ($CDCl_3$, δ 77.16; [D_6] DMSO, δ 39.52). Data are represented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (*J*) in Hertz (Hz), integration and assignment. In the NMR data given hereafter, Cq denotes a quaternary carbon atom. Flash chromatography was performed as described by Still et al.,[42] employing Geduran SI (E. Merck, 0.040-0.063 mm) silica. Routine thin-layer chromatography analyses were carried out by using plates coated with Merck Kieselgel 60 GF254. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie (CNRS), Strasbourg. Melting points were determined with a Büchi 535 capillary melting-point apparatus and are uncorrected. Diimine **1a** and complexes **5h** and **5i** were prepared following procedures described in the literature.[27]

IV - B) General procedures

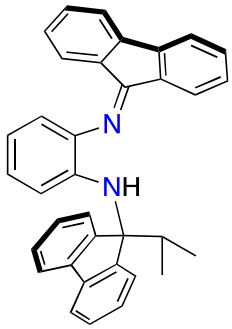
General procedure for palladium-catalysed Suzuki-Miyaura cross-coupling reactions

A mixture of the palladium complex (0.01 mmol), phenylboronic acid (0.183 g, 1.50 mmol) and Cs_2CO_3 (0.652 g, 2 mmol) was suspended in dioxane (3 mL). After the addition of *para*-tolyl chloride (0.126 g, 1 mmol), the mixture was vigorously stirred at 80°C for a given period of time. The hot mixture was filtered through Celite. 1,4-dimethoxybenzene (0.069 g, 0.5 mmol; internal standard) was then added to the filtrate. The solvent was removed under reduced pressure, and the crude mixture was analysed by ^{1}H NMR spectroscopy. The yields were determined by comparing the intensity of the methyl signal of the product [δ(Me) = 2.41 ppm] with that of the internal reference [δ(Me) = 3.78 ppm]. In some experiments the product was isolated chromatographically. The isolated yield

turned out to be very close (deviation less than 5%) to that determined by using the internal reference.

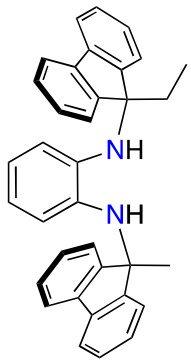
IV - C) Syntheses of amines

***N*-(2-((9*H*-fluoren-9-ylidene)amino)phenyl)-9-isopropyl-9*H*-fluoren-9-amine (2e).** A



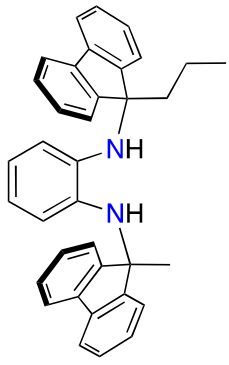
solution of *i*-PrBr (0.598 g, 4.86 mmol) in Et_2O (5mL) was added dropwise to a suspension of Mg (0.118 g, 4.86 mmol) in Et_2O (5 mL), at a rate to maintain a steady reflux (about 30 min). The suspension was maintained at reflux for 3 h and then allowed to reach room temperature. The *i*-PrMgBr solution (C ≈ 0.48 M, 6 mL, 2.90 mmol) was added dropwise at 0°C to a stirred solution of diimine **1** (1.05 g, 2.43 mmol) in CH_2Cl_2 (10 mL). The dark solution was heated at refluxed for 4 h and then allowed to reach room temperature. Water was slowly added (40 mL) and the product was extracted with AcOEt (3 × 40 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether, 10:90) to afford **2e** as a red solid (0.845 g, 73%). ^{1}H NMR ($CDCl_3$, 300 MHz), δ 8.11 (1H, d, ^3J = 7.4 Hz, ArH), 7.74 (2H, d, ^3J = 7.5 Hz, ArH), 7.67 (2H, d, ^3J = 7.5 Hz, ArH), 7.53 (1H, dd, ^3J = 7.5 Hz, ^4J = 1.2 Hz, ArH), 7.47-7.32 (4H, m, ArH), 7.31-7.24 (2H, m, ArH), 7.22-7.10 (3H, m, ArH), 7.01 (1H, dd, ^3J = 7.6 Hz, ^4J = 1.0 Hz, ArH), 6.82-6.76 (1H, m, ArH), 6.53-6.44 (2H, m, ArH), 5.54-5.47 (1H, m, ArH), 5.08 (1H, s, NH), 2.37-2.20 (1H, m, CH), 0.67 (6H, d, ^3J = 6.7 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 163.9 (C=N), 147.6 (2 overlapped arom. Cq), 143.8 (arom. Cq), 141.9 (arom. Cq), 140.8 (2 overlapped arom. Cq), 138.1 (arom. Cq), 137.8 (arom. Cq), 136.9 (arom. Cq), 132.1 (arom. CH), 131.9 (arom. CH), 131.5 (arom. Cq), 128.6 (arom. CH), 128.0 (3 overlapped arom. CH), 127.3 (2 overlapped arom. CH), 127.1 (arom. CH), 125.9 (arom. CH), 124.2 (2 overlapped arom. CH), 123.3 (arom. CH), 120.3 (arom. CH), 119.9 (2 overlapped arom. CH), 119.8 (arom. CH), 118.1 (arom. CH), 116.8 (arom. CH), 113.4 (arom. CH), 71.4 (Cq), 65.5 (Cq), 39.1 (CH), 17.7 (CH_3). Found C, 87.85; H, 6.02; N, 6.12. Calc. for $C_{35}H_{28}N_2$ (M_r = 476.62): C, 88.20; H, 5.92; N, 5.88%.

***N*-(9-ethyl-9*H*-fluoren-9-yl)-*N'*-(9-methyl-9*H*-fluoren-9-yl)benzene-1,2-diamine (3a).**



A solution of ethyl bromide (1.04 g, 9.72 mmol) in pentane (10 mL) was added to a suspension of lithium powder (25 wt% in mineral oil 0.551 g, 19.7 mmol) in pentane (9 mL) at a rate to maintain a steady reflux (about 1 h). The suspension was maintained at reflux for 3 h and then allowed to reach room temperature. The EtLi solution (C ≈ 0.5 *M*) was used without further purification. To a stirred solution of diimine **1** (1.06 g, 2.45 mmol) in THF (10 mL) cooled to -78°C, was added dropwise MeLi (1.6 *M* in Et_2O, 1.8 mL, 2.88 mmol). The dark solution obtained was allowed to reach room temperature and was stirred for 1 h. The mixture was then cooled to -78°C and the EtLi solution previously prepared (10 mL, 5 mmol), was added dropwise. The mixture was allowed to reach room temperature and was stirred 1 h. Water was slowly added (30 mL) and the product was extracted with AcOEt (3 × 30 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether, 0.5:99.5) to afford **3a** as a pale red solid (0.962 g, 82%); mp 164°C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.77-7.72 (4H, m, ArH), 7.41-7.34 (8H, m, ArH), 7.30-7.24 (4H, m, ArH), 6.11-6.08 (2H, m, ArH), 5.68-5.65 (1H, m, ArH), 5.63-5.60 (1H, m, ArH), 4.39 (2H, br s, NH), 2.20 (2H, q, ^3J = 7.4 Hz, CH_2), 1.76 (3H, s, CH_3), 0.57 (3H, t, ^3J = 7.4 Hz, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 149.9 (arom. Cq), 148.26 (arom. Cq), 140.12 (arom. Cq), 139.1 (arom. Cq), 136.3 (arom. Cq), 135.3 (arom. Cq), 128.1 (arom. CH), 128.0 (arom. CH), 127.7 (arom. CH), 127.6 (arom. CH), 123.4 (arom. CH), 123.2 (arom. CH), 120.3 (arom. CH), 120.1 (arom. CH), 119.3 (arom. CH), 117.7 (arom. CH), 116.8 (arom. CH), 68.8 (Cq), 65.4 (Cq), 36.4 (CH_2) 30.4 (CH_3), 8.31 (CH_2CH_3). Found C, 87.52; H, 6.46; N, 5.96. Calc. for $C_{35}H_{30}N_2$ (M_r = 478.63): C, 87.83; H, 6.32; N, 5.85%.

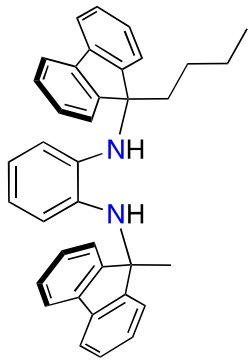
***N*-(9-propyl-9*H*-fluoren-9-yl)-*N'*-(9-methyl-9*H*-fluoren-9-yl)benzene-1,2-diamine**



(3b). A solution of *n*-propyl bromide (0.950 g, 7.72 mmol) in pentane (10 mL) was added to a suspension of lithium powder (25 wt% in mineral oil 0.514 g, 18.3 mmol) in pentane (9 mL) at a rate to maintain a steady reflux (about 1 h). The suspension was maintained at reflux for 3 h and then allowed to reach room temperature. The *n*-PrLi solution (C ≈ 0.4 *M*) was used without further purification. To a stirred solution of diimine **1** (0.950 g, 2.20 mmol) in THF (10 mL) cooled to -78°C, was

added dropwise MeLi (1.6 *M* in Et_2O, 1.7 mL, 2.72 mmol). The dark solution obtained was allowed to reach room temperature and was stirred for 1 h. The mixture was then cooled to -78°C and the *n*-PrLi solution previously prepared (11 mL, 4.40 mmol), was added dropwise. Water was slowly added (30 mL) and the product was extracted with AcOEt (3 × 30 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether, 0.5:99.5) to afford **3b** as a pale red solid (0.864 g, 80%); mp 148 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.67-7.61 (4H, m, ArH), 7.45-7.34 (8H, m, ArH), 7.34-7.24 (4H, m, ArH), 6.14-6.11 (2H, m, ArH), 5.71-5.69 (1H, m, ArH), 5.65-5.62 (1H, m, ArH), 4.42 (2H, br s, NH), 2.18-2.13 (2H, m, $CqCH_2$), 1.79 (3H, s, CH_3), 0.99-0.89 (2H, m, CH_2CH_3), 0.82 (3H, t, ^3J = 7.3 Hz, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 150.0 (arom. Cq), 148.7 (arom. Cq), 140.1 (arom. Cq), 139.1 (arom. Cq), 136.2 (arom. Cq), 135.5 (arom. Cq), 128.1 (arom. CH), 128.1 (arom. CH), 127.8 (arom. CH), 127.7 (arom. CH), 123.5 (arom. CH), 123.2 (arom. CH), 120.4 (arom. CH), 120.2 (arom. CH), 120.1 (arom. CH), 117.4 (arom. CH), 117.6 (arom. CH), 116.9 (arom. CH), 68.7 (Cq), 65.5 (Cq), 45.9 ($CqCH_2$) 30.6 (CH_3), 17.1 (CH_2CH_3), 14.3 (CH_2CH_3). Found C, 87.62; H, 6.66; N, 5.51. Calc. for $C_{36}H_{32}N_2$ (M_r = 492.67): C, 87.77; H, 6.55; N, 5.69%.

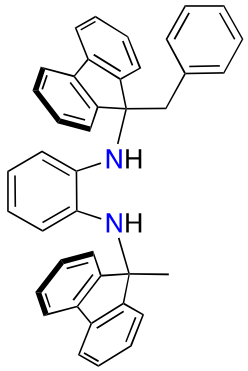
***N*-(9-butyl-9*H*-fluoren-9-yl)-*N*'-(9-methyl-9*H*-fluoren-9-yl)benzene-1,2-diamine (3c).**



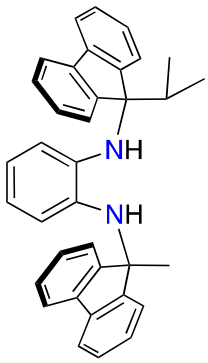
To a stirred solution of diimine **1** (1.04g, 2.40 mmol) in THF (8 mL) cooled to -78°C, was added dropwise MeLi (1.6 *M* in Et_2O, 1.7 mL, 2.72 mmol). The dark solution obtained was allowed to reach room temperature and was stirred for 1 h. The mixture was then cooled to -78°C and *n*-BuLi, (1.6 *M* in hexanes, 2 mL, 3.20 mmol) was added dropwise. The mixture was allowed to reach room temperature and was stirred 1h. Water was slowly added (30 mL) and the product was extracted with AcOEt (3 × 30 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether, 0.5:99.5) to afford **3c** as a pale red solid (0.947 g, 78%); mp 90 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.78-7.74 (4H, m, ArH), 7.42-7.34 (8H, m, ArH), 7.31-7.24 (4H, m, ArH), 6.14-6.09 (2H, m, ArH), 5.72-5.69 (1H, m, ArH), 5.63-5.60 (1H, m, ArH), 4.39 (2H, br s, NH), 2.18-2.11 (2H, m, $CqCH_2$), 1.78 (3H, s, CH_3), 1.22 (2H, tq, ^3J = $^3J'$ = 7.5 Hz, CH_2CH_3), 0.95-0.86 (2H, m, $CqCH_2CH_2$), 0.80 (3H, t, ^3J = 7.5 Hz, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 150.0 (arom. Cq), 148.7 (arom. Cq), 140.0 (arom.

Cq), 139.1 (arom. Cq), 136.3 (arom. Cq), 135.4 (arom. Cq), 128.1 (arom. CH), 128.0 (arom. CH), 127.8 (arom. CH), 127.6 (arom. CH), 123.5 (arom. CH), 123.2 (arom. CH), 120.4 (arom. CH), 120.2 (arom. CH), 120.1 (arom. CH), 119.3 (arom. CH), 117.7 (arom. CH), 116.9 (arom. CH), 68.6 (Cq), 65.5 (Cq), 43.4 (CqCH_2), 30.5 (CH_3), 25.9 (CqCH$_2$$CH_2$), 23.0 ($CH_2CH_3$), 14.1 ($CH_2CH_3$). Found C, 87.30; H, 6.83; N, 5.68. Calc. for $C_{37}H_{34}N_2$ (M_r = 506.69): C, 87.71; H, 6.76; N, 5.53%.

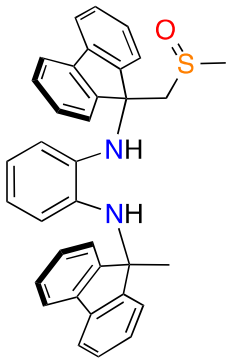
***N*-(9-benzyl-9*H*-fluoren-9-yl)-*N*'-(9-methyl-9*H*-fluoren-9-yl)benzene-1,2-diamine**



(3d). *n*-BuLi (1.6 *M* in hexanes, 3.80 mL, 6.10 mmol) was added dropwise at -78°C to a suspension of toluene (0.645 mL, 6.10 mmol) and *t*-BuOK (0.685 g, 6.10 mmol) in THF (5 mL). The red solution was allowed to reach room temperature and was stirred 1 h. The benzyl lithium solution obtained (C ≈ 0.7 *M*) was used without further purification. To a stirred solution of diimine **1** (1.30 g, 3.00 mmol) in THF (12 mL) cooled to -78°C, was added dropwise MeLi (1.6 *M* in Et_2O, 2.0 mL, 3.20 mmol). The dark solution obtained was allowed to reach room temperature and was stirred for 1 h. The mixture was then cooled to -78°C and the benzyl lithium solution previously prepared (9 mL, 6.10 mmol), was added dropwise. The mixture was allowed to reach room temperature and stirred 1h. Water was slowly added (30 mL) and the product was extracted with AcOEt (3 × 30 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether, 0.5:99.5) to afford **3d** as a pale orange solid (1.36 g, 84%); mp 110 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.80 (2H, d, ^3J = 7.5 Hz, ArH), 7.73 (2H, d, ^3J = 7.5 Hz ArH), 7.44-7.20 (15H, m, ArH), 7.05 (2H, dd, ^3J = 7.6 Hz, ^4J = 1.8 Hz, ArH), 6.05-6.01 (2H, m, ArH), 5.65-5.62 (1H, m, ArH), 5.48-5.45 (1H, m, ArH), 4.92-4.11 (2H, overlapped br s, NH), 3.30 (2H, s, C$H_2C_6H_5$), 1.86 (3H, s, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 150.0 (arom. Cq), 148.2 (arom. Cq), 139.6 (arom. Cq), 139.2 (arom. Cq), 136.1 (arom. Cq), 135.7 (arom. Cq), 135.2 (arom. Cq), 131.2 (arom. CH), 128.2 (arom. CH), 128.1 (arom. CH), 128.0 (arom. CH), 127.9 (arom. CH), 127.2 (arom. CH), 127.1 (arom. CH), 124.3 (arom. CH), 123.0 (arom. CH), 120.4 (arom. CH), 120.3 (arom. CH), 119.8 (arom. CH), 119.1 (arom. CH), 116.7 (arom. CH), 115.8 (arom. CH), 68.5 (Cq), 65.3 (Cq), 45.9 ($CH_2C_6H_5$) 31.1 (CH_3). Found C, 88.46; H, 5.99; N, 4.99. Calc. for $C_{40}H_{32}N_2$ (M_r = 540.71): C, 88.85; H, 5.97; N, 5.18%.

***N*-(9-*iso*-propyl-9*H*-fluoren-9-yl)-*N'*-(9-methyl-9*H*-fluoren-9-yl)benzene-1,2-diamine (3e).** 

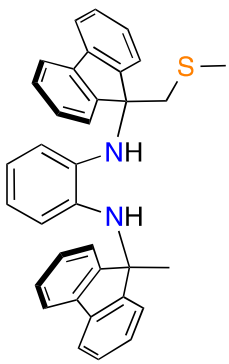
To a stirred solution of amine **2e** (0.829 g, 1.54 mmol) in THF (10 mL) cooled to -78°C, was added MeLi (1.6 *M* in Et_2O, 2.1 mL, 3.40 mmol). The dark solution obtained was allowed to reach room temperature and was stirred for 1 h. Water was slowly added (30 mL) and the product was extracted with AcOEt (3 × 30 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether, 0.5:99.5) to afford **3e** as a pale brown solid (0.777 g, 90%); mp 80 °C. ^{1}HNMR ($CDCl_3$, 300 MHz), δ 7.76 (2H, d, ^3J = 7.4 Hz, ArH), 7.73 (2H, d, ^3J = 7.4 Hz, ArH), 7.41-7.21 (12H, m, ArH), 6.08-6.06 (2H, m, ArH), 5.74-5.72 (1H, m, ArH), 5.51-5.48 (1H, m, ArH), 4.72 (1H, br s, NH), 4.20 (1H, br s, NH), 2.44 (1H, hept, ^3J = 6.8 Hz, C*H*$(CH_3)_2$), 1.78 (3H, s, CH_3), 0.84 (6H, d, ^3J = 6.8 Hz, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 150.0 (arom. Cq), 147.6 (arom. Cq), 140.8 (arom. Cq), 139.2 (arom. Cq), 137.1 (arom. Cq), 134.8 (arom. Cq), 128.1 (arom. CH), 128.0 (arom. CH), 127.8 (arom. CH), 127.3 (arom. CH), 124.0 (arom. CH), 123.2 (arom. CH), 120.6 (arom. CH), 120.4 (arom. CH), 119.9 (arom. CH), 118.7 (arom. CH), 118.2 (arom. CH), 115.7 (arom. CH), 71.4 (Cq), 65.5 (Cq), 39.7 (*C*H$(CH_3)_2$), 30.4 (CH_3), 17.7 (CH(*C*H$_3)_2$). Found C, 87.72; H, 6.65; N, 6.00. Calc. for $C_{36}H_{32}N_2$ (M_r = 492.67): C, 87.77; H, 6.55; N, 5.69%.

***N*-(9-methyl-9*H*-fluoren-9-yl)-*N'*-(9-methylsulfinylmethyl-9*H*-fluoren-9-yl)benzene-1,2-diamine (3f).** 

A solution of *n*-BuLi (1.6 *M* in hexanes, 4.6 mL, 7.40 mmol) was added dropwise at -78°C to a solution of dimethylsulfoxyde (DMSO, 526 µL, 0.578 g, 7.40 mmol) in THF (10 mL). The white suspension was allowed to reach room temperature and was stirred 1 h. The dimsyl lithium (LiDMSO) suspension (C ≈ 0.5 *M*) was used without further purification. To a stirred solution of diimine **1** (2.05 g, 4.73 mmol) in THF (10 mL) cooled to -78°C, was added a solution of MeLi (1.6 *M* in Et_2O, 3.5 mL, 5.67 mmol). The dark solution obtained was allowed to reach room temperature and was stirred for 1 h. The mixture was then cooled to -78°C and the LiDMSO solution previously prepared (15 mL, 7.40 mmol), was then added dropwise. The mixture was allowed to reach room temperature and was stirred 1h. Water was slowly added (30 mL) and the product was extracted with AcOEt (3 × 30 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude

product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether, 70:30) to afford **3f** as a pale red solid (1.99 g, 80%); mp 185°C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.87-7.78 (5H, m, ArH), 7.67-7.59 (3H, m, ArH), 7.54-7.29 (8H, m, ArH), 5.99 (1H, ddd, $^3J = {}^3J' = 7.6$ Hz, $^4J = 1.3$ Hz, ArH), 5.90 (1H, ddd, $^3J = {}^3J' = 7.6$ Hz, $^4J = 1.3$ Hz, ArH), 5.59 (1H, br s, NH), 5.40 (2H, d, $^3J = 7.6$ Hz, ArH), 5.23 (1H, br s, NH), 3.76 (1H, d, $^2J = 13.5$ Hz, CH_2SCH$_3$), 2.66 (1H, d, $^2J = 13.5$ Hz, CH_2SCH$_3$), 2.63 (3H, s, CH$_2$SCH_3), 1.95 (3H, s, CH$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 150.32 (arom. Cq), 150.19 (arom. Cq), 148.17 (arom. Cq), 146.03 (arom. Cq), 139.46 (arom. Cq), 139.14 (arom. Cq), 138.89 (arom. Cq), 138.49 (arom. Cq), 135.69 (arom. Cq), 132.71 (arom. Cq), 129.07 (2 overlapped arom. CH), 128.40 (arom. CH), 127.92 (arom. CH), 127.85 (arom. CH), 127.81 (3 arom. CH), 125.03 (arom. CH), 123.29 (arom. CH), 123.17 (arom. CH), 122.82 (arom. CH), 120.80 (arom. CH), 120.69 (arom. CH), 120.33 (arom. CH), 120.29 (arom. CH), 119.40 (arom. CH), 117.40 (arom. CH), 114.51 (arom. CH), 113.37 (arom. CH), 68.11 (Cq), 66.84 (*C*H$_2$SCH$_3$), 65.06 (Cq), 39.67 (CH$_2$S*C*H$_3$), 31.51 (CH$_3$). Found C, 79.57; H, 5.92; N, 5.11. Calc. for $C_{35}H_{30}N_2OS$ (M_r = 526.70): C, 79.82; H, 5.74; N, 5.32%.

***N*-(9-methyl-9*H*-fluoren-9-yl)-*N*'-(9-methylthiomethyl-9*H*-fluoren-9-yl)benzene-1,2-diamine (3g).** $NaBH_4$ (0.224 g, 5.92 mmol) was added under vigorous stirring at 0°C to a solution of diamine **3f** (1.29 g, 2.45 mmol) and I_2 (1.50 g, 5.90 mmol) in THF (40 mL). Gas emission was observed. The reaction mixture was allowed to reach room temperature and was stirred 1 h. A 10% aqueous sodium hydroxide solution was slowly added (80 mL) and the product was extracted with AcOEt (3 × 60 mL). The combined organic layers were washed with a 10% aqueous sodium thiosulfate solution (2 × 80 mL), water (80 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; AcOEt/petroleum ether, 10:90) to afford **3g** as a white solid (0.988 g, 79%); mp 84°C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.83 (4H, d, $^3J = 7.5$ Hz, ArH), 7.61 (2H, d, $^3J = 7.5$ Hz, ArH), 7.54 (2H, d, $^3J = 7.3$ Hz, ArH), 7.49-7.40 (4H, m, ArH), 7.40-7.30 (4H, m, ArH), 6.19-6.05 (2H, m, ArH), 5.17-5.60 (2H, m, ArH), 5.29-4.30 (2H, overlapped br s, NH), 3.21 (2H, s, CH_2SCH$_3$), 2.21 (3H, s, CH$_2$SCH_3), 1.88 (3H, s, CH$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 149.9 (arom. Cq), 147.8 (arom. Cq), 139.6 (arom. Cq), 139.1 (arom. Cq), 135.9 (arom. Cq), 135.2 (arom. Cq), 128.6 (arom. CH), 128.1 (arom. CH), 127.8 (arom. CH), 127.6 (arom. CH), 124.0 (arom. CH), 123.1 (arom. CH), 120.4 (arom. CH), 120.3 (arom. CH), 119.8 (arom. CH), 119.4 (arom. CH),



116.6 (arom. CH), 116.4 (arom. CH), 68.0 (Cq), 65.3(Cq), 49.6 (CH_2SCH_3), 30.8 (CH_2SCH_3), 18.4 (CH_3). Found C, 82.60; H, 5.82; N, 5.23. Calc. for $C_{35}H_{30}N_2S$ (M_r = 510.70): C, 82.32; H, 5.92; N, 5.49%.

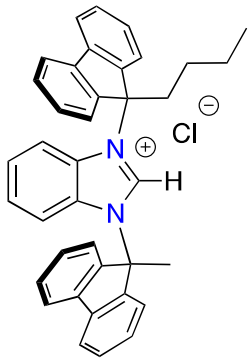
IV - D) Syntheses of benzimidazolium salts

1-(9-ethyl-9*H*-fluoren-9-yl)-3-(9-methyl-9*H*-fluoren-9-yl)benzimidazolium chloride (4a). Diamine **3a** (0.512 g, 1.07 mmol) was dissolved under magnetic stirring in $HC(OEt)_3$. HCl (12 *M*, 116 µL, 1.39 mmol) was added, and the mixture was heated at 80°C for 15 h. The mixture was then cooled to room temperature and petroleum ether was added (*ca.* 20 mL). The precipitate was collected by filtration and washed with petroleum ether (3 × 15 mL). Compound **4a** (0.507 g, 90%) was obtained as a hygroscopic white solid; mp 192°C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 11.16 (1H, s, NCHN), 7.86-7.78 (8H, m, ArH), 7.51-7.43 (4H, m, ArH), 7.38-7.29 (4H, m, ArH), 6.78-6.72 (2H, m, ArH), 6.26-6.16 (2H, m, ArH), 3.70 (2H, q, ^3J = 7.0 Hz, CH_2CH_3), 2.91 (3H, s, CH_3), 0.51 (3H, t, ^3J = 7.0 Hz, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 145.1 (arom. Cq), 143.1 (arom. Cq), 142.4 (NCHN), 140.4 (arom. Cq), 139.0 (arom. Cq), 131.1 (arom. Cq), 130.7 (arom. Cq), 130.2 (2 overlapped arom. CH), 129.4 (2 overlapped arom. CH), 126.1 (2 overlapped arom. CH), 125.0 (arom. CH), 124.9 (arom. CH), 120.8 (arom. CH), 120.5 (arom. CH), 114.9 (arom. CH), 114.7 (arom. CH), 75.3 (Cq), 71.4 (Cq), 31.4 (CH_2CH_3), 27.3 (CH_3), 7.4 (CH_2CH_3). Found C, 80.30; H, 5.70; N, 5.34. Calc. for $C_{36}H_{29}ClN_2 \cdot 0.6\ H_2O$ (M_r = 525.09 + 10.81): C, 80.69; H, 5.68; N, 5.23%.

1-(9-methyl-9*H*-fluoren-9-yl)-3-(9-propyl-9*H*-fluoren-9-yl)benzimidazolium chloride (4b). Diamine **3b** (0.271 g, 0.550 mmol) was dissolved under magnetic stirring in $HC(OEt)_3$ (2 mL) and then HCl 12 *M* (58 µL, 0.70 mmol) was added. The mixture was heated at 80°C for 15 h. The mixture was then cooled to room temperature and petroleum ether was added (*ca.* 20 mL). The precipitate was collected by filtration and washed with petroleum ether (3 × 15 mL). Compound **4b** (0.274 g, 93%) was obtained as a hygroscopic white solid; mp 192°C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 11.15 (1H, s, NCHN), 7.87-7.81 (8H, m, ArH), 7.48 (4H, t, ^3J = 7.5 Hz, ArH), 7.38-7.31 (4H, m, ArH), 6.79-6,73 (2H, m, ArH), 6.24-6.19 (2H, m, ArH), 3.67-3.62 (2H, m, $CqCH_2$), 2.93 (3H, s, CH_3), 0.91 (3H, t, ^3J = 7.5 Hz, CH_2CH_3), 0.85-0.75 (2H, m, CH_2CH_3). ^{13}C{^{1}H} NMR

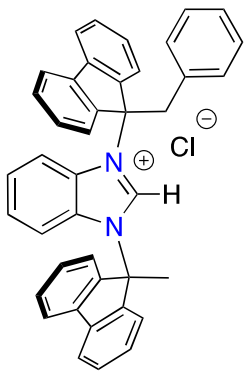
($CDCl_3$, 75 MHz), δ 145.1 (arom. Cq), 143.6 (arom. Cq), 142.3 (NCHN), 140.3 (arom. Cq), 139.0 (arom. Cq), 131.0 (arom. Cq), 130.8 (arom. Cq), 130.3 (2 overlapped arom. CH), 129.5 (arom. CH), 129.4 (arom. CH), 126.2 (arom. CH), 126.2 (arom. CH), 125.0 (arom. CH), 124.9 (arom. CH), 120.8 (arom. CH), 120.5 (arom. CH), 115.0 (arom. CH), 114.7 (arom. CH), 74.8 (Cq), 71.4 (Cq), 39.9 (Cq*C*H_2) 27.3 (CH_3), 16.5 (*C*H_2CH_3), 13.9 (CH_2*C*H_3). Found C, 79.73; H, 5.90; N, 4.80. Calc. for $C_{37}H_{31}ClN_2 \cdot 0.9\ H_2O$ (M_r = 539.12 + 16.21): C, 80.03; H, 5.95; N, 5.04%.

1-(9-butyl-9*H*-fluoren-9-yl)-3-(9-methyl-9*H*-fluoren-9-yl)benzimidazolium chloride (4c). Diamine **3c** (0.902 g, 1.78 mmol) was dissolved under magnetic stirring in $HC(OEt)_3$ (8 mL) and then HCl 12 *M* (195 µL, 2.34 mmol) was added. The mixture was heated at 80°C for 15 h. The mixture was then cooled to room temperature and petroleum ether was added (*ca.* 20 mL). The precipitate was collected by filtration and washed with petroleum ether (3 × 25 mL). Compound **4c** (0.865 g, 88%) was obtained as a hygroscopic white solid; mp 163°C.



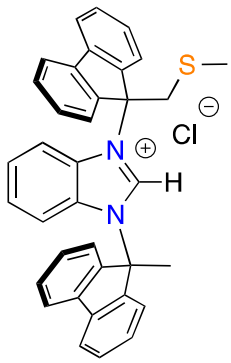
^{1}H NMR ($CDCl_3$, 300 MHz), δ 11.15 (1H, s, NCHN), 7.89-7.82 (8H, m, ArH), 7.52-7.41 (4H, m, ArH), 7.38-7.30 (4H, m, ArH), 6.80-6.73 (2H, m, ArH), 6.25-6.19 (2H, m, ArH), 3.71-3.66 (2H, m, $CqCH_2$), 2.94 (3H, s, CH_3), 1.38 (2H, tq, ^3J = $^3J'$ = 7.5 Hz, C*H*$_2$CH$_3$), 0.79-0.67 (5H, m, overlapped signals, $CqCH_2CH_2$ and CH_2CH_3,). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 145.1 (arom. Cq), 143.5 (arom. Cq), 142.2 (NCHN), 140.3 (arom. Cq), 139.0 (arom. Cq), 131.0 (arom. Cq), 130.8 (arom. Cq), 130.2 (2 overlapped arom. CH), 129.4 (arom. CH), 129.4 (arom. CH), 126.2 (arom. CH), 126.2 (arom. CH), 125.0 (arom. CH), 124.9 (arom. CH), 120.8 (arom. CH), 120.5 (arom. CH), 115.0 (arom. CH), 114.7 (arom. CH), 74.8 (Cq), 71.4 (Cq), 37.7 (Cq*C*H_2), 27.3 (CH_3), 25.2 ($CqCH_2CH_2$), 22.5 (C*H*$_2$CH$_3$), 14.2 (CH_2*C*H_3). Found C, 80.80; H, 6.03; N, 5.10. Calc. for $C_{38}H_{33}ClN_2 \cdot 0.5\ H_2O$ (M_r = 553.15 + 9.01): C, 81.19; H, 6.10; N, 4.98%.

1-(9-benzyl-9*H*-fluoren-9-yl)-3-(9-methyl-9*H*-fluoren-9-yl)benzimidazolium chloride (4d). Diamine **3d** (0.612 g, 1.13 mmol) was dissolved under magnetic stirring in $HC(OEt)_3$ (4 mL) and then HCl 12 *M* (122 µL, 1.47 mmol) was added. The mixture was heated at 120°C for 15 h. After cooling to room temperature petroleum ether was added (*ca.* 20 mL). The precipitate was collected by filtration and washed with petroleum ether (3 × 15 mL). Compound **4d** (0.510 g, 77%) was obtained as a hygroscopic white solid; mp 209°C. ^{1}H NMR ([D_6] DMSO, 300 MHz), δ

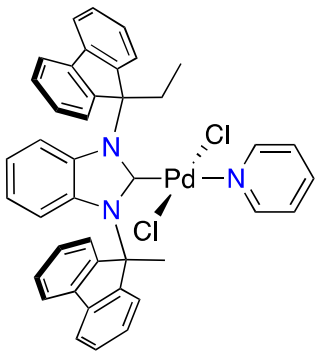


10.70 (1H, s, NCHN), 8.12 (4H, dd, ^3J = $^3J'$ = 8.8 Hz, ArH), 7.99 (2H, d, ^3J = 7.4 Hz, ArH), 7.72 (2H, d, ^3J = 7.2 Hz, ArH), 7.56 (2H, dd, ^3J = $^3J'$ = 7.4 Hz, ArH), 7.46-7.35 (6H, m, ArH), 7.00-6.80 (5H, m, ArH), 6.45 (2H, d, ^3J = 7.4 Hz, ArH), 6.14-6.05 (2H, m, ArH), 4.88 (2H, CH_2(C_6H_5), 2.70 (3H, s, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 145.2 (arom. Cq), 143.6 (NCHN), 142.6 (arom. Cq), 140.0 (arom. Cq), 138.6 (arom. Cq), 132.5 (arom. Cq), 130.3 (arom. CH), 130.2 (arom. CH), 130.1 (arom. CH), 130.0 (arom. Cq), 129.8 (arom. Cq), 129.0 (arom. CH), 128.4 (arom. CH), 127.1 (arom. CH), 126.6 (arom. CH), 126.3 (arom. CH), 126.2 (arom. CH), 125.3 (arom. CH), 124.6 (arom. CH), 121.5 (arom. CH), 120.8 (arom. CH), 114.2 (arom. CH), 113.9 (arom. CH), 73.9 (Cq), 70.3 (Cq), 42.4 (*C*H_2(C_6H_5)), 26.2 (CH_3). Found C, 79.72; H, 5.50; N, 4.20. Calc. for $C_{41}H_{31}ClN_2$·1.7 H_2O (M_r = 587.16 + 30.63): C, 79.71; H, 5.61; N, 4.53%.

1-(9-methyl-9*H*-fluoren-9-yl)-3-(9-*iso*-propyl-9*H*-fluoren-9-yl)benzimidazolium chloride (4e). Diamine **3e** (0.455 g, 0.92 mmol) was dissolved under magnetic stirring in $HC(OEt)_3$ (3 mL) and then HCl 12 *M* (110 µL, 1.32 mmol) was added. The mixture was heated at 80°C for 15 h. The solution was then cooled to room temperature and petroleum ether was added (*ca.* 20 mL). The precipitate was collected by filtration and washed with petroleum ether (3 × 15 mL). Compound **4e** (0.391 g, 79%) was obtained as a hygroscopic white solid; mp 175°C. ^1H NMR ($CDCl_3$, 300 MHz), δ 11.67 (1H, s, NCHN), 7.90 (2H, d, ^3J = 7.5 Hz, ArH), 7.82 (4H, dd, ^3J = $^3J'$ = 7.3 Hz, ArH), 7.77 (2H, d, ^3J = 7.5 Hz, ArH), 7.49 (4H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 7.34 (4H, dd, ^3J = $^3J'$ = 7.3 Hz, ArH), 6.79-6.71 (2H, m, ArH), 6.19-6.13 (1H, m, ArH), 5.99-5.93 (1H, m, ArH), 4.88 (1H, hept, ^3J = 6.5 Hz, C*H*(CH_3)$_2$), 2.97 (3H, s, CH_3), 1.05 (6H, d, ^3J = 6.5 Hz, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 145.0 (arom. Cq), 144.2 (NCHN), 142.8 (arom. Cq), 140.6 (arom. Cq), 139.1 (arom. Cq), 131.4 (arom. Cq), 130.7 (arom. Cq), 130.4 (arom. CH), 130.3 (arom. CH), 129.4 (arom. CH),129.0 (arom. CH), 126.2 (arom. CH), 126.2 (arom. CH), 126.1 (arom. CH), 124.7 (arom. CH), 120.9 (arom. CH), 120.5 (arom. CH), 115.4 (arom. CH), 114.8 (arom. CH), 78.8 (Cq), 71.7 (Cq), 33.7 (*C*H(CH_3)$_2$) 27.8 (CH_3), 17.9 (CH(*C*H_3)$_2$). Found C, 79.46; H, 6.15; N, 4.77. Calc. for $C_{37}H_{31}ClN_2$·1.2 H_2O (M_r = 539.12 + 21.62): C, 79.25; H, 6.00; N, 5.00%.

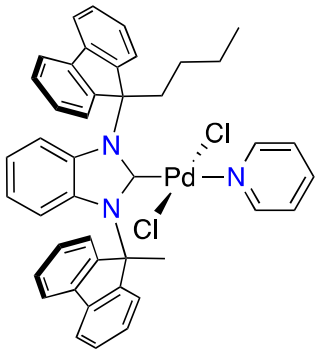
1-(9-methyl-9*H*-fluoren-9-yl)-3-(9-methylthiomethyl-9*H*-fluoren-9-yl)benzimidazolium chloride (4g).  Diamine **3g** (0.292 g, 0.57 mmol) was dissolved under magnetic stirring in $HC(OEt)_3$ (2 mL) and then HCl 12 *M* (65 µL, 0.78 mmol) was added. The mixture was heated at 80°C for 15 h. The solution was then cooled to room temperature and petroleum ether was added (*ca.* 20 mL). The precipitate was collected by filtration and washed with petroleum ether (3 × 15 mL). Compound **4g** (0.235 g, 73%) was obtained as a hygroscopic white solid; mp 178°C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 11.61 (1H, s, NCHN), 8.03 (2H, d, ^3J = 7.7 Hz, ArH), 7.84 (6H, d, ^3J = 7.7 Hz, ArH), 7.55-7.46 (4H, m, ArH), 7.39-7.31 (4H, m, ArH), 6.80-6.76 (2H, m, ArH), 6.21-6.17 (1H, m, ArH), 6.10-6.06 (1H, m, ArH), 4.74 (2H, s, C*H*$_2$SCH$_3$), 2.94 (3H, s, CH$_2$SC*H*$_3$), 2.31 (3H, s, CH$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 145.0 (arom. Cq), 144.4 (NCHN), 143.2 (arom. Cq), 139.9 (arom. Cq), 139.0 (arom. Cq), 130.8 (arom. Cq), 130.6 (arom. CH), 130.5 (arom. Cq), 130.3 (arom. CH), 129.4 (arom. CH), 129.1 (arom. CH), 126.2 (arom. CH), 126.1 (2 overlapped arom. CH), 124.9 (arom. CH), 120.8 (arom. CH), 120.7 (arom. CH), 114.8 (arom. CH), 114.7 (arom. CH), 73.7 (Cq), 71.3 (Cq), 42.6 (*C*H$_2$SCH$_3$), 27.2 (CH$_2$S*C*H$_3$), 17.4 (CH$_3$). Found C, 77.86; H, 5.30; N, 4.78. Calc. for $C_{36}H_{29}ClN_2S$ (M_r = 557.15): C, 77.61; H, 5.25; N, 5.03%.

IV - E) Syntheses of palladium complexes

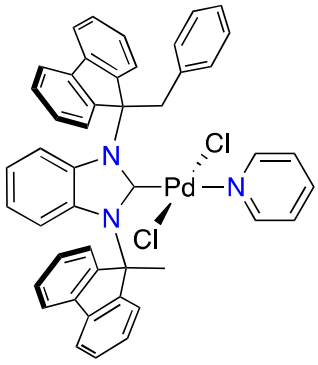
***trans*-[1-(9-ethyl-9*H*-fluoren-9-yl)-3-(9-methyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene](pyridine)palladium(II) dichloride (5a).**  A suspension of benzimidazolium salt **4a** (0.310 g, 0.59 mmol), finely crushed K_2CO_3 (0.407 g, 2.95 mmol), and $PdCl_2$ (0.126 g, 0.71 mmol) in pyridine (2 mL) was heated at 80°C for 15 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the filtered solid was washed with CH_2Cl_2 (*ca.* 20 mL). The combined washings and the filtrate were evaporated to dryness. The residue was then purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50:50) to afford **5a** as a yellow solid (0.373 g, 85%); mp > 240°C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 9.17-9.12 (2H, m, *ortho*-NC_5H_5), 7.89-7.73 (9H, m, 8H ArH and 1H *para*-NC_5H_5), 7.48-7.37 (6H, m, 4H ArH and 2H *meta*-NC_5H_5), 7.35-7.26 (4H, m, ArH), 6.41-6.35 (2H, m, ArH), 6.22-6.17 (1H, m, ArH), 6.11-6.05 (1H, m, ArH), 5.45 (2H, q, ^3J = 7.1 Hz, C*H*$_2$CH$_3$), 4.06 (3H, s, CH$_3$), 0.46 (3H, t, ^3J = 7.1 Hz, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75

MHz), δ 161.0 (NCN), 151.7 (arom. CH), 149.3 (arom. Cq), 146.3 (arom. Cq), 140.3 (arom. Cq), 138.3 (arom. Cq), 138.2 (arom. CH), 134.6 (arom. Cq), 134.2 (arom. Cq),129.2 (arom. CH), 129.1 (arom. CH), 129.0 (arom. CH), 124.9 (arom. CH), 124.8 (arom. CH), 124.7 (arom. CH), 122.5 (arom. CH), 120.7 (arom. CH), 120.0 (arom. CH), 113.4 (arom. CH), 113.1 (arom. CH), 76.7 (Cq), 72.3 (Cq), 36.7 (CH$_2$CH$_3$) 33.9 (CH$_3$), 6.7 (CH$_2$$CH_3$). Found C, 65.91; H, 4.80; N, 5.51. Calc. for $C_{41}H_{33}Cl_2N_3Pd$ (M_r = 745.06): C, 66.10; H, 4.46; N, 5.64%.

***trans*-[1-(9-methyl-9*H*-fluoren-9-yl)-3-(9-propyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene](pyridine)palladium(II) dichloride (5b).** A suspension of benzimidazolium salt **4b** (0.307 g, 0.57 mmol), finely crushed K_2CO_3 (0.407 g, 2.95 mmol), and $PdCl_2$ (0.120 g, 0.67 mmol) in pyridine (2 mL) was heated at 80°C for 15 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the filtered solid was washed with CH_2Cl_2 (*ca.* 20 mL). The combined washings and the filtrate were evaporated to dryness. The residue was then purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50:50) to afford **5b** as a yellow solid (0.412 g, 95%); mp > 240°C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 9.19-9.14 (2H, m, *ortho*-NC_5H_5), 7.88-7.76 (9H, m, 8H ArH and 1H *para*-NC_5H_5), 7.48-7.37 (6H, m, 4H ArH and 2H *meta*-NC_5H_5), 7.35-7.27 (4H, m, ArH), 6.41-6.35 (2H, m, ArH), 6.21-6.14 (1H, m, ArH), 6.11-6.05 (1H, m, ArH), 5.47-5.41 (2H, m, CqCH_2), 4.07 (3H, s, CH_3), 0.95 (3H, t, ^3J = 7.1 Hz, CH_2CH_3), 0.76-0.50 (2H, m, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 161.1 (NCN), 151.8 (arom. CH), 149.3 (arom. Cq), 146.9 (arom. Cq), 140.1 (arom. Cq), 138.3 (arom. Cq), 138.2 (arom. CH), 134.5 (arom. Cq), 134.3 (arom. Cq), 129.1 (arom. CH), 129.0 (arom. CH), 124.8 (arom. CH), 124.7 (arom. CH), 124.6 (arom. CH), 122.4 (arom. CH), 120.7 (arom. CH), 120.0 (arom. CH), 113.4 (arom. CH), 113.1 (arom. CH), 75.9 (Cq), 72.3 (Cq), 46.0 (CqCH_2) 33.9 (CH_3), 17.5 (CH_2CH_3), 14.5 (CH_2CH_3). Found C, 66.17; H, 4.86; N, 5.17. Calc. for $C_{42}H_{35}Cl_2N_3Pd$ (M_r = 759.08): C, 66.46; H, 4.65; N, 5.54%.

***trans*-[1-(9-butyl-9*H*-fluoren-9-yl)-3-(9-methyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene](pyridine)palladium(II) dichloride (5c).** 

A suspension of benzimidazolium salt **4c** (0.498 g, 0.90 mmol), finely crushed K_2CO_3 (0.622 g, 4.50 mmol), and $PdCl_2$ (0.191 g, 1.08 mmol) in pyridine (2 mL) was heated at 80°C for 15 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the filtered solid was washed with CH_2Cl_2 (*ca.* 20 mL). The combined washings and the filtrate were evaporated to dryness. The residue was then purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50:50) to afford **5c** as a yellow solid (0.330 g, 47%); mp > 240°C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 9.19-9.14 (2H, m, *ortho*-NC_5H_5), 7.87-7.70 (9H, m, 8H ArH and 1H *para*-NC_5H_5), 7.46-7.36 (6H, m, 4H ArH and 2H *meta*-NC_5H_5), 7.33-7.24 (4H, m, ArH), 6.39-6.33 (2H, m, ArH), 6.18-6.12 (1H, m, ArH), 6.09-6.03 (1H, m, ArH), 5.45-5.39 (2H, m, $CqCH_2$), 4.04 (3H, s, CH_3), 1.37 (2H, tq, ^3J = $^3J'$ = 7.4 Hz, CH_2CH_3), 0.71 (3H, t, ^3J = 7.4 Hz, CH_2CH_3), 0.64-0.51 (2H, m, $CqCH_2CH_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 161.0 (NCN), 151.8 (arom. CH), 149.4 (arom. Cq), 146.9 (arom. Cq), 140.2 (arom. Cq), 138.3 (arom. Cq), 138.2 (arom. CH), 134.6 (arom. Cq), 134.3 (arom. Cq), 129.1 (arom. CH), 129.0 (arom. CH), 128.6 (arom. CH), 124.8 (arom. CH), 124.7 (arom. CH), 122.4 (arom. CH), 120.7 (arom. CH), 120.1 (arom. CH), 113.4 (arom. CH), 113.1 (arom. CH), 75.9 (Cq), 72.3 (Cq), 43.6 ($CqCH_2$) 34.0 (CH_3), 26.1 ($CqCH_2CH_2$), 23.0 (CH_2CH_3), 15.1 (CH_2CH_3). Found C, 65.51; H, 4.93; N, 5.42. Calc. for $C_{43}H_{37}Cl_2N_3Pd$ (M_r = 773.11): C, 66.80; H, 4.82; N, 5.44%.

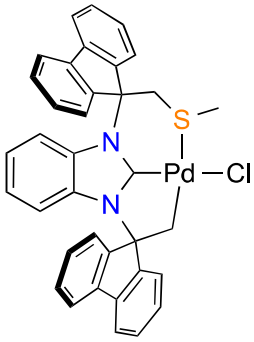
***trans*-[1-(9-benzyl-9*H*-fluoren-9-yl)-3-(9-methyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene](pyridine)palladium(II) dichloride (5d).** 

A suspension of benzimidazolium salt **4d** (0.211 g, 0.39 mmol), finely crushed K_2CO_3 (0.282 g, 2.04 mmol), and $PdCl_2$ (0.085 g, 0.48 mmol) in pyridine (2 mL) was heated at 80°C for 15 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the filtered solid was washed with CH_2Cl_2 (*ca.* 20 mL). The combined washings and the filtrate were evaporated to dryness. The residue was then purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50:50) to afford **5d** as a yellow solid (0.205 g, 65%); mp > 212°C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 9.11-9.05 (2H, m, *ortho*-NC_5H_5), 7.97-7.93 (2H, m, ArH), 7.87 (4H, d, ^3J = 7.9 Hz, ArH), 7.73 (1H, m, 8H, *para*-NC_5H_5), 7.51-7.26 (12H, m, 10H ArH and 2H

meta-NC_5H_5), 6.94 (1H, t, ^3J = 7.5 Hz, ArH), 6.80 (2H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 6.73 (2H, s, $CH_2C_6H_5$), 6.43-6.33 (4H, m, ArH), 6.14-6.09 (2H, m, ArH), 4.09 (3H, s, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 161.5 (NCN), 151.6 (arom. CH), 149.3 (arom. Cq), 146.2 (arom. Cq), 140.1 (arom. Cq), 138.4 (arom. Cq), 138.1 (arom. CH), 134.6 (arom. Cq), 134.5 (arom. Cq), 134.3 (arom. Cq), 131.1 (arom. CH), 129.2 (arom. CH), 129.1 (arom. CH), 129.0 (2 overlapped arom. CH), 128.5 (arom. CH),126.6 (arom. CH), 125.9 (arom. CH), 125.3 (arom. CH), 125.0 (arom. CH), 124.7 (arom. CH), 122.5 (arom. CH), 120.7 (arom. CH), 120.0 (arom. CH),113.7 (arom. CH), 113.2 (arom. CH), 76.0 (Cq), 72.4 (Cq), 49.9 ($CH_2C_6H_5$), 34.0 (CH_3). Found C, 68.33; H, 4.59; N, 4.89. Calc. for $C_{46}H_{35}Cl_2N_3Pd$ (M_r = 807.13): C, 68.45; H, 4.37; N, 5.21%.

***trans*-[1-(9-methyl-9*H*-fluoren-9-yl)-3-(9-*iso*-propyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene](pyridine)palladium(II) dichloride (5e).** A suspension of benzimidazolium salt **4e** (0.518 g, 0.96 mmol), finely crushed K_2CO_3 (0.656 g, 4.75 mmol), and $PdCl_2$ (0.199 g, 1.12 mmol) in pyridine (3 mL) was heated at 80°C for 15 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the filtered solid was washed with CH_2Cl_2 (*ca.* 20 mL). The combined washings and the filtrate were evaporated to dryness. The residue was then purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50:50) to afford **5e** as a yellow solid (0.539 g, 74%); mp > 203°C. ^1H NMR ($CDCl_3$, 300 MHz), δ 9.14-9.09 (2H, m, *o*-NC_5H_5), 7.86-7.76 (9H, m, 8H ArH and 1H *para*-NC_5H_5), 7.46-7.38 (6H, m, 4H ArH and 2H *meta*-NC_5H_5), 7.32-7.22 (4H, m, ArH), 7.00 (1H, hept, ^3J = 6.6 Hz, $CH(CH_3)_2$), 6.39-6.23 (2H, m, ArH), 6.11-6.05 (1H, m, ArH), 5.86-5.80 (1H, m, ArH), 4.13 (3H, s, CH_3), 1.32 (6H, d, ^3J = 7.1 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 161.7 (NCN), 151.7 (arom. CH), 149.7 (arom. Cq), 146.1 (arom. Cq), 140.2 (arom. Cq), 138.2 (overlapped arom. CH and arom. Cq), 135.8 (arom. Cq), 134.6 (arom. Cq), 129.1 (2 overlapped arom. CH), 128.9 (arom. CH), 128.0 (arom. CH), 126.4 (arom. CH), 125.0 (arom. CH), 124.7 (arom. CH), 122.5 (arom. CH), 122.3 (arom. CH), 120.7 (arom. CH), 120.0 (arom. CH), 113.9 (arom. CH), 113.3 (arom. CH), 82.1 (Cq), 73.1 (Cq), 34.2 ($CH(CH_3)_2$) 33.7 (CH_3), 22.4 ($CH(CH_3)_2$). Found C, 66.13; H, 4.85; N, 5.17. Calc. for $C_{42}H_{35}Cl_2N_3Pd$ (M_r = 759.02): C, 66.46; H, 4.65; N, 5.54%.

Palladium complex 5g. A suspension of benzimidazolium salt **4g** (0.234 g, 0.42 mmol, finely crushed K_2CO_3 (0.291 g, 2.10 mmol), and $PdCl_2$ (0.089 g, 0.50 mmol) in pyridine (3 mL) was heated at 80°C for 15 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the filtered solid was washed with CH_2Cl_2 (*ca.* 20 mL). The combined washings and the filtrate were evaporated to dryness. The residue was then purified by flash chromatography (SiO_2; CH_2Cl_2/MeOH ether, 92:8) to afford **5g** as a yellow solid (0.260 g, 93%); mp > 240°C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.90 (2H, d, ^3J = 7.5 Hz, ArH), 7.78 (2H, d, ^3J = 7.5 Hz, ArH), 7.72 (2H, d, ^3J = 7.5 Hz, ArH), 7.60-7.52 (4H, m, ArH), 7.45-7.24 (6H, m, ArH), 6.65-6.42 (2H, m, ArH), 5.96-5.90 (1H, m, ArH), 5.77-5.71 (1H, m, ArH), 3.70 (2H, s, CH_2Pd), 3.33 (2H, br s, CH_2SCH_3), 2.70 (3H, s, CH_2SCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 176.5 (NCN), 147.3 (arom. CH), 144.2 (arom. Cq), 139.2 (arom. Cq), 138.9 (arom. Cq), 132.0 (arom. Cq), 131.7 (arom. Cq), 130.6 (arom. CH), 129.1 (arom. Cq), 128.7 (arom. CH), 128.5 (arom. CH), 124.8 (arom. CH), 123.8 (2 overlapped arom. CH), 123.2 (arom. CH), 121.3 (arom. CH), 120.4 (arom. CH), 113.4 (arom. CH), 111.3 (arom. CH), 77.3 (Cq), 72.1 (Cq), 47.4 (CH_2Pd) 38.8 (CH_2SCH_3), 19.4 (CH_2SCH_3). Found C, 65.61; H, 4.32; N, 4.51. Calc. for $C_{36}H_{27}ClN_2PdS$ (M_r = 661.56): C, 65.36; H, 4.11; N, 4.23%.



IV - F) Crystal data

Crystal data for complex 5d

Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a dichloromethane solution of the complex: $C_{98}H_{75}Cl_9N_6Pd_2$, M_r = 1868.49, monoclinic, space group $P2_1/c$, a = 20.5938(5), b = 18.5018(4), c = 24.0322(7) Å, □□ = 103.048(3), V = 8920.4(4) Å^3, Z = 4, □ = 0.723 mm^{-1}, F(000) = 3800. Crystals of the compound were mounted on a Oxford Diffraction CCD Safire 3 Xcalibur diffractometer. Data collection with Mo-K□ radiation (□ = 0.71073 Å) was carried out at 150 K. 67669 reflections were collected (2.60 < □□□< 27.00°), 19447 were found to be unique and 9064 were observed (merging R = 0.0689). The structure was solved with SHELXS-97.[43] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.1375, 0.0661, 0.2058, 0.1846, 0.705. Residual electron density minimum/maximum = -1.039/1.335 e Å^{-3}.

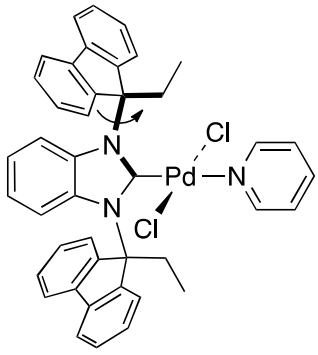
Crystal data for complex 5g

Crystals suitable for X-ray diffraction were obtained by slow diffusion of ether into a dichloromethane solution of the complex: $C_{36}H_{27}ClN_2PdS$, M_r = 661.51, orthorhombic, space group *Pbca*, *a* = 14.5752(3), *b* = 19.1704(4), *c* = 22.6020(5) Å, □□ = 90.00, *V* = 6315.3(2) Å^3, *Z* = 8, □ = 0.765 mm^{-1}, *F*(000) = 2688. Crystals of the compound were mounted on a Oxford Diffraction CCD Safire 3 Xcalibur diffractometer. Data collection with Mo-K□ radiation (□ = 0.71073 Å) was carried out at 100 K. 84941 reflections were collected (2.70 < □□□< 27.00°), 6894 were found to be unique and 4643 were observed (merging *R* = 0.0799). The structure was solved with SHELXS-97.[43] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.0703, 0.0365, 0.1002, 0.0916, 0.866. Residual electron density minimum/maximum = -0.271/1.737 e Å^{-3}.

CCDC-970760 (for **5d**) and -862359 (for **5g**) 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.

IV - G) Computational details

Calculations were performed using the ADF 2013 package.[44] All electron Slater type orbitals were used with all-electron triple-ζ quality basis sets at DFT level with PBE functional.[45,46] Dispersive interactions were taken into account through Grimme corrections.[47] Scalar relativistic effects were included through ZORA Hamiltonian.[48] Full geometry optimisation was performed on the complex. Then the barrier was computed through the calculation of the relaxed potential energy surface. The C-C-N-C dihedral angle (below in bold) was varied from 0° to 180°.



V - Notes and References

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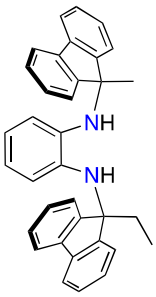

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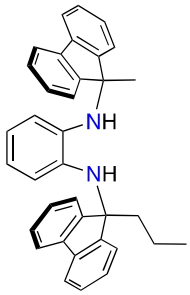

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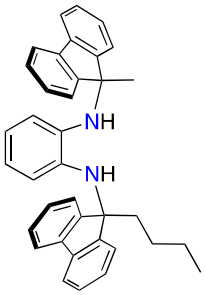

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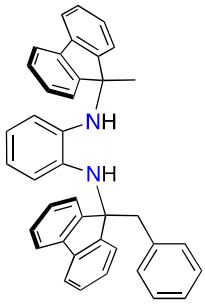

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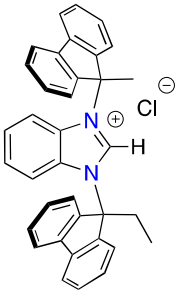

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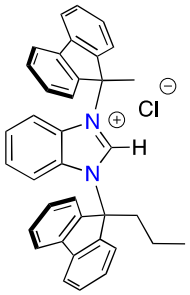

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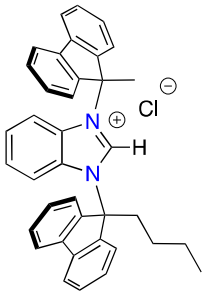

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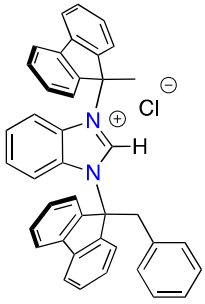

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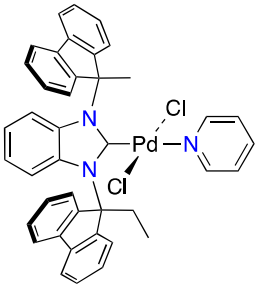

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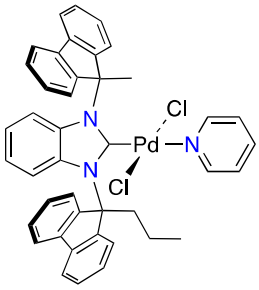

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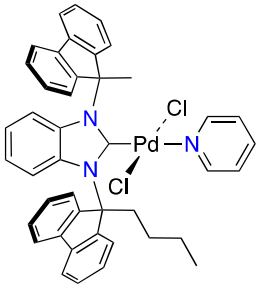

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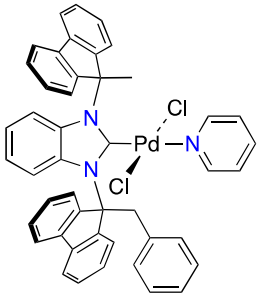

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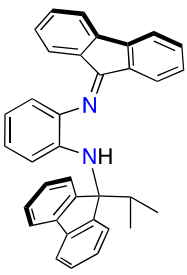

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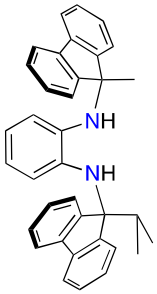

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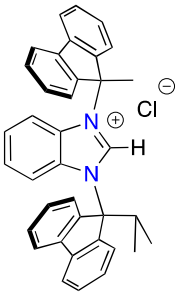

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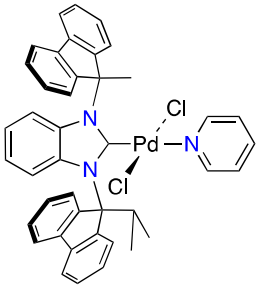

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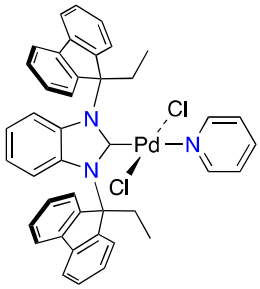

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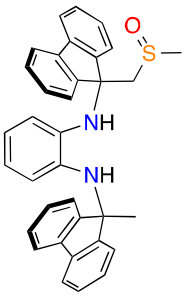

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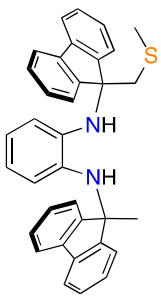

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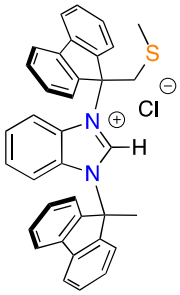

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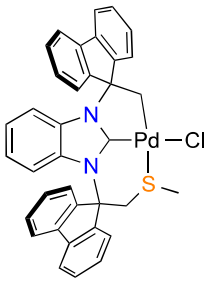

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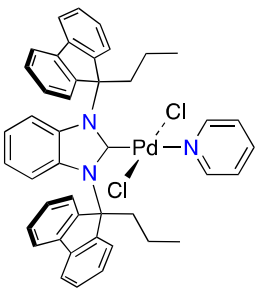


5i

Chapter III :

N-Alkylfluorenyl-substituted *N*-heterocyclic carbenes as bimodal pincers.

Chapter III:

N-Alkylfluorenyl-substituted *N*-heterocyclic carbenes as bimodal pincers

Abstract

Two *N*-heterocyclic carbene precursors having their nitrogen atoms substituted by the large 9-ethyl-9-fluorenyl (EF) group, namely imidazolinium chloride **6** and imidazolium chloride **7**, have been synthesized in high yields from fluorenone (**1**). The key intermediate of these syntheses is the new primary amine 9-ethyl-9-fluorenylamine (**3**)**,** which could be prepared in 75% yield. Both salts were readily converted into the corresponding PEPPSI-type palladium complexes, **8** and **9** (PEPPSI: pyridine-enhanced precatalyst preparation stabilisation and initiation). Despite rotational freedom of the EF moieties about their C-N bond in their cationic precursors, the carbene ligands of the Pd(II)-complexes **8** and **9** both behave as clamp-like ligands in solution and in the solid state, the resulting confinement being essentially due to (weak) attractive anagostic interactions between the C*H*$_2$(fluorenyl) groups and the metal centre. Unlike in **8** and **9**, there was no indication for similar anagostic interactions in the imidazolylidene chlorosilver complex **11**, which could be obtained from **7**. In the solid state, however, 11 adopts a remarkable "open sandwich" structure, with the two fluorenylidene planes η^2-bonded to the silver, this constituting a further bimodal pincer-type bonding mode of this ligand class. Complexes **8** and **9** were assessed in Suzuki-Miyaura cross-coupling reactions. The imidazolylidene complex **9** displayed high activity towards unencumbered aryl chlorides. Its efficiency is comparable to that of the previously reported, highly efficient benzimidazolylidene analogue **10**.

I - Introduction

The current increasing interest in *N*-heterocyclic carbenes (NHCs) as metallocatalyst components is primarily due to the strong donor ability of these ligands, which in most cases, exceeds that of tertiary phosphines.[1] Their particular electronic properties alone do not, however, necessarily confer optimised reactivity on their metal complexes. Improved ligand efficiency is often achieved, exactly as in phosphine chemistry, through subtle control of the NHC sterics. For example, in palladium-catalysed Suzuki-

Miyaura cross-coupling reactions, *N*-heterocyclic carbenes with N atoms substituted by side-expanded aryl rings have been shown to result in much higher activities than those obtained with analogs bearing smaller *N*-substituents (e.g. Me, *t*-Bu, phenyl).[2] In fact, the high degree of crowding created with the former ligands not only facilitates the final reductive elimination step of the coupling reaction, but also favours monoligation and increases the lifetime of key intermediates. Further, Glorius et al. have exposed the beneficial role in these reactions of bulky *N*-substituents that display structural flexibility, thereby enabling their adaptation to the steric requirements of each individual step of the catalytic cycle.[3]

In some recent publications, we have described a series of benzimidazole-based NHCs bearing nitrogen-grafted AF substituents (Figure 1).[4]

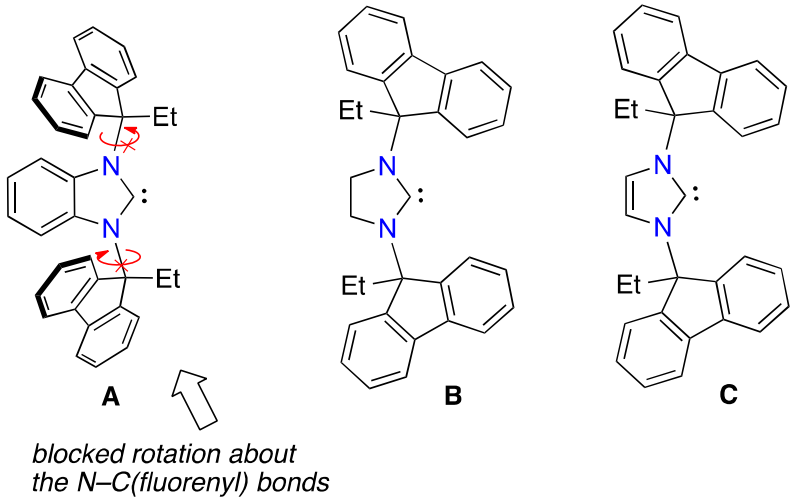


Figure 1: Carbene ligands used in this study: benzimidazol-2-ylidene (**A**), imidazolin-2-ylidene (**B**) and imidazol-2-ylidene (**C**).

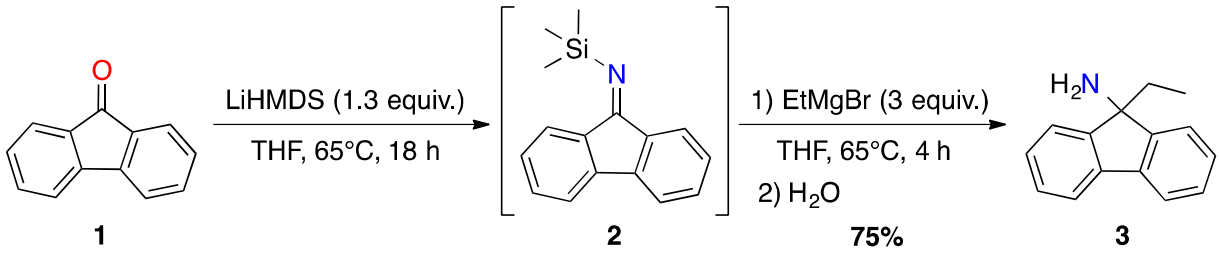
In their complexes, the metal centre was shown to be firmly protected in a permanent manner by the alkyl groups as a consequence of the orientating properties of the large, planar fluorenylidene unit combined with a high rotational barrier of the AF group about its C–N bond. In the case of Pd(II) complexes obtained with these ligands, anagostic CH···M interactions between the metal and the alkyl chains were shown to contribute to the high steric protection. In the present study we describe the coordinative properties of related ligands, which instead of the benzimidazolylidene moiety contain the smaller imidazolylidene and imidazolinylidene moieties. These were expected to confer rotational freedom to the AF groups and accordingly to modify the confining properties of the ligand. In the following, the term *bimodal pincer* designates any tridentate ligand containing a strongly coordinated atom (in our case a carbenic C atom) and two other

donor atoms (or functions) able to interact in a non-covalent manner with the complexed metal ion.

II - Results and discussion

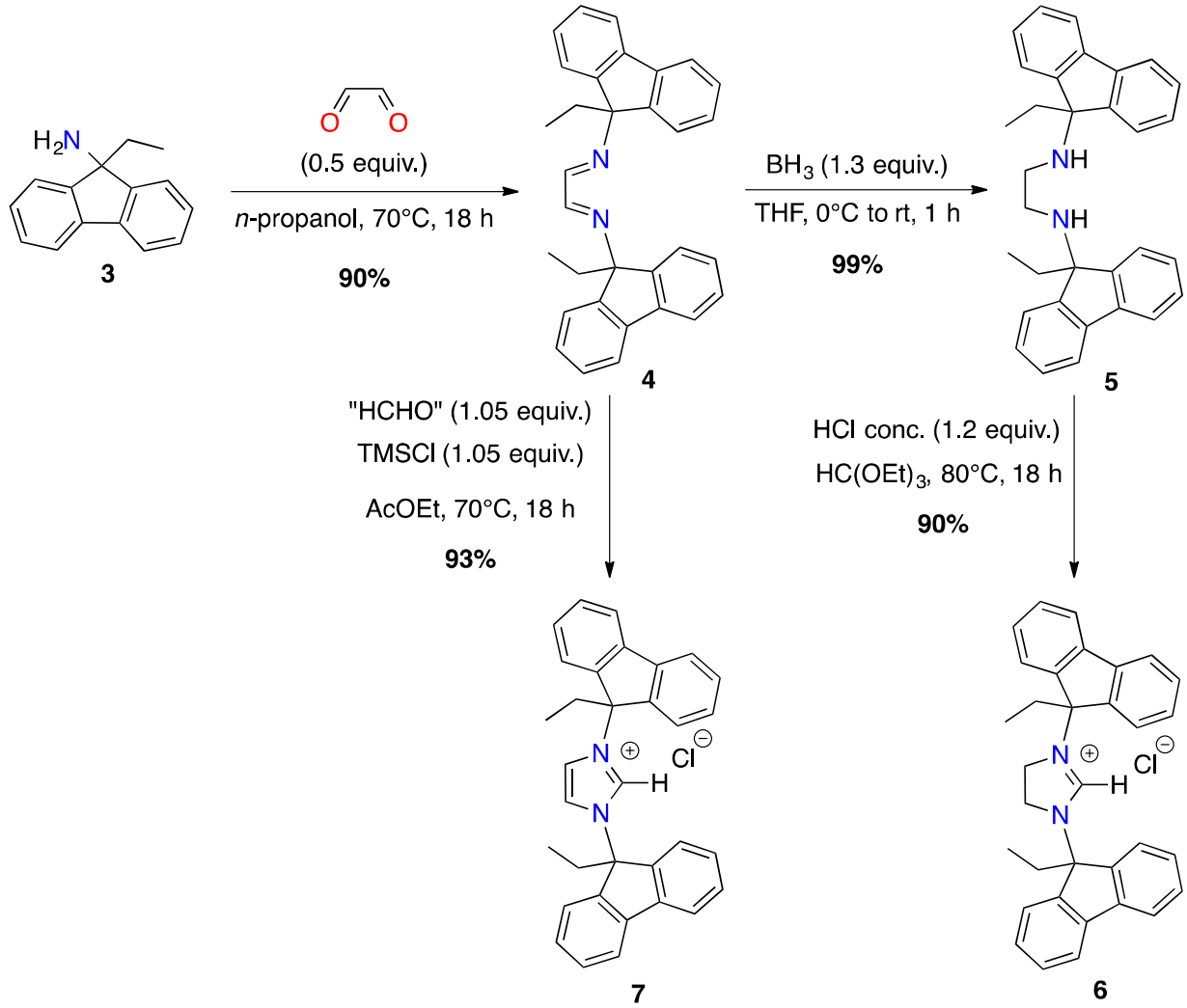
II - A) Syntheses of *N*-heterocyclic carbene precursors

The syntheses of imidazolinium chloride **6** and imidazolium chloride **7** required the preparation of the (new) primary amine **3**, which was obtained by applying a one-flask procedure inspired from the literature (Scheme 1).[5] Thus, reaction of fluorenone with lithium bis(trimethylsilyl)amide (LiHMDS) (1.3 equiv.) in refluxing THF afforded a pale orange solution, which was subsequently treated with EtMgBr in excess. Silyl imine **2**, formed in the first step of this sequence, was not isolated. After workup, amine **3** was obtained in 75% yield.



Scheme 1: Preparation of primary amine **1**

Reaction of **3** with glyoxal in *n*-propanol at 70°C then gave diimine **4** in high yield. Reduction of 4 with BH_3 in THF, followed by reaction of the resulting diamine with $HC(OEt)_3 \cdot HCl$ gave **6** in 90% overall yield (scheme 2). Applying Hintermann's nonclassical protocol for the synthesis of imidazolium salts,[6] **4** was further reacted with paraformaldehyde and Me_3SiCl (**4**:HCHO:Me_3SiCl ratio 1:1:1) in AcOEt, giving **7** in 93% yield.

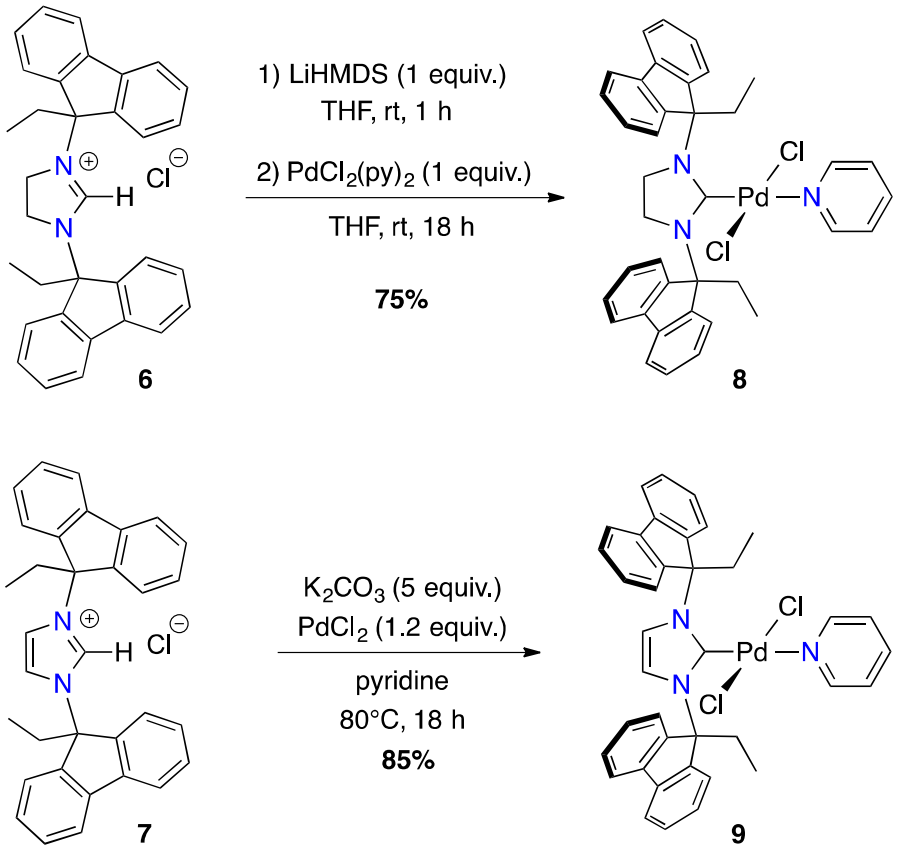


Scheme 2: Synthesis of imidazolinium salt **6** and imidazolium salt **7**.

In the ^{1}H NMR spectra of both salts, **6** and **7**, the signal of the NCHN proton appears, as expected, at relatively low field (10.25 (**6**) and 11.85 (**7**) ppm). Furthermore, the 2D-^{1}H NMR ROESY spectra of both salts revealed correlations between the methylene protons of the Et groups and the protons connected to all three C atoms of the NHC ring, this being a clear indication of freely rotating AF goups. Both salts are strongly hygroscopic and therefore need to be kept in a dry atmosphere.

II - B) Syntheses of Metal Complexes

The PEPPSI-type complex **8** was obtained in 75% yield by the following two-step, one-flask synthesis: 1) reaction of imidazolinium salt **6** with LiHDMS in THF at room temperature; 2) after 1h, addition of $[PdCl_2(Py)_2]$ to the reaction mixture with subsequent heating for 18 h at 65°C (Scheme 3). The related imidazolylidene complex **9** was obtained in 85% yield by refluxing a suspension of precursor **7**, K_2CO_3 and $PdCl_2$ in pyridine for 18 h.



Scheme 3: Synthesis of palladium complexes **8** and **9**.

The ^{13}C NMR spectrum of both complexes shows a signal corresponding to a carbenic C atom, respectively at 174.9 (**8**) and 144.2 (**9**) ppm. As previously observed for a benzimidazolylidene analogue, the NCC*H*$_2$ signals of **8** and **9** are considerably downfield shifted with respect to those of the corresponding precursor salts ($\delta\Delta$ = 1.59 (**8** vs. **6**), and 1.42 (**9** vs. **7**) ppm).

The observed chemical shifts of these protons, together with relatively "standard" ^1J(CH) values (all close to 130 Hz) are indicative of anagostic C–H···Pd interactions, that is of interactions being essentially electrostatic in nature (with the d_z^2 orbital being not significantly involved). 2D-^{1}H NMR ROESY experiments further revealed that while for the precursors **6** and **7** the EF groups freely rotate about their corresponding C-N bonds, these are blocked in **8** and **9**, with the ethyl groups being permanently turned towards the "Pd(pyridine)" unit. The particular orientation of the ethyl groups was confirmed by single crystal X-ray analyses carried out for each complex (Figure 2 and Figure 3).

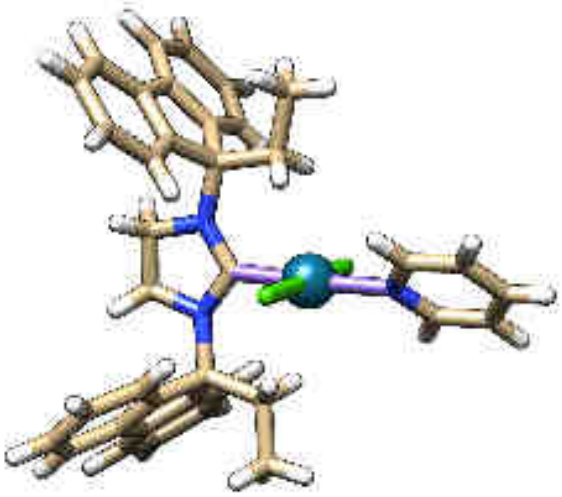


Figure 2: Molecular structure of complex **8**. Pd···H(Et) anagostic bond separations : 2.61, 2.78, 2.60, 2.72 Å.

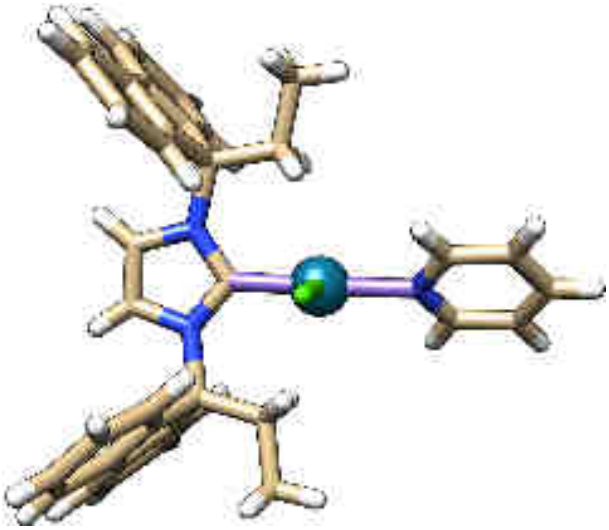
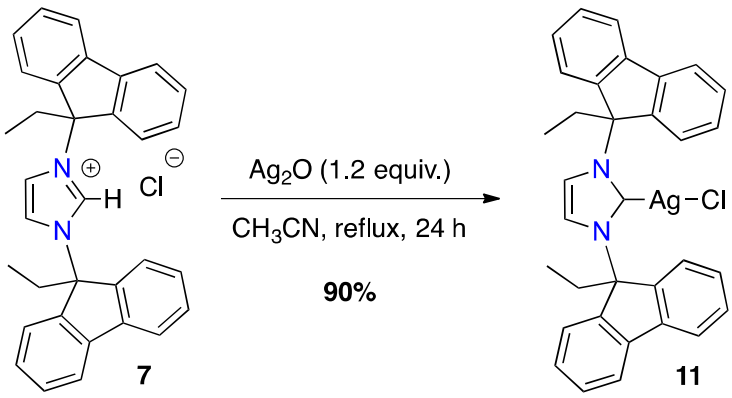


Figure 3: Molecular structure of complex **9**. Pd···H(Et) anagostic bond separations : 2.74, 2.62, 2.60, 2.80 Å.

Imidazolium salt **7** was further successfully converted into silver salt **11**, which formed in 90% yield upon reaction with Ag_2O in refluxing acetonitrile (scheme 4).



Scheme 4: Synthesis of silver complex 11.

Complex **11** is highly stable under light. The 2D-^{1}H NMR ROESY spectrum of **11** displayed cross peaks between the CH_2CH$_3$ and the NCH protons, thus suggesting that the alkyl groups are remote from the silver centre and that therefore the fluorenylidene plane is turned towards the silver ion. In contrast to those of **8-10** (Figure 4), the chemical shift of the CH_2CH$_3$ protons of **11** (2.75 ppm) is normal, this ruling out significant Ag···H(Et) interactions.

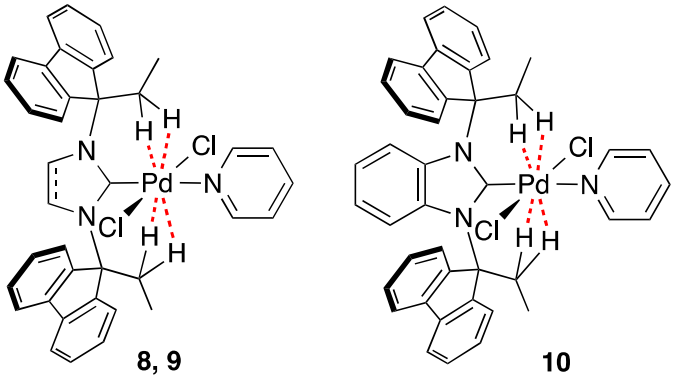


Figure 4: Anagostic interactions (red) observed in the palladium complexes **8-10**.

Crystals of **11** suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a solution of the complex. In the solid state two distinct molecules, **A** and **B**, are present (Figure 5).

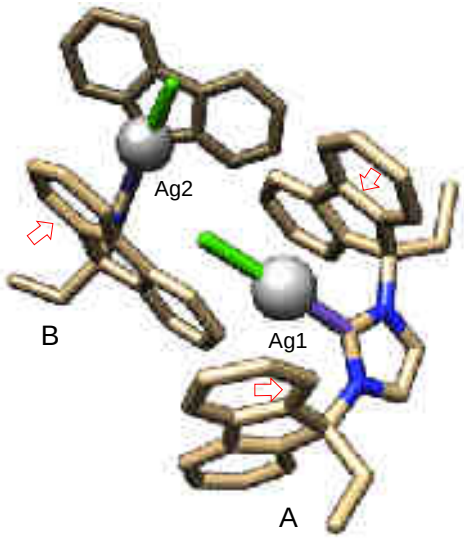


Figure 5: Silver complex **11** existing in the solid state as two distinct molecules with "sandwiched" metal atoms. The red arrows indicate C=C bonds π-interacting with the metal centres (Ag···C separations 2.93-3.18 Å).

Their most striking feature concerns the orientation of the fluorenylidene planes, which, in keeping with the NMR data (*vide supra*), are both bent towards the metal atom,

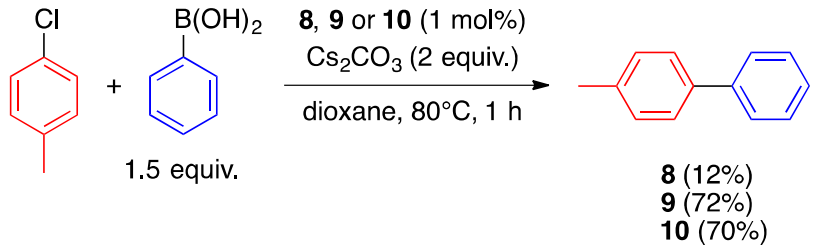
thus resulting in an "open sandwich" structure. The X-ray data indicate that molecule **A** has both fluorenylidene moieties η^2-coordinated to the metal (see Figure 5; shortest Ag···C distances: 2.93 and 3.02 Å for fluorenylidene **A1**; 3.10 and 3.12 Å for fluorenylidene **A2**). A similar π-arene-metal interaction can also be seen in molecule **B**, but only for one of its two fluorenylidene planes (shortest Ag···C distances: 3.00 and 3.18 Å). DFT calculations (see computational details) revealed that conformers having both fluorenylidene planes bent towards the silver atom (exactly as observed for **11** in the solid state) are favoured over those in which these planes are turned away from the metal. However, the interaction energy of each fluorenylidene with the silver atom is only of *ca.* 2 kcal mol^{-1}. Molecules of type **A** and **B** are further supramolecularly linked (in the solid state) through H···Cl bonds involving H atoms of the EF substituents and the imidazolyl rings.

It is noteworthy that in the palladium complexes **8** and **9**, the AF planes are turned away from the metal as a result of anagostic interactions between the CH_2CH_3 protons and the palladium atom (Figure 4). These interactions are seemingly dominant over other possible weak interactions in the palladium complexes. Overall, the present study shows that AF substituted NHCs may behave as carbene-centered bimodal pincers functioning in two possible bonding modes, one involving two weak CH···M interactions, the other two weak η^2-arene···M interactions. It is further interesting to note that determination of the percent buried volume[7] (%*V*bur) of the carbene ligand resulted in markedly different values (35.8% and 58.3%, respectively) according to which structure, **9** or **11**, was used for the calculation. This makes the relevance of the %*V*bur concept questionable, as it does not take into account time dependent conformational changes. For comparison, the two bulkiest monodentate NHCs with the highest reported percent buried volume are NHC which caps a cyclodextrin unit (%*V*bur = 58.5%),[8] and IPr*$^{(2\text{-Np})}$ (%*V*bur = 57.4%).[9]

II - C) Catalysis

Complexes **8** and **9** were assessed in Suzuki-Miyaura cross-coupling between phenylboronic acid and various aryl chlorides. The catalytic runs were performed in dioxane at 80°C using 1 mol% of complex and 2 equiv. of Cs_2CO_3 per aryl chloride. Preliminary tests carried out with *para*-tolyl chloride revealed that the activity of the imidazolylidene complex **9** was six times higher than that of **8** (Scheme 5). In fact its performance for this particular reaction compares with that of the previously reported

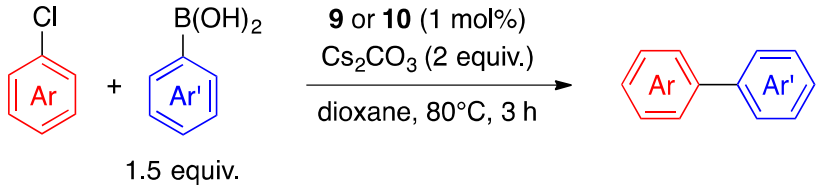
benzimidazolidene complex **10**,[4a] which is one of the fastest Suzuki-Miyaura cross-coupling catalysts prepared so far for this reaction.

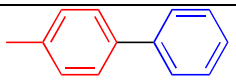
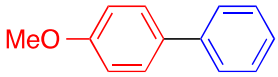
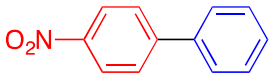
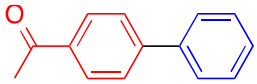
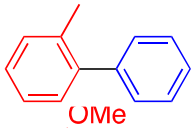
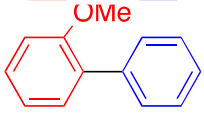
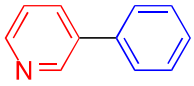


Scheme 5: Suzuki-Miyaura cross-coupling of $PhB(OH)_2$ with *para*-tolyl chloride using palladium complexes **8-10**.

The relatively low activity of **8** *vs.* that of **9** is possibly due to the high donating properties of the corresponding carbene, which makes the metal richer and consequently disfavours the transmetallation step. Tests with other aryl chlorides (Table 1) were therefore ran with **9** and **10** only. The relative activity of these complexes turned out to be dependent on the substrate.

Table 1: Efficiency of complexes **9** and **10** in Suzuki-Miyaura cross-coupling of aryl chlorides[a]



Entry	Product	Yield (%)[b]	
		9	**10**
1		99	99
2		96	29
3		96	90
4		98	96
5		9 (24 h)	15
6		20	23
7		20	20

[a]aryl chloride (1 mmol), phenyboronic acid (1.5 mmol), Cs_2CO_3 (2 mmol), [Pd] (1 mol%), dioxane (3 mL), 3 h. [b]Isolated yields; average of two runs.

Thus, aryl chlorides bearing electron-withdrawing groups in *para* position resulted in activities similar to those obtained for *para*-tolyl chloride (Table 1, entries 3 and 4), whether **9** or **10** was used. In contrast, for *para*-chloroanisole, the coupling reaction occurred *ca*. 3 times faster with **9** than with **10** (Table 1, entry 2). This possibly reflects the better donor properties of the carbene ligand of **9**, which consequently facilitates the oxidative addition step. With *ortho*-substituted arylchlorides, the activity of both catalysts dropped significantly (Table 1, entris 5 and 6), suggesting that the encumbrance of the carbene ligand hinders the approach of the reagent. A similar decrease in activity was observed with 3-chloropyridine. Probably competition occurs in that case between the expected oxidative addition step and (reversible) coordination of the heteroarylchloride through its nitrogen atom, this slowing down the coupling reaction. Overall, complex **9** should be considered as a highly reactive Suzuki-Miyaura cross-coupling catalyst, but only for unencumbered aryl chlorides.

III - Conclusion

In summary, a useful synthetic route for the preparation of imidazolinium salt **6** and imidazolium salt **7** has been described. The key intermediate for these syntheses is the primary amine **3**, which could be obtained according to a one-flask procedure starting from fluorenone. Both salts were converted into the PEPPSI-type palladium complexes **8** and **9** by applying the classical procedure developped by Organ.[2l,10] While complex **8** showed low efficiency, complex **9** behaved as a fast catalyst for the cross-coupling of phenylboronic acid with *para*-substituted aryl chlorides, its activity being comparable to the best commercially available Pd-PEPPSI-NHC reported to date. In solution as well as in the solid state, anagostic interactions were seen in both complexes between the CH_2(fluorenyl) groups and the palladium centre, thus confirming that these carbene ligands may behave as bimodal pincers. As suggested by the solid state structure of the "open sandwich" silver complex **11**, another type of bimodal pincer may be envisaged with such carbenes. Overall, our findings also demonstrate that AF-substituted NHCs may behave as ligands with variable encumbrance.

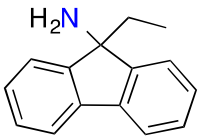
IV - Experimental section

IV - A) General information

All commercial reagents were used as supplied. The syntheses were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. Routine ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a FT Bruker AVANCE 300 (^{1}H: 300.1 MHz, ^{13}C: 75.5 MHz) instrument at 25°C. ^{1}H NMR spectral data were referenced to residual protonated solvent ($CHCl_3$, δ 7.26), ^{13}C chemical shifts are reported relative to deuterated solvent ($CDCl_3$, δ 77.16). In the NMR data given hereafter, Cq denotes a quaternary carbon atom. Flash chromatography was performed as described by Still et al.,[11] employing Geduran SI (E. Merck, 0.040-0.063 mm) silica. Routine thin-layer chromatography analyses were carried out by using plates coated with Merck Kieselgel 60 GF254. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie (UDS-CNRS), Strasbourg. Melting points were determined with a Büchi 535 capillary melting-point apparatus and are uncorrected. Palladium complex **10** was prepared following a procedure described in the literature.[4a]

IV - B) Syntheses of *N*-heterocyclic carbene precursors

(9-ethyl-9*H*-fluoren-9-yl)amine (3). LiHMDS (1 *M* in THF, 21.7 mL, 21.7 mmol) was added to a stirred solution of fluorenone (**1**) (3.0 g, 16.7 mmol) in THF (10 mL) at room temperature. The reaction mixture was then heated at 65°C for 18 h. The resulting dark solution was then cooled to 0°C and ethylmagnesium bromide (1.5 *M* in THF, 33.5 mL, 50.3 mmol) was added dropwise. The mixture was heated at 65°C during 4 h and then cooled to 0°C. Water (100 mL) was slowly added and the mixture was extracted with AcOEt (3 × 100 mL). The combined organic layers were dried over Na_2SO_4 and the solvent removed under vacuum. The crude product was purified by flash chromatography (SiO_2; AcOEt) to afford **3** as a pale yellow oil (2.62 g, 75%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.63-7.56 (m, 2 H, ArH), 7.50-7.45 (m, 2 H, ArH), 7.39-7.30 (m, 4 H, ArH), 2.10 (q, ^{3}J = 7.5 Hz, 2 H, CH_2), 2.02 (br s, 2 H, NH_2), 0.47 (t, ^{3}J = 7.5 Hz, 3 H, CH_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz): δ 150.8 (arom. Cq), 139.9 (arom. Cq), 128.1 (arom. CH), 127.8 (arom. CH), 123.0 (arom. CH), 120.0 (arom. CH), 66.0 (Cq), 34.1 (CH_2), 8.8 (CH_3). Anal. Calcd for $C_{15}H_{15}N$ (209.29): C, 86.08; H, 7.22; N, 6.69. Found: C, 86.15; H, 6.92; N, 6.4.



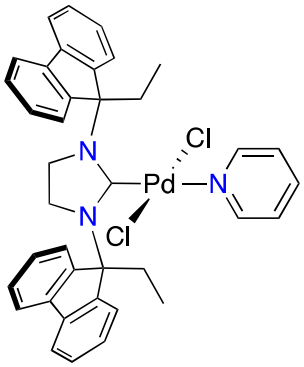
***N,N'*-(ethane-1,2-diylidene)bis(9-ethyl-9*H*-fluoren-9-amine) (4).** To a solution of amine **3** (2.47 g, 11.8 mmol) in *n*-propanol (23 mL) was added glyoxal (40%, 0.675 mL, 5.89 mmol). The solution was then heated at 70°C for 18 h under vigorous stirring. A white precipitate was observed. The suspension was allowed to reach room temperature and was then concentrated under vacuum. The residue was recrystallized from *n*-propanol to afford pure diimine **4** as a white crystalline solid (2.33 g, 90%); mp > 220°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.74 (s, 2 H, NCH), 7.68-7.61 (m, 4 H, ArH), 7.37-7.23 (m, 12 H, ArH), 2.28 (q, ^3J = 7.5 Hz, 4 H, CH_2), 0.47 (t, ^3J = 7.5 Hz, 6 H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 159,3 (NCH), 146.6 (arom. Cq), 140.6 (arom. Cq), 128.4 (arom. CH), 127.8 (arom. CH), 124.7 (arom. CH), 120.3 (arom. CH), 78.4 (Cq), 32.8 (CH_2), 8.4 (CH_3). Anal. Calcd for $C_{32}H_{28}N_2$ (440.59): C, 87.24; H, 6.41; N, 6.36. Found C: 87.15; H, 6.35; N, 6.39.

***N,N'*-bis(9-ethyl-9*H*-fluoren-9-yl)ethane-1,2-diamine (5).** BH_3 (1 *M* in THF, 3 mL, 3.00 mmol) was added dropwise to a stirred solution of diimine **4** (1.0 g, 2.27 mmol) in THF (10 mL) at 0°C. The reaction mixture was allowed to reach room temperature and stirred for 1 h. Water was slowly added (40 mL) and the reaction mixture was extracted with AcOEt (3 x 40 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The light yellow crude diamine was taken in CH_2Cl_2 and charcoal was added. The black mixture was heated to reflux and then allowed to reach room temperature. After filtration through Celite the filtrate was concentrated under reduced pressure to afford pure diamine **5** as a white solid (997 mg, 99%); mp 174°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (d, ^3J = 7.3 Hz, 4 H, ArH), 7.35-7.24 (m, 12 H, ArH), 2.04-1.96 (m, 6 H, overlapping signals, 4 H C*H*$_2$CH$_3$ and 2 H NH), 1.85 (s, 4 H, NCH_2), 0.41 (t, ^3J = 7.5 Hz, 6 H, CH_2CH_3).^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 148.1 (arom. Cq), 141.0 (arom. Cq), 128.0 (arom. CH),127.5 (arom. CH), 123.4 (arom. CH), 119.8 (arom. CH), 71.0 (Cq), 43.5 (NCH_2), 33.9 (*C*H_2CH$_3$), 8.3 (CH_2*C*H$_3$). Anal. Calcd for $C_{32}H_{32}N_2$ (444.62): C, 86.44; H, 7.25; N, 6.30. Found: C, 86.20; H, 7.32; N, 6.55.

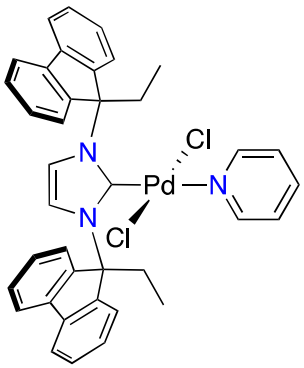
1,3-bis(9-ethyl-9*H*-fluoren-9-yl)imidazolinium chloride (6). Diamine **5** (512 mg, 1.15 mmol) was dissolved under magnetic stirring in $HC(OEt)_3$ (3 mL). HCl (12 M, 116 µL, 1.39 mmol) was added and he mixture was heated at 80°C for 18 h. A white precipitate was observed. The suspension was then cooled to room temperature, and petroleum ether was added (*ca.* 20 mL). The precipitate was collected by filtration and washed with petroleum ether (3 × 15 mL) to afford **6** (507 mg, 90%) as a hygroscopic white solid; mp > 230°C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 10.25 (s, 1 H, NCHN), 7.99-7.92 (m, 4 H, ArH), 7.68-7.61 (m, 4 H, ArH), 7.46-7.38 (m, 8 H, ArH), 3.27 (q, ^3J = 7.4 Hz, 4 H, CH_2CH$_3$), 3.01 (s, 4 H, NCH_2), 0.41 (t, ^3J = 7.4 Hz, 6 H, CH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 156.1 (NCHN), 142.2 (arom. Cq), 140.7 (arom. Cq), 130.0 (arom. CH), 129.1 (arom. CH), 124.5 (arom. CH), 120.3 (arom. CH), 73.6 (Cq), 45.2 (NCH$_2$), 29.4 (*C*H$_2$CH$_3$), 7.9 (CH$_2$*C*H$_3$). Anal. Calcd for $C_{33}H_{31}ClN_2$ (491.08): C, 80.71; H, 6.36; N, 5.70. Found: C, 80.91; H, 6.36; N, 5.40.

1,3-bis(9-ethyl-9*H*-fluoren-9-yl)imidazolium chloride (7). TMSCl (189 µL, 1.50 mmol) was slowly added to a mixture of diimine **4** (635 mg, 1.44 mmol) and paraformaldehyde (45 mg, 1.50 mmol) in AcOEt (5 mL). The mixture was then heated at 70°C for 18 h. A white precipitate was observed. The suspension was then cooled to room temperature and petroleum ether was added (*ca.* 20 mL). The precipitate was collected by filtration and washed with petroleum ether (3 × 15 mL) to afford compound **7** (654 mg, 93%) was obtained as a hygroscopic white solid; mp 212°C. ^{1}H NMR ($CDCl_3$, 500 MHz), δ 11.85 (s, 1 H, NCHN), 7.87 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.71 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.46 (dd, ^3J = $^3J'$ = 7.5 Hz, 4 H, ArH), 7.40 (dd, 4 H, ^3J = $^3J'$ = 7.5 Hz, ArH), 6.37 (s, 2 H, NCH), 3.47 (q, 4 H, ^3J = 6.3 Hz, CH$_2$), 0.50 (t, 6 H, ^3J = 6.3 Hz, CH$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz), δ 143.0 (arom. Cq), 140.3 (arom. Cq), 137.7 (NCHN), 130.4 (arom. CH), 129.2 (arom. CH), 124.7 (arom. CH), 120.6 (arom. CH), 119.8 (NCH), 75.7 (Cq), 30.5 (CH$_2$), 8.0 (CH$_3$). Anal. Calcd for $C_{33}H_{29}ClN_2$ (489.06): C, 81.05; H, 5.98; N, 5.73. Found: C, 81.38; H, 5.97; N, 5.55.

IV - C) Syntheses of palladium and silver complexes

***trans*-[1,3-bis(9-ethyl-9*H*-fluoren-9-yl)imidazolin-2-ylidene](pyridine)palladium(II) dichloride (8).** 

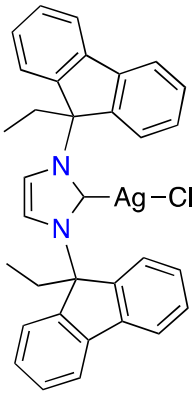
To a suspension of imidazolinium salt **6** (491 mg, 1,00 mmol) in THF (5 mL) cooled at 0°C, was added LiHMDS (1 *M* in THF, 1 mL, 1,00 mmol). The suspension was allowed to reach room temperature and was stirred for 1 h. To the resulting orange solution was added $PdCl_2(pyridine)_2$ (335 mg, 1 mmol) and the mixture was stirred at room temperature for 18 h. The mixture was filtered through Celite and the collected solid washed with CH_2Cl_2 (*ca.* 20 mL). The filtrate was concentrated under reduced pressure and the residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50:50) to afford **8** as a yellow solid (534 mg, 75%); mp > 230°C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 9.11-9.06 (m, 2 H, *o*-NC_5H_5), 7.95-7.89 (m, 4 H, ArH), 7.84-7.77 (m, 1 H, *para*-NC_5H_5), 7.64-7.57 (m, 4 H, ArH), 7.44-7.31 (m, 10 H, overlapping signals, 8 H ArH and 2 H *meta*-NC_5H_5), 4.86 (q, ^3J = 7.2 Hz, 4 H, CH_2CH_3), 2.57 (s, 4 H, NCH_2), 0.36 (t, ^3J = 7.2 Hz, 6 H, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 174.9 (NCN), 151.7 (arom. CH), 146.0 (arom. Cq), 140.6 (arom. Cq), 138.1 (arom. CH), 128.9 (arom. CH), 128.8 (arom. CH), 124.9 (arom. CH), 124.7 (arom. CH), 119.8 (arom. CH), 75.2 (Cq), 45.7 (NCH_2), 33.8 (CH_2CH_3), 9.06 (CH_2CH_3). Anal. Calcd for $C_{38}H_{35}Cl_2N_3Pd$ (711.04): C, 64.19; H, 4.96; N, 5.91. Found: C, 64.42; H, 5.08; N, 5.66.

***trans*-[1,3-bis(9-ethyl-9*H*-fluoren-9-yl)imidazol-2-ylidene](pyridine)palladium(II) dichloride (9).** 

A suspension of imidazolium salt (**7**) (1.23 g, 2.51 mmol), finely crushed K_2CO_3 (1.72 g, 12.4 mmol), and $PdCl_2$ (534 mg, 3.01 mmol) in pyridine (5 mL) was heated at 80°C for 18 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the collected solid washed with CH_2Cl_2 (*ca.* 20 mL). The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50:50) to afford **9** as a yellow solid (1.51 g, 85%); mp > 220°C. ^{1}H NMR ($CDCl_3$, 500 MHz), δ 9.14-9.12 (m, 2 H, *o*-NC_5H_5), 7.82 (tt, ^3J = 7.6 Hz, ^4J = 1.7 Hz, 1 H, *para*-NC_5H_5), 7.75 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.66 (d, ^3J = 7.5 Hz, 4 H, ArH), 7.44-7.40 (m, 2 H, *meta*-NC_5H_5), 7.37 (ddd, ^3J = $^3J'$ = 7.5 Hz, ^4J = 1.2 Hz, 4 H, ArH), 7.31 (ddd, ^3J = $^3J'$ = 7.5 Hz, ^4J = 1.2 Hz, 4 H, ArH), 5.85 (s, 2 H, NCH), 4.99 (q, ^3J = 7.3 Hz, 4 H, CH_2), 0.47 (t, ^3J = 7.3 Hz, 6 H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 151.8 (arom. CH), 147.6 (arom. Cq), 144.2 (NCN),

140.1 (arom. Cq), 138.1 (arom. CH), 129.2 (arom. CH), 129.0 (arom. CH), 125.0 (arom. CH), 124.8 (arom. CH), 122.8 (arom. CH), 120.0 (arom. CH), 75.8 (Cq), 33.1 (CH_2), 8.9 (CH_3). Anal. Calcd for $C_{38}H_{33}Cl_2N_3Pd$ (709.02): C, 64.37; H, 4.69; N, 5.93. Found: C, 64.52; H, 4.62; N, 5.65.

***trans*-[1,3-bis(9-ethyl-9*H*-fluoren-9-yl)imidazol-2-ylidene]silver(I) chloride (11).** A



mixture of imidazolium salt **7** (210 mg, 0.43 mmol) and Ag_2O (119 mg, 0.516 mmol) in CH_3CN (8 mL) was stirred at reflux for 24 h, protected from light. The mixture was cooled to room temperature, filtered through Celite and the collected solid washed with CH_2Cl_2 (*ca.* 20 mL). The filtrate was evaporated to dryness to afford **11** as a white solid (230 mg, 90%); mp 215°C decomposition. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 7.77 (d, ^3J = 7.6 Hz, 4 H, ArH), 7.46 (dd, ^3J = $^3J'$ = 7.6 Hz, 4 H, ArH), 7.29 (dd, ^3J = $^3J'$ = 7.6 Hz, 4 H, ArH), 7.22 (d, ^3J = 7.6 Hz, 4 H, ArH), 7.02 (s, 2 H, NCH), 2.75 (q, 4 H, ^3J = 7.2 Hz, CH_2), 0.39 (t, 6 H, ^3J = 7.2 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz), δ 145.8 (arom. Cq), 140.3 (arom. Cq), 129.7 (arom. CH), 128.5 (arom. CH), 123.4 (arom. CH), 121.0 (arom. CH), 119.0 (NCH), 73.9 (Cq), 32.2 (CH_2), 8.2 (CH_3). The signal of the carbenic C atom was not detected. Anal. Calcd for $C_{33}H_{28}AgClN_2$ (595.92): C, 66.51; H, 4.74; N, 4.70. Found: C, 66.32; H, 4.81; N, 4.65.

IV - D) General Procedure for Suzuki-Miyaura Cross-couplings.

Scheme 4

A mixture of palladium complex (0.01 mmol), phenylboronic acid (183 mg, 1.50 mmol) and Cs_2CO_3 (652 mg, 2 mmol) was suspended in dioxane (3 mL). After the addition of *para*-tolyl chloride (126 mg, 1 mmol), the mixture was vigorously stirred at 80°C for 1 h. The hot mixture was filtered through Celite. 1,4-Dimethoxybenzene (69 mg, 0.5 mmol; internal standard) was then added to the filtrate. The solvent was removed under reduced pressure, and the crude mixture was analysed by ^{1}H NMR spectroscopy. The yields were determined by comparing the intensity of the methyl signal of the product [δ(Me) = 2.41 ppm] with that of the internal reference [δ(Me) = 3.78 ppm]. In some experiments the product was isolated chromatographically. The isolated yield turned out to be very close (deviation less than 5 %) to that determined by using the internal reference.

Table 1

A mixture of palladium complex (0.01 mmol), phenylboronic acid (183 mg, 1.50 mmol) and Cs_2CO_3 (652 mg, 2 mmol) was suspended in dioxane (3 mL). After the addition of the arylchloride (1 mmol), the mixture was vigorously stirred at 80°C for 3 h. The hot mixture was filtered through Celite and the collected solid washed with CH_2Cl_2 (*ca.* 20 mL). The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO_2; AcOEt/petroleum ether, 0.5:99.5) to afford the desired product. All products were unambiguously identified by NMR after their isolation. The NMR spectra were compared to those reported in the literature.[2u]

IV - E) Crystal data

Crystal Data for Complex 8

Crystals suitable for X-ray diffraction were obtained by slow diffusion of ether into a dichloromethane solution of the complex: $C_{38}H_{35}Cl_2N_3Pd$, M_r = 710.99, orthorhombic, space group $P2_12_12_1$, a = 11.6715(2), b = 13.6877(2), c = 20.5488(4) Å, β = 90.00, V = 3282.79(10) Å^3, Z = 4, μ = 0.760 mm^{-1}, F(000) = 1456. Crystals of the compound were mounted on a Oxford Diffraction CCD Safire 3 Xcalibur diffractometer. Data collection with Mo-Kα radiation (λ = 0.71073 Å) was carried out at 120 K. 23091 reflections were collected (2.64 < θ < 27.00°), 7149 were found to be unique and 5389 were observed (merging R = 0.0620). The structure was solved with SHELXS-97.[12] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.0592, 0.0378, 0.0631, 0.0598, 0.869. Residual electron density minimum/maximum = –0.460/0.899 e Å^{-3}.

Crystal Data for Complex 9

Crystals suitable for X-ray diffraction were obtained by slow diffusion of ether into a dichloromethane solution of the complex: $C_{38}H_{33}Cl_2N_3Pd$, M_r = 708.97, orthorhombic, space group $P2_12_12_1$, a = 11.6469(2), b = 13.7077(2), c = 20.4229(3) Å, β = 90.00, V = 3260.56(9) Å^3, Z = 4, μ = 0.765 mm^{-1}, F(000) = 1448. Crystals of the compound were mounted on a Oxford Diffraction CCD Safire 3 Xcalibur diffractometer. Data collection with Mo-Kα radiation (λ = 0.71073 Å) was carried out at 120 K. 27148 reflections were collected (2.65 < θ < 27.00°), 7099 were found to be unique and 6467 were observed (merging R = 0.0335). The structure was solved with SHELXS-97.[12] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.0289, 0.0244, 0.0526, 0.0517, 0.969. Residual electron density minimum/maximum = –0.251/0.476 e Å^{-3}.

Crystal Data for Complex 11

Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a dichloromethane solution of the complex: $C_{66}H_{56}Ag_2Cl_2N_4$, M_r = 1191.79, triclinic, space group *P*–1, a = 10.2170(7), b = 13.5390(10), c = 20.073(2) Å, β = 78.226(8), V = 2660.9(4) Å^3, Z = 2, μ = 0.883 mm^{-1}, F(000) = 1216. Crystals of the compound were mounted on a Oxford Diffraction CCD Safire 3 Xcalibur diffractometer. Data collection with Mo-Kα radiation (λ = 0.71073 Å) was carried out at 140 K. 21631 reflections were collected ($3.05 < \theta < 27.00°$), 11591 were found to be unique and 6846 were observed (merging R = 0.0708). The structure was solved with SHELXS-97.[12] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.1315, 0.0645, 0.1176, 0.0941, 1.019. Residual electron density minimum/maximum = –0.621/0.759 e Å^{-3}.

IV - F) Computational details

Calculations were performed using the ADF 2013 package.[13] All-electron Slater type orbitals were used with all-electron triple-ζ quality basis sets at DFT level with PBE functional.[14] Dispersive interactions were taken into account applying Grimme corrections.[15] Scalar relativistic effects were included through ZORA Hamiltonian.[16] Full geometry optimisation was performed on the complexes. Interaction energy between the silver atom of 11 and the fluorenyl moiety was calculated by two methods. First, the EF groups were rotated around the corresponding N–C bond moving the fluorenylidene plane from a position in which it is bent towards the metal centre to the opposite one (calculation 1). Secondly, we computed the substitution energy of a NHC-complex having two *n*-propyl chains instead of EF groups by the NHC bearing two EF groups (calculation 2). Both calculations showed that the complex where interaction between the silver atom and the fluorenyl groups occurs is more stable (ΔE= 3.2 kcal mol^{-1} for calculation 1; ΔE = 3.8 kcal mol^{-1} for calculation 2).

V - Notes and references

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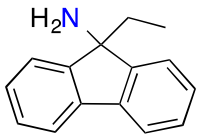

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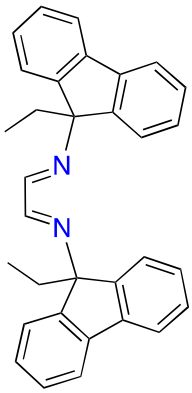

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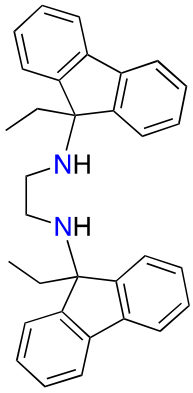

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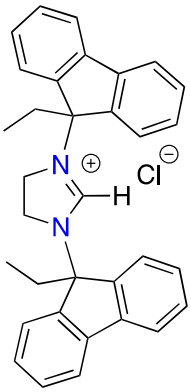

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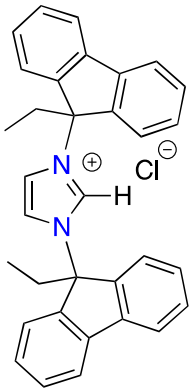

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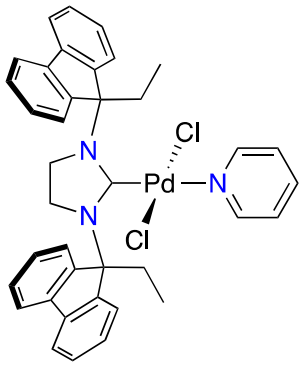

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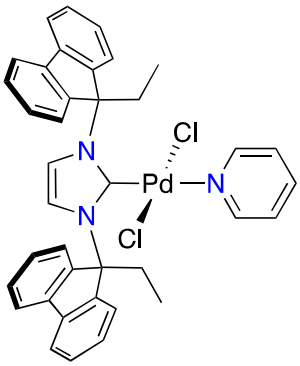

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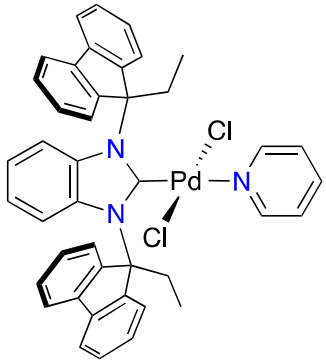

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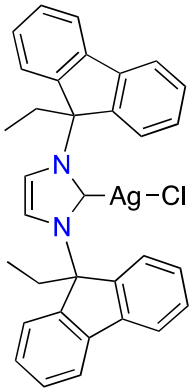

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Chapter IV :

"Hummingbird" behaviour of *N*-heterocyclic carbenes stabilises out-of-plane bonding of AuCl and CuCl units.

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Abstract

An *N*-heterocyclic carbene substituted by two expanded 9-ethyl-9-fluorenyl groups was shown to bind an AuCl unit in an unusual manner, namely with the Au–X rod sitting *out of the plane* defined by the central imidazolium unit. As shown by X-ray studies and DFT calculations, the observed large pitch angle (21°) arises from an easy displacement of the gold(I) atom out the carbene lone pair axis, combined with the stabilisation provided by weak CH···Au interactions involving aliphatic and aromatic H atoms of the NHC wingtips. A general belief until now was that tilt angles in NHC complexes arise only from steric effects.

I - Introduction

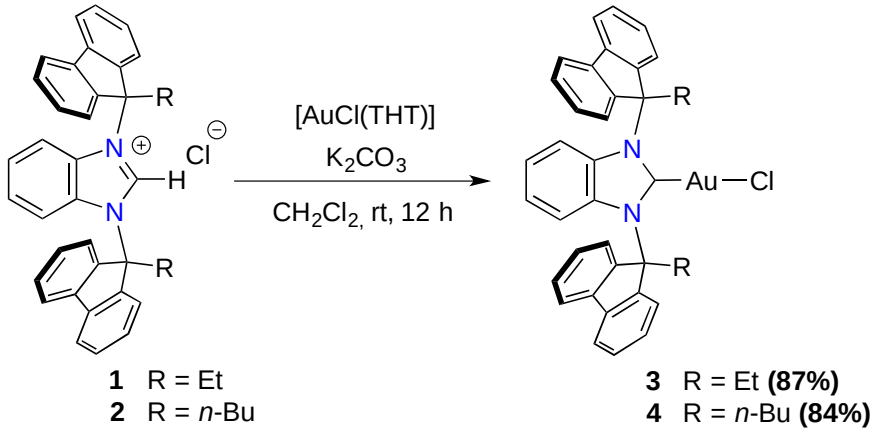
The discovery in 1991[1] of the first stable, "bottleable" *N*-heterocyclic carbene (NHC) triggered an explosion of interest for this class of compounds in many fields of contemporary chemistry.[2] In organometallic chemistry and catalysis, NHCs have become valuable ligands which are frequently preferred over the conventional phosphine and amine ligands, mainly because of the higher stability and activity of their metal complexes.[3] Many theoretical and experimental studies provide evidence and rationale for the high stability of such complexes, shown to be a consequence of the particular nature of the metal-carbene bond ($M–C_{carb}$), that combines high ligand σ-donor properties with a possible π-donor contribution of the NHC as well as π-back donation from the metal to the whole NHC-metal bonding (ambivalent π-bonding character).[4] A crucial role with respect to catalytic activity is further played by the steric influence of the NHC unit, which is completely controlled by the nitrogen substituents. Thus, in NHC coordination chemistry it is now well established that steric encumbrance favours the formation of monoligated complexes, reductive elimination steps, and efficient stabilisation of coordinatively unsaturated catalytic intermediates. In palladium-catalysed Suzuki-Miyaura cross-

couplings, encumbered NHCs with some flexibility were found superior in terms of activity to more rigid analogues.[5]

In some complexes featuring non-chelating NHCs, the C_{carb}–M bond undergoes an out-of-NHC-plane tilting, characterised by a so-called pitch angle.[6] X-ray structural analyses combined with DFT studies showed that in the vast majority of complexes showing a non-zero pitch angle, the observed deviation can be assigned to steric interactions involving the wingtip substituents, rather than to electronic factors.[6] In the present study we report the first NHC chlorogold (I) complex in which the metal ion lies out of the NHC plane in the solid, the pitch angle created being exclusively due to non-steric factors. The NHCs employed in this study, all containing AF substituents, have been previously shown to behave as "bimodal pincers", that is tridentate ligands containing a strongly coordinating atom (the carbenic C) and two C*H* atoms able to interact in a non-covalent manner with the metal ion.[7]

II - Results and discussion

The gold (I) complexes considered in this study, **3** and **4**, were obtained in high yield by reacting the corresponding benzimidazolium salts, respectively **1** and **2**, with [AuCl(tetrahydrothiophene)] in the presence of K_2CO_3 (Scheme 1).



Scheme 1: Synthesis of gold (I) complexes **3** and **4**

A single crystal X-ray diffraction study (Figure 1, top) revealed that while the C_{carb}–Au–Cl unit of **3** adopts the expected linear coordination geometry, the gold atom lies out of the plane defined by the NHC ring, providing a remarkable pitch angle of 21°.

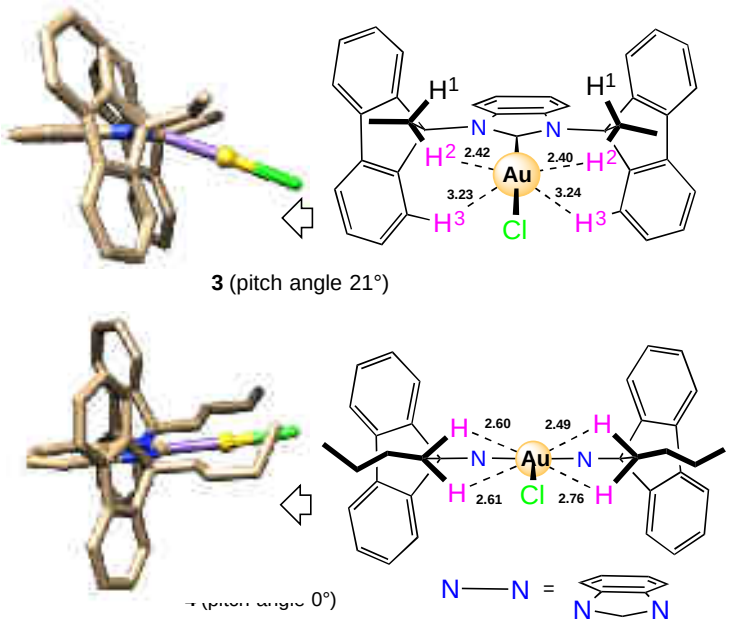


Figure 1: Solid-state structures of chlorogold complexes **3** (top) and **4** (bottom) showing the out-of-plane (**3**) or in-plane (**4**) positioning of the metal centre. Au···H[1]. Distances in complex **3**: 3.12 and 3.13 Å.

In addition, both fluorenylidene planes display an inclination of 11° with respect to the direction orthogonal to the benzimidazolyl unit, this leading to two different methylenic Au•••H separations (Au•••H[1] : 3.12 and 3.13 Å; Au•••H[2]: 2.40 and 2.42 Å; see Figure 1) and two aromatic H atoms coming close to the metal (Au•••H[3]: 3.23 and 3.24 Å; Figure 1). Note also that the Au-C_{carb} bond length (2.001 Å) lies in the range reported for undistorted [(NHC)AuCl] complexes.[8]

What makes such a large C_{carb}–M tilt possible ? As the two large AF groups are far apart, and the gold atom possesses no ligand in *cis* position to the carbene, steric grounds should be excluded for rationalising the bending. An interesting observation comes from the solid state structure of the *n*-butyl analogue **4**, in which the gold atom sits, unlike in **3**, perfectly in the NHC plane (Figure 1, bottom). Thus, here the two C-H bonds of each NC*H_2* group are nearly symmetrically positioned with respect to the NHC plane, with the corresponding H•••Au distances (aver. 2.62 Å) being somewhat longer than the shortest Au•••H(of CH_2) observed in **3**. These findings are a clear indication that the pitch found in **3** cannot arise from repulsive interactions between the metal atom and the alkyl side groups.

A DFT calculation carried out for an analogue of **4** in which the two alkyl groups (R) have been substituted by hydrogen revealed that the energy difference between a minimised in-plane conformer and its analogue having the C–Au bond pitched by 21° is

only *ca.* 2.5 kcal mol^{-1}.[9] In other terms, in such a complex the gold atom can, *a priori*, occupy a position along the carbene lone pair or remote from it.

Carrying out the same calculations for the complex with R = Et (*i.e.* **3**) showed that in this case the "in" and "out" conformers have nearly the same energy, thus confirming that the Au•••H interactions "seen" the solid-state structure play a stabilising role. This study also revealed that while the interactions between the gold atom and the methylenic H^2 atoms of **3** can be regarded as hydrogen bonds (being electrostatic in nature, they may be termed anagostic[10]), those with the aromatic H^3 atoms involve dispersive forces (see experimental part). No interactions were found to occur between the gold atom and the methylenic H^1 atoms.

In the solid, the individual molecules forming **3** are linked through Cl•••H(aromatic) bonds involving the two fluorenylidene moieties of each ligand (Cl•••H : 2.67 and 2.71 Å), this resulting in an infinite chain structure (Figure 2).

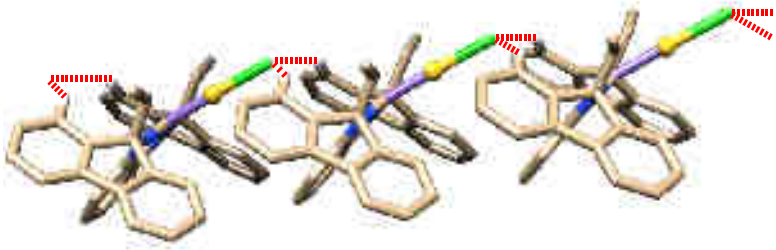


Figure 2: Supramolecular chain structure of **3** in the solid state

We wondered whether such interactions might have contributed to stabilise the out-of-plane conformer detected in the solid state. For this purpose, the energy of a dimer extracted from the solid-state supramolecular chain structure (thus having two out-of-plane gold atoms), was compared with that of a dimer in which the gold atoms were forced to stay in the plane. These calculations unambigously demonstrated the beneficial role of the intermolecular interactions, the dimer with the two out-of-plane gold atoms being more stable by 3 kcal mol^{-1} than the other one.

It is worth mentioning that complex **4** having a zero pitch angle, does not have a chain structure. Here pairs of molecules form an AA' dimer (not shown), this assembly involving in addition to H···Cl bonds analogous to those creating the superstructure in **3**, CH-π interactions between the butyl groups of molecule A and the fluorenylidene moieties of sister molecule A' also.

Overall, the observed out-of-plane conformation found for **3** in the solid (leading to a structure reminiscent of a flying hummingbird) is most likely the result of a solid-state

effect which renders the out-of-plane conformer slightly more stable. More importantly, the unexpected observation of a pitch angle in **3** constitutes a hint that, in solution, gold (I) atoms may readily move away from the carbenic lone pair axis (Figure 3), although such an oscillation has never been reported in the literature.

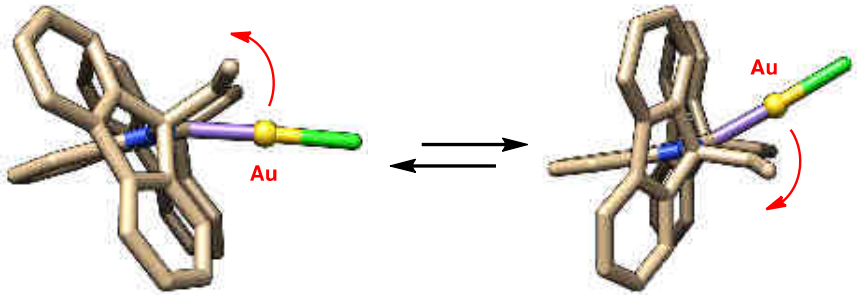
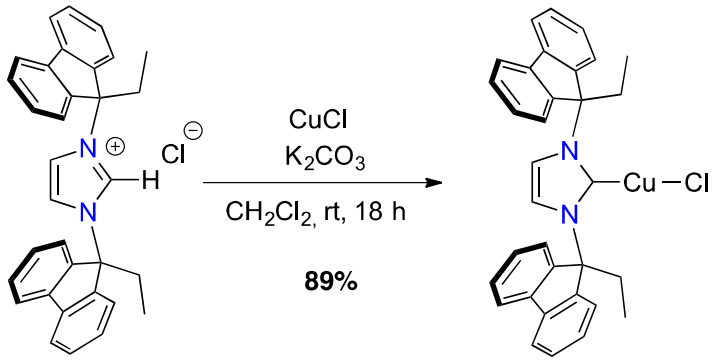


Figure 3: Oscillating behaviour of the AuCl unit in complex **3**

The demonstration that the bending seen for **3** is not limited to Au(I), nor to NHCs built on a benzimidazolyl unit was provided by examining the structure of the chloro copper(I) complex **6**, obtained from imidazolinium salt **5** (Scheme 2).



Scheme 2: Synthesis of copper (I) complexes **6**

Indeed, the molecular structure of **6** (Figure 4) is basically similar to that of **3**, the pitch being here 16° (average value for the two independent molecules of the unit cell). The separations between the copper atom and the closest H atoms are slightly smaller than the corresponding ones in **3** (Figure 4).

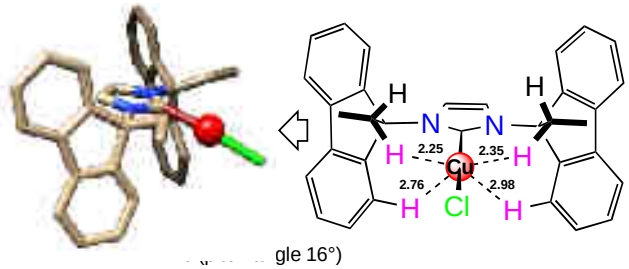


Figure 4: Solid state structures of copper complex **6** with an out-of-plane metal atom (only one molecule of the unit cell is shown).

To get an insight into the dynamic behaviour of **3** in solution, a variable temperature ^{1}H NMR study was carried out (Figure 5).

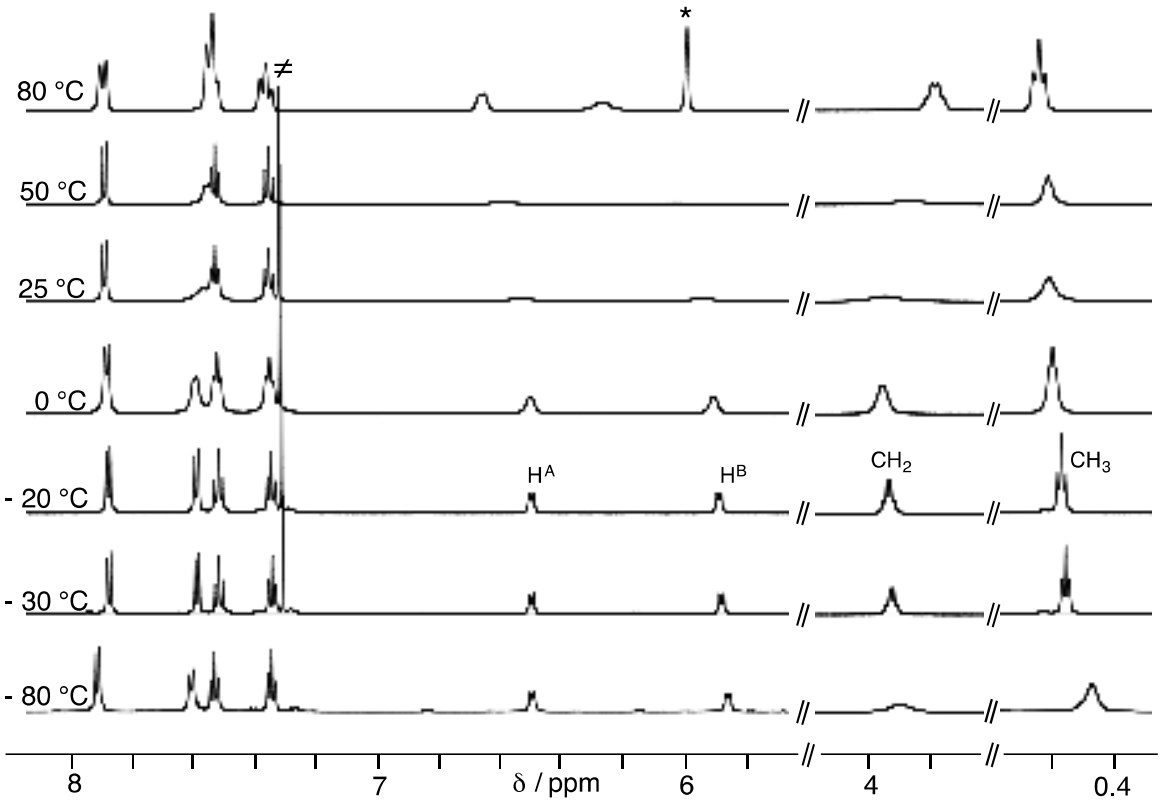


Figure 5: Variable temperature study for **3**. Conditions: –80 °C (CD_2Cl_2, 600 MHz); –30 °C- +50 °C ($CDCl_3$, 600 MHz); +80 °C ($C_2D_2Cl_4$, 400 MHz). Hashtag and asterisk denote protonated $CDCl_3$ and $C_2D_2Cl_4$, respectively. H^A and H^B are protons of the benzimidazolylidene unit.

The spectrum measured at -30°C is consistent with a C_{2v}-symmetrical structure, as it shows a sharp quartet for the CH_2 groups (the two H atoms are thus equivalent), a typical AA'BB' spectrum for the protons of the benzimidazolyl unit, and a sharp doublet for the H-1 protons of the fluorenylidene moiety. These observations together with the unsymmetrical structure observed in the solid, suggest that in solution the gold atom switches rapidly

from one side of the carbenic lone pair axis to the other concomitantly with a rapid partial oscillation of the ethyl group about the C(ethyl)–C(fluorenylidene) bond (this latter movement creating alternately bonding to each of the two methylenic protons). On raising the temperature, the above signals first broadened, then coalesced, and finally reappeared with their original line shape at nearly identical chemical shifts. Thus, whether high or low temperature, the spectrum of **3** was consistent with a C_{2v} symmetrical complex. The observed line broadening probably reflects conformational changes within the wingtips, these being set off only at higher temperatures. A likely motion is the full rotation of the two Et groups about the C(ethyl)–C(fluorenylidene) bond only at higher temperatures, these rotations occurring not necessarily in a synchronous manner (calculated rotational barrier : *ca.* 15 kcal mol^{-1}).[11] That the fluorenylidene plane keeps its orientating properties in the temperature range -30 – +80°C was deduced from a series of comparative 2D-^{1}H NMR ROESY experiments. Note that lowering the temperature to -80°C (using CD_2Cl_2 instead of $CDCl_3$) induced again broadening of the signals of the ethyl groups, however it was not possible to freeze out a motion involving these groups. This broadening probably corresponds to a slowing down of the Au–H/Au–H' bonding exchange involving geminal CH_2 protons (calculated barrier *ca.* 7 kcal mol^{-1}).[12]

III - Conclusion

In conclusion, we have described the first example of a linear [AuCl(NHC)] complex in which the metal atom is kept out of the plane defined by the coordinated *N*-heterocyle. The observed large tilt angle results from the energetically weakly demanding out-of-plane displacement of the Au(I) atom, combined with a stabilisation of the resulting bent structure by weak Au···H interactions involving aliphatic and aromatic H atoms of the wingtips, the NHC operating here *de facto* as a bimodal pincer. Subtle supramolecular forces between the individual molecules clearly help stabilising the unusal NHC–Au bending in the solid. While numerous previous studies have illustrated the capacity of bulky NHC substituents to sterically protect metal centres and/or to promote metal-centred coupling reactions, this study has revealed that NHCs able to act as bimodal pincers may display "hummigbird dynamics" towards bound M–X units (M = Au, Cu), and thus allow visualisation of oscillating metal atoms. Further studies are aimed at investigating whether the coordinative flexibility of such NHCs has an impact on catalytic reactions.

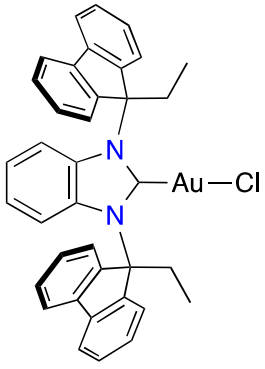
IV - Experimental section

IV - A) General information

All commercial reagents and solvents were used as supplied. The syntheses were performed using Schlenk-type flasks in air. Routine ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a FT Bruker AVANCE 400 (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz), AVANCE 500 (^{1}H: 500.1 MHz, ^{13}C: 125.6 MHz) or AVANCE 600 (^{1}H: 600.1 MHz, ^{13}C: 150.5 MHz) instrument at 25°C otherwise stated. ^{1}H NMR spectral data were referenced to residual protonated solvents ($CDCl_3$, δ 7.26; $C_2D_2Cl_4$, δ ??????? CD_2Cl_2, δ 5.30), ^{13}C chemical shifts are reported relative to deuterated solvents ($CDCl_3$, δ 77.16; $C_2D_2Cl_4$, δ ??????? CD_2Cl_2 δ 53.8). Data appear in the following order: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constant (J) in Hz and assignment. In the NMR data given hereafter, Cq denotes a quaternary carbon atom. Geduran SI (E. Merck, 0.040-0.063 mm) silica was employed for filtrations over silica gel. Routine thin-layer chromatography analyses were carried out by using plates coated with Merck Kieselgel 60 GF254. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie UMR 7177 CNRS-UDS, Strasbourg. Melting points were determined with a Büchi 535 capillary melting-point apparatus and are uncorrected. NHC precursors **1**,[13] **2**,[13] and **5**[14] and [AuCl(THT)][15] were prepared according to literature procedures.

IV - B) Syntheses of chlorogold(I) and chlorocopper(I) complexes

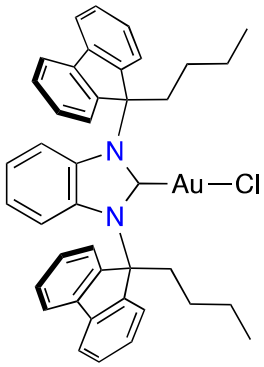
1,3-bis(9-ethyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene)gold(I) chloride (3) : A



suspension of benzimidazolium salt **1** (0.300 g, 0.56 mmol), finely crushed K_2CO_3 (1.041 g, 7.89 mmol) and [AuCl(THT)] (0.178 g, 0.56 mmol) in CH_2Cl_2 (20 mL) was stirred for 12h in air at room temperature. The mixture was filtered through a pad of silica gel and the pad was washed with CH_2Cl_2 (*ca.* 3 × 20 mL). The filtrate was concentrated under vacuum to *ca.* 1 mL. Pentane (6 mL) was added and the resulting white precipitate was decanted. After removal of the supernatant, the solid was washed with pentane (3 × 6 mL) to afford pure **3** as a white solid (0.358 g, 87%); m.p. > 202°C. Crystals suitable for X-Ray analysis were grown by slow diffusion of pentane into a CH_2Cl_2 solution of the complex. ^{1}H NMR ($CDCl_3$, 500 MHz, -30°C), δ 7.83 (d, 4H, ^{3}J = 7.6 Hz, arom. H of fluorenylidene), 7.52 (d, 4H, ^{3}J = 7.6 Hz, arom. H of

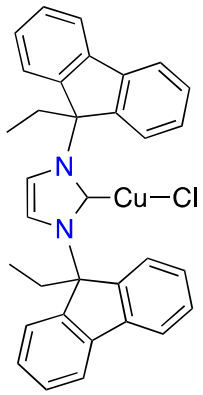
fluorenylidene), 7.45 (dd, 4H, ^3J = $^3J'$ = 7.6 Hz, arom. H of fluorenylidene), 7.30 (dd, 4H, ^3J = $^3J'$ = 7.5 Hz, arom. H of fluorenylidene), 6.50 (A part of AB spectrum, 2H, ArH of benzimidazolylidene unit), 5.92 (B part of AB spectrum, 2H, arom. H of benzimidazolylidene unit), 3.90 (q, 4H, ^3J = 7.2 Hz, CH_2), 0.63 (t, 6H, ^3J = 7.2 Hz, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 25°C): δ 145.8 (arom. Cq), 139.9 (arom. Cq), 133.7 (arom. Cq), 129.7 (arom. CH), 129.6 (arom. CH), 128.8 (arom. CH), 128.7 (arom. CH), 124.2 (arom. CH), 123.4 (arom. CH), 120.7 (arom. CH), 114.6 (arom. CH), 75.4 (N*C*-Et), 36.7 (CH_2), 9.0 (CH_3), signal of carbenic C not detected; Elemental analysis: found C, 60.25; H, 4.22; N, 3.66. Calc. for $C_{37}H_{30}AuClN_2$ (M_r = 735.07): C, 60.46; H, 4.11; N, 3.80.

(1,3-bis(9-butyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene)gold(I) chloride (4) A



suspension of benzimidazolium salt **2** (0.200 g, 0.34 mmol), finely crushed K_2CO_3 (0.620 g, 4.70 mmol), and [AuCl(THT)] (0.107 g, 0,33 mmol) in CH_2Cl_2 (8 mL) was stirred for 12 h in air at room temperature. The mixture was filtered through a pad of silica gel and the pad was washed with CH_2Cl_2 (*ca.* 3 × 20 mL). The filtrate was concentrated under vacuum to *ca.* 1 mL. Pentane (6 mL) was added and the resulting white precipitate was decanted. After removal of the supernatant, the solid was washed with pentane (3 × 6 mL). The product was dried under vacuum to afford pure complex **4** as a white solid (0.218 g, 84%); m.p. > 185°C. Crystals suitable for X-Ray analysis were grown by slow diffusion of pentane into a CH_2Cl_2 solution of the complex. ^1H NMR ($CDCl_3$, 400 MHz, 25°C), δ 7.84 (d, 4H, ^3J = 7.5 Hz, arom. H of fluorenylidene), 7.86 (br, 4H, arom. H of fluorenylidene), 7.49 (dd, 8H, ^3J = $^3J'$ = 7.5 Hz, arom. H of fluorenylidene), 7.30 (dd, 4H, ^3J = $^3J'$ = 7.5 Hz, arom. H), 6.05 (br, 2H, H of benzimidazolylidene unit), 5.90 (br, 2H, H of benzimidazolylidene unit), 3.90 (br, 4H, $CH_2CH_2CH_2CH_3$), 1.39 (br, 4H, $CH_2CH_2CH_2CH_3$), 0.98 (br, 4H, $CH_2CH_2CH_2CH_3$), 0.83 (t, 6H, ^3J = 7.1 Hz, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25°C), δ 146.3 (arom. Cq), 139.7 (arom. Cq), 133.7 (arom. Cq), 129.5 (arom. CH), 128.6 (arom. CH), 124.2 (arom. CH), 123.3 (arom. CH), 120.8 (arom. CH), 114.6 (arom. CH), 75.0 (br, N*C*-Bu), 43.3 (br, CH_2-$CH_2CH_2CH_3$), 26.5 ($CH_2CH_2CH_2CH_3$), 22.5 ($CH_2CH_2CH_2CH_3$), 14.1 (CH_3), carbenic C signal not detected; Elemental analysis: found C, 62.19; H, 4.84; N, 3.54. Calc. for $C_{41}H_{38}AuClN_2$ (M_r = 791.17): C, 62.24; H, 4.84; N, 3.54.

1,3-bis(9-ethyl-9*H*-fluoren-9-yl)imidazol-2-ylidene)copper(I) chloride (6): A



suspension of imidazolium salt **5** (0.200 g, 0.41 mmol), finely crushed K_2CO_3 (0.773 g, 5.85 mmol) and CuCl (0.059 g, 0.60 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature overnight (in air). The mixture was filtered through a pad of silica gel and the pad was washed with CH_2Cl_2 (*ca*. 3 × 20 mL). The filtrate was concentrated under vacuum to *ca.* 1 mL. Pentane (6 mL) was added and the resulting white precipitate was decanted. After removal of the supernatant, the solid was washed with pentane (3 × 6 mL), then dried under vacuum to afford pure **5** as a white solid (0.200 g, 89%); m.p. > 220 °C. Crystals suitable for X-ray analysis were grown by slow diffusion of pentane into a CH_2Cl_2 solution of the complex.^{1}H NMR ($CDCl_3$, 500 MHz, 25°C), δ 7.75 (4H, d, ^3J = 7.5 Hz, arom. H), 7.46 (4H, dd, ^3J = $^3J'$ = 7.5 Hz, arom. H), 7.41 (4H, d, ^3J = 7.5 Hz, ArH), 7.32 (4H, dd, ^3J = $^3J'$ = 7.5 Hz, arom. H), 6.62 (2H, s NCH), 3.05 (4H, q, ^3J = 7.2 Hz, CH_2), 0.47 (6H, t, ^3J = 7.2 Hz, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, 25°C): δ 173.8 (NCN), 145.8 (arom. Cq), 140.4 (arom. Cq), 129.6 (arom. CH), 128.5 (arom. CH), 123.9 (arom. CH), 120.8 (arom. CH), 119.0 (N=*C*H), 74.0 (N*C*-Et), 32.9 (CH_2), 8.3 (CH_3); elemental analyses: found C, 71.56; H, 5.44; N, 4.94; calc. for $C_{33}H_{28}ClCuN_2$ (M_r = 551.59): C, 71.86; H, 5.12; N, 5.08.

IV - C) Crystal data

Crystal Data for Complex 3

Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a dichloromethane solution of the complex: $C_{37}H_{30}AuClN_2$, M_r = 735.05, orthorhombic, space group $P2_12_12_1$, a = 7.9679(1), b = 17.3273(3), c = 20.9327(3) Å, □ = 90.00, V = 2890.01(7) Å^3, Z = 4, □ = 5.213 mm^{-1}, F(000) = 1448. Crystals of the compound were mounted on an Oxford Diffraction CCD Safire 3 Xcalibur diffractometer. Data collection with Mo-Kα radiation (□ = 0.71073 Å) was carried out at 150 K. 24331 reflections were collected (2.98 < □ < 26.99°), 6169 were found to be unique and 5871 were observed (merging R = 0.0422). The structure was solved with SHELXS-97.[16] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.0242, 0.0216, 0.0409, 0.0399, 1.015. Residual electron density minimum/maximum = –0.816/1.018 e Å^{-3}. CCDC 1002895.

Crystal Data for Complex 4

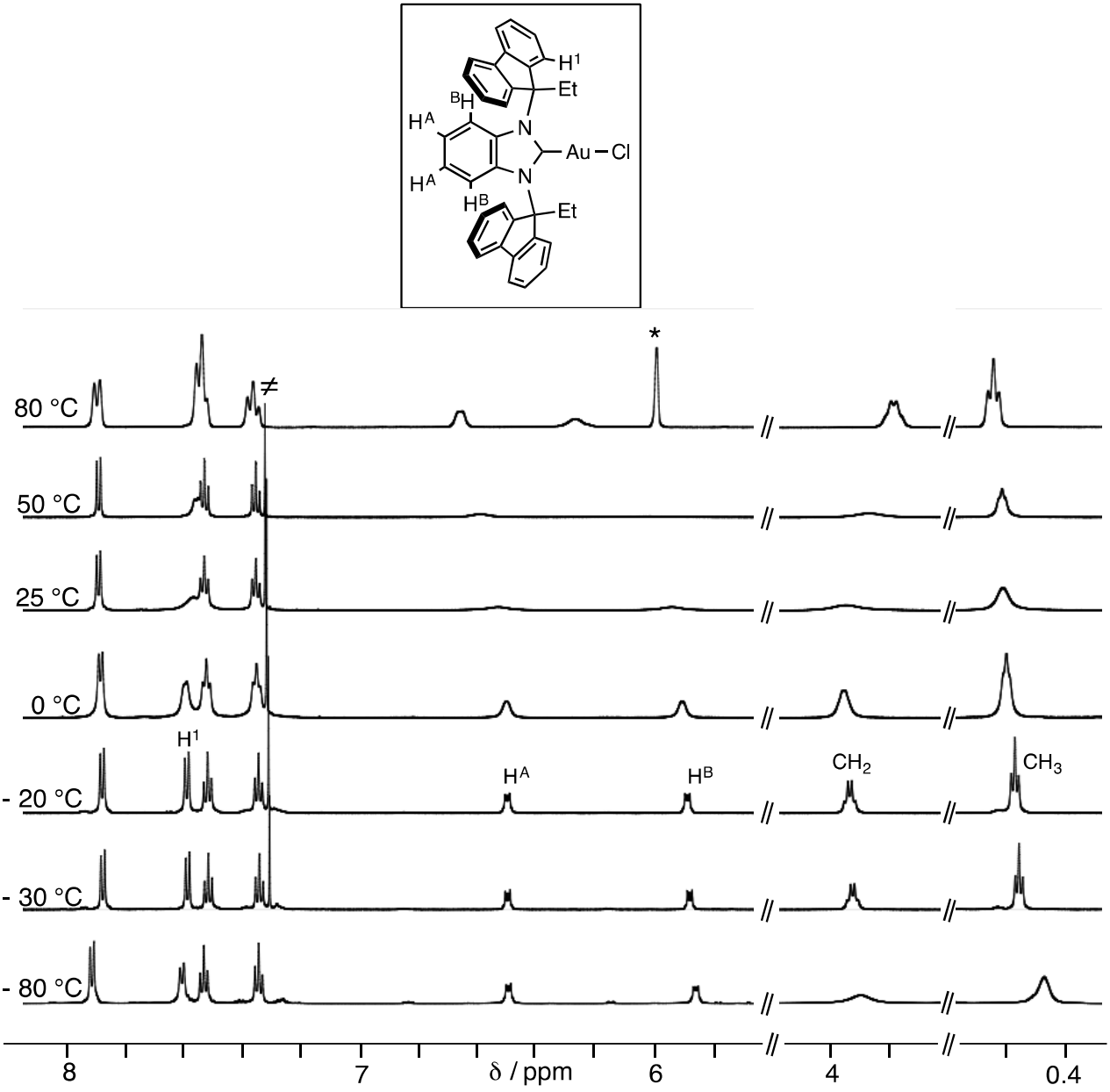
Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a dichloromethane solution of the complex: $C_{41}H_{38}AuClN_2 \bullet CH_2Cl_2$, M_r = 876.08, triclinic, space group *P*-1, *a* = 12.1680(6), *b* = 12.3688(4), *c* = 13.1028(5) Å, □ = 90.968(3), □ = 115.666(4), □ = 91.862(3), *V* = 1775.5(1) Å^3, *Z* = 2, μ = 4.402 mm^{-1}, *F*(000) = 872. Crystals of the compound were mounted on an Oxford Diffraction CCD Safire 3 Xcalibur diffractometer. Data collection with Mo-Kα radiation (□ = 0.71073 Å) was carried out at 140 K. 13709 reflections were collected (3.04 < □ < 27.00°), 7755 were found to be unique and 7234 were observed (merging *R* = 0.0284). The structure was solved with SHELXS-97.[16] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.0301, 0.0594, 0.0617, 0.0594, 1.053. Residual electron density minimum/maximum = –1.199/1.689 e Å^{-3}. The product crystallises with a molecule of dichloromethane. CCDC 995380.

Crystal Data for Complex 6

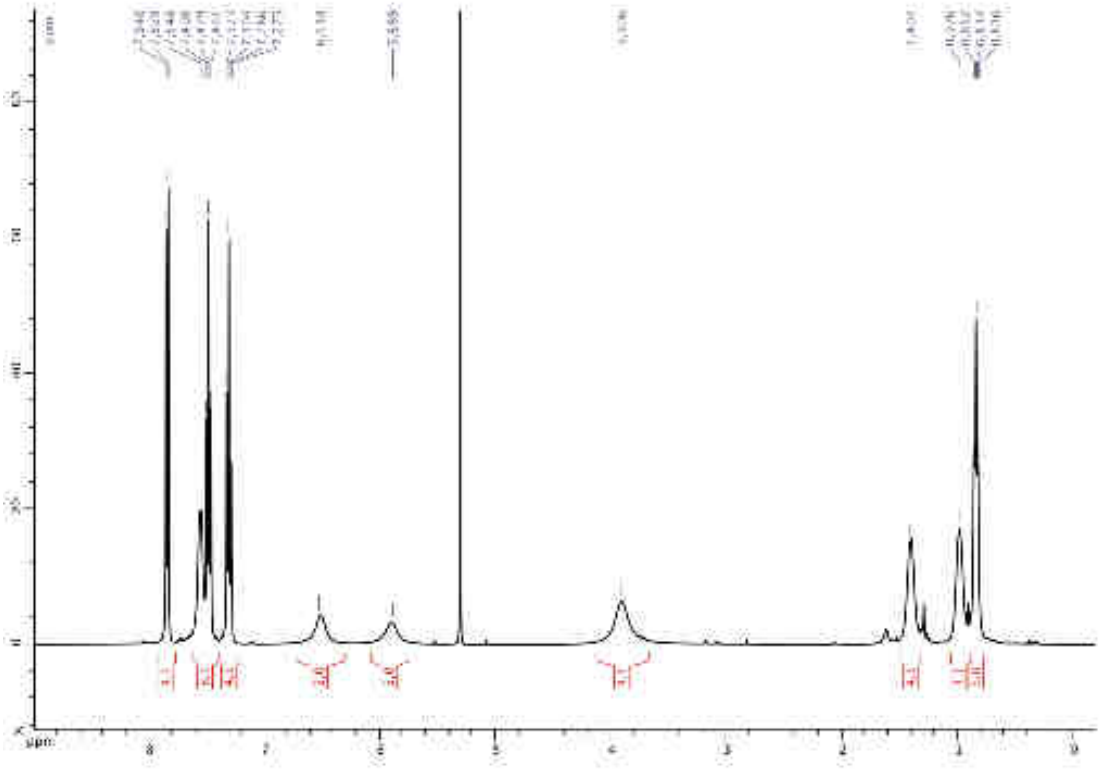
Crystals suitable for X-ray analysis were grown by slow diffusion of pentane into a CH_2Cl_2 solution of the complex: $C_{33}H_{28}ClCuN_2$, M_r = 551.57, monoclinic, space group $P2_1/n$, *a* = 12.1680(6), *b* = 12.3688(4), *c* = 13.1028(5) Å, □ = 97.169(2), *V* = 5227.8(2) Å^3, *Z* = 8, □ = 0.963 mm^{-1}, *F*(000) = 2288. Crystals of the compound were mounted on an Oxford Diffraction CCD Safire 3 Xcalibur diffractometer. Data collection with Mo-Kα radiation (□ = 0.71073 Å) was carried out at 140 K. 44785 reflections were collected (3.18 < □ < 27.00°), 11384 were found to be unique and 8420 were observed (merging *R* = 0.0438). The structure was solved with SHELXS-97.[16] Final results: R_2, R_1, wR_2, wR_1, Goof; 0.0642, 0.0436, 0.1236, 0.1100, 1.027. Residual electron density minimum/maximum = –1.199/1.689 e Å^{-3}. The unit cell contains two nearly identical molecules. CCDC 1013278.

Variable temperature study for 3

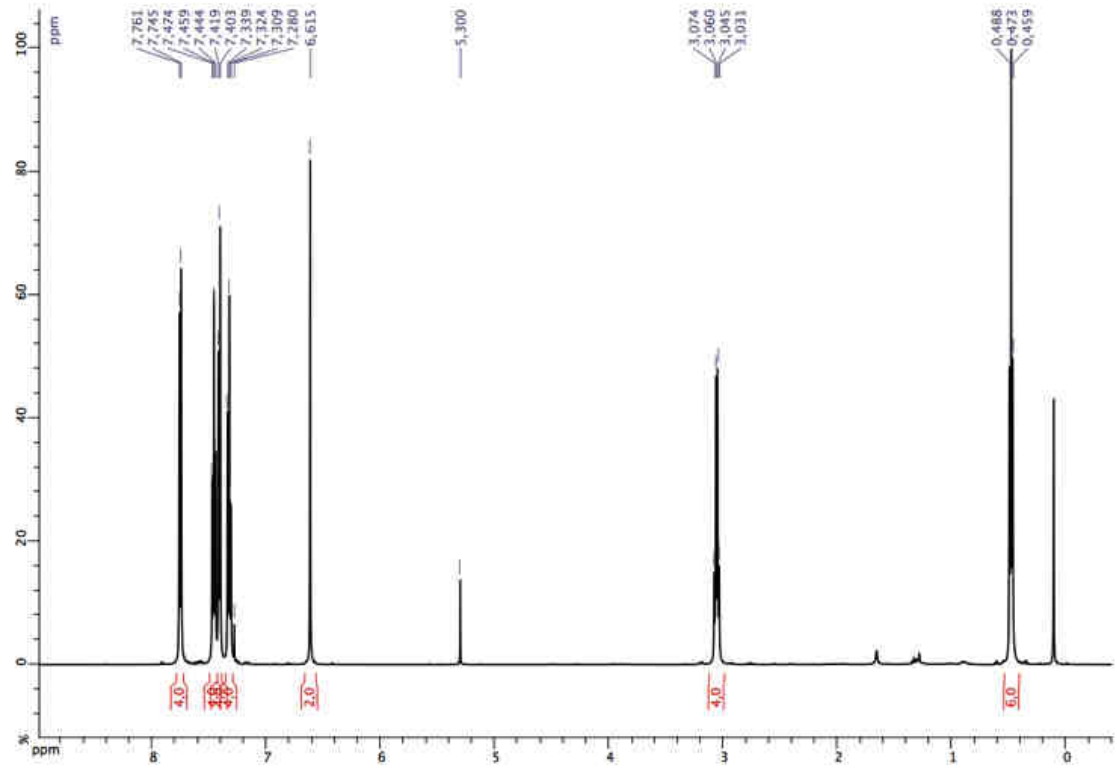
Conditions: –80 °C (CD_2Cl_2, 600 MHz); –30 °C- +50 °C ($CDCl_3$, 600 MHz); +80 °C ($C_2D_2Cl_4$, 400 MHz). The asterisk denotes the presence of $C_2D_2Cl_4$.



^{1}H NMR (600 MHz, $CDCl_3$, 25°C) spectrum of gold complex 4:



^{1}H NMR (300 MHz, $CDCl_3$, 25°C) spectrum of copper complex 6:



IV - D) Computational details

Calculations were performed using the ADF 2013 package.[eric][17] All-eletron Slater type orbitals were used with all-electron triple-ζ quality basis sets at DFT level with PBE functional.[18,19] Dispersive interactions were taken into account through Grimme corrections.[20] Scalar relativistic effects were included through ZORA Hamiltonian.[21] Full geometry optimisation was performed on each structures. The rotation barriers of respectively the ethyl group or the whole 9-ethyl-9-fluorenyl group were estimated through successive constrained optimisations along the adequate dihedral angle.

Single points with Gaussian 09[22] package were done at DFT level with PBE functional on ADF optimized structure in order to compute wavefunction suitable for topological analyses. The atoms were described by the 6-31+G** basis sets on H, C and N and the SDD pseudopotentials and associated basis set for Au.[23] The weak interactions were studied through the NCI analysis[24] of the Gaussian wavefunction.

Additional calculations made for gold complex 3

1) The energy barrier between conformer **3** as seen in the solid state and its analogue **3'** in which the gold-bonded H atom of *one* of the two Et groups has been exchanged with the geminal H atom (noted H') was found to be *ca.* 7 kcal mol^{-1} (Figure S1). Note that during this move, the gold atom is temporarely bonded to both atoms in exchange while remaining permanently located below the NHC plane. Thus, the 7 kcal mol^{-1} value reflects the combined Au···H dissociation and the Au···H' bond formation. It takes also into account the resistance to positional changes of the metal atom imposed by the other CH_2 group the position of which has been blocked.

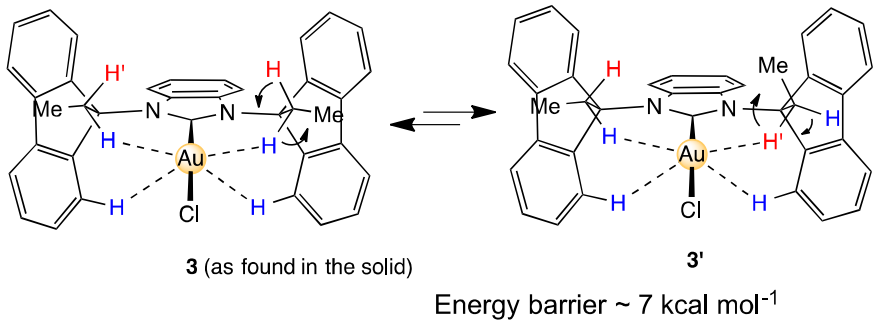


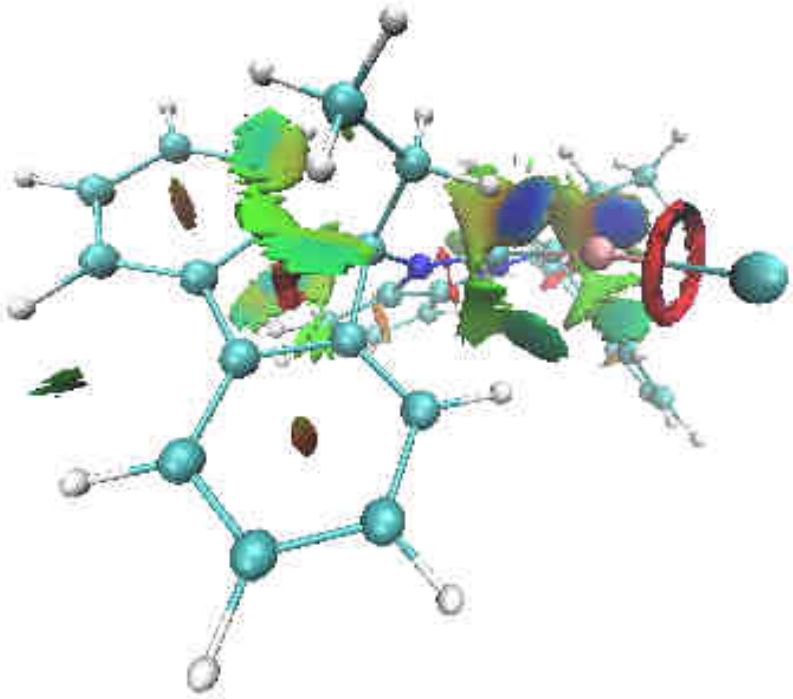
Figure S1: Au···HC / Au···H_{gem}C switch involving two geminal H atoms (partial rotation about the C(Et)–C(fluorenyl) bond).

2) Another calculation established a 15 kcal mol^{-1} energy barrier for a full rotation of the individual ethyl groups about the corresponding C(ethyl)–C(fluorenylidene) bond.

This relatively high value reflects essentially the above Au···H (methylene) bond breaking energy and to a lesser extend steric interactions with the gold atom.

Visualising the non covalent interactions in 3

Attractive electrostatic interactions are in blue, dispersive Van der Waals forces in green and repulsive congestion in red (gold atom in pink).



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[11] A calculation established a 15 kcal mol^{-1} energy barrier for a full rotation of the individual ethyl groups about the corresponding C(ethyl)–C(fluorenylidene) bond. This relatively high value reflects essentially the Au···H(of CH_2) bond breaking energy and to a lesser extend steric interactions with the gold atom.

[12] The energy barrier for a Au–H/Au–H' bonding exchange involving two geminal methylenic protons of **3** was found to be *ca.* 7 kcal mol^{-1}. During this move, which corresponds to a partial rotation of the Et group about the C(fluorenylidene)–C(Et), the gold atom is temporarely bonded to both atoms in exchange while remaining permanently located below the NHC plane. Thus, the 7 kcal mol^{-1} value reflects the combined Au···H dissociation and the Au···H' bond formation. It takes also into account the resistance to positional changes of the metal atom imposed by the other CH_2 group the position of which has been blocked.

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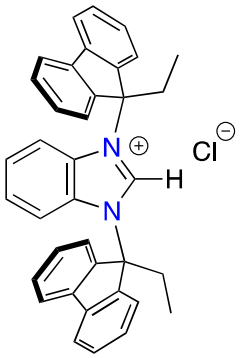

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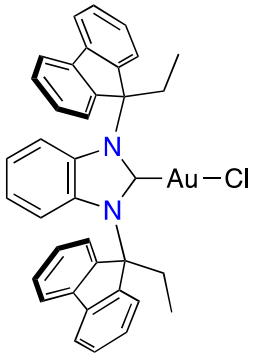

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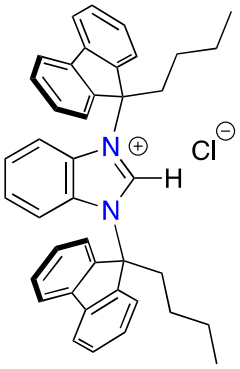

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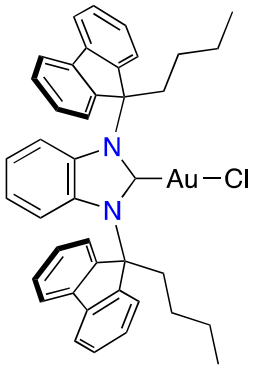

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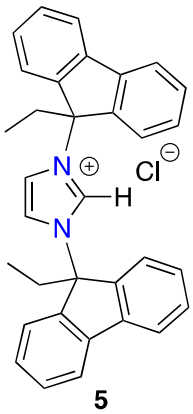

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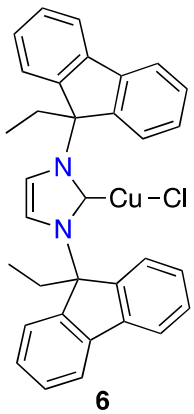


6

Chapter V :

Alkylfluorenyl substituted *N*-heterocyclic carbenes in copper(I) catalysed hydrosilylation of aldehydes and ketones

Chapter V :

Alkylfluorenyl substituted *N*-heterocyclic carbenes in copper(I) catalysed hydrosilylation of aldehydes and ketones

Abstract

Copper(I) complexes featuring *N*-heterocyclic carbenes (NHCs) in which the nitrogen atoms are substituted by a 9-alkyl-9-fluorenyl group (AF) have been synthesised and tested in the hydrosylilation of functionalized and/or sterically demanding ketones and aldehydes. These reactions, carried out with triethylsilane as hydride source, were best achieved with the imidazolylidene copper complex **2d** in which the EF substituents (alkyl = ethyl) can freely rotate about their corresponding C-N bonds. The remarkable stability of the active species, which surpasses that of previously reported Cu(imidazol-2-ylidene) catalysts relies on the ability of the NHC to protect the copper centre during the catalytic cycle by forming sandwich-like intermediates, but also on its steric flexibility enabling coordination of encumbered substrates. TONs up to 1000 were reached.

I - Introduction

Hydrosilylation of ketones, when followed by hydrolysis of the resulting silyl ethers, is a well-established method for the preparation of a variety of alcohols, including chiral ones.[1] Current research in this area focuses on the development of new, cost-effective catalysts with the hope to move away from the expensive Rh- or Ru-catalysts which are traditionally employed for these reactions.[2] Efforts to achieve this goal, logically, also require the concomitant development of appropriate ligands.

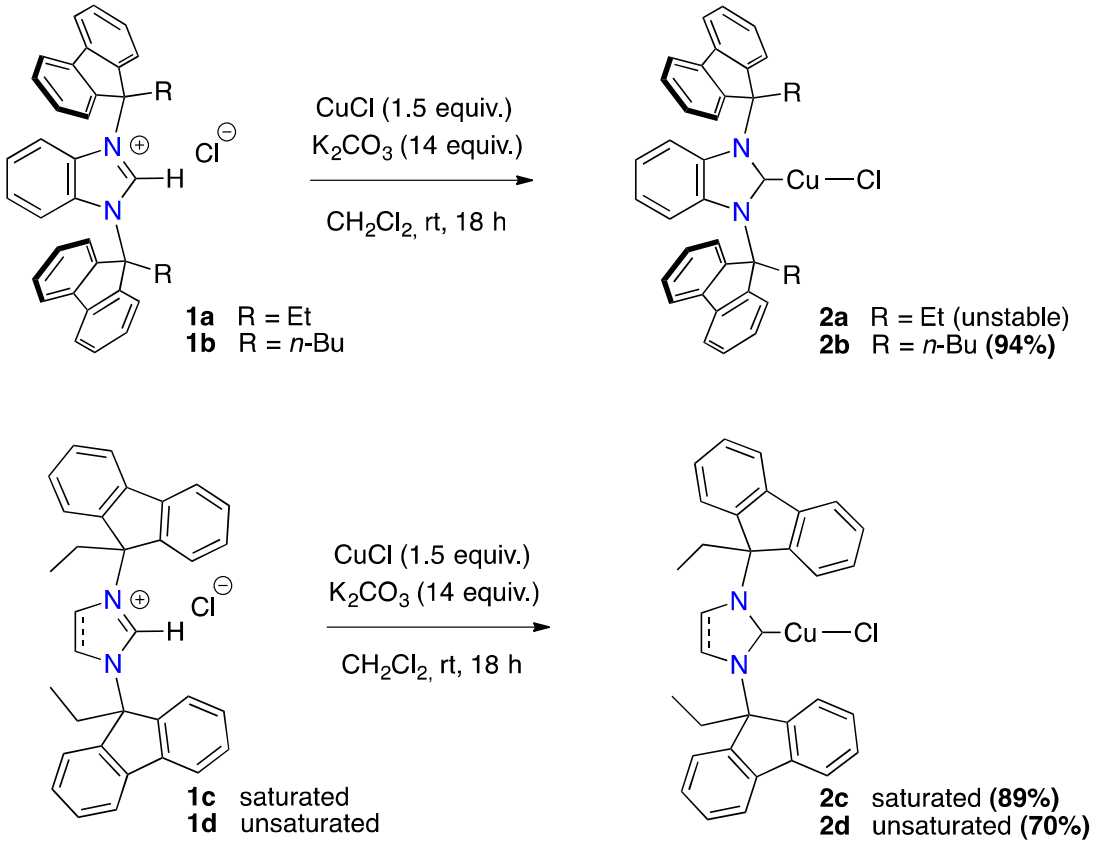
As part of a program aimed at exploring the catalytic properties of N-heterocyclic carbenes (NHCs) bearing expanded 9-alkyl-9-fluorenyl (AF) substituents, we examined the hydrosylilation of ketones and aldehydes with copper(I) complexes based on such ligands. Previously, we had shown that in their complexes AF-substituted NHCs derived from benzimidazolium salts display a preorganised structure in which the alkyl groups are turned towards the metal centre, so as to promote a terdentate, clamp-like bonding mode of the ligand, involving the carbenic C atom and two weakly coordinating CH atoms of the alkyl side groups.[3] As they may form two non-covalent bonds with the metal,

ligands of this type have been termed bimodal pincers. In analogues in which the benzannulated moiety has been replaced by smaller imidazolinylidene or imidazolylidene rings, rotation of the AF unit about the N–C^{AF} bond may occur, this enabling the ligand to adapt to the steric requirements of the metal environment. It is worth mentioning that copper complexes containing other bulky NHCs have recently been applied in the hydrosylilation of carbonyl compounds.[4]

II - Results and discussion

II - A) Syntheses of copper(I) complexes

The complexes used in this study (**2a-d**) were obtained by reacting the appropriate azolium precursor (**1a-d**) with CuCl in CH_2Cl_2 in the presence of K_2CO_3 (Scheme 1).



Scheme 1: Synthesis of copper complexes **2a-d**.

Complex **2d** has been briefly described in a Chapter IV. As complex **2a** underwent rapid oxidation in air, both in solution and in the solid state (colour change from white to blue), this complex was not considered for hydrosylilation tests. In contrast, complexes **2b**

and **2c** were found stable in air up to *ca.* 150° over long periods. The most stable complex is **2d**, which is fully air stable below 220°.

In keeping with freely rotating AF groups (Chapter III) in **2c** and **2d**, the corresponding 2D-^{1}H NMR ROESY spectra measured at room temperature showed strong through-space correlations between the NCC*H*$_2$ hydrogen atoms (termed hereafter □-CH_2 protons) and the CH atoms of the NHC ring (see experimental part). Such correlations were not observed for **2b**, the □-CH_2 protons remaining here permanently oriented towards metal centre. We further noted that while the □-CH_2 protons of **2c** appear at nearly the same chemical shifts as those of their precursor salt, those of **2d** have undergone a significant upfield shift (0.42 ppm) with respect to those of **1d**. This could merely reflect a shielding effect of the π electrons of the aromatic NHC ring of **2d** on the □-CH_2 protons, which may temporarely approach the backside of the NHC ring.

Palladium and silver complexes containing the carbene ligands derived from **1b-1d** have been crystallographically characterised in previous studies.[3, Chapter III] These revealed that the corresponding ligands have the fluorenylidene planes either turned towards the metal or folded back to the CC bond of the NHC ring. This leads respectively to percent buried volumes (%*V*bur) of *ca.* 58% for the former carbenes and of 37 % for the latter (Figure 1). Thus, when AF groups can freely rotate (as in **1c** and **1d**), the %*V*bur of the corresponding carbenes must be regarded as a time-dependent variable.

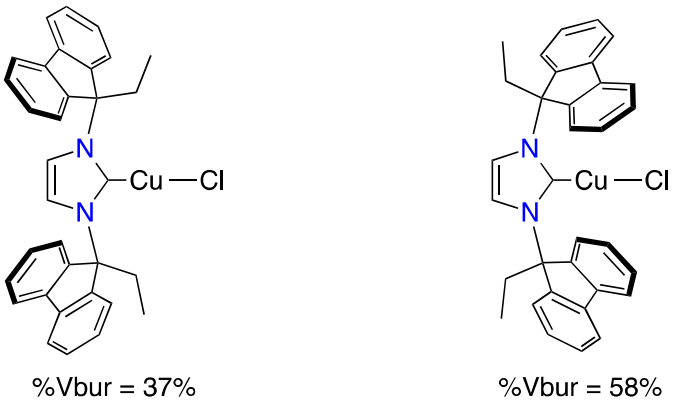


Figure 1: Percent buried volume (*%V*bur) for the two extreme ligand conformations of **2d** calculated from previously reported X-ray studies. Parameters used for the calculations: C-M distance: 2.1 Å; sphere radius: 3.5 Å.

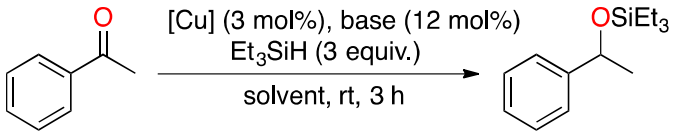
II - B) Catalysis

We began the catalytic investigations by examining the properties of **2b-d** in the hydrosilylation of acetophenone (taken as the model substrate), using either THF or

toluene as solvent, and *t*-BuOK or *t*-BuONa as base. The runs were carried out applying a slight modification of a procedure described by Nolan et al. (Table 1).[5] Triethylsilane, a mild and economical hydride source, was chosen as conditions consisted in carrying out 3 hour runs in toluene at room temperature. Optimal with 3 equivalents of silane, 3 mol% of copper catalyst, and 12 mol% of *t*-BuONa. Complex **2d** proved to be the most efficient catalyst, the corresponding runs affording 93% of the silyl ether after 3 h. In comparaison, under similar conditions the complex [CuCl(IPr)], which is regarded as a very performing NHC-copper catalyst for this reaction,[5] resulted in 97% yield (Table 1 entries 6 and 7). Control experiments showed that no reaction takes place in the absence of catalyst, nor in the presence of ligand free copper(I) chloride (Table 1, entries 1 and 2). Complex **2b** displayed a significantly lower activity than **2d** (Table 1, entry 8), probably due to gradual degradation of the active species. This is likely due to a lower steric protection of the metal by the carbene ligand of **2b** that provided by the (time-averaged) sterically bulkier carbene ligand of **2d**, the fluorenylidene planes of which may be bent towards the metal atom, so as to sandwich it.

Interestingly, complex **2d** proved also to be more efficient than **2c** in the hydrosilylation of acetophenone (Table 1, entry 9). Note that the corresponding carbenes do not differ by their steric properties, only by their electronic ones, the carbene ligand in **2d** being a weaker donor. This finding is consistent with a recently reported theoretical study by Leyssens et al., who showed that as a general trend Cu-catalysed hydrosilylation is facilitated with electronically poorer NHCs.[6]

Table 1: Catalytic hydrosilylation of acetophenone with Et_3SiH using complexes **2b-d** or [**CuCl(IPr)**]: influence of the base and the solvent.[a]



Entry	Complex	Base	Solvent	Conv. [%][b]
1	–	*t*-BuOK	THF	0
2	**CuCl**	*t*-BuOK	THF	0[c]
3	**2d**	*t*-BuOK	THF	15
4	**2d**	*t*-BuONa	THF	10
5	**2d**	*t*-BuOK	toluene	29
6	**2c**	*t*-BuONa	toluene	93
7	[CuCl(IPr)]	*t*-BuONa	toluene	97
8	**2b**	*t*-BuONa	toluene	26
9	**2c**	*t*-BuONa	toluene	29

[a]complex (3 mol%), base (12 mol%), Et_3SiH (6 mmol), solvent (2 mL), acetophenone (2 mmol), 25°C, 3 h; [b]Conversion determined by ^1H NMR; [c]9 mol% of **CuCl**.

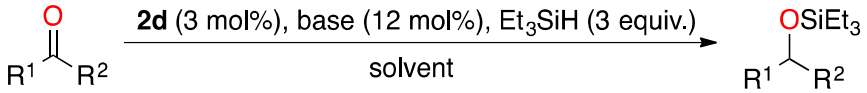
In order to assess the scope of the reaction, tests were then run with 14 other ketones (Table 2) applying conditions similar to those described above. We observed that neither with *t*-BuOK nor with *t*-BuONa were aldolisation products observed (Table 2, entries 1-13). As expected, the reaction rates were higher with less demanding and/or activated ketones. In these cases, hydrosilylation could be carried out efficiently at room temperature within 2-3 h (Table 2, entries 1-3, 6-7, 9 and 12). For bulkier ketones and/or non-activated ones, longer reaction times or higher temperatures were required (Table 2, entries 4, 5, 8, 10 and 11). For the reactions carried out at 65°C, the use of *t*-BuOK/THF gave significantly better results than with *t*-BuONa-toluene (Table 2, entries 8, 11, 13 and 14).

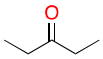
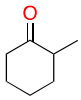
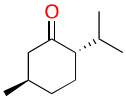
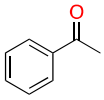
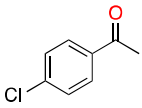
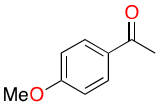
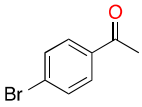
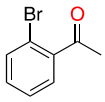
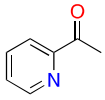
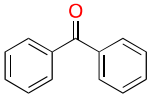
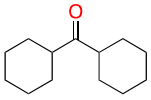
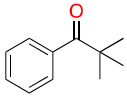
The hydrosilylation of norcamphor, which was achieved at room temperature, gave a 80:20 mixture of *endo*:*exo* products (Table 2, entry 3). The observed diastereoselectivity is consistent with a preferential attack of the hydride on the less encumbered *exo* face. The hydrosilylation of 2-methylcyclohexanone (Table 2, entry 4), which was best achieved at 65°C, afforded the expected silylated alcohol as a mixture of *syn*/*anti* diastereomers (45:55). Starting from the bulkier menthone (Table 2, entry 5) did not increase the selectivity (*syn*:*anti* ratio = 40:60; configuration with respect to the C-O/C-(*i*-Pr) bonds).

Full conversion to the silylether was achieved at room temperature with benzophenone (Table 2, entry 12). Remarkably, bromo- and chloroacetophenone derivatives were fully converted without dehalogenation (Table 2, entries 7, 9 and 10). The deactivated *para*-methoxyacetophenone was also readily hydrosilylated (at 65°C) (Table 2, entry 8). Other successful hydrosilylations include that of acetylpyridine (using *t*-BuOK as base in THF; (Table 2, entry 11), as well as those of the sterically demanding ketones dicyclohexylketone and 2,2-dimethylpropiophenone and (Table 2, entries 13 and 14).

Notably, *para*-cyano or *para*-nitro substituted acetophenone (not drawn) could not be hydrosilylated under conditions similar to the ones reported above. The electron-withdrawing cyano and nitro groups supposed to inductively activate the conjugated ketone did in fact not result in the expected effect. Lipshutz *et al*. have already made similar observations for 3-acetyl-benzonitrile.[7] Possibly, the nitrile and nitro groups coordinate strongly to the copper atom so as to prevent binding of the keto groups.

Table 2: Hydrosilylation of ketones catalysed by complex **2d**.[a]

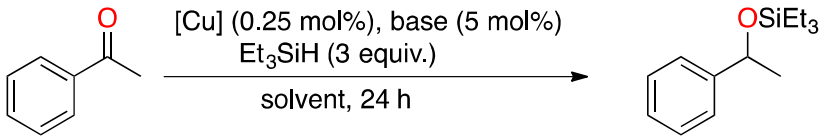


Entry	Substrate	Base/Solvent	Temp.[°C]	Time [h]	Conv. [%][b]	Yield [%][c]
1		*t*-BuONa / toluene	25	2	> 99	96
2		*t*-BuONa / toluene	25	2	> 99	94
3		*t*-BuONa / toluene	25	2	> 99	94 (endo : exo / 80 : 20)
4		*t*-BuONa / toluene	65	2	> 99	97 (syn : anti / 45 : 55)
5		*t*-BuONa / toluene	65	2	> 99	96 (syn : anti / 40 : 60)
6		*t*-BuONa / toluene	25	3	93	90
7		*t*-BuONa / toluene	25	3	98	97
8		*t*-BuONa / toluene *t*-BuOK / THF	25 65	2 2	10 92	- 87
9		*t*-BuONa / toluene	25	3	> 99	97
10		*t*-BuONa / toluene	65	6	> 99	92
11		*t*-BuONa / toluene *t*-BuOK / THF	65 65	18 4	> 99 > 99	- 95
12		*t*-BuONa / toluene	25	1	> 99	97
13		*t*-BuONa / toluene *t*-BuOK / THF	65 65	2 4	4 > 99	 98
14		*t*-BuONa / toluene *t*-BuOK / THF	65 65	2 2	50 > 99	- 94

[a]complex **2d** (3 mol%), base (12 mol%), Et_3SiH (6 mmol), solvent (2 mL), ketone (2 mmol); [b] Conversion determined by ^1H NMR; [c] Isolated yields.

In order to test the endurance of **2d** under catalytic conditions, additional hydrosylilation runs were carried out for acetophenone over longer reaction periods (Table 3), these runs being performed at 65°C with only 0.25 mol% of catalyst (a lower catalyst concentration being required for monitoring the reaction progress).

Table 3: Hydrosilylation of acetophenone catalysed by complexes **2b-d** and [IPrCuCl] (0.25 mol%) in the presence of Et_3SiH: influence of the base and the solvent.[a]



Entry	Complex	Base / Solvent	Temp. [°C]	Conv. [%][b]
1	–	*t*-BuOK / THF	65	0
2	CuCl	*t*-BuOK / THF	65	0[c]
3	[CuCl(IPr)]	*t*-BuONa / toluene	RT	10
4	**2d**	*t*-BuONa / toluene	RT	23
5	[CuCl(IPr)]	*t*-BuONa / toluene	65	23
6	**2d**	*t*-BuONa / toluene	65	41
7	[CuCl(IPr)]	*t*-BuOK / THF	RT	5
8	**2d**	*t*-BuOK / THF	RT	11
9	[CuCl(IPr)]	*t*-BuOK / THF	65	35
10	**2d**	*t*-BuOK / THF	65	97
11	**2d**	*t*-BuONa / THF	65	23
12	**2b**	*t*-BuOK / THF	65	12
13	**2c**	*t*-BuOK / THF	65	13
14	**2d**	*t*-BuOK / THF	65	>99[d]

[a]complex (0.25 mol%), base (5 mol%), Et_3SiH (6 mmol), acetophenone (2 mmol), solvent (2 mL), RT, 24 h. [b]Conversion determined by ^1H NMR. [c]9 mol% of CuCl. [d] Reaction performed with 0.1 mol% of **2d**, 70h.

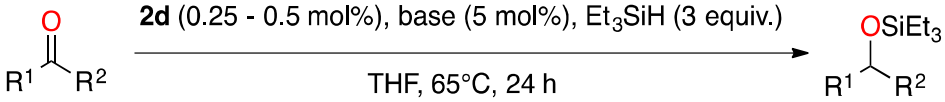
At the applied temperature, the best conversions were obtained with the couple *t*-BuOK/THF. Under these conditions, the conversion reached 97 % after 24 h (TON = 388) (Table 3, entry 10). In comparison, for the same experiment, [CuCl(IPr)] resulted in a yield of only 35% (TON = 140), this being indicative of a higher stability of the **2d** catalyst (Table 3, entry 9). Note that, consistent with the observations made for the low-temperature

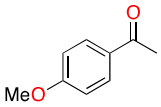
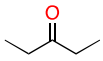
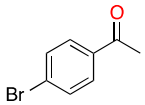
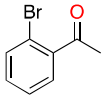
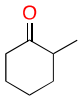
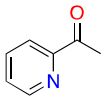
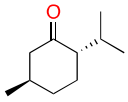
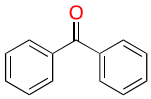
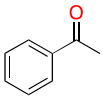
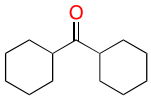
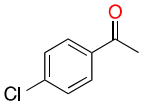
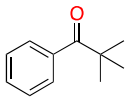
experiments (see above), catalysts **2b** and **2c** displayed lower activities at 65°C than **2d** and [CuCl(IPr)] (Table 3, entries 12 and 13).

In order to test catalyst **2d** over a still longer period, the runs (at 65°C) were then repeated with only 0.1 mol% of catalyst. In this case, no catalyst deactivation occurred and the reaction was complete after 70 h (Table 3, entry 14), this corresponding to one of the highest TONs (TON = 1000) ever reported for NHC-copper catalysts containing a five-membered diaminocarbene.

Low-charge hydrosylilation reactions using 0.25 or 0.5 mol% of **2d** were also successfully applied to all the ketones discussed above (Table 4).

Table 4: Hydrosilylation of ketones using complex **2d**.[a]



Entry	Substrate	Conv. [%][b]	Yield [%][c]	Entry	Substrate	Conv. [%][b]	Yield [%][c]
1		> 99	97	8		> 99	96[e]
2		> 99	93	9		> 99	93
3		> 99	96	10		> 99	94[e]
4		> 99	94	11		> 99	96[e]
5		> 99	94	12		> 99	97[d]
6		97	93	13		> 99	95[e]
7		> 99	95	14		> 99	94

[a]complex **2d** (0.25 mol%), *t*-BuOK (5 mol%), Et_3SiH (6 mmol), ketone (2 mmol), THF (2 mL), 65°C, 24 h. [c]Conversion determined by ^1H NMR. [c]Isolated yields. [d]Reaction performed at RT, 18 h. [e] 0.5 mol% of **2d**.

The considerable longer lifetime of catalyst **2d** *vs.* [CuCl(IPr)] is best explained by the steric differences between the corresponding carbenes. In fact, the steric protection of the Cu atom is significantly better in **2d** than in [CuCl(IPr)]. This can be seen, *e.g.*, by

comparing the percent buried volumes of the ligands, namely 37%-58% for the sterically flexible carbene ligand of **2d** (noted NHC^{2d}), and 29% for that of [CuCl(IPr)].

The recently reported solid state structure of [AgCl(NHC^{2d})] (Figure 2) provides proof that both fluorenylidene planes of NHC^{2d} may be turned simultaneously towards the bound metal centre, this resulting then in an efficient steric protection of the metal (sandwich type structure) in possible Pd(0) intermediates.

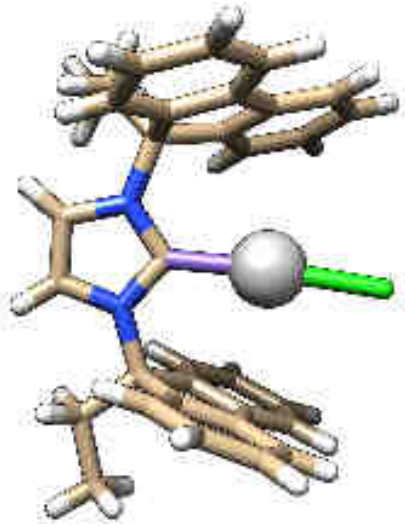
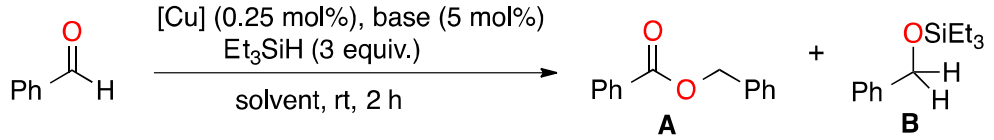


Figure 2: Solid state structure of [AgCl(NHC^{2d})][Chapter III] showing the flexible carbene ligand NHC^{2d} when it displays its highest possible encumbrance.

The reactivity of aldehydes was also examined (Table 6). Benzaldehyde was first studied (Table 5).

Table 5: Hydrosilylation of benzaldehyde catalysed by **2d** using Et_3SiH: influence of the base and the solvent.[a]



Entry	Complex	Base / Solvent	Conv. [%][b]	A:B
1	**2d**	*t*-BuOK / THF	98	50:50
2	**2d**	*t*-BuOK / toluene	95	55:45
3	**2d**	*t*-BuONa / THF	88	7:93
4	**2d**	*t*-BuONa / toluene	100	15:85
5	-	*t*-BuOK / THF	100	100:0
6	-	*t*-BuONa / THF	0	-
7	CuCl	*t*-BuONa / THF	0[c]	-

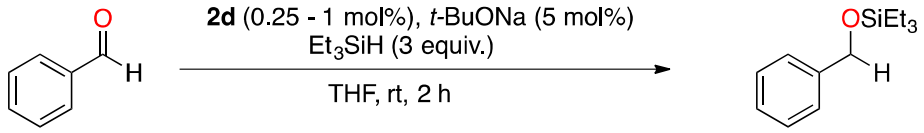
[a]**2d** (0.25 mol%), base (5 mol%), Et_3SiH (6 mmol), benzaldehyde (2 mmol), solvent (2 mL), rt, 2 h. [b]Conversions determined by ^1H NMR. [c]9 mol% of CuCl.

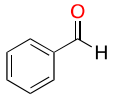
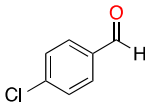
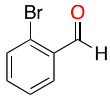
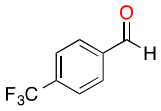
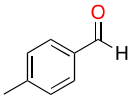
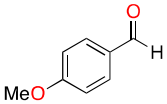
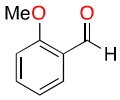
Surprisingly, independently of the solvent used, hydrosilylation proceeded with concomitant formation of benzyl benzoate (**A**) (Table 5, entries 1-4). The formation of this homoester arose from a competitive Tishchenko reaction.[8] It was found to be strongly cation dependent, *t*-BuOK favoring formation of the ester (Table 5, entries 1 and 2) and *t*-BuONa that of the hydrosilylation product (Table 5, entries 3 and 4). When using *t*-BuONa with Et_3SiH in the absence of any copper catalyst, no reaction took place (Table 5, entry 6). In contrast, with *t*-BuOK instead of *t*-BuONa the same reaction led to selective and quantitative formation of the homoester within 2 h at room temperature (Table 5, entry 5), thus showing that ester formation may occur *through a copper–free mechanism*. It is noteworthy that in the absence of silane, the latter reaction did not take place, demonstrating that the silane may operate as a hydride transfer catalyst.

Overall, effective hydrosylilation of benzaldehyde was best performed with **2d** (0.25 mol%) in THF *at room temperature* with *t*-BuONa as base, this resulting in a $PhCH_2OSiEt_3$:$PhC(O)OCH_2Ph$ ratio of 93:7 after 2 h reaction time (Table 5, entry 3). No Tishchenko products were observed with benzaldehyde derivatives containing electron-donating groups, notably *para*-methylbenzaldehyde, *para*-methoxybenzaldehyde and *ortho*-methoxybenzaldehyde (Table 5, entries 5-7). Note that hydrosilylation of *para*-methoxybenzaldehyde required to carry out the reaction at 65°C (Table 5, entry 6), the other two aldehydes being readily converted at 25°C.

In the presence of 0.25 mol% of catalyst and with *t*-BuONa/THF, the hydrosilylation of benzaldehyde derivatives bearing electron-withdrawing groups, led again to mixtures of silylether and homoester, the proportion of ester being here higher than in the case of benzaldehyde. Obviously, the competitive Tishchenko reaction occurred faster than in the case of benzaldehyde. Thus, in order to favor the hydrosilylation process over the Tishchenko reaction, the **2d**:*t*-BuONa ratio was increased to 1:5 instead of 0.25:5. In that case no ester formed (Table 6, entry 2-4). It should also be mentioned that with the chloro- and bromo- substrates, the reaction took place without dehalogenation.

Table 6: Hydrosilylation of aromatic aldehydes catalysed by complex **2d**.[a]



Entry	Substrate	Conv. [%][b]	Yield [%][c]
1		>99[e]	95
2		<99[e]	94
3		<99[e]	92[f]
4		<99[e]	94
5		<99	96
6		<99[d]	91
7		<99	91

[a]Activation of complex **2d** (0.25 mol%) with *t*-BuONa (5 mol%) and Et_3SiH (6 mmol) in THF (2 mL) at room temperature, then addition of the aldehyde (2 mmol). Reaction mixture stirred at room temperature for 2 h. [b]Conversion to product based on starting material determined by ^1H NMR. [c]Isolated yields. [d]Reaction performed at 65°C for 1 h. [e]Reaction performed with 1 mol% of **2d**. [f]Reaction mixture stirred at room temperature for 4 h.

III - Conclusion

We have demonstrated that the 9-ethyl-9-fluorenyl-substituted imidazolylidene copper complex **2d** efficiently catalyses the hydrosilylation of functionalized and/or sterically demanding carbonyl compounds, using triethylsilane as cost-effective hydride source. Its intrinsic activity compares with that of [CuCl(IPr)], presently considered as the most performing copper-based NHC complex based on a five-membered NHC. Remarkably, the activity of **2d** was not altered after 70 h reaction time (TONs up to 1000), thereby contrasting with its less stable IPr analogue. The high stability of complex **2d** is likely to arise from the capacity of the carbene ligand to sterically protect temporarly the metal centre by forming intermediates with a sandwiched metal atom. On the other hand, the

steric flexibility of the ligand related to rotational freedom of the EF groups facilitates conversation of encumbered substrates. The reported results are a new illustration of the potential of NHCs displaying variable steric encumbrance.

IV - Experimental section

IV - A) General information

All commercial reagents were used as supplied, except liquid aldehydes, which were treated with a $NaHCO_3$(aq.)/CH_2Cl_2 mixture prior to use. The syntheses and catalytic tests were performed in Schlenk-type flasks under dry nitrogen. Solvents were used as received except for tetrahydrofuran (THF) (distilled from sodium/benzophenone) and toluene (distilled from sodium). Routine ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a FT Bruker AVANCE 300 instrument (^1H: 300.1 MHz, ^{13}C: 75.5 MHz) at 25°C. ^1H NMR spectral data were referenced to residual protonated solvents ($CHCl_3$, δ 7.26), ^{13}C chemical shifts are reported relative to deuterated solvents ($CDCl_3$, δ 77.16). Data are represented in the following order: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (*J*) in Hz, and assignment. In the NMR data given hereafter, Cq denotes a quaternary carbon atom. Flash chromatography was performed as described by Still *et al.* employing Geduran SI (E. Merck, 0.040-0.063 mm) silica.[9] Routine thin-layer chromatography analyses were carried out by using plates coated with Merck Kieselgel 60 GF254. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie (UMR 7177 CNRS), Strasbourg. Melting points were determined with a Büchi 535 capillary melting-point apparatus and are uncorrected. Complex **2d**[Chapter IV] and CuCl(IPr)[5] were synthetised according to known procedures.

IV - B) General procedures

General procedure for copper-catalysed hydrosilylation reactions:

In a Schlenk tube under nitrogen were introduced the copper complex (3×10^{-2}–10^{-5} mmol) and the appropriate base (0.24 mmol) followed by the solvent (2 mL). The mixture was stirred at room temperature for 10 min. Triethylsilane (6 mmol) was then added and the mixture stirred at room temperature for 10 min. After activation, the carbonyl compound (2 mmol) was added and the reaction mixture was stirred at room temperature for a period of time indicated in the corresponding Table. The mixture was filtered through a short pad of Celite using CH_2Cl_2 as solvent. The residue was then purified by flash

chromatography (SiO_2; AcOEt–petroleum ether) to afford the hydrosilylated product as a colourless oil.

General procedure for the hydrosilylation of acetophenone catalysed by 3 mol% of complexes 2b-d and [IPrCuCl] using Et_3SiH (influence of the base and the solvent) as shown in Table 1:

In a Schlenk tube under nitrogen were introduced the copper complex (6.0×10^{-3} mmol) and *t*-BuOK (2.7×10^{-4} g; 0.24 mmol) or *t*-BuONa (2.3×10^{-4} mg; 0.24 mmol) followed by THF or toluene (2 mL). The mixture was stirred at room temperature for 10 min. Triethylsilane (6 mmol) was then added and the mixture stirred at room temperature for a futher 10 min. After this period of activation, acetophenone (2 mmol) was added and the reaction mixture was stirred at room temperature for 3 h. The mixture was filtered through a short pad of Celite using CH_2Cl_2. The solvent was removed under reduced pressure and the residue analysed by ^1H NMR spectroscopy.

General procedure for the hydrosilylation of ketones catalysed by 3 mol% of complex 2d using Et_3SiH as shown in Table 2:

In a Schlenk tube under nitrogen were introduced the **2d** (3.3×10^{-4} g; 0.06 mmol) and *t*-BuOK (2.7×10^{-4} g; 0.24 mmol) or *t*-BuONa (2.3×10^{-4} g; 0.24 mmol) followed by THF or toluene (2 mL). The mixture was stirred at room temperature for 10 min. Triethylsilane (6 mmol) was then added and the mixture stirred at room temperature for 10 min. After this activation period, the ketone (2 mmol) was added and the reaction mixture was stirred at room temperature for 3 h. The mixture was filtered through a short pad of Celite using CH_2Cl_2 as solvent. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (SiO_2; AcOEt–petroleum ether) to afford the hydrosilylated products as colourless oils.

General procedure for the hydrosilylation of acetophenone catalysed by 0.25 mol% of complexes 2b-d and [IPrCuCl] using Et_3SiH (influence of the base and the solvent) as shown in Table 3:

In a Schlenk tube under nitrogen were introduced the complex (5.0×10^{-3} mmol) and *t*-BuOK (1.1×10^{-3} g; 1.0×10^{-2} mmol) or *t*-BuONa (1×10^{-3} g; 1.0×10^{-2} mmol) followed by THF or toluene (2 mL). The mixture was stirred at room temperature for 10 min. Triethylsilane (6 mmol) was then added and the mixture stirred at room temperature for a

further 10 min. After the activation period, acetophenone (2 mmol) was added and the reaction mixture was stirred at 65°C for 24 h. The mixture was filtered through a short pad of Celite using CH_2Cl_2. The solvent was removed under reduced pressure and the residue analysed by ^1H NMR spectroscopy.

General procedure for the hydrosilylation of ketones catalysed by 0.25 mol% of complex 2d as shown in Table 4:

In a Schlenk tube under nitrogen were introduced the **2d** (2.8×10^{-3} g; 5.0×10^{-3} mmol) and *t*-BuOK (1.1×10^{-3} g; 1.0×10^{-2} mmol) followed by THF (2 mL). The mixture was stirred at room temperature for 10 min. Triethylsilane (6 mmol) was then added and the mixture stirred at room temperature for 10 min. After this period of activation, the ketone (2 mmol) was added and the reaction mixture was stirred at 65°C for 24 h. The mixture was cooled to room temperature and filtered through a short pad of Celite using CH_2Cl_2 as solvent. The mixture was filtered through a short pad of Celite using CH_2Cl_2. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (SiO_2; AcOEt–petroleum ether) to afford the hydrosilylated products as colourless oils.

General procedure for the hydrosilylation of benzaldehyde catalysed by 0.25 mol% of complex 2d using Et_3SiH (influence of the base and the solvent) as shown in Table 5:

In a Schlenk tube under nitrogen were introduced the **2d** (2.8×10^{-3} g; 5.0×10^{-3} mmol) and *t*BuOK (1.1×10^{-3} g; 1.0×10^{-2} mmol) or *t*BuONa (1×10^{-3} g; 1.0×10^{-2} mmol) followed by THF or toluene (2 mL). The mixture was stirred at room temperature for 10 min. Triethylsilane (6 mmol) was then added and the mixture stirred at room temperature for 10 min. After this period of activation, benzaldehyde (2 mmol) was added and the reaction mixture was stirred at room temperature for 2 h. The mixture was filtered through a short pad of Celite using CH_2Cl_2 as solvent. The solvent was removed under reduced pressure and the residue analysed by ^1H NMR spectroscopy.

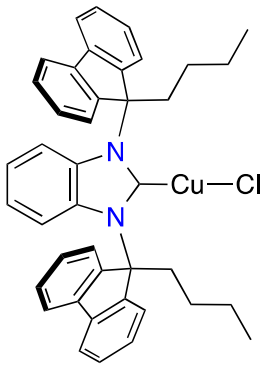
General procedure for the hydrosilylation of benzaldehyde derivatives catalysed by 0.25 mol% of complex 2d as shown in Table 6:

In a Schlenk tube under nitrogen were introduced the **2d** (2.8×10^{-3} g; 5.0×10^{-3} mmol) and *t*BuONa (1×10^{-3} g; 1.0×10^{-2} mmol) followed by THF (2 mL). The mixture was

stirred at room temperature for 10 min. Triethylsilane (6 mmol) was then added and the mixture stirred at room temperature for 10 min. After this period of activation, the aldehyde (2 mmol) was added and the reaction mixture was stirred at room temperature for 2 h. The mixture was filtered through a short pad of Celite using CH_2Cl_2 as solvent. The solvent was removed under reduced pressure and the residue analysed by ^1H NMR spectroscopy.

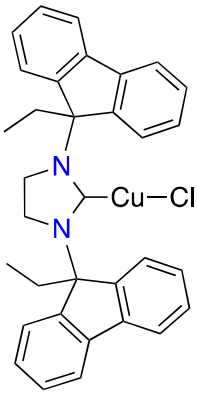
IV - C) Syntheses of the complexes

1,3-bis(9-ethyl-9*H*-fluoren-9-yl)benzimidazol-2-ylidene)copper(I) chloride (3) A



suspension of benzimidazolium salt **1b** (0.400 g, 0.67 mmol), finely crushed K_2CO_3 (1.290 g, 9.77 mmol), and CuCl (0.098 g, 0.99 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature overnight. The mixture was filtered through a pad of silica gel and the pad was washed with CH_2Cl_2 (*ca.* 3 × 30 mL). The filtrate was concentrated in vacuo to *ca.* 1 mL. Pentane (10 mL) was added and the resulting white precipitate was decanted. After removal of the supernatant, the solid was washed with pentane (3 × 10 mL) to afford pure complex **2b** as a white solid (0.411 g, 94%); m.p. decomp. 200 °C. ^1H NMR ($CDCl_3$, 500 MHz), δ 7.78 (4H, d, ^3J = 7.3 Hz, ArH of fluorenylidene), 7.42 (4H, dd, ^3J = $^3J'$ = 7.3 Hz, ArH of fluorenylidene), 7.32-7.27 (4H, m, ArH of fluorenylidene), 6.48 (2H, br signal, NCCCH of benzimidazolylidene unit), 5.98 (2H, br signal, NCCH of benzimidazolylidene unit), 3.77 (4H, br s, $CH_2CH_2CH_2CH_3$), 1.38 (4H, m, $CH_2CH_2CH_2CH_3$), 0.77 (6H, t, ^3J = 7.3 Hz, $CH_2CH_2CH_2CH_3$), 0.67 (4H, m, $CH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz), δ 145.9 (arom. Cq), 140.2 (arom. Cq), 133.8 (arom. Cq), 129.6 (arom. CH), 128.8 (arom. CH), 123.5 (arom. CH), 123.2 (arom. CH), 120.7 (arom. CH), 113.9 (arom. CH), 73.7 (N*C*Bu), 43.4 ($CH_2CH_2CH_2CH_3$), 25.9 ($CH_2CH_2CH_2CH_3$), 22.5 ($CH_2CH_2CH_2CH_3$), 14.1 ($CH_2CH_2CH_2CH_3$), carbene signal not detected. Found C, 74.57; H, 5.79; N, 4.12. Calc. for $C_{41}H_{38}ClCuN_2$ (M_r = 656.20): C, 74.87; H, 5.82; N, 4.26%.

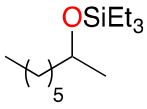
(1,3-bis(9-ethyl-9-fluoren-9-yl)imidazolin-2-ylidene)copper(I) chloride (2c): A



suspension of imidazolinium salt (**1c**) (0.204 g, 0.42 mmol), finely crushed K_2CO_3 (0.773 g, 5.85 mmol) and CuCl (0.068 g, 0.69 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature overnight. The mixture was filtered through a pad of silica gel and the pad was washed with CH_2Cl_2 (*ca.* 3 × 20 mL). The filtrate was concentrated in vacuum to *ca.* 1 mL. Pentane (6 mL) was added and the resulting white precipitate was decanted. After removal of the supernatant, the solid was washed with pentane (3 × 20 mL) to afford pure complex **2c** as a white solid (0.161 g, 69%); m.p. > 220 °C. ^{1}H NMR ($CDCl_3$, 500 MHz), δ 7.68 (4H, d, ^3J = 7.3 Hz, ArH), 7.48 (4H, d, ^3J = 7.2 Hz, ArH), 7.42 (4H, dd, ^3J = $^3J'$ = 7.3 Hz, ArH), 7.35 (4H, dd, ^3J = $^3J'$ = 7.4 Hz, ArH), 3.10 (4H, q, ^3J = 6.2 Hz, CH_2CH$_3$), 3.04 (4H, s, NCH_2), 0.44 (6H, t, ^3J = 6.2 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz), δ 196.4 (NCN), 145.4 (arom. Cq), 140.6 (arom. Cq), 129.3 (arom. CH), 128.4 (arom. CH), 123.6 (arom. CH), 120.5 (arom. CH), 73.2 (N*C*Et), 46.2 (N*C*H$_2$), 33.5 (*C*H$_2$CH$_3$), 8.4 (CH$_2$*C*H$_3$). Found C, 71.56; H, 5.44; N, 4.94. Calc. for $C_{33}H_{30}ClCuN_2$ (M_r = 552.14) C, 71.60; H, 5.46; N, 5.06%.

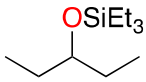
IV - D) List of hydrosilylation products synthesised in this study

Triethyl(octan-2-yloxy)silane (see main text: Table 2, entry 1 and Table 4, entry 1):



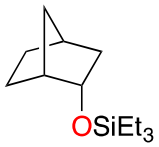
This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; neat petroleum ether) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature.[9]

Triethyl(pentan-3-yloxy)silane (see main text: Table 2, entry 2 – Table 4, entry 2):



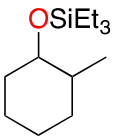
This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; neat petroleum ether) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature.[9]

(bicyclo[2.2.1]heptan-2-yloxy)triethylsilane (see Table 2, entry 3 – Table 4, entry 3):



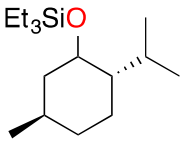
This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; neat petroleum ether) and obtained as colourless oil. The exo product could not be isolated purely, however, *endo* / *exo* ratios could be determine by comparison of the respective C*H*OSiEt$_3$ integrations. Spectroscopic data were consistent with those described in the literature.[9]

Triethyl(2-methylcyclohexyloxy)silane (see main text: Table 2, entry 4 – Table 4, entry 4):



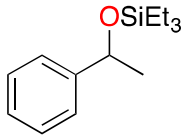
This compound (diastereomeric mixture) was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; neat petroleum ether) and obtained as colourless oil. Spectroscopic data for the *syn* and *anti* products were consistent with those described in the literature.[10]

Triethyl(((1*R+S*,2*S*,5*R*)-2-*iso*-propyl-5-methylcyclohexyl)oxy)silane (see main text: Table 2, entry 5 – Table 4, entry 8):



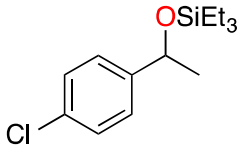
This compound was prepared as described above. It was purified by flash chromatography (SiO_2; neat petroleum ether) and obtained as colourless oil. The compound was obtained as a diastereomeric mixture of triethyl-(2(*S*)-isopropyl-5(*R*)-methylcyclohexyloxy)silane. The diastereomeric ratio (40:60) was determined by NMR. Spectroscopic data for both diatereomers were consistent with those described in the literature, but only the NMR spectra of the pure (1*R*,2*S*,5*R*) disatereomer is shown below.[11]

Triethyl(1-phenylethoxy)silane (see main text: Table 2, entry 6 – Table 4, entry 6):



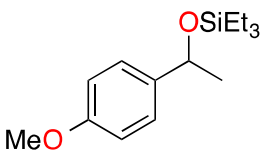
This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; neat petroleum ether) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature.[12]

(1-(4-chlorophenyl)ethoxy)triethylsilane (see main text: Table 2, entry 7 – Table 4, entry 7):

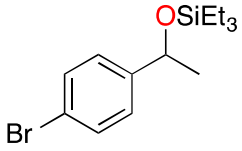


This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; neat petroleum ether) and obtained as colourless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.26 (s, 4H, ArH), 4.83 (q, ^3J = 6.3 Hz, 4H, OCH), 3.75 (d, ^3J = 6.3 Hz, 3H, CH_3), 0.91 (t, ^3J = $^3J'$ = 8.1 Hz, 9 H, CH_2-CH_3), 0.61-0.52 (m, 6H, CH_2CH$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 145.6 (arom. Cq), 132.5 (arom. Cq), 128.3 (arom. CH), 126.7 (arom. CH), 70.1 (OCH), 27.4 (CH_3), 6.9 (CH_2CH_3), 4.9 (CH_2CH_3). Anal. Calcd for $C_{14}H_{23}ClOSi$ (M_r = 270.87) C, 62.08; H, 8.56; Found: C, 62.17; H, 8.35.

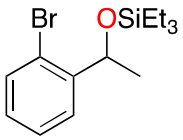
[1-(4-methoxyphenyl)ethoxy]triethylsilane (see main text: Table 2, entry 7 – Table 4, entry 7): This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; AcOEt : petroleum ether (10 : 90)) and obtained as colourless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.29-7.27 (m, 2H, ArH), 6.89-6.86 (m, 2H, ArH), 4.85 (q, ^3J = 6.4 Hz, 1H, CH), 3.82 (s, 3H, OCH_3), 1.43 (d, ^3J = 8.1 Hz, 9 H, CH_2CH_3), 0.63-0.53 (m, 6H, CH_2CH$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 158.6 (arom. Cq), 139.3 (arom. Cq), 126.5 (arom. CH), 113.6 (arom. CH), 70.3 (CH), 55.3 (OCH_3), 27.4 (CH_3), 7.0 (CH_2CH_3), 5.0 (CH_2CH_3). Anal. Calcd for $C_{15}H_{26}O_2Si$ (M_r = 266.46) C, 67.62; H, 9.84 Found: C, 67.72; H, 9.96.



[1-(4-bromophenyl)ethoxy]triethylsilane (see main text: Table 2, entry 8 – Table 4, entry 8):This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; neat petroleum ether) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature.[13]

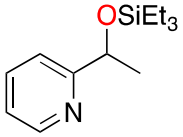


[1-(2-bromophenyl)ethoxy]triethylsilane (see main text: Table 2, entry 9 – Table 4, entry 9):



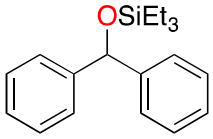
This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; AcOEt : petroleum ether (10 : 90)) and obtained as colourless oil. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.64 (dd, ^3J = 7.3 Hz, $^3J'$ = 1.8 Hz, 1H, ArH), 7.47 (dd, ^3J = 7.8 Hz, $^3J'$ = 1.3 Hz, 1H, ArH), 7.36-7.28 (m, 1H, ArH), 7.09 (ddd, ^3J = 7.8 Hz, $^3J'$ = 7.3 Hz, ^4J = 1.8 Hz, 1H, ArH), 5.19 (q, ^3J = 6.2 Hz, 1H, CH), 1.40 (d, ^3J = 6.2 Hz, 3H, CH_3), 0.92 (t, ^3J = 7.9 Hz, 9H, CH_2CH_3), 0.58 (m, AB part of ABX_3, ^3J = 7.9 Hz, ^2J = 2.7 Hz, 9H, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 146.1 (arom. Cq), 132.3 (arom. CH), 128.3 (arom. CH), 127.7 (arom. CH), 127.5 (arom. CH), 120.9 (arom. Cq), 69.7 (CH), 25.8 (CH_3), 6.9 (CH_2CH_3), 4.9 (CH_2CH_3). Anal. Calcd for $C_{14}H_{23}BrOSi$ (M_r = 315.33) C, 53.33; H, 7.35. Found: C, 53.12; H 7.49,

2-(1-(triethylsilyloxy)ethyl)pyridine (see main text: Table 2, entry 11 – Table 4, entry 11):



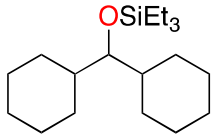
This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; AcOEt : petroleum ether (50 : 50)) and obtained as colourless oil. Spectroscopic were consistent with those described in the literature.[13]

Benzhydryloxytriethylsilane (see main text: Table 2, entry 12 – Table 4, entry 12):



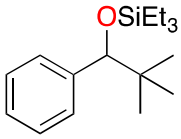
This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; neat petroleum ether) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature.[13]

(dicyclohexylmethoxy)triethylsilane (see main text: Table 2, entry 13 – Table 4, entry 13):



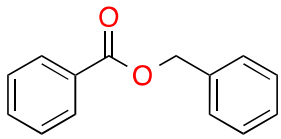
This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; neat petroleum ether) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature.[13]

(2,2-dimethyl-1-phenylpropoxy)triethylsilane (see main text: Table 2, entry 14 – Table 4, entry 14):



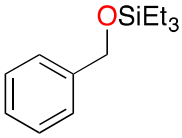
This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; neat petroleum ether) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature.[13]

Benzyl benzoate (see main text: Table 5, entry 5):



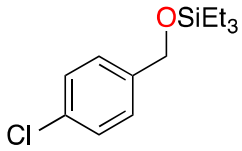
This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; neat petroleum ether) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature.[14]

Benzyloxytriethylsilane (see main text: Table 5, entry 1):



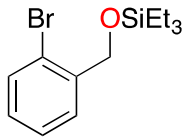
This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; neat petroleum ether) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature.[12]

(4-chlorobenzyloxy)triethylsilane (see main text: Table 5, entry 2):



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; AcOEt : petroleum ether (10 : 90)) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature.[15]

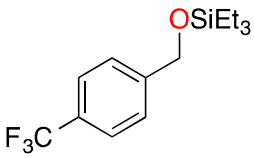
(2-bromobenzyloxy)triethylsilane (see main text: Table 5, entry 3):



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; AcOEt : petroleum ether (10 : 90)) and obtained as colourless oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.64 (d, ^3J = 8.1 Hz, 1 H, ArH), 7.53 (d, ^3J = 7.9 Hz, 1H, ArH), 7.36 (t, ^3J = 8.1 Hz, 1H, ArH), 7.14 (t, ^3J = 7.9 Hz, 1H, ArH), 4.8 (s, 2H, CH_2), 1.40 (d, ^3J = 6.2 Hz, 3H, CH_3), 1.05 (t, ^3J = 7.9 Hz, 9H, CH_2CH_3), 0.74 (q, ^3J = 7.9 Hz, 9H, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 140.4 (arom. Cq), 132.1 (arom. CH), 128.3 (arom. CH), 127.7 (arom. CH), 127.4 (arom. CH), 121.2 (arom. Cq), 64.4

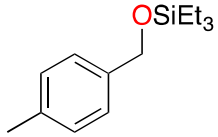
(CH_2), 29.8 (CH_3), 6.9 (CH_2CH_3), 4.7 (CH_2CH_3). Anal. Calcd for $C_{13}H_{21}BrOSi$ (M_r = 301,30) C, 51.82; H, 7.03. Found: C, 51.56; H, 7.33.

(4-trifluoromethylbenzyloxy)triethylsilane (see main text: Table 5, entry 4):



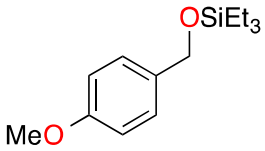
This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; neat petroleum ether) and obtained as colourless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.59 (d, ^3J = 7.9 Hz, 2H, ArH), 7.45 (m, ^3J = 7.9 Hz, 2H, ArH), 4.79 (s, 2H, CH_2), 0.99 (d, ^3J = 7.9 Hz, 9H, CH_2CH_3), 0.68 (q, ^3J = 7.9 Hz, 6H, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 145.6 (arom. Cq), 129.3 (t, ^2J = 32.3 Hz, CF_3), 126.2 (arom. CH), 125.3 (broad signal, arom. CH), 64.1 (CH_2), 27.4 (CH_3), 6.9 (CH_2CH_3), 4.6 (CH_2CH_3). Anal. Calcd for $C_{14}H_{21}F_3OSi$ (M_r = 290,40) C, 57.90; H, 7.29. Found: C, 57.65; H, 7.36.

(4-methylbenzyloxy)triethylsilane (see main text: Table 5, entry 5):



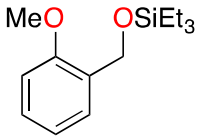
This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; neat petroleum ether) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature. [16]

(4-methoxybenzyloxy)triethylsilane (see main text: Table 5, entry 6):



This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; AcOEt : petroleum ether (10 : 90)) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature.[15]

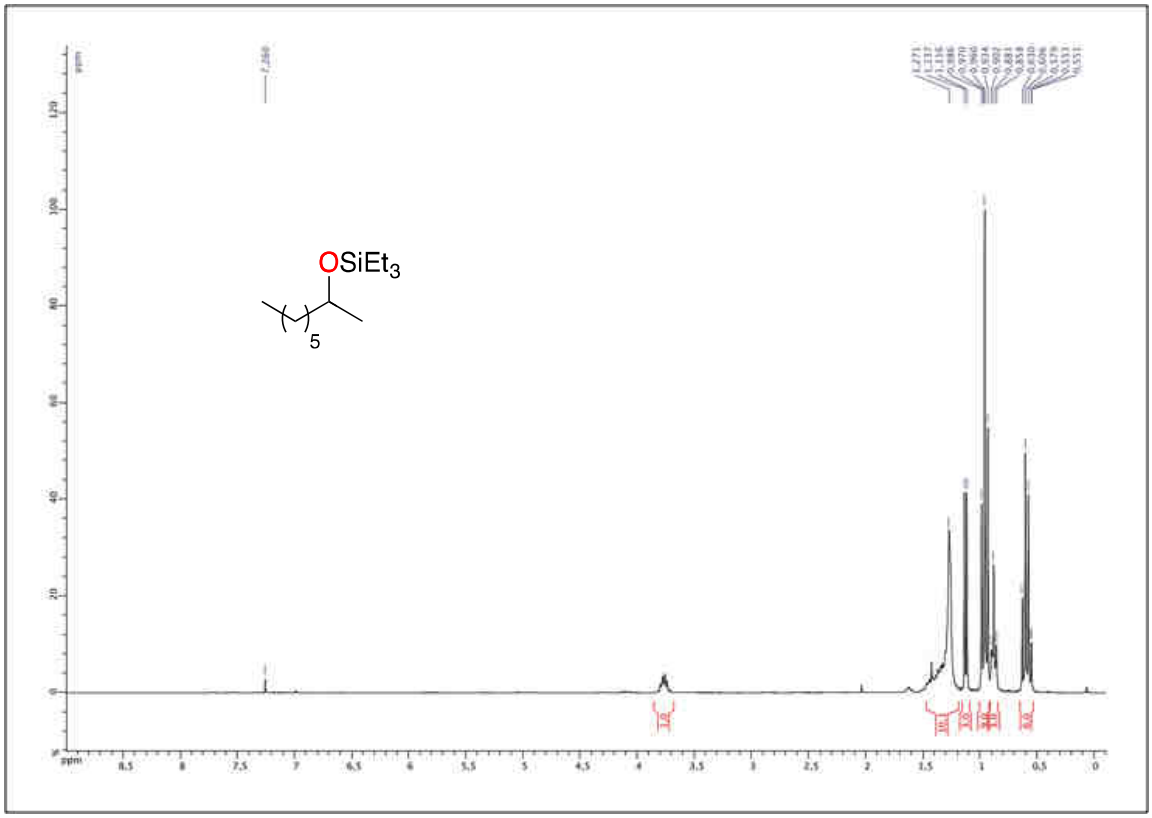
(2-methoxybenzyloxy)triethylsilane (see main text: Table 5, entry 7):

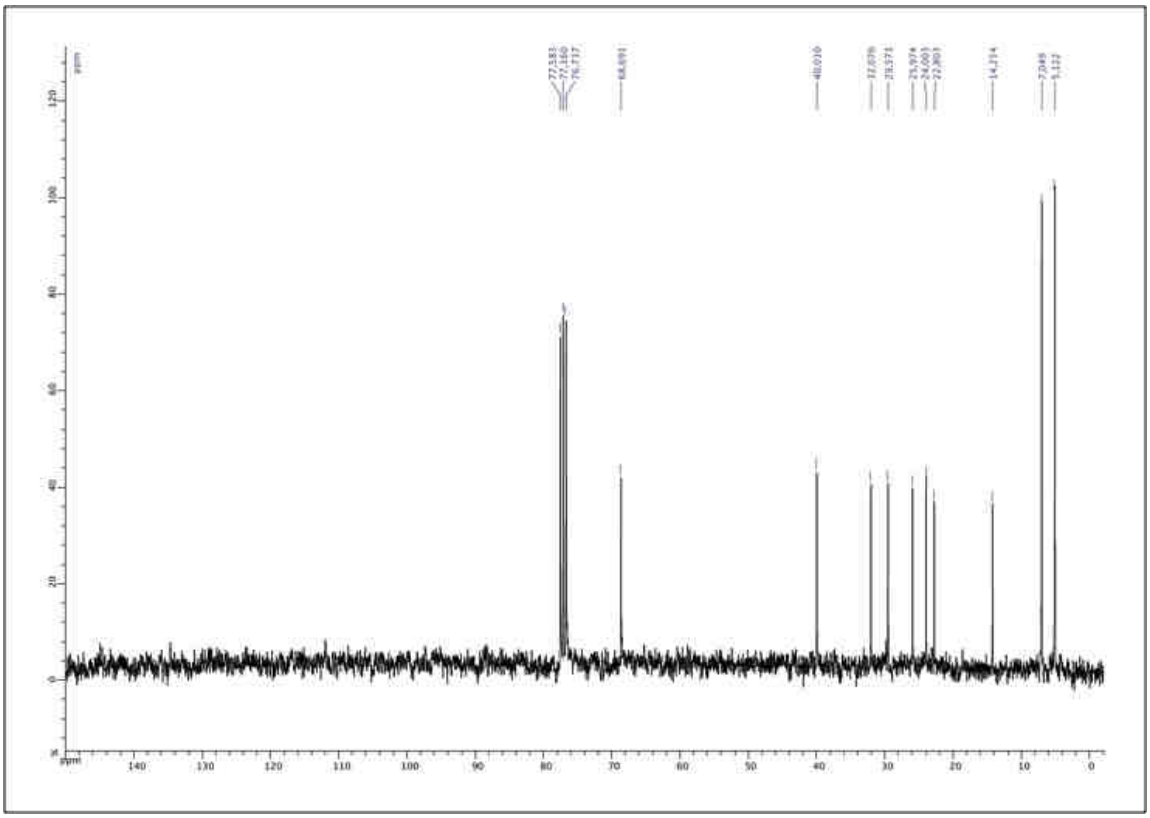


This compound was prepared as described in the general procedures. It was purified by flash chromatography (SiO_2; AcOEt : petroleum ether (10 : 90)) and obtained as colourless oil. Spectroscopic data were consistent with those described in the literature.[16]

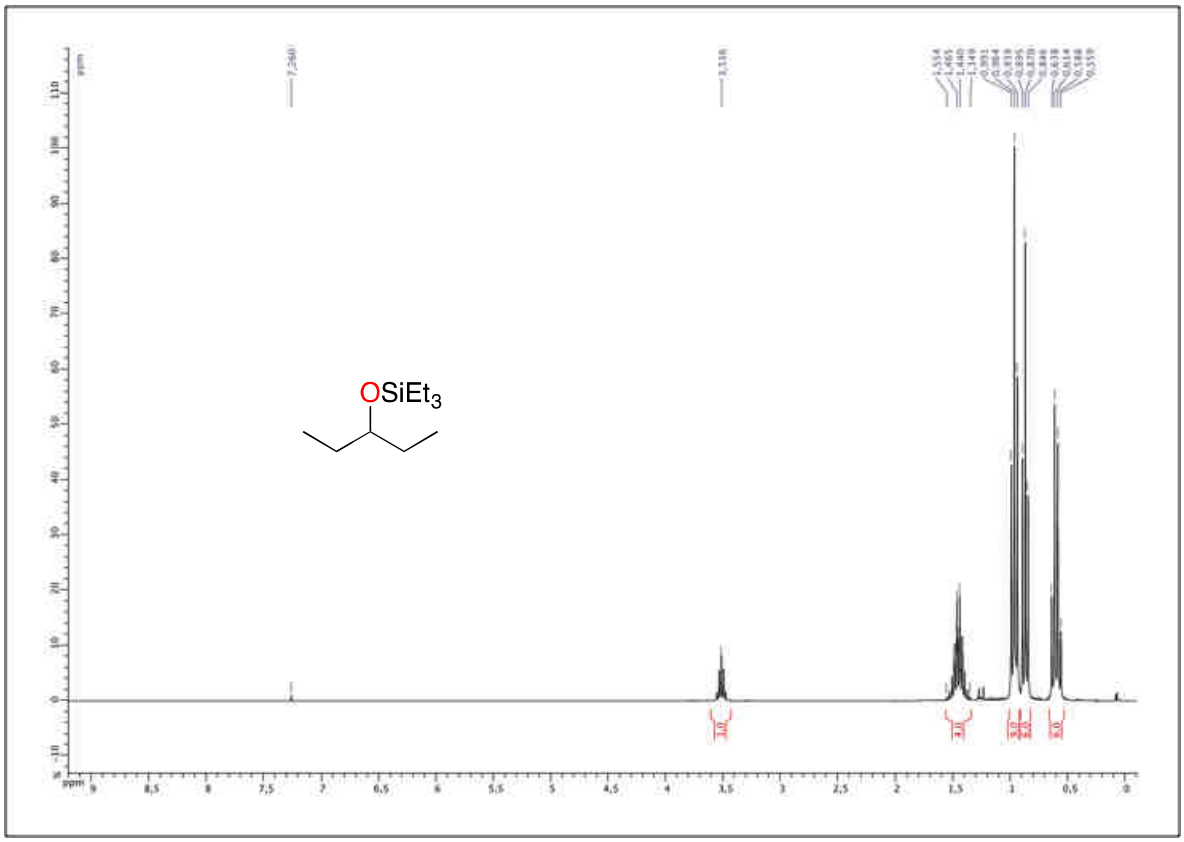
^{1}H NMR and ^{13}C NMR spectra of the hydrosilylation products ($CDCl_3$, 300 MHz, 75 MHz)

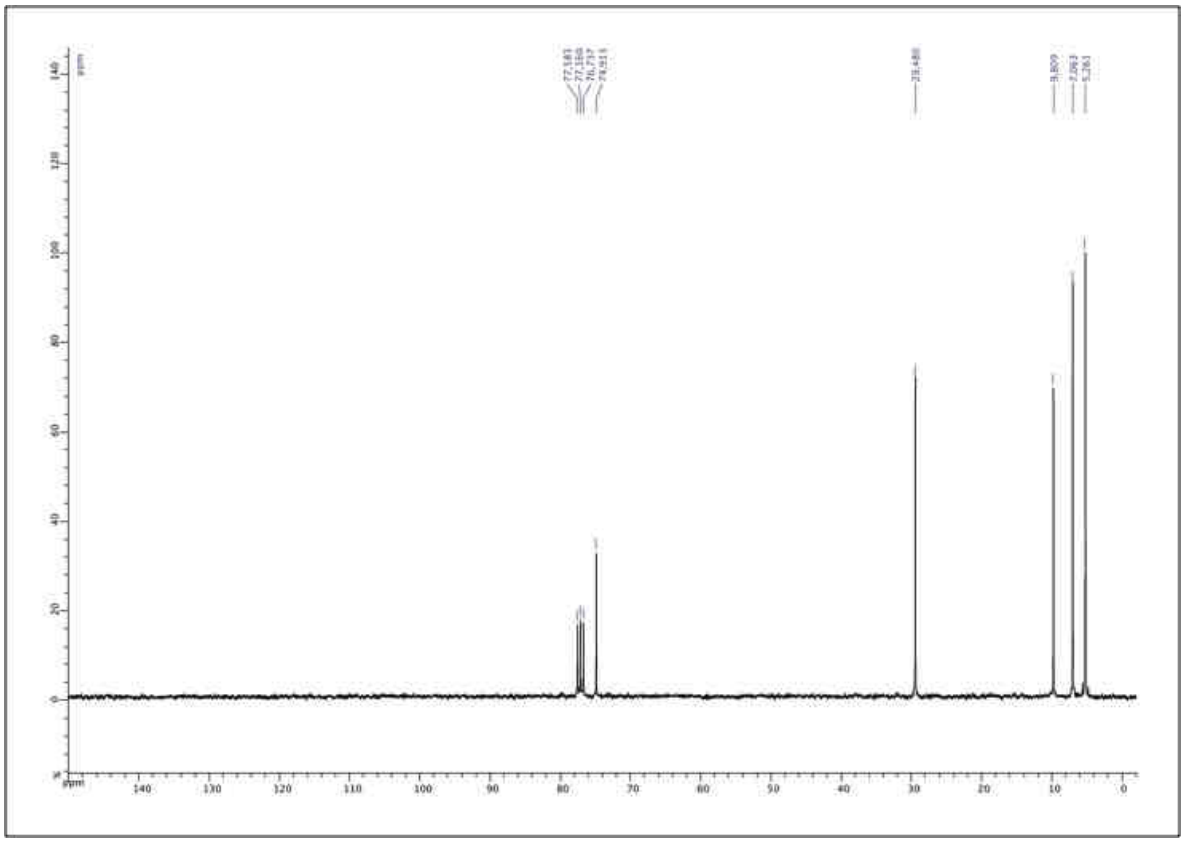
Triethyl(octan-2-yloxy)silane (Table 2, entry 2 – Table 4, entry 2):



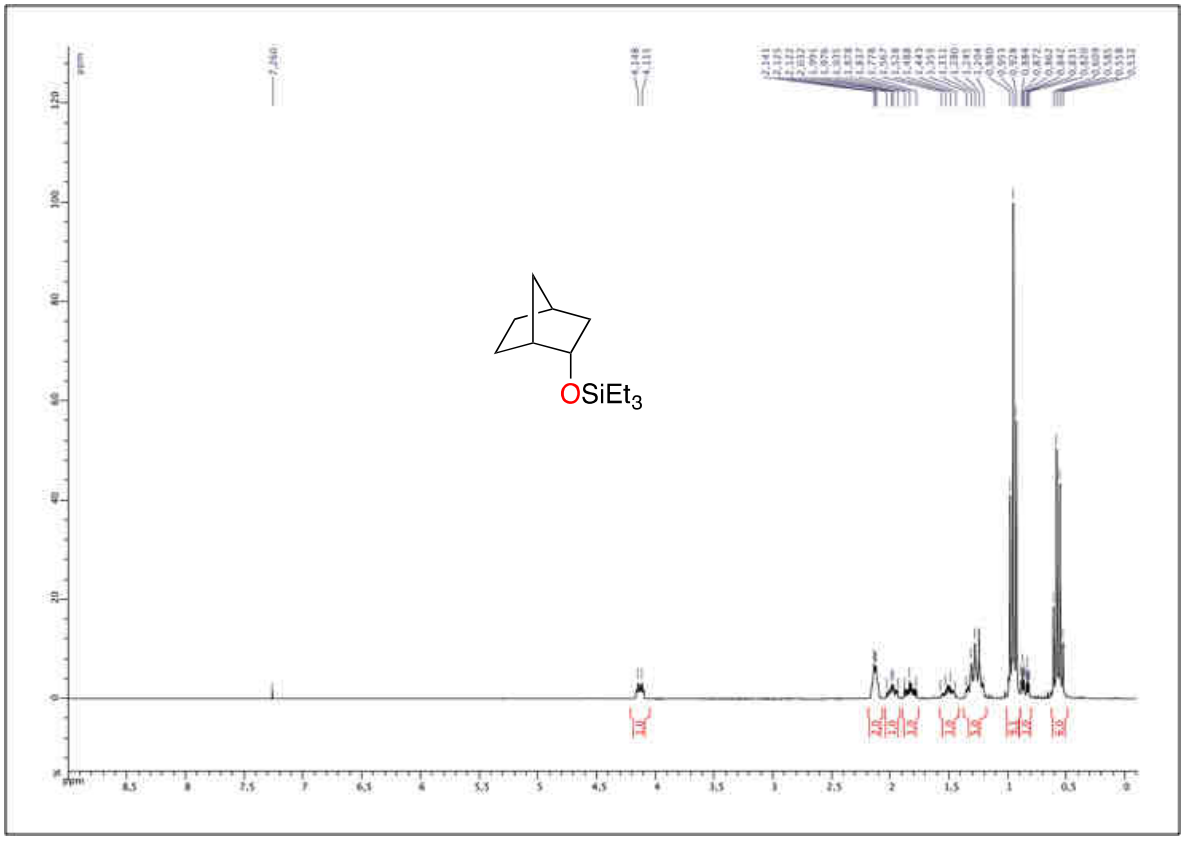


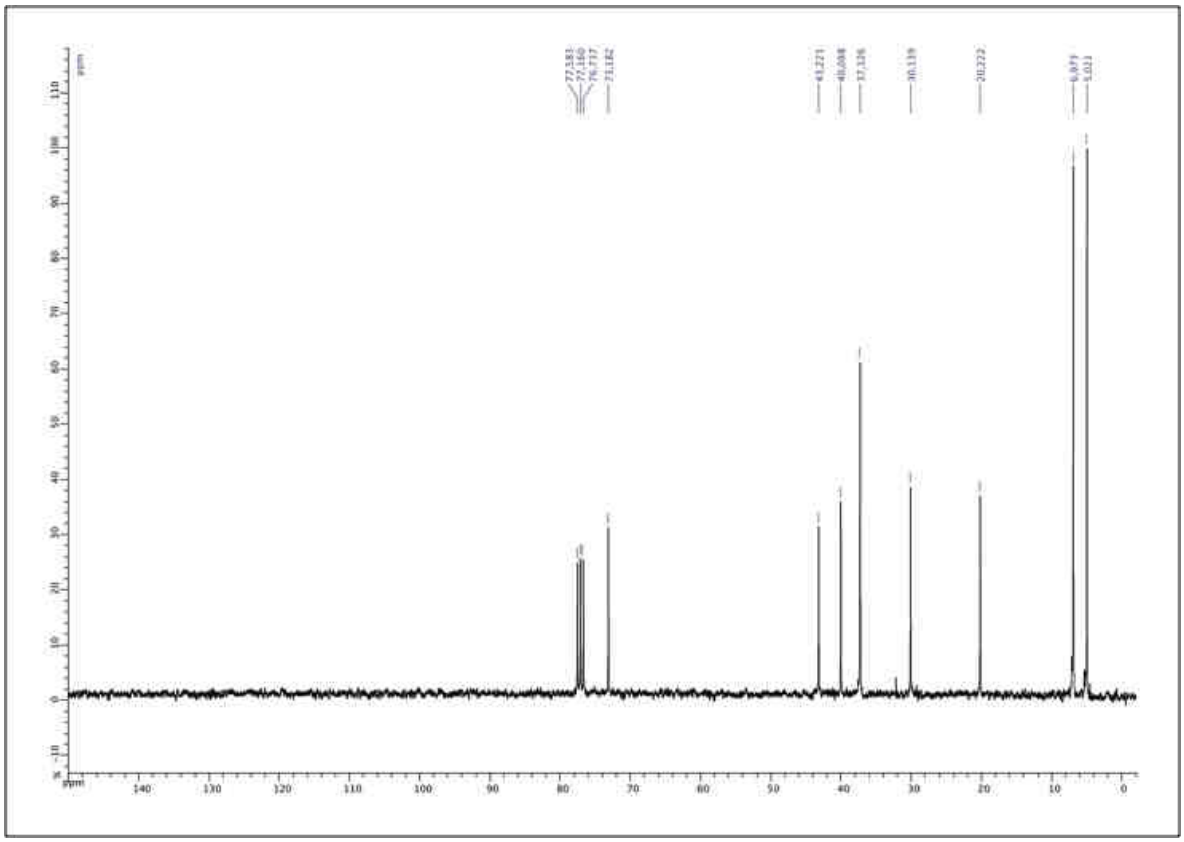
Triethyl(pentan-3-yloxy)silane (Table 2, entry 2 – Table 4, entry 2):



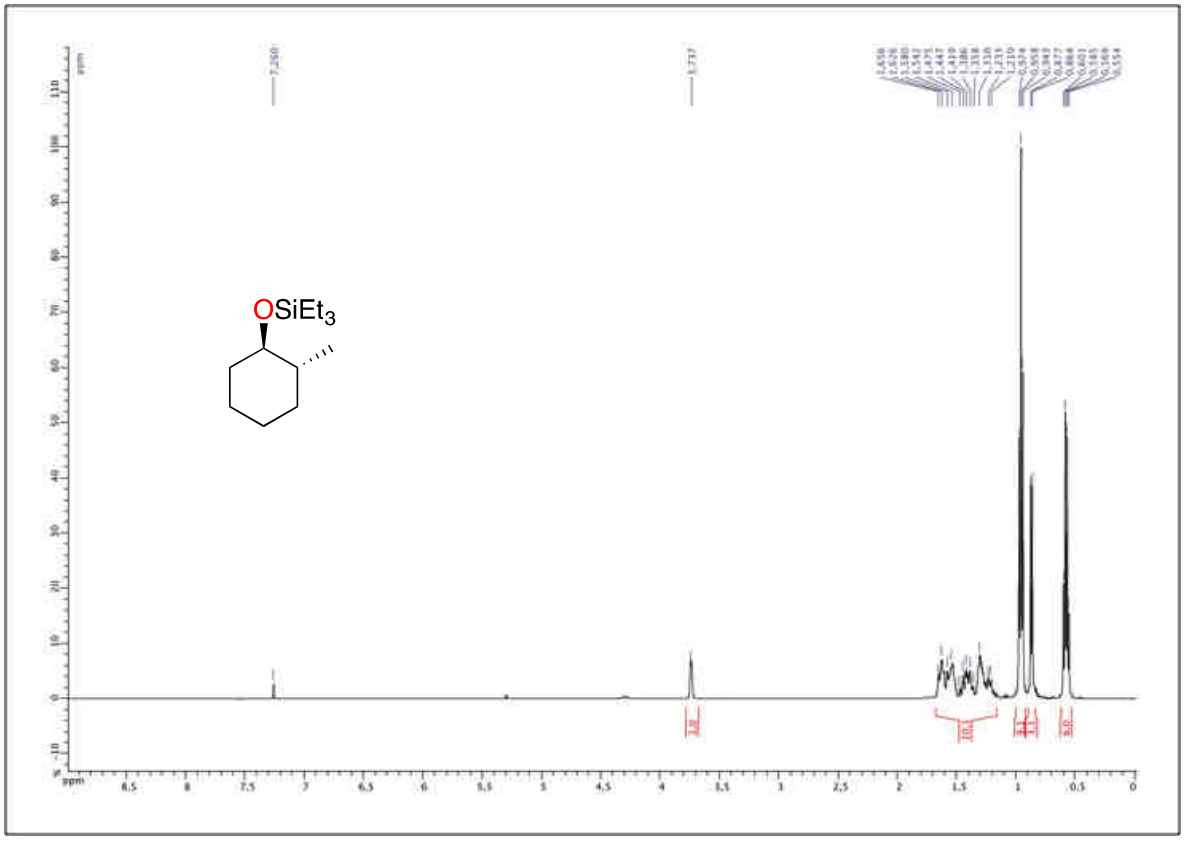


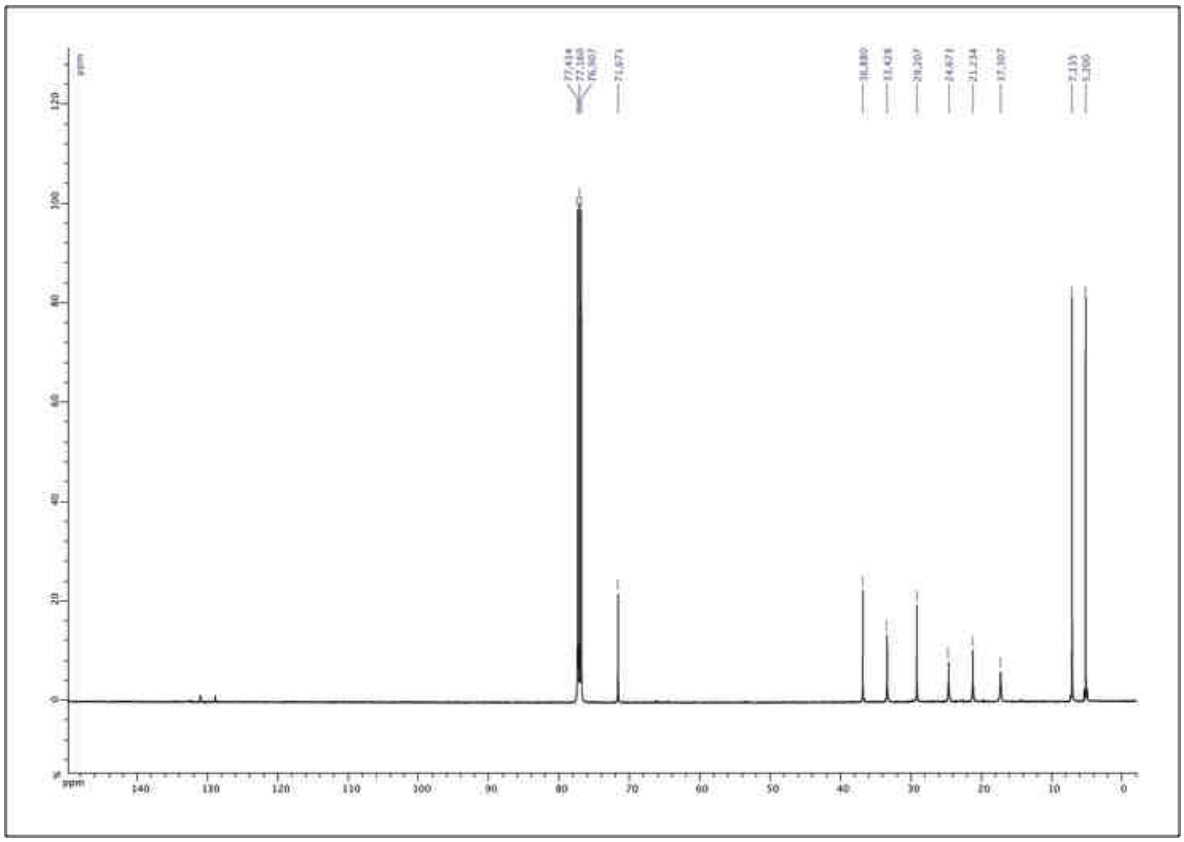
(bicyclo[2.2.1]heptan-2-yloxy)triethylsilane (Endo product) (Table 2, entry 3 – Table 4, entry 3):



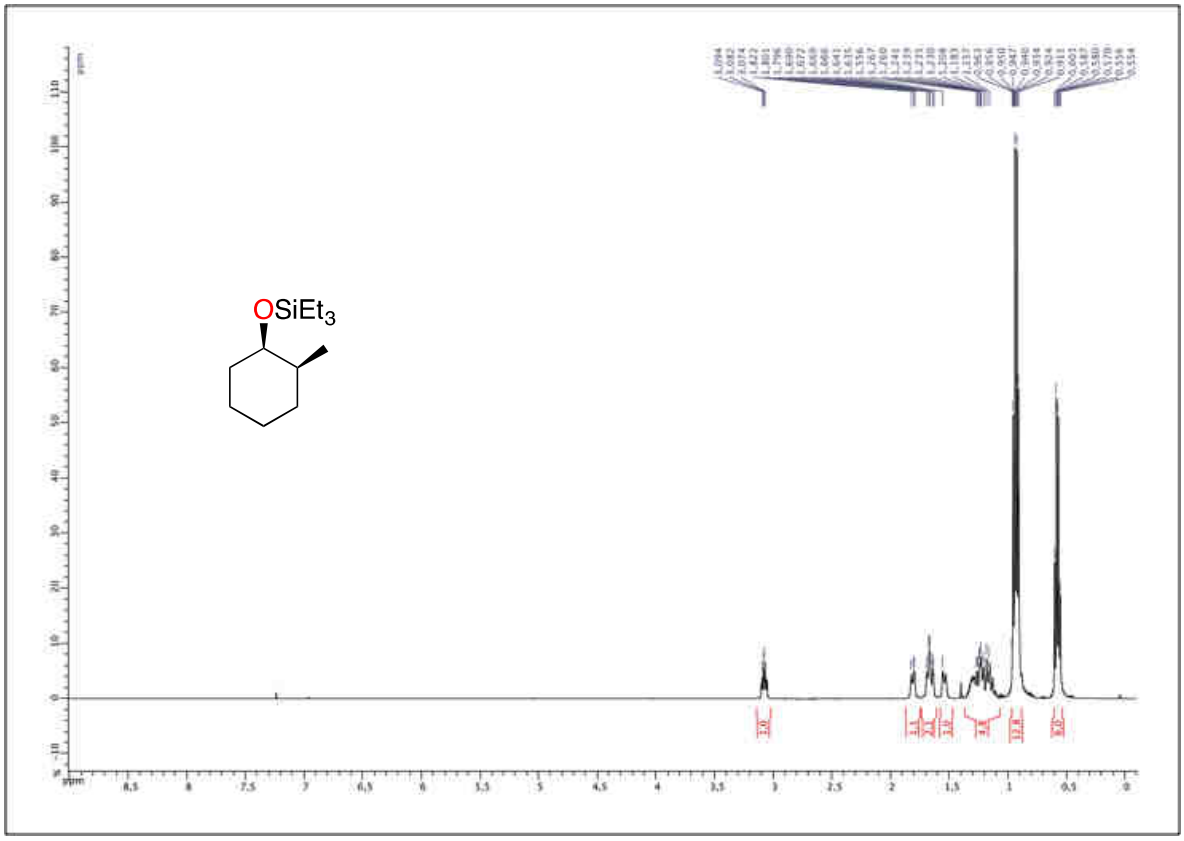


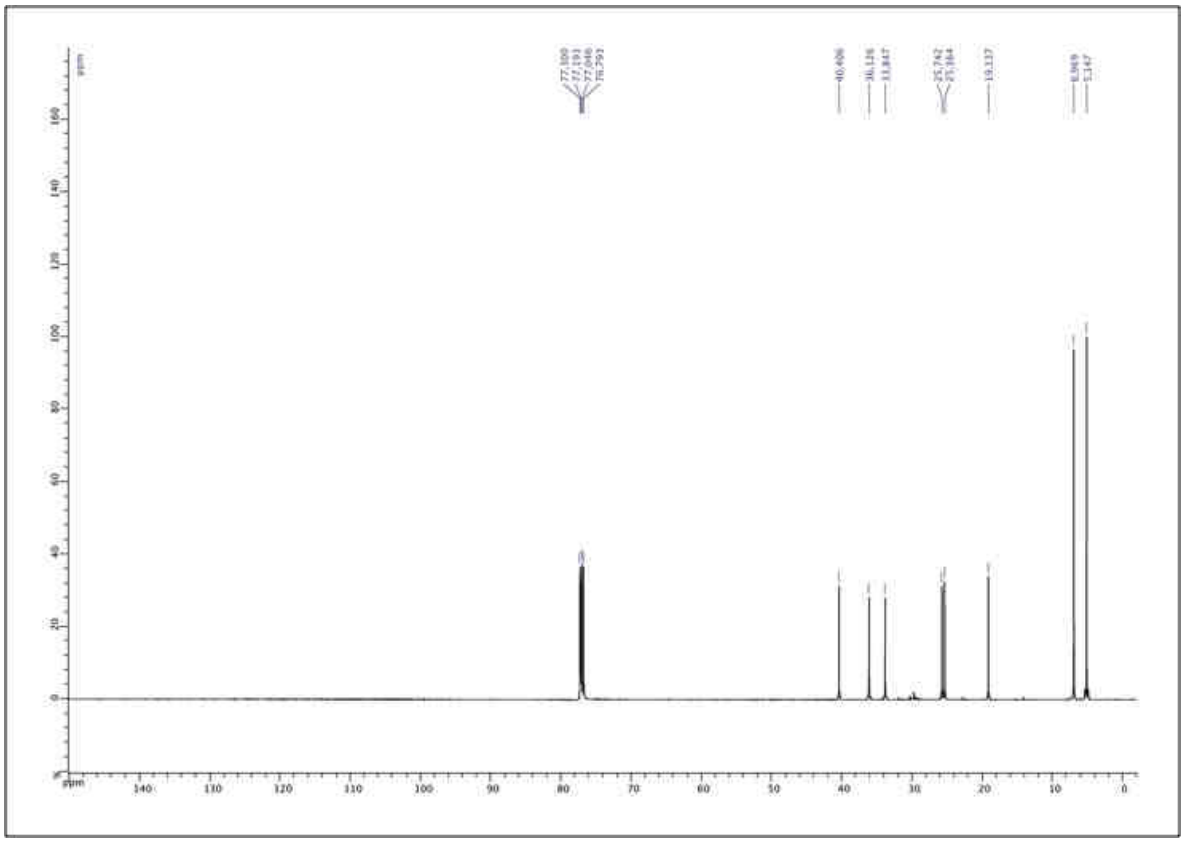
Triethyl(2-methylcyclohexyloxy)silane (*anti*-product) (Table 2, entry 4 – Table 4, entry 4):



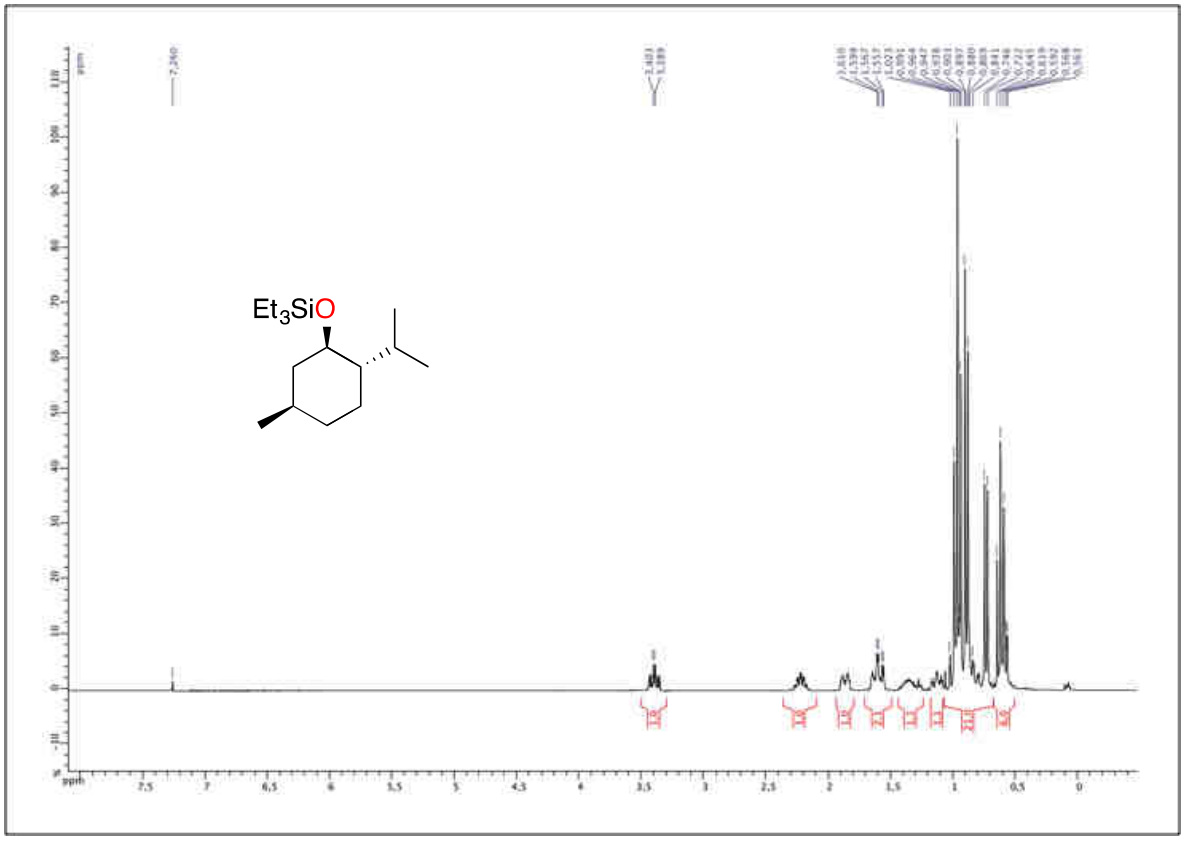


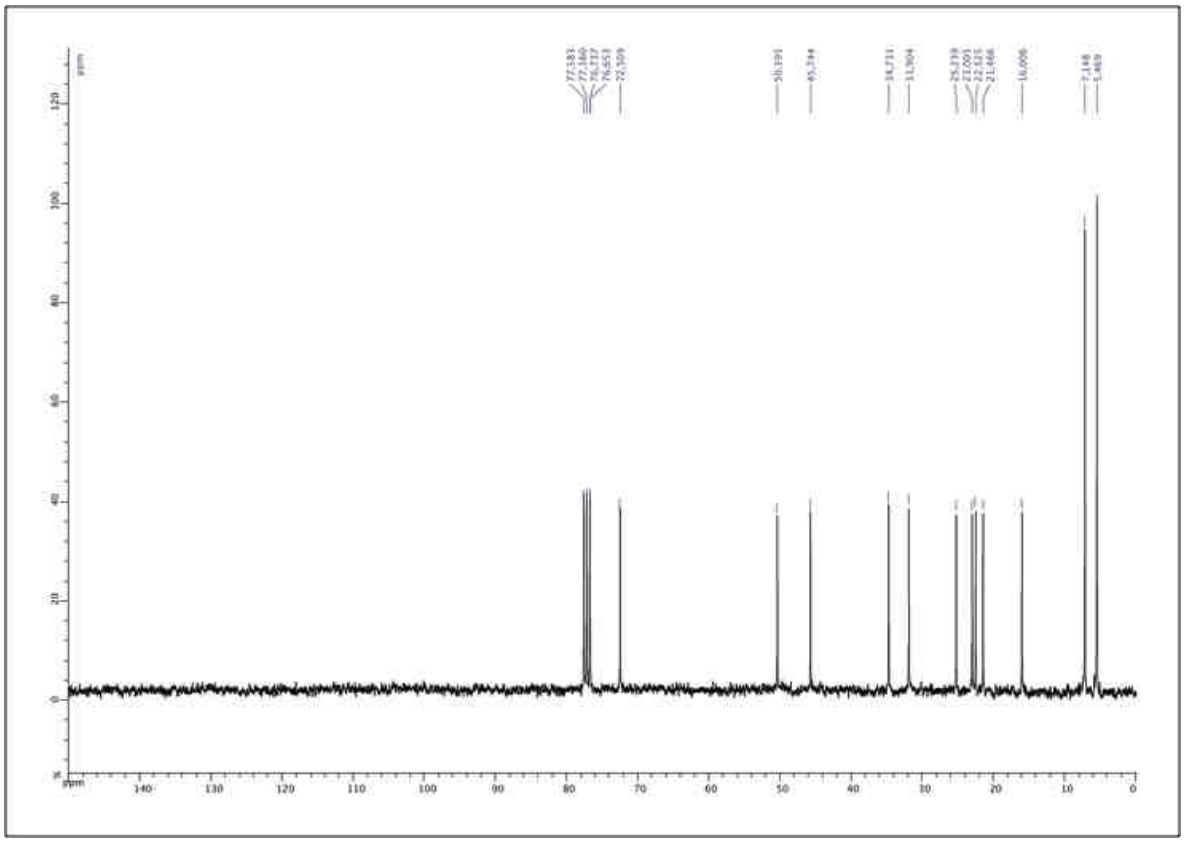
Triethyl(2-methylcyclohexyloxy)silane (*syn*-product) (Table 2, entry 4 – Table 4, entry 4):



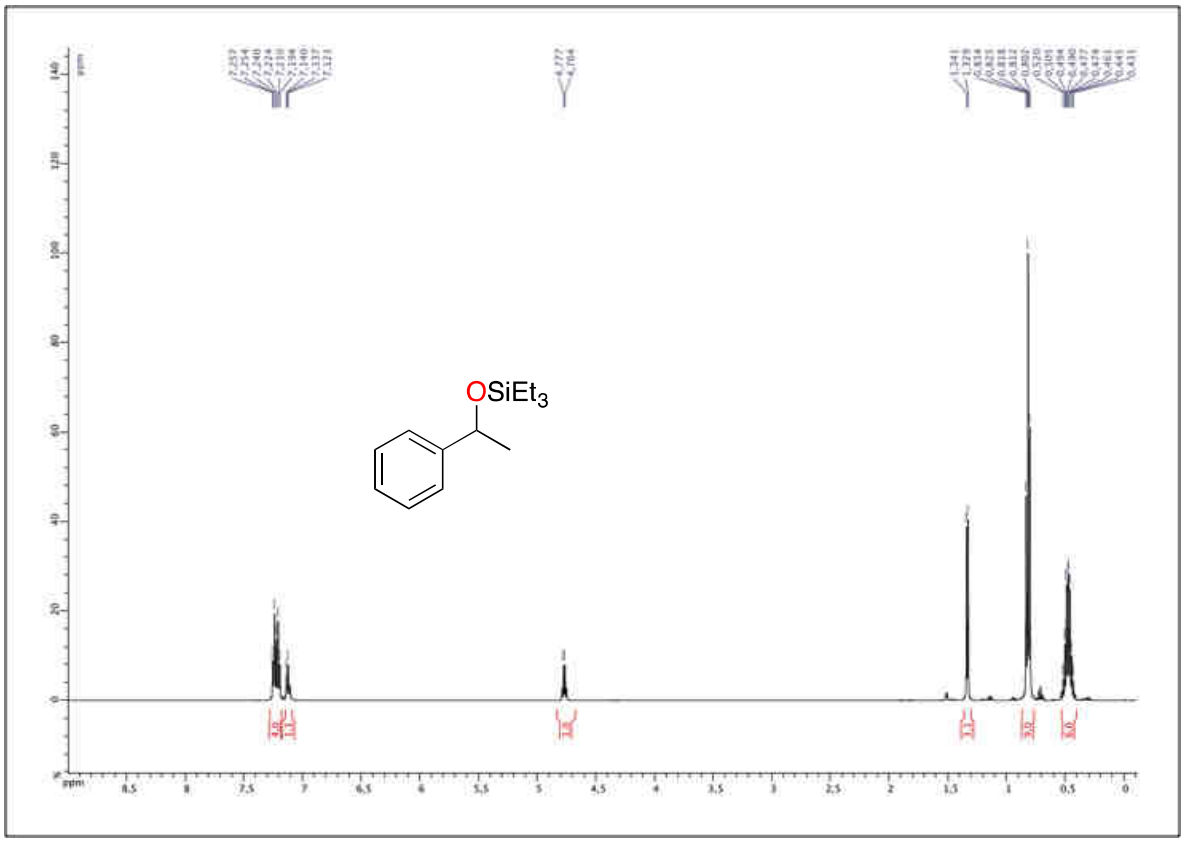


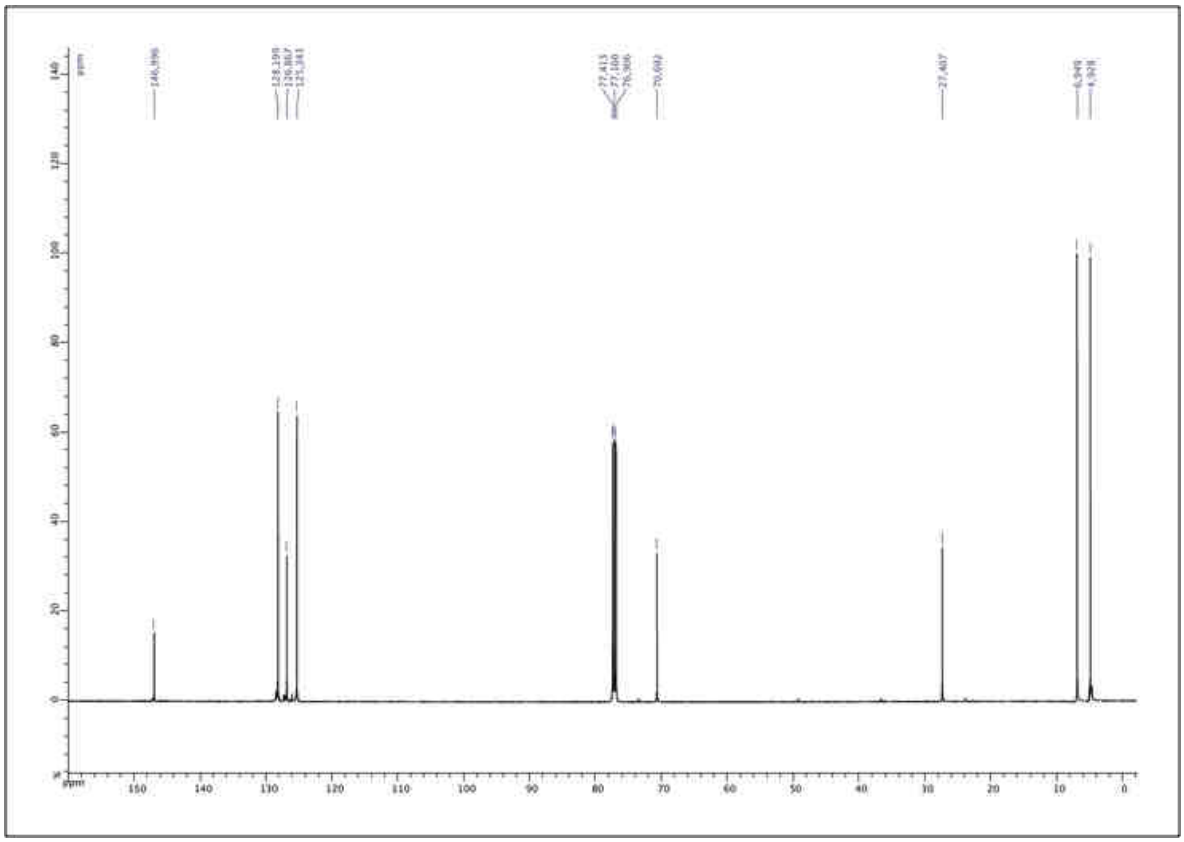
Triethyl((1R, 2*S*, 5R)-2-*iso*-propyl-5-methylcyclohexyloxy)silane (Table 2, entry 5 – Table 4, entry 5):



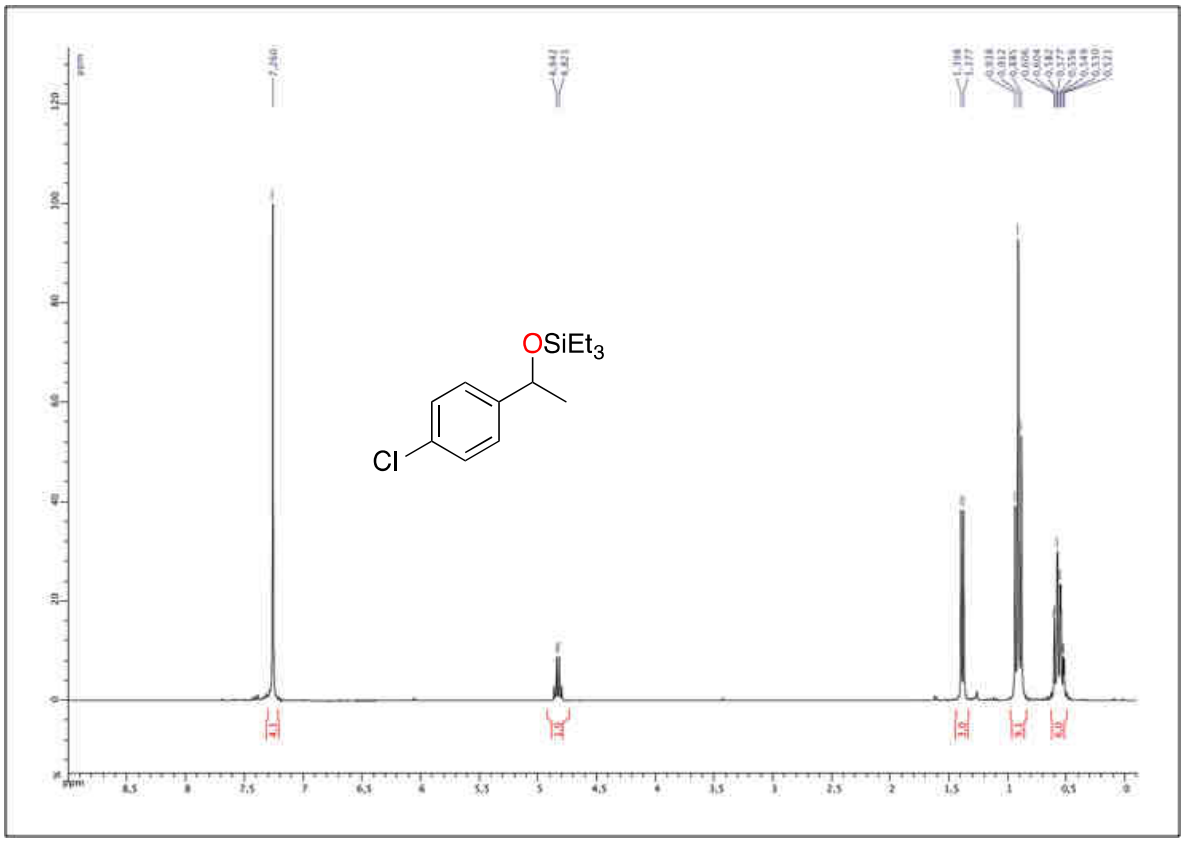


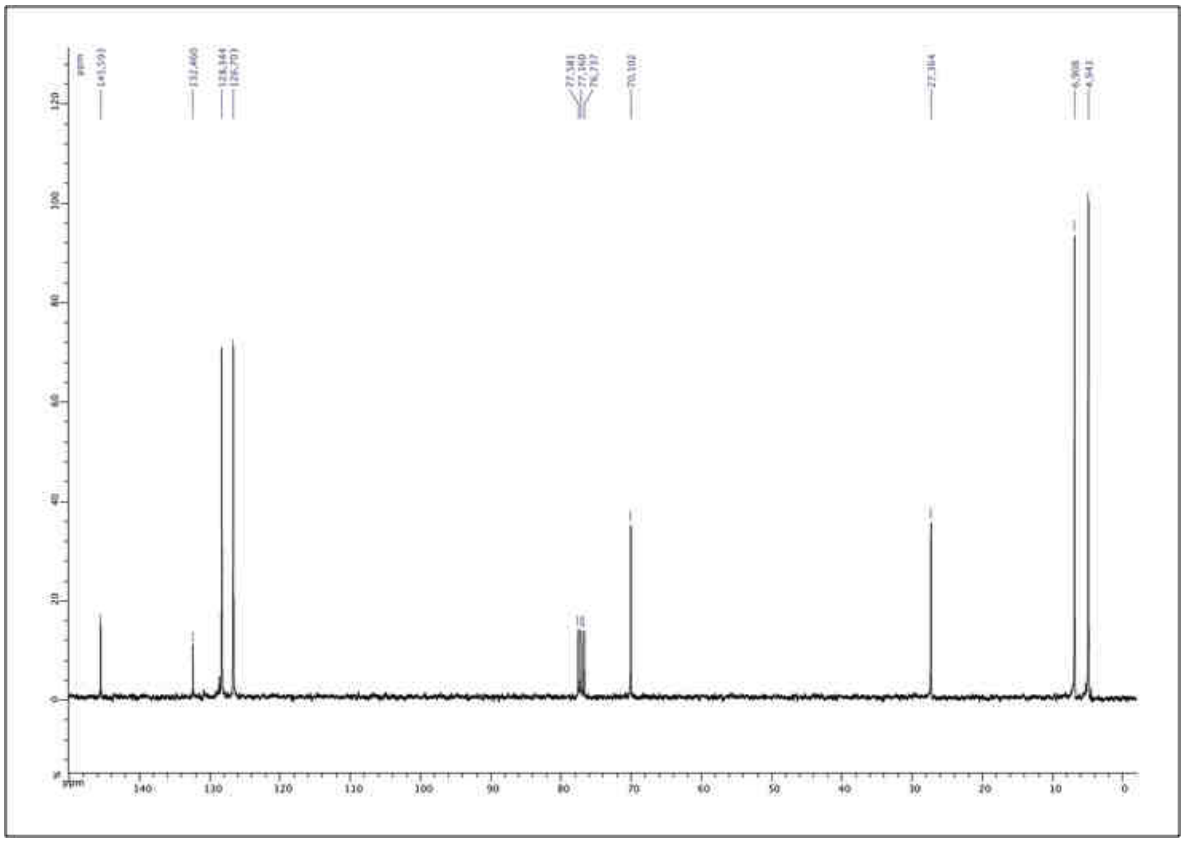
Triethyl(1-phenylethoxy)silane (Table 2, entry 6 – Table 4, entry 6):



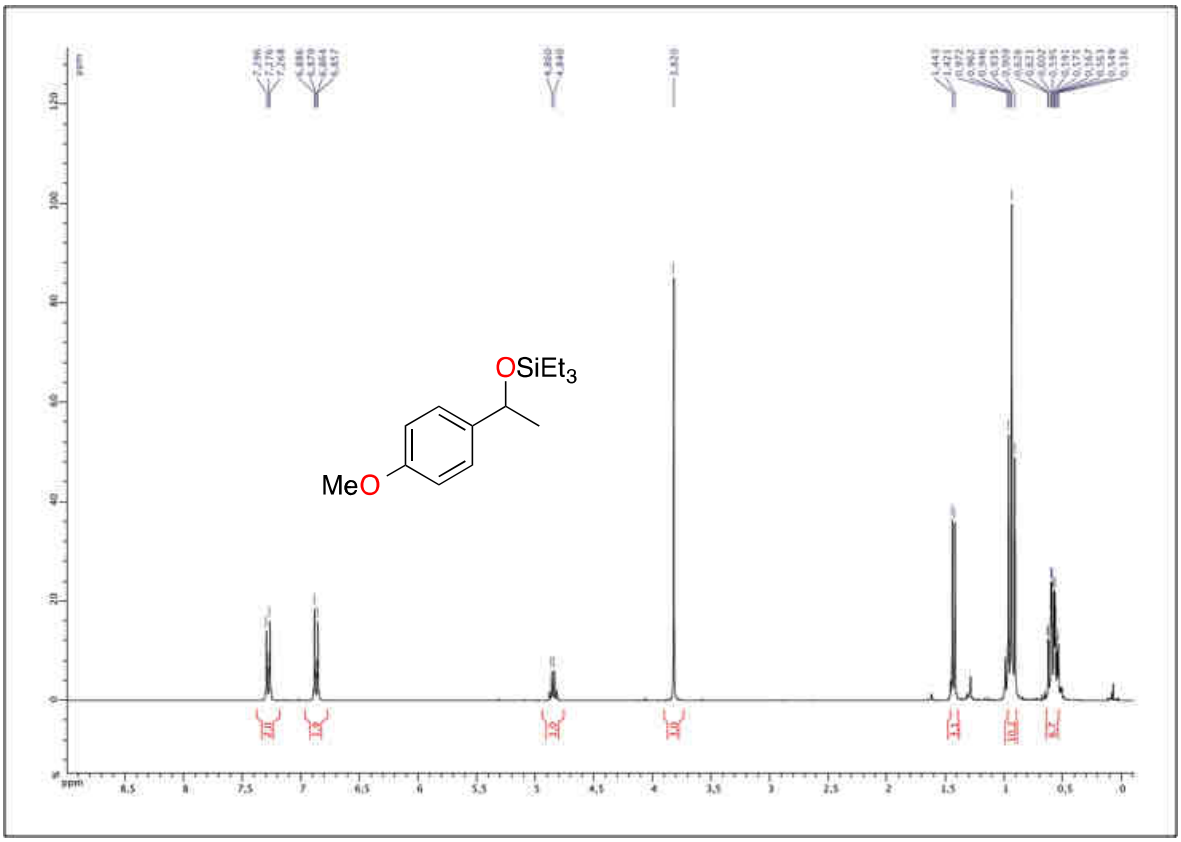


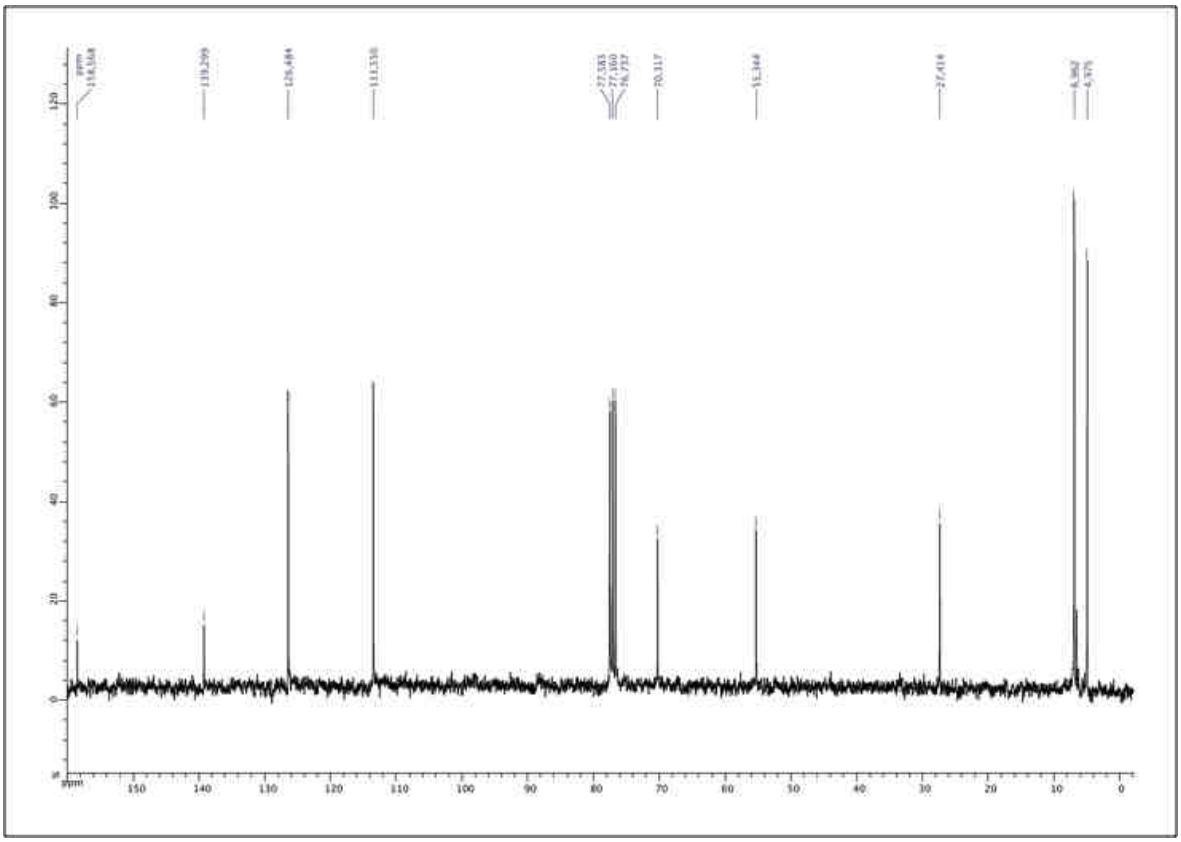
[1-(4-chlorophenyl)ethoxy]triethylsilane (Table 2, entry 7 – Table 4, entry 7):



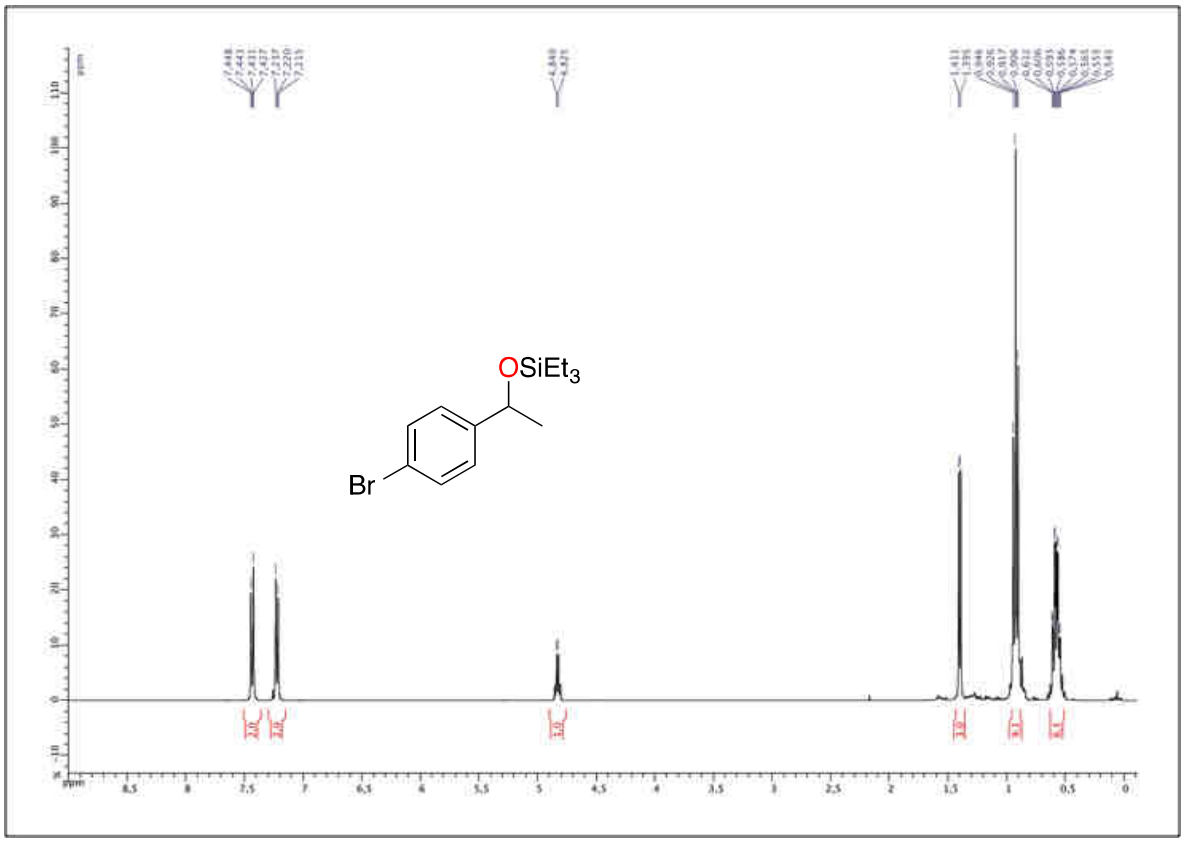


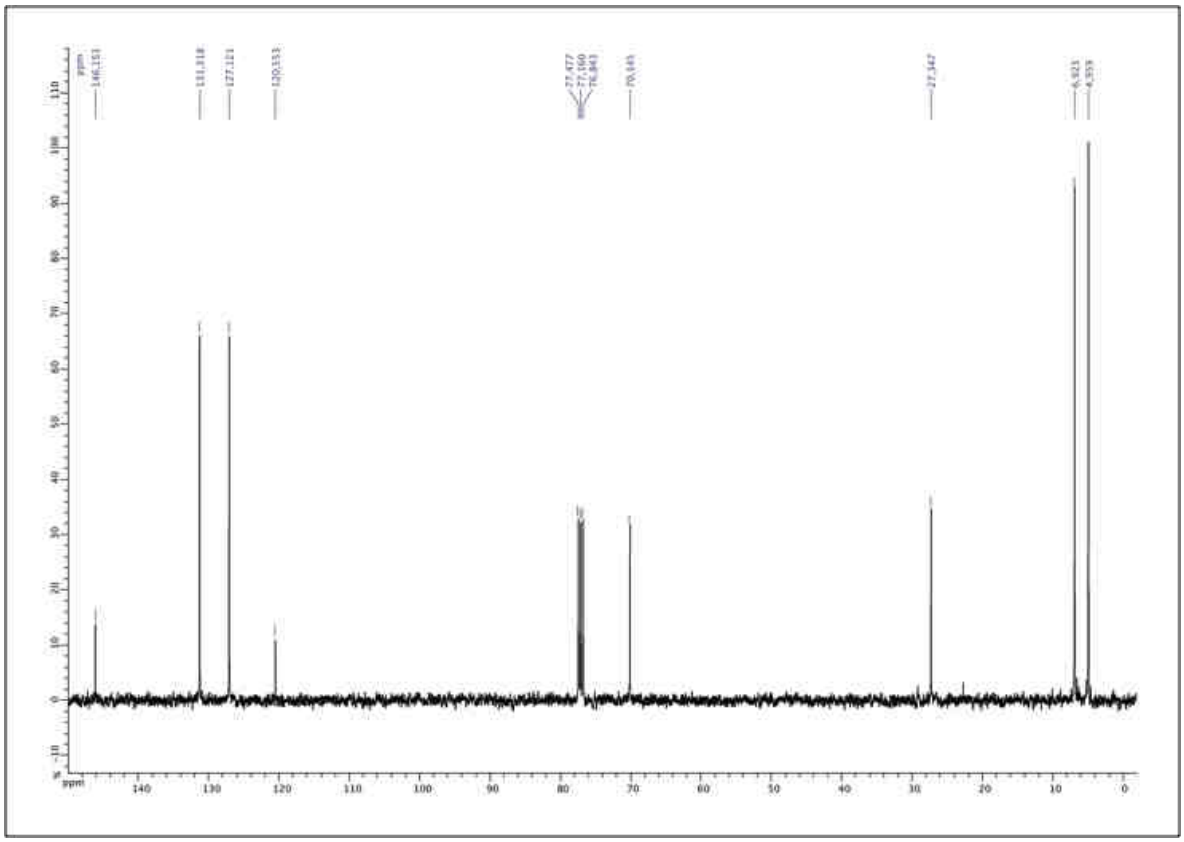
[1-(4-methoxy)ethoxy]triethylsilane (Table 2, entry 8 – Table 4, entry 7):



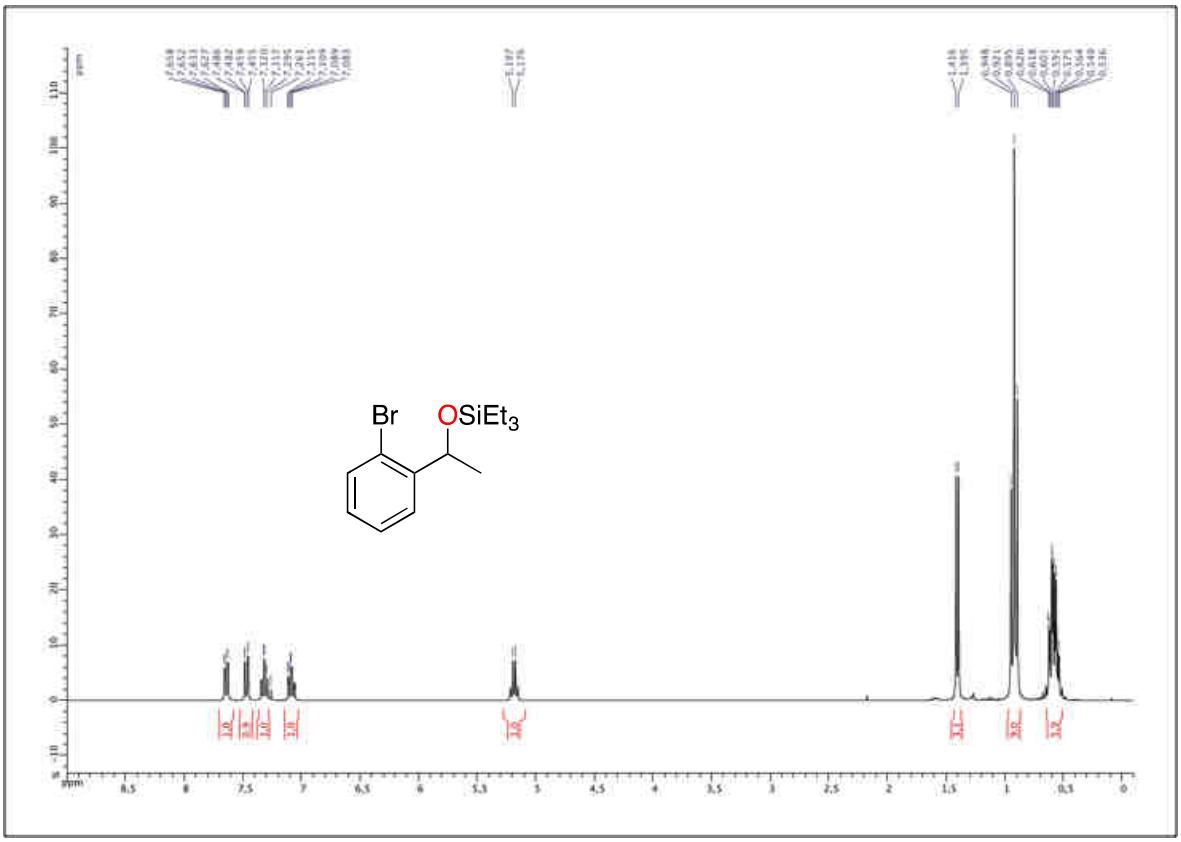


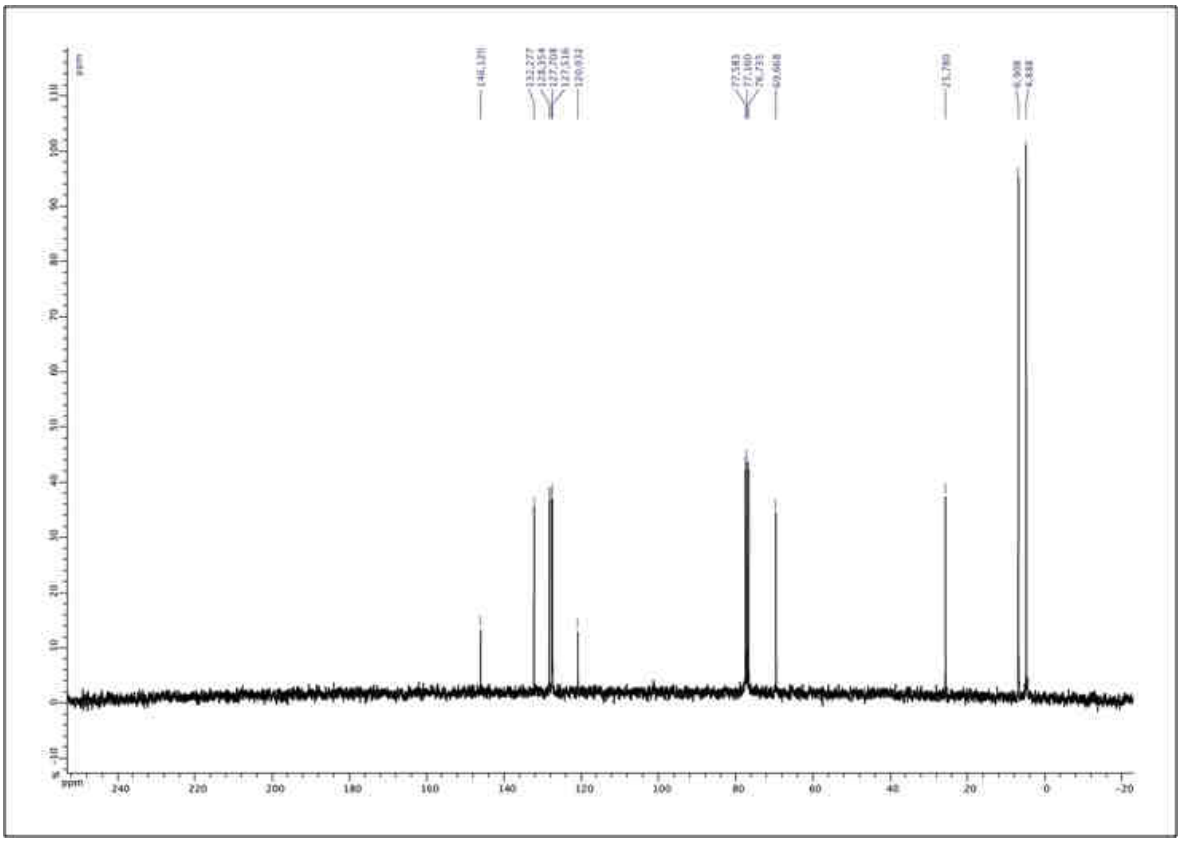
[1-(4-bromophenyl)ethoxy]triethylsilane (Table 2, entry 8 – Table 4, entry 8):



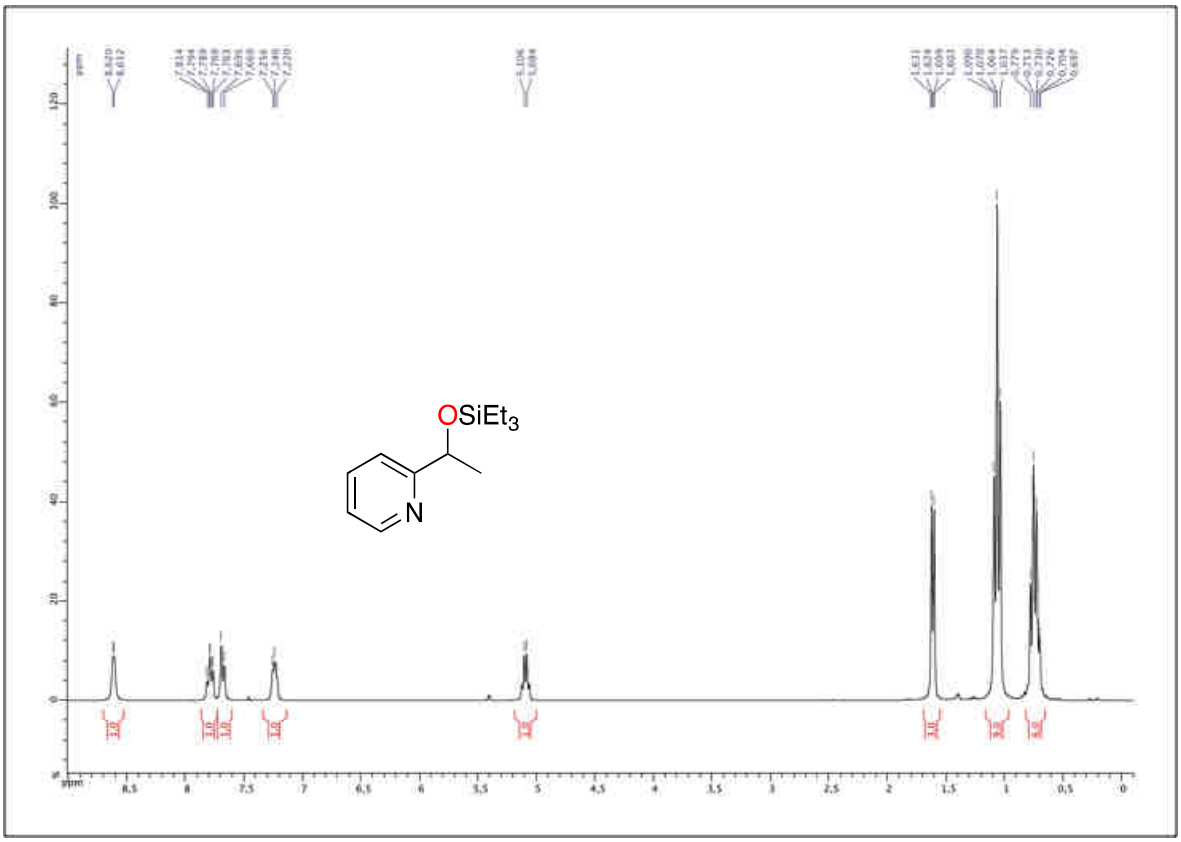


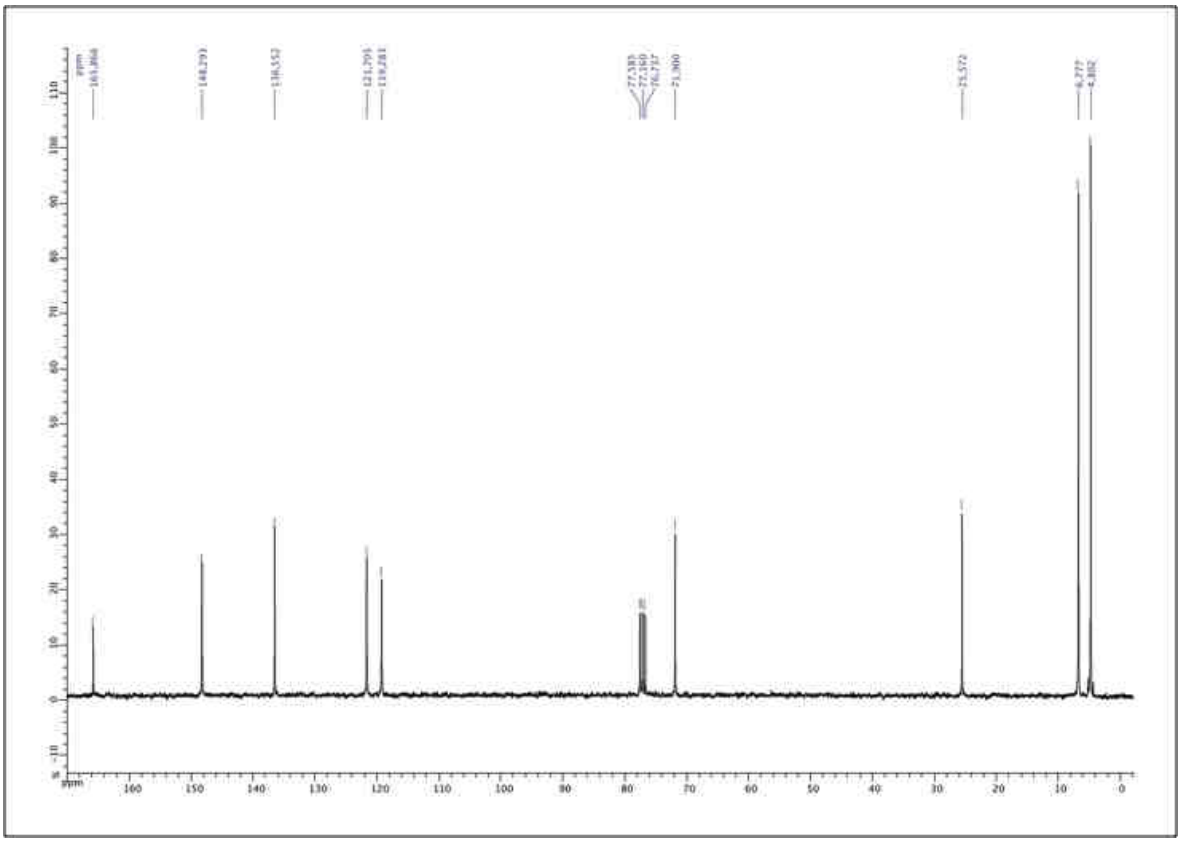
[1-(2-bromophenyl)ethoxy]triethylsilane (Table 2, entry 9 – Table 4, entry 9):



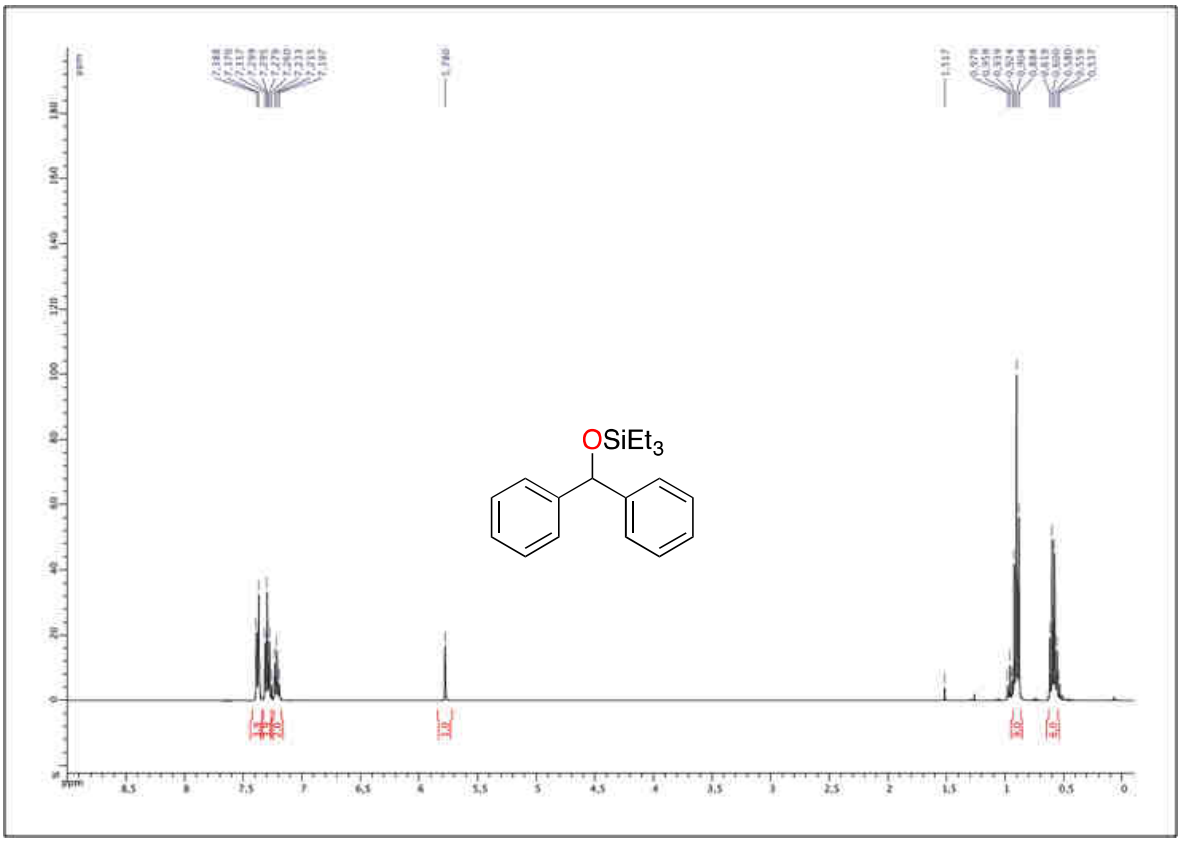


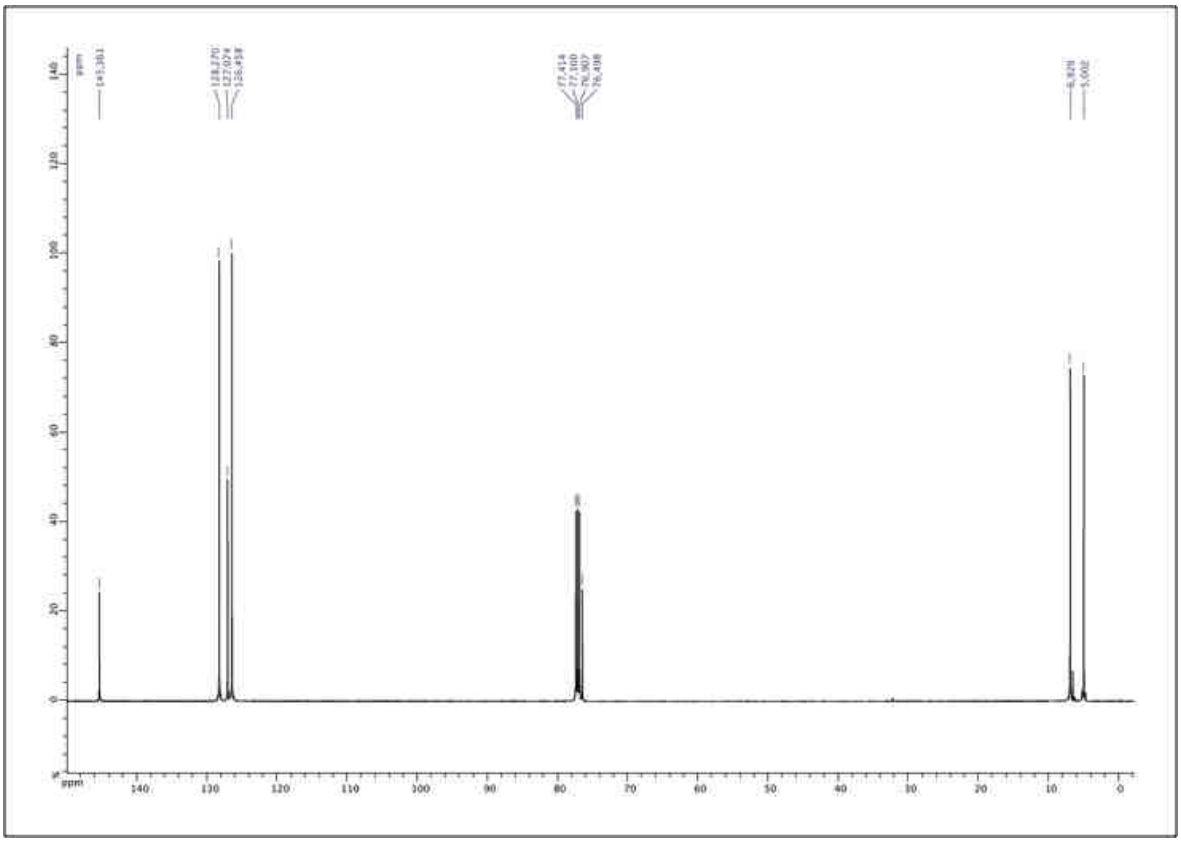
[2-(1-(triethylsilyloxy)ethyl]pyridine (Table 2, entry 11 – Table 4, entry 11):



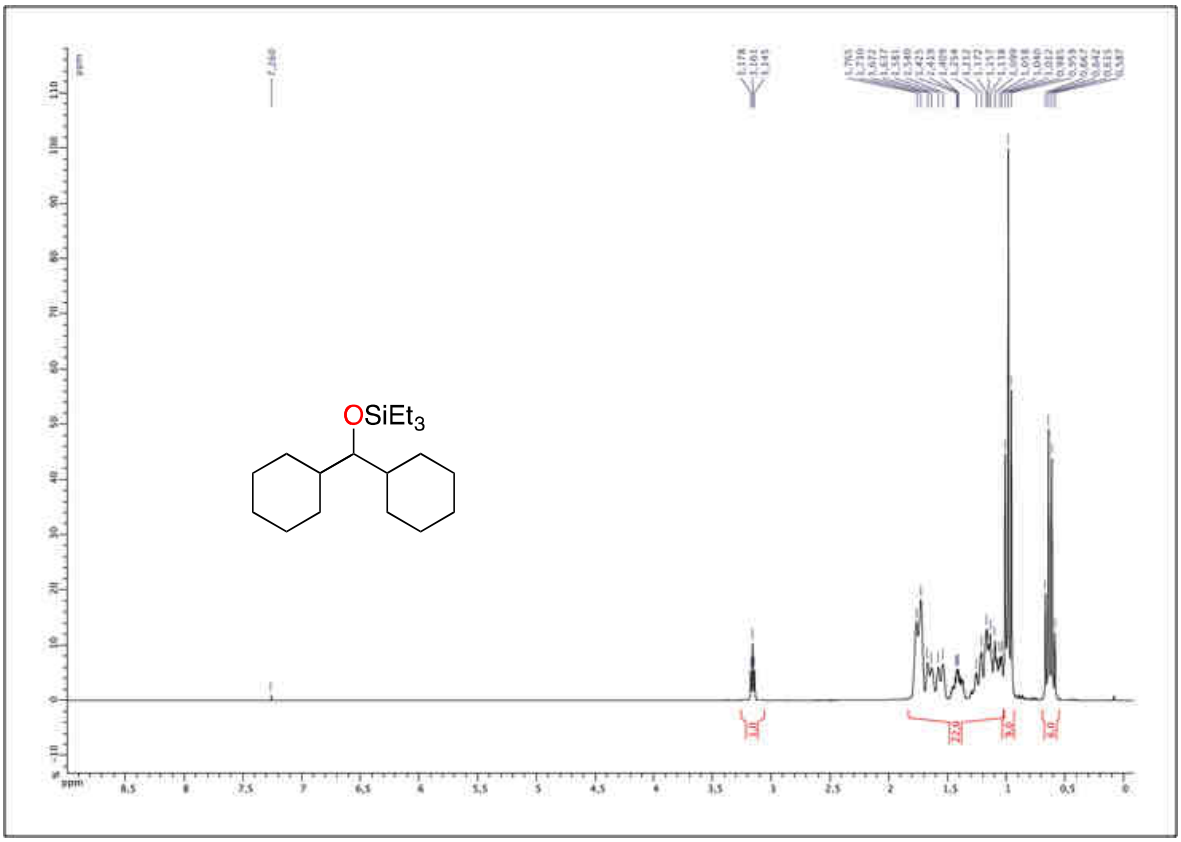


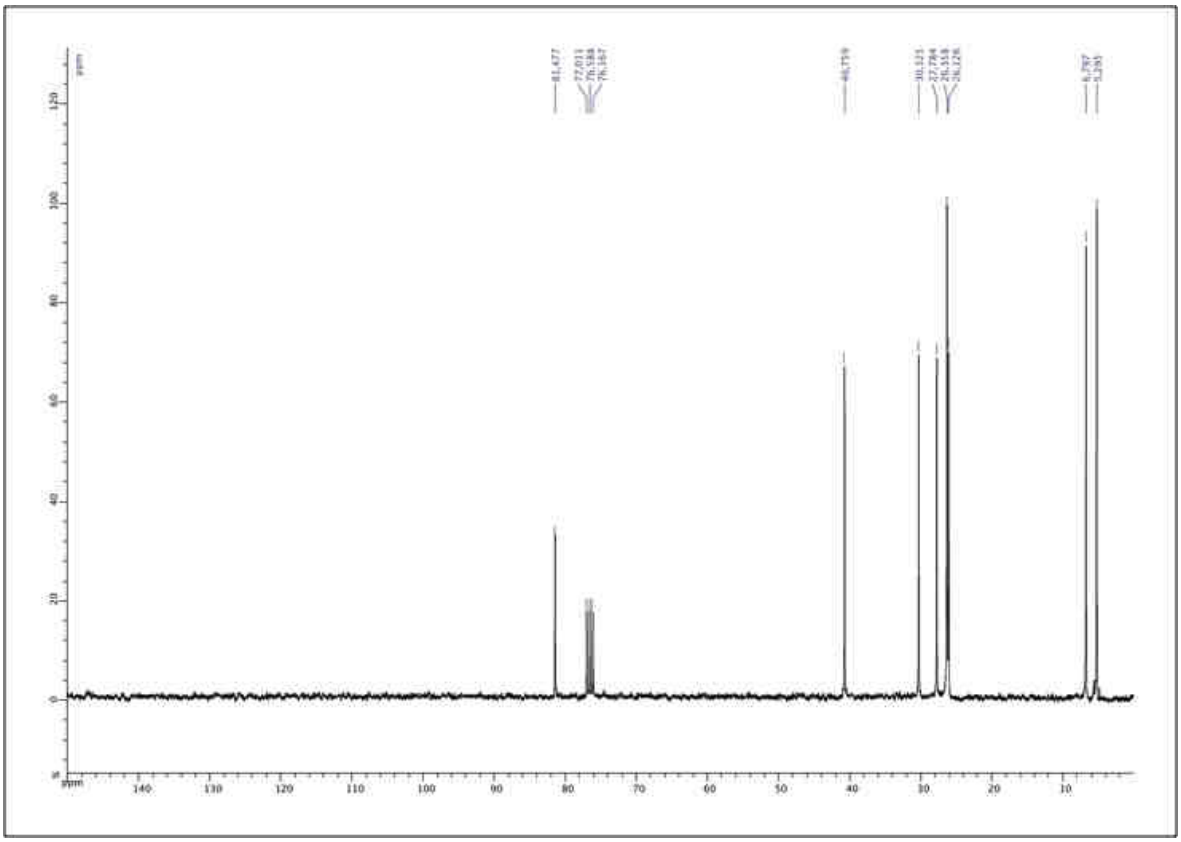
Benzhydryloxytriethylsilane (Table 2, entry 12 – Table 4, entry 12):



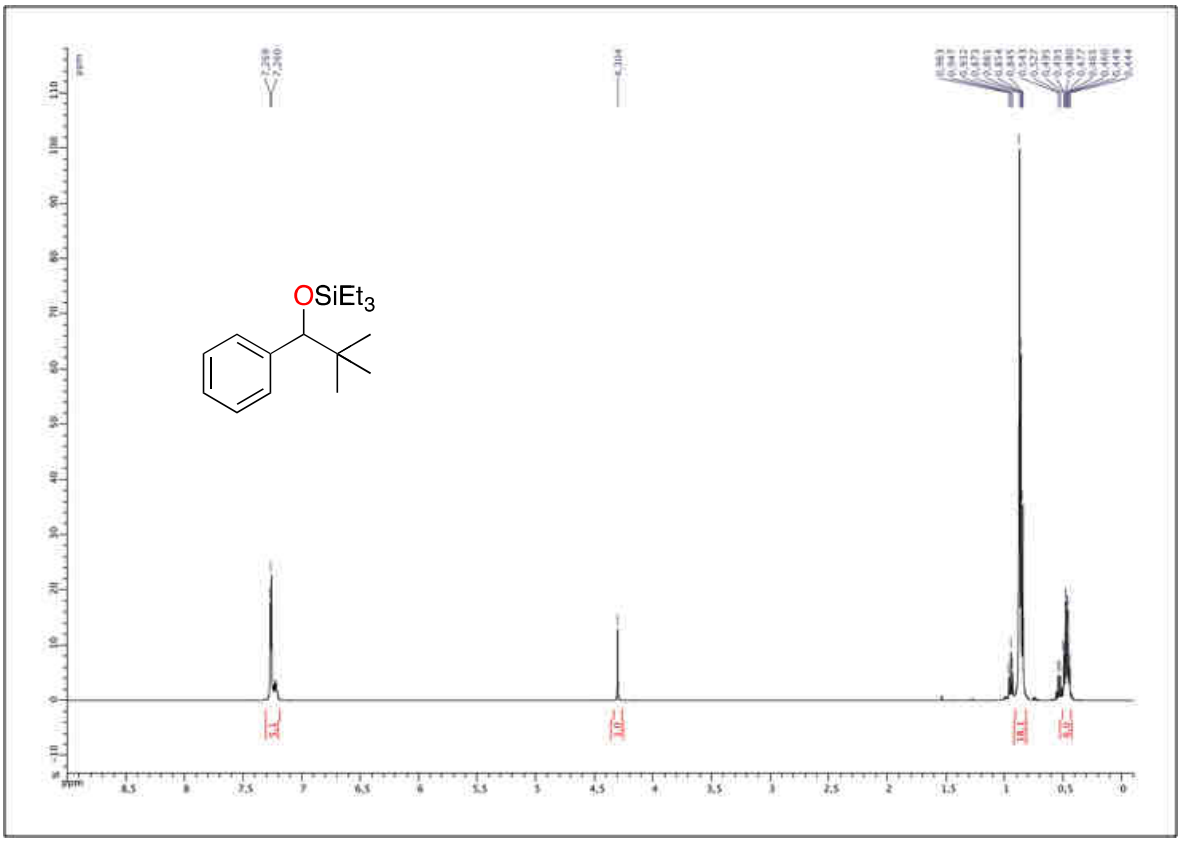


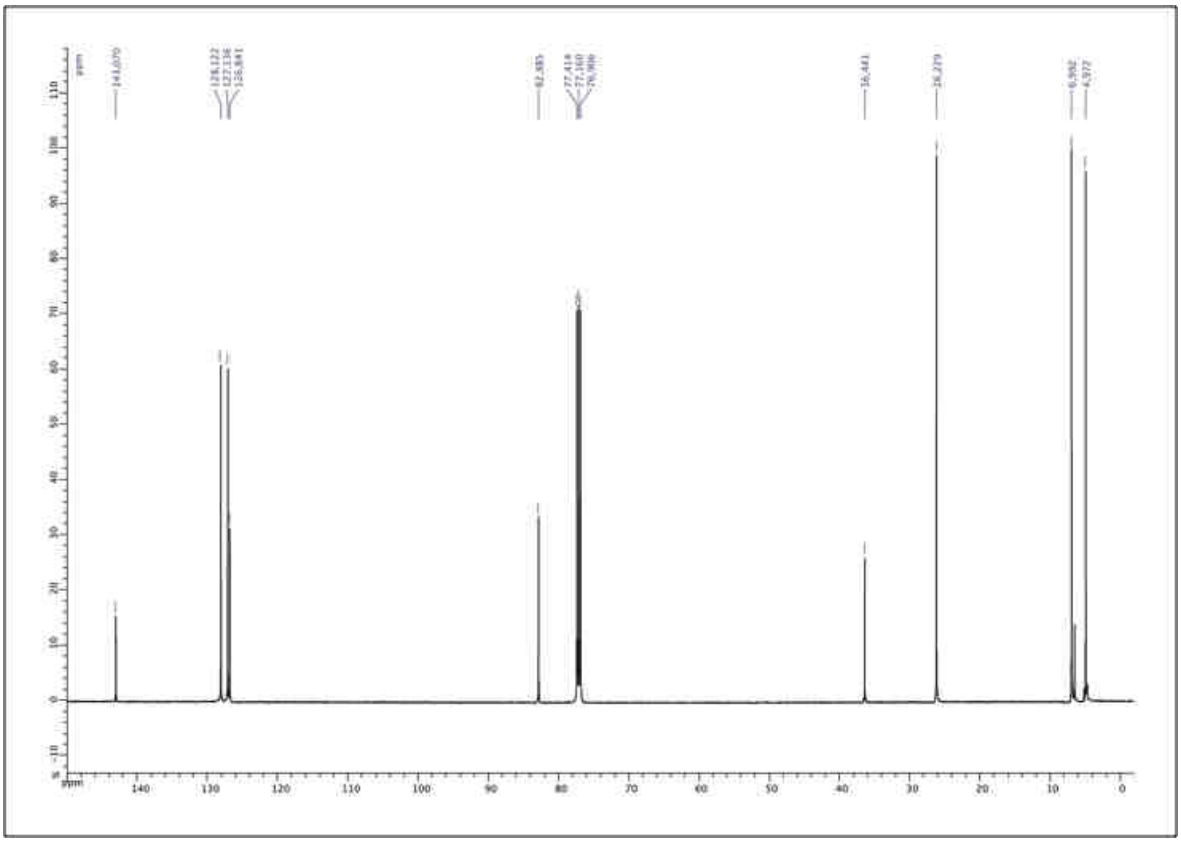
(dicyclohexylmethoxy)triethylsilane (Table 2, entry 13 – Table 4, entry 13):



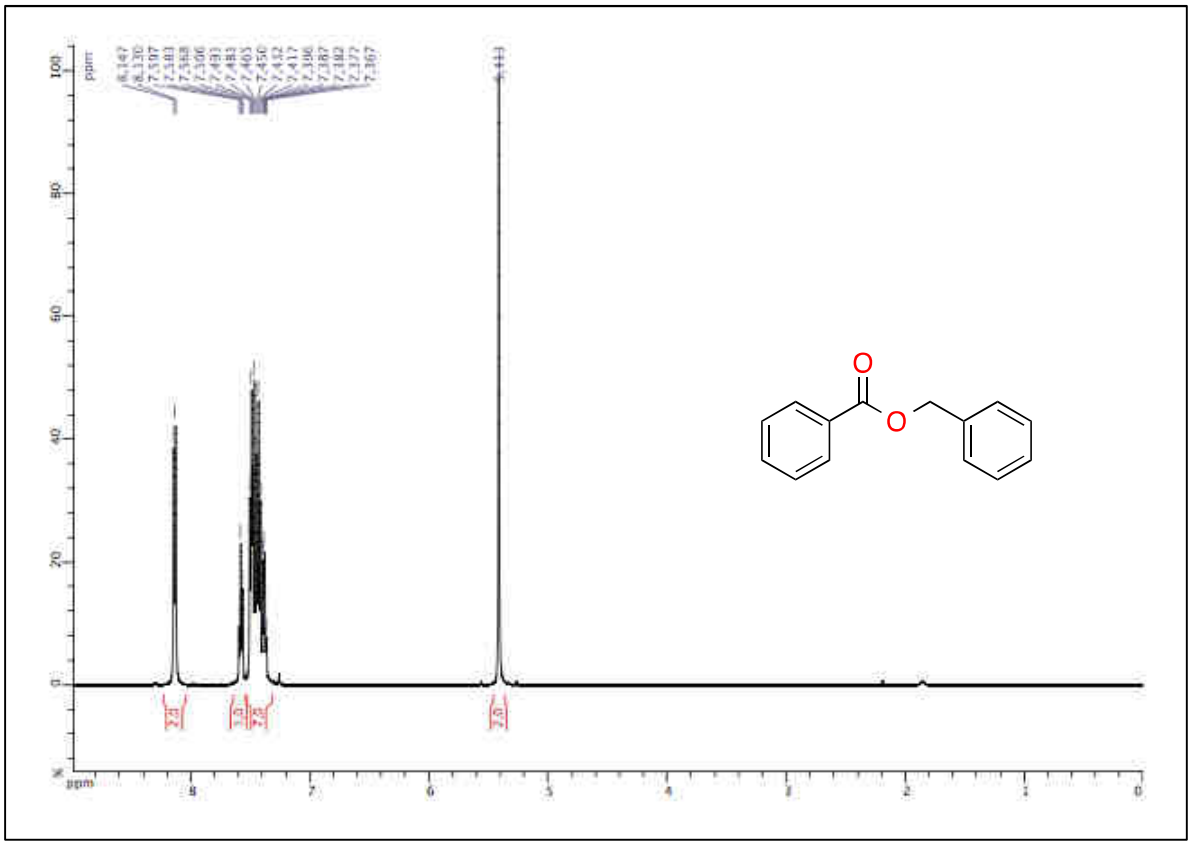


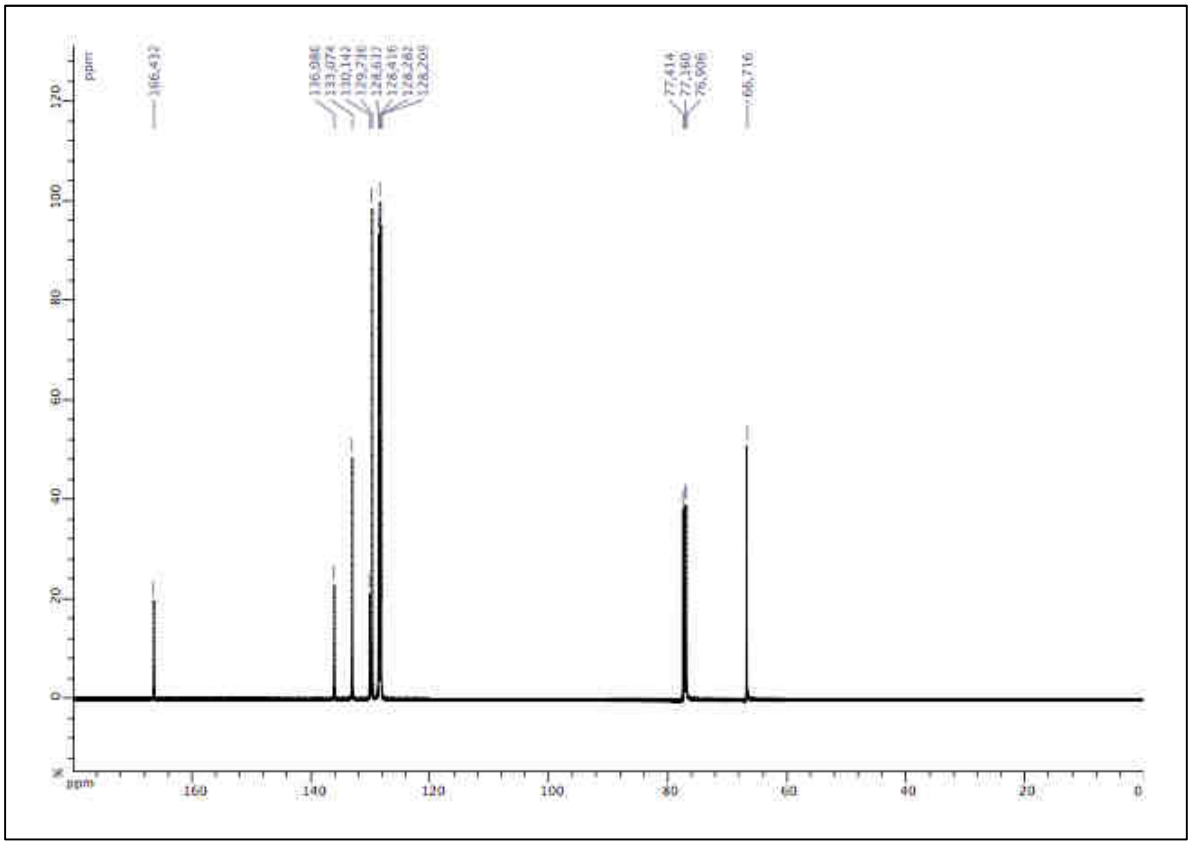
(2,2-dimethyl-1-phenylpropoxy)triethylsilane (Table 2, entry 14 – Table 4, entry 14):



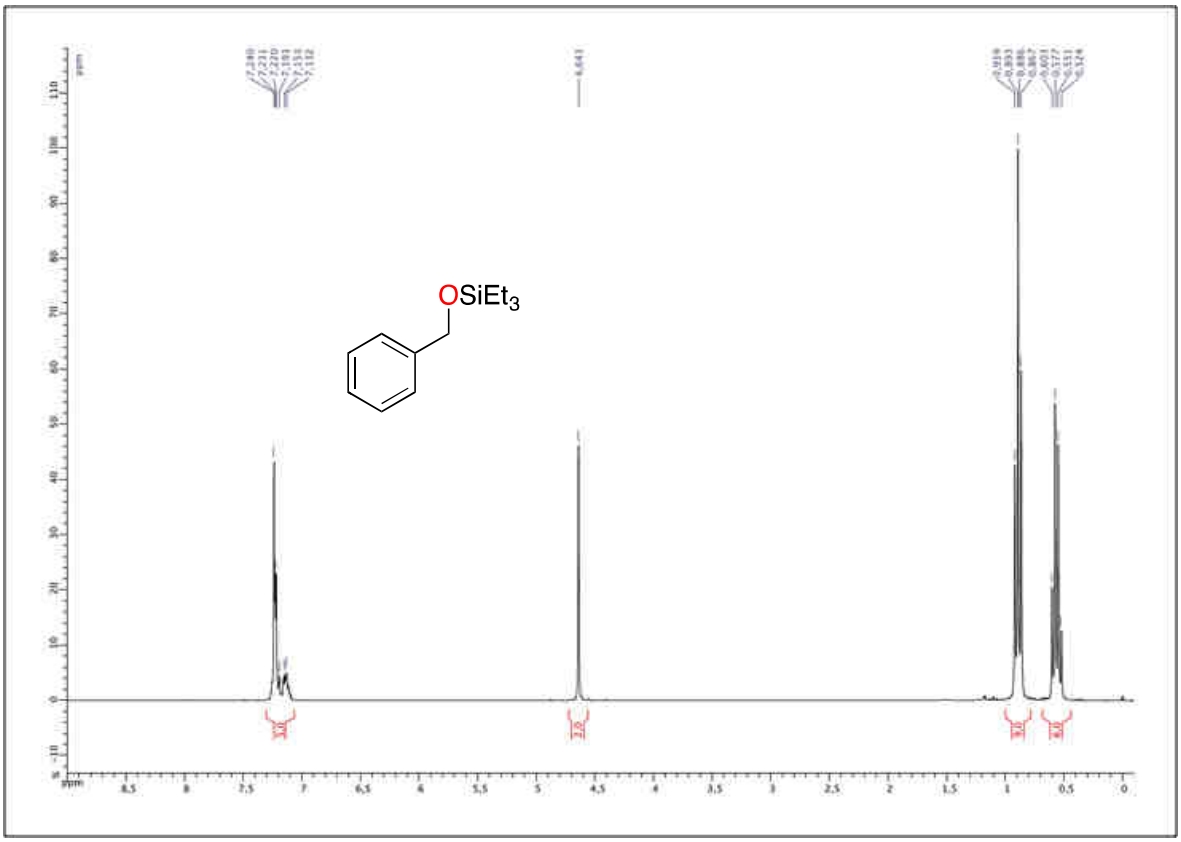


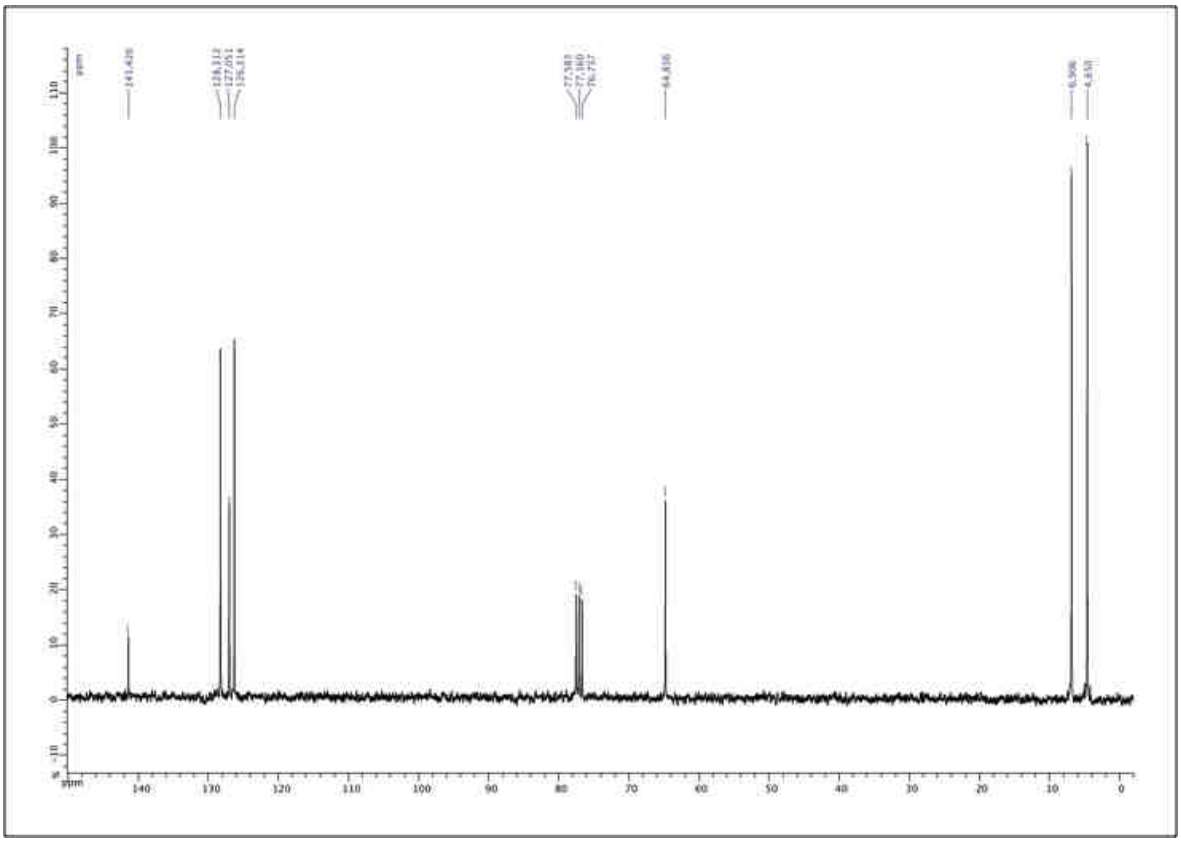
Benzylbenzoate (Table 5, entry 5):



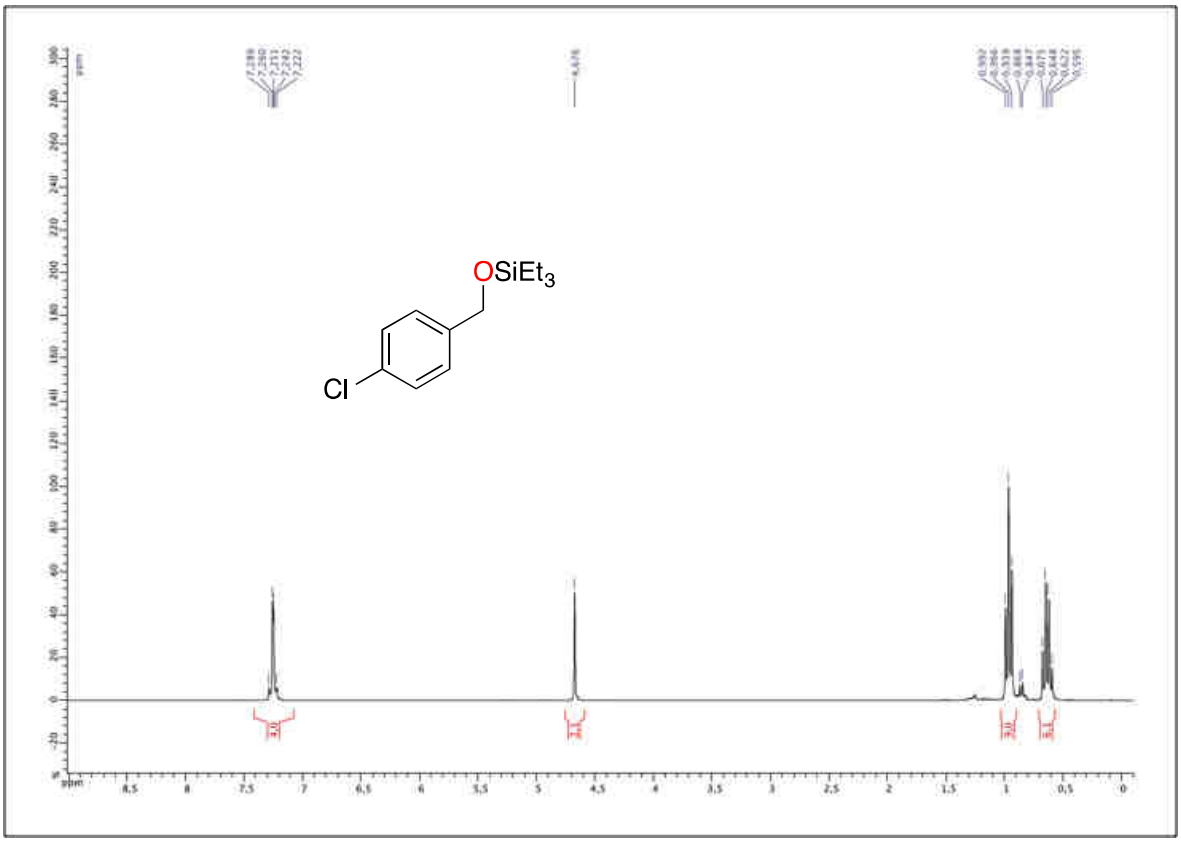


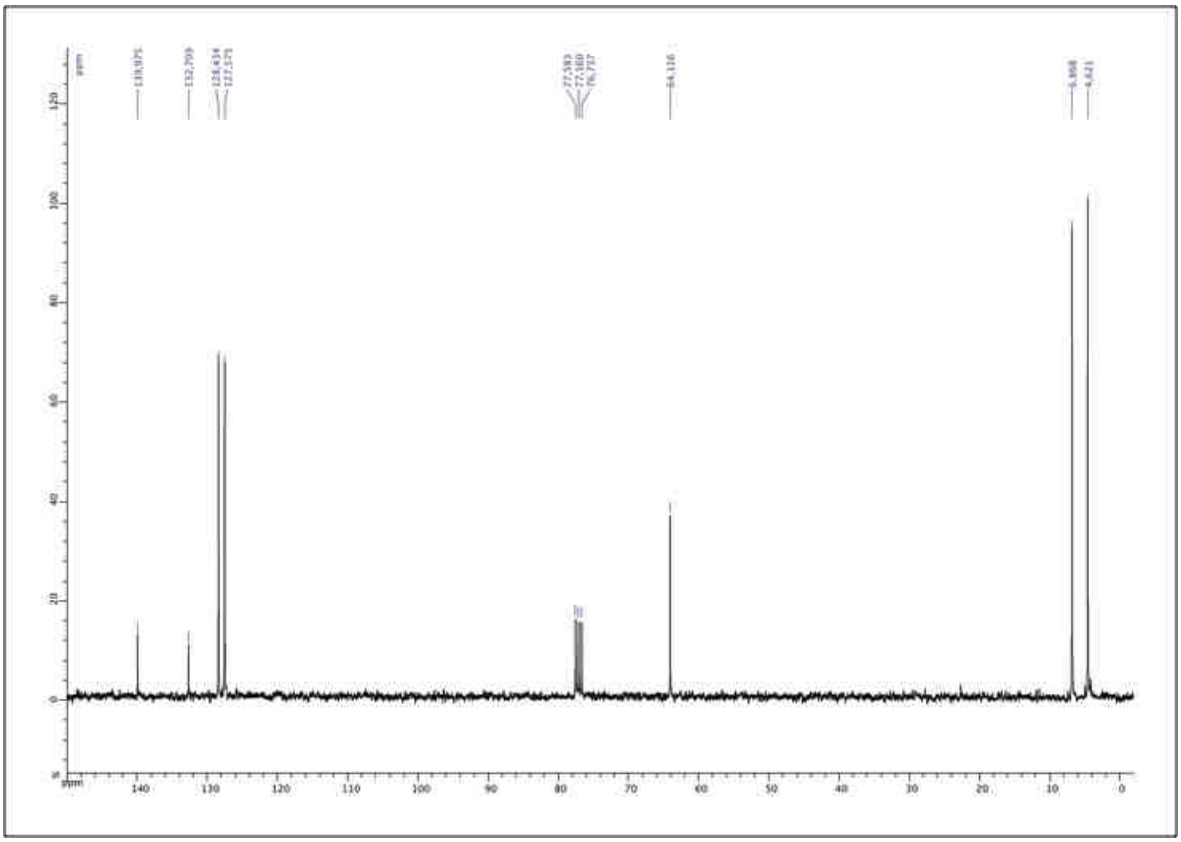
Benzyloxytriethylsilane (Table 5, entry 1):



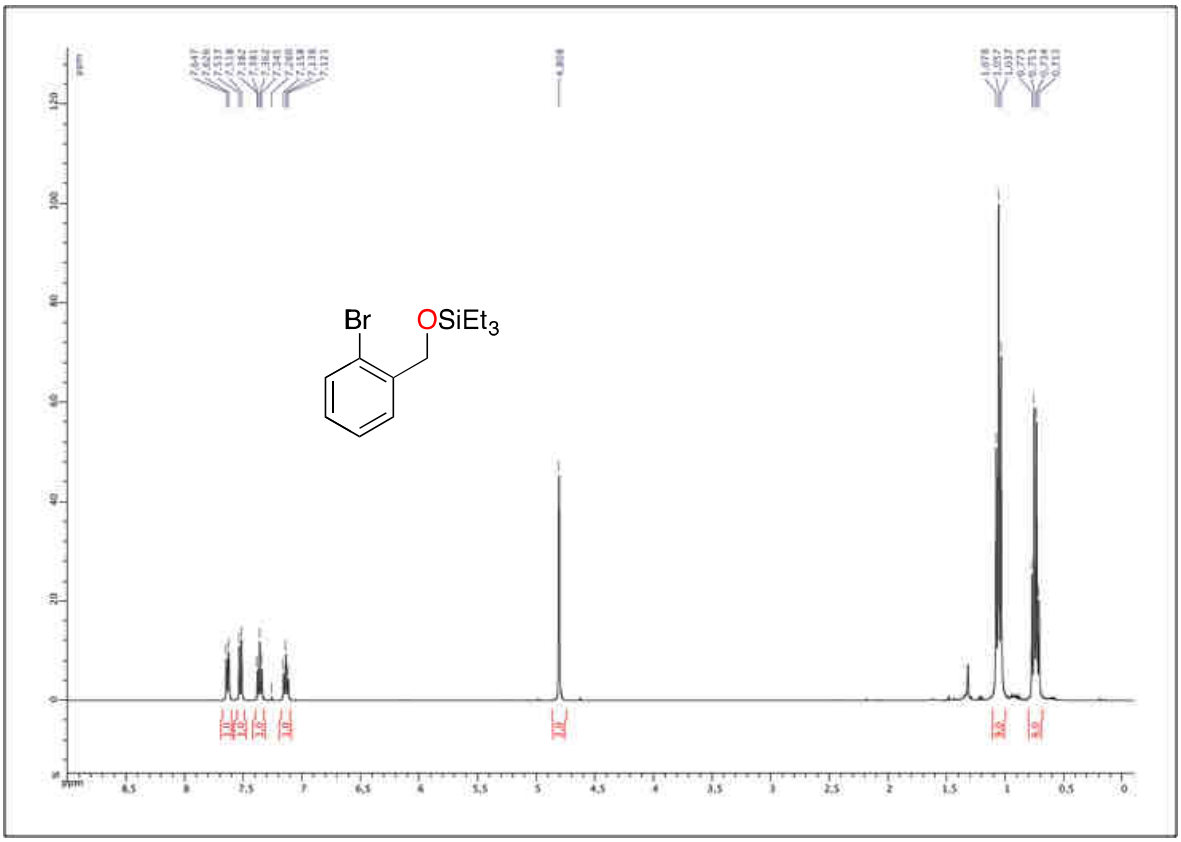


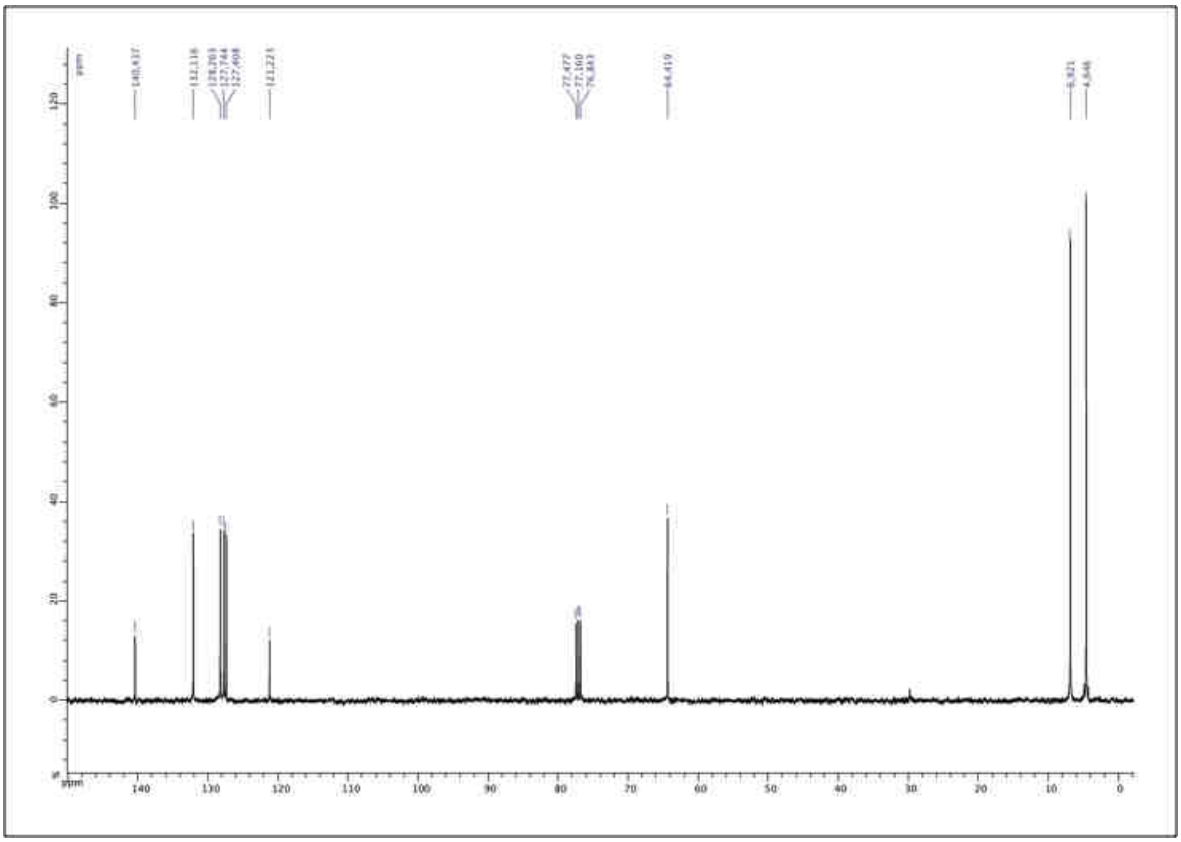
(4-chlorobenzyloxy)triethylsilane (Table 5, entry 2):



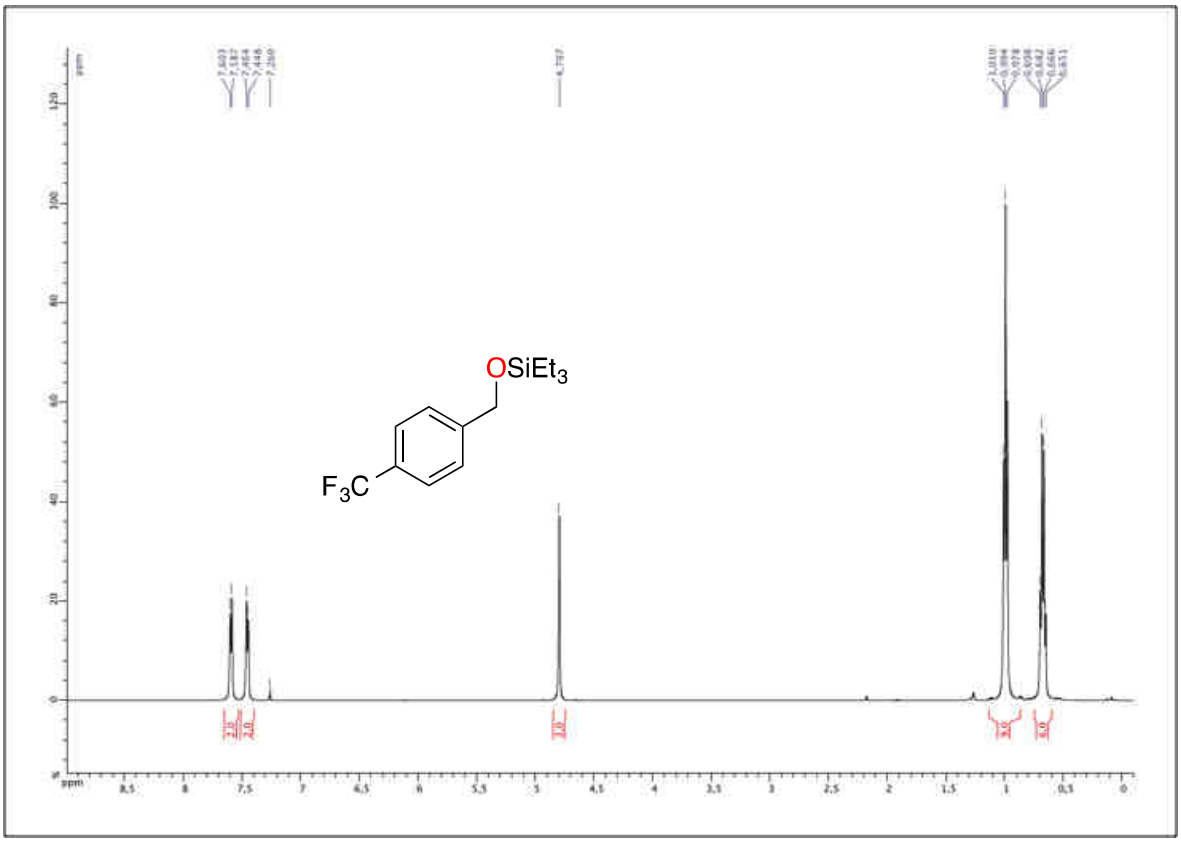


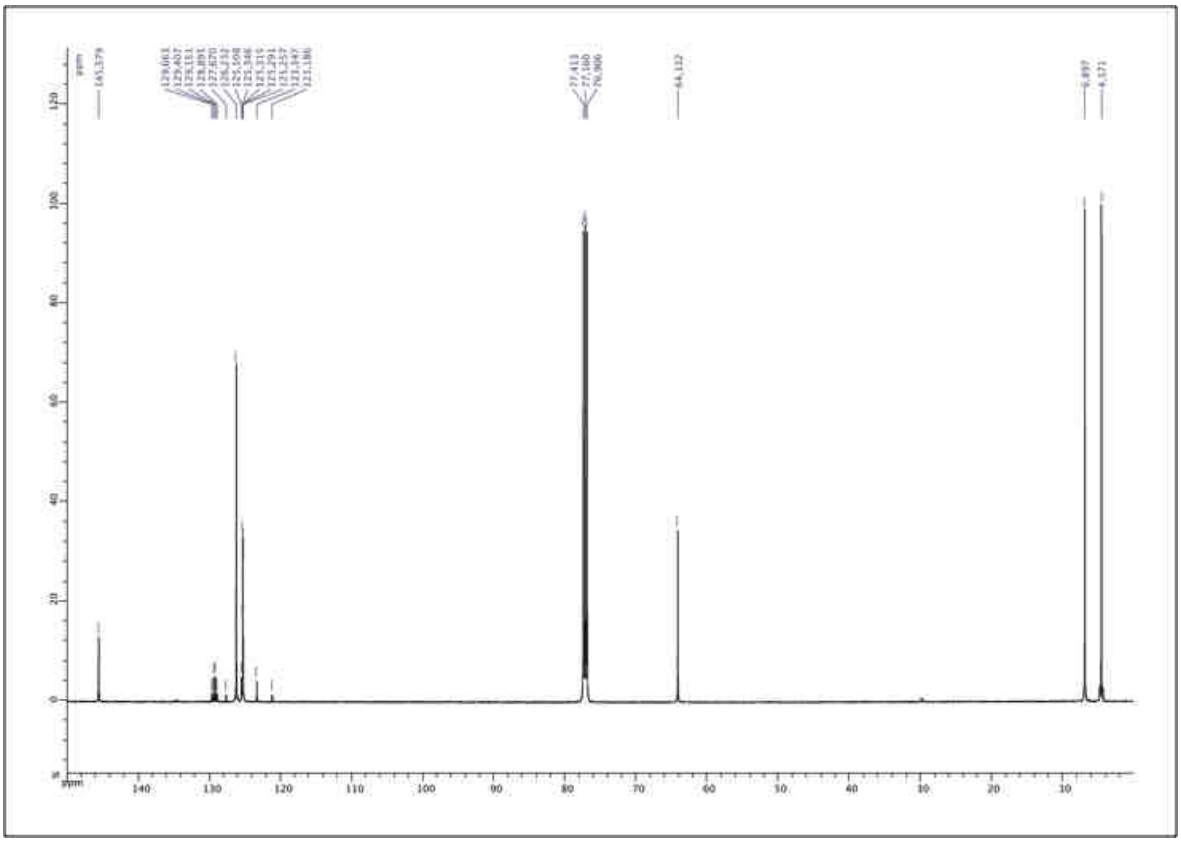
(2-bromobenzyloxy)triethylsilane (Table 5, entry 3):



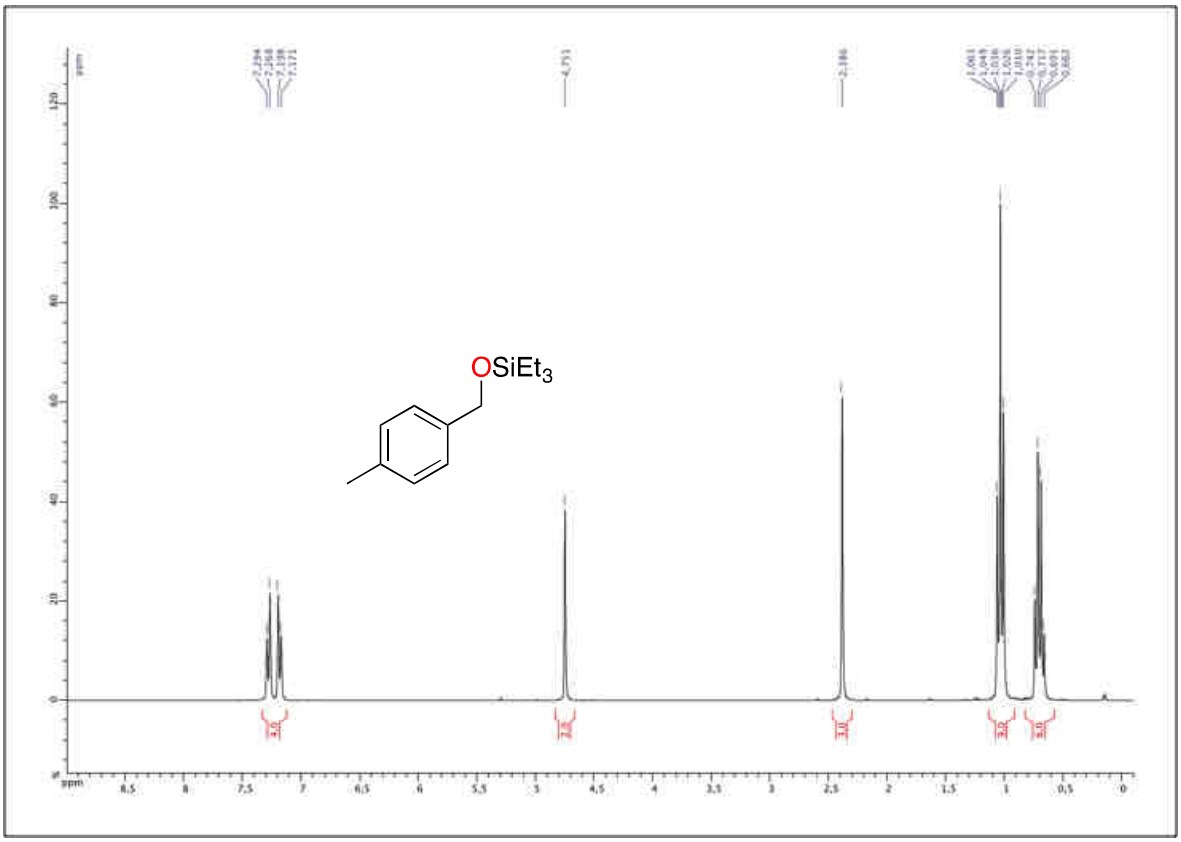


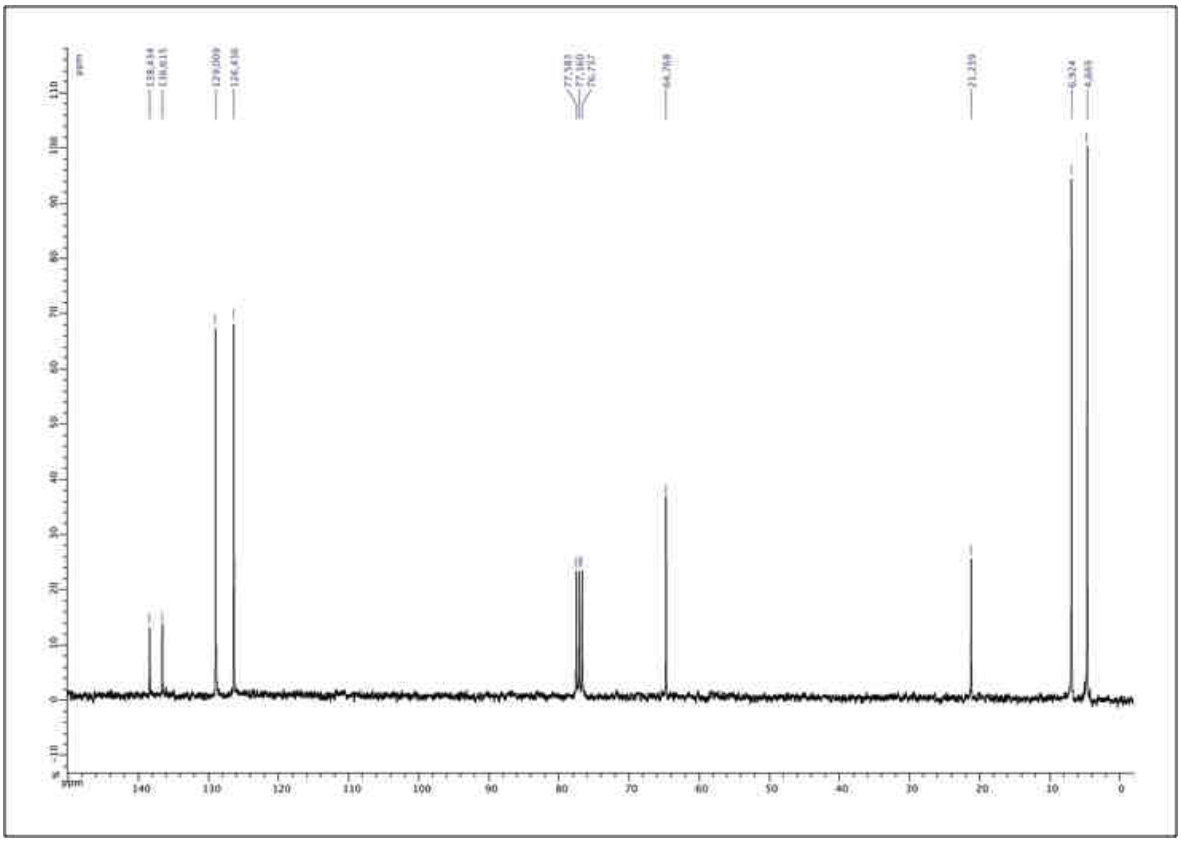
(4-trifluoromethylbenzyloxy)triethylsilane (Table 5, entry 4):



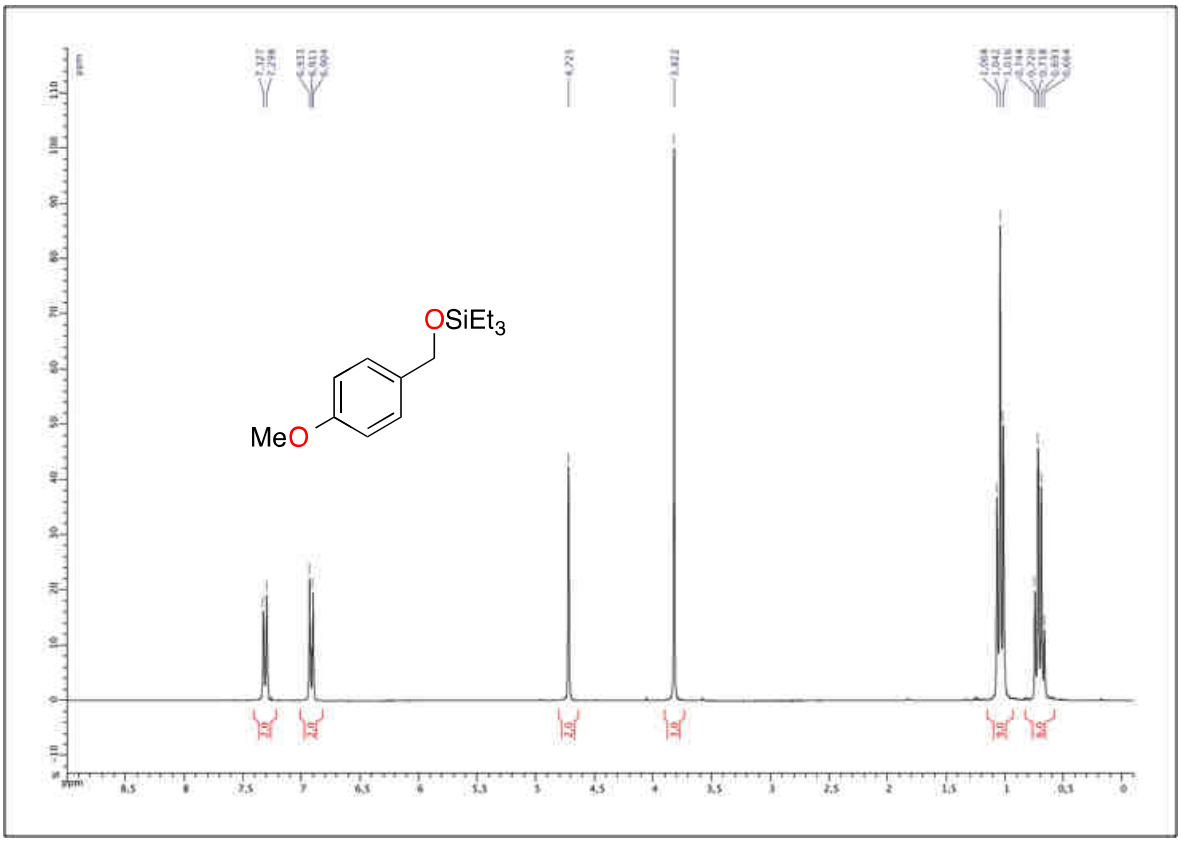


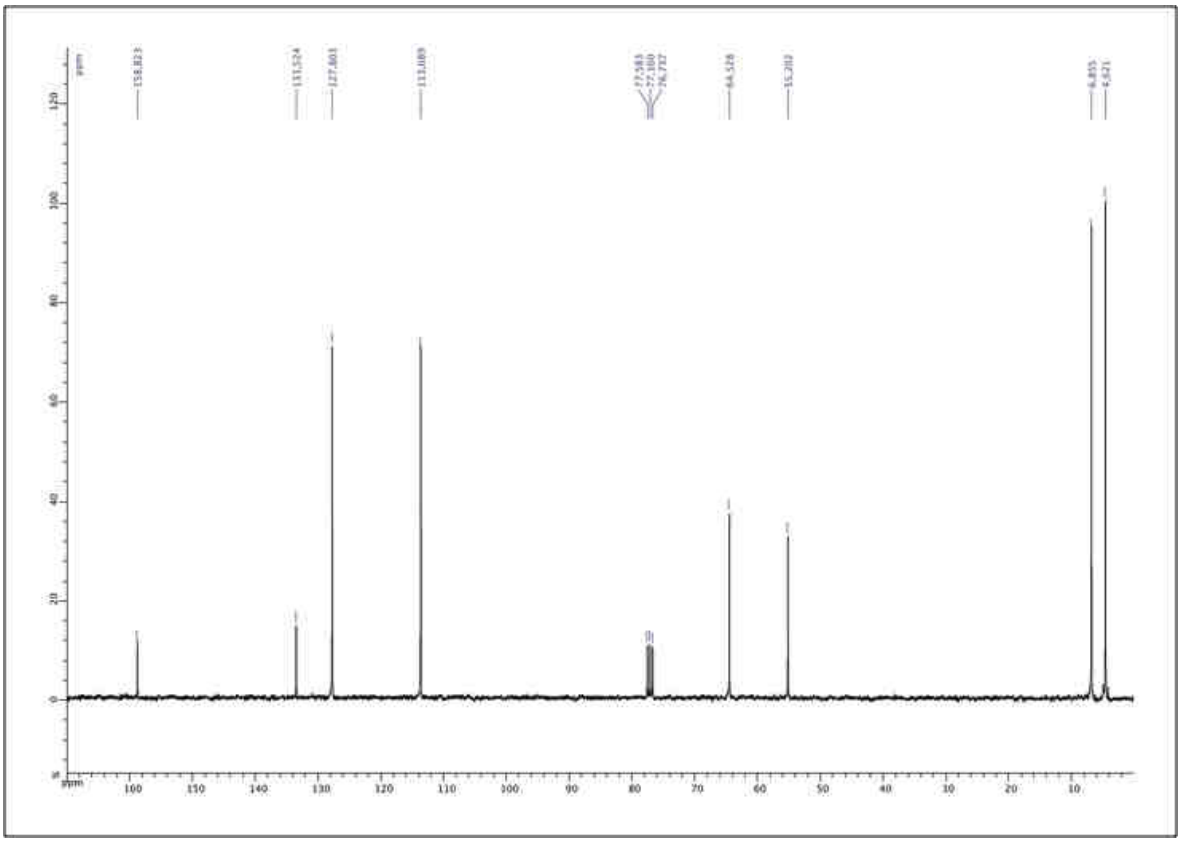
(4-methylbenzyloxy)triethylsilane (Table 5, entry 5):



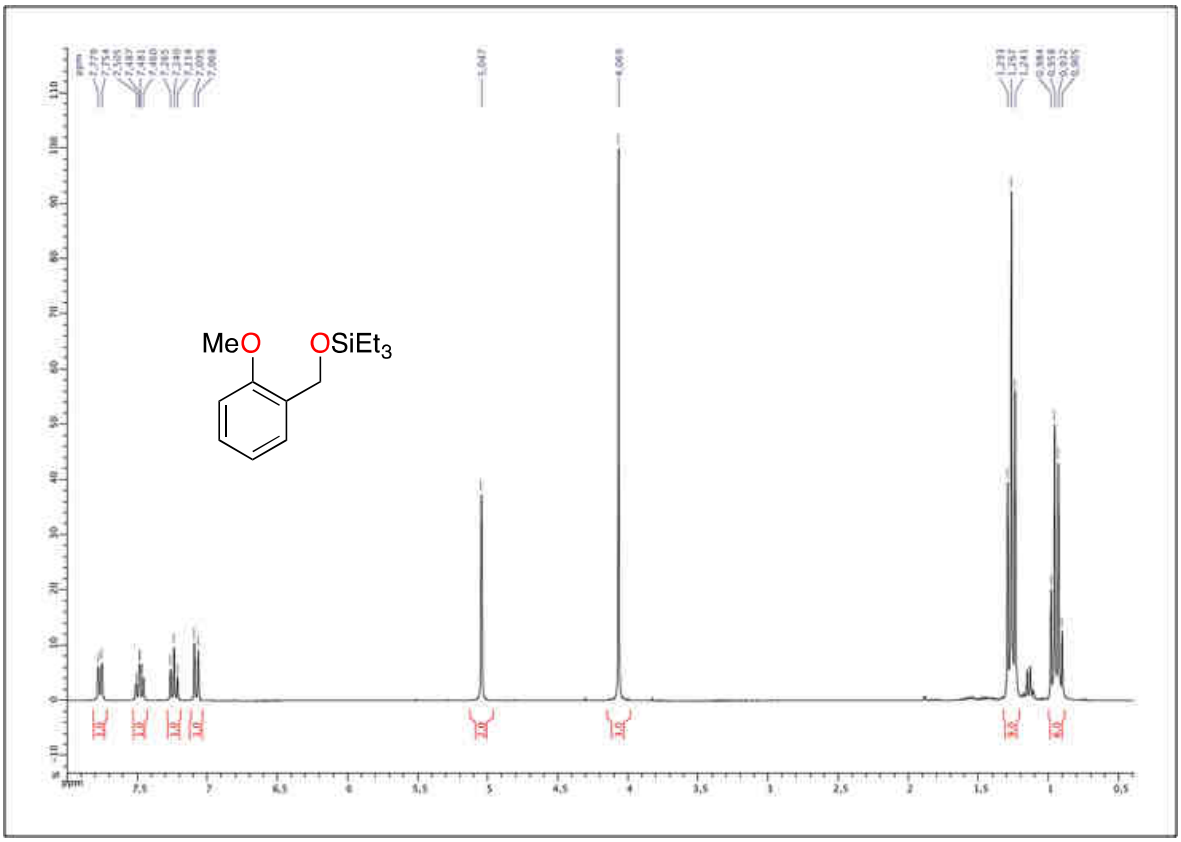


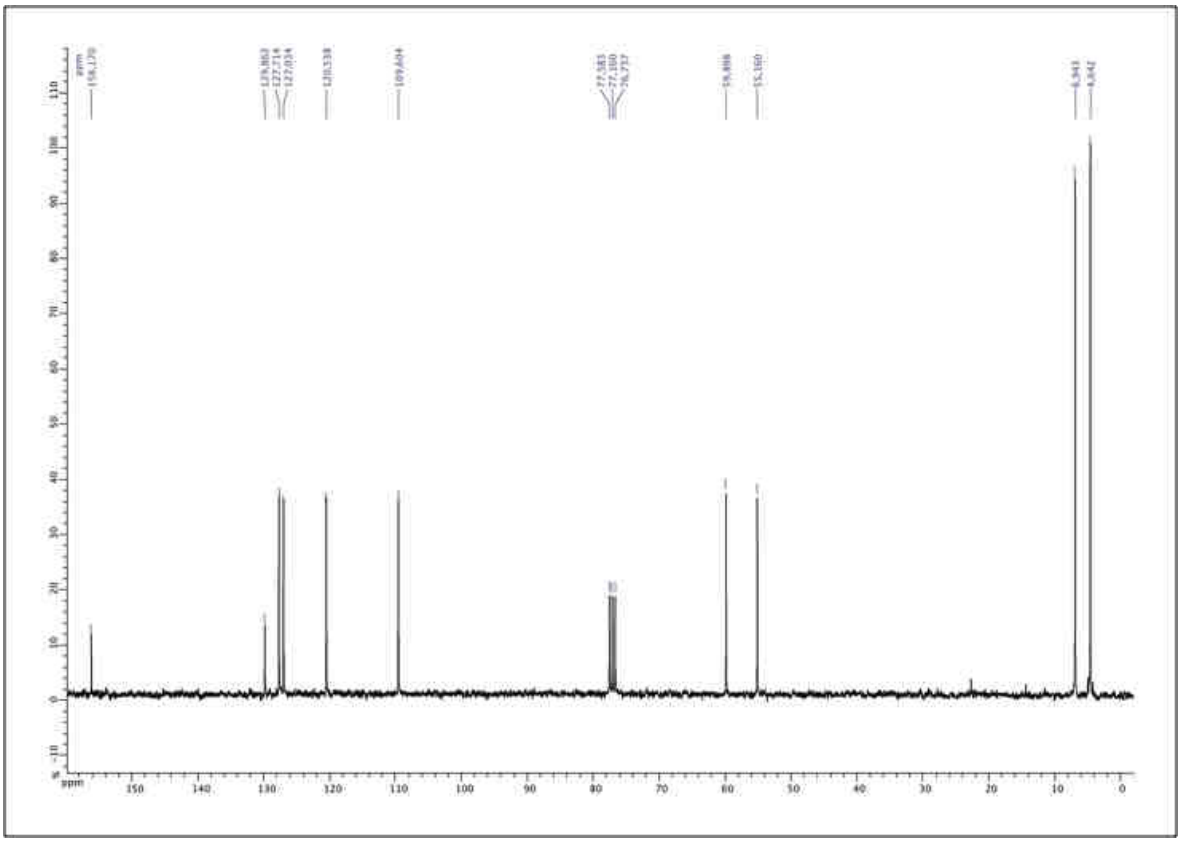
(4-methoxybenzyloxy)triethylsilane (Table 5, entry 6):





(2-methoxybenzyloxy)triethylsilane (Table 5, entry 7):





V - Notes and references

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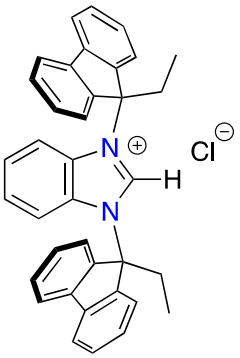

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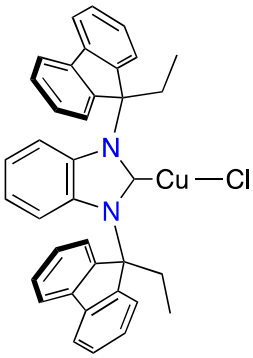

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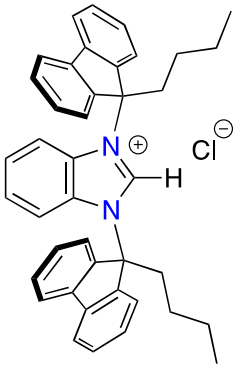

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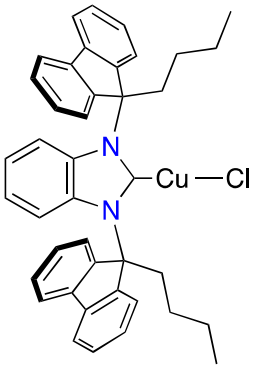

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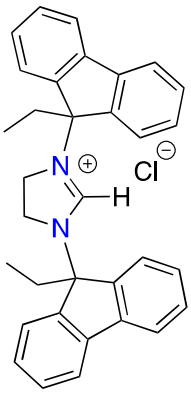

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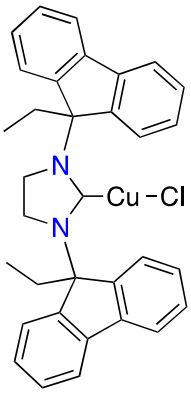

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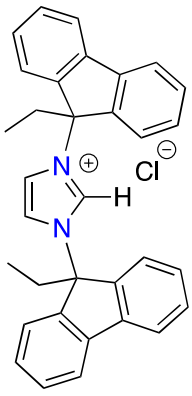

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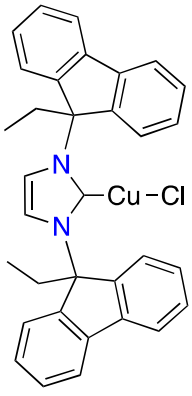

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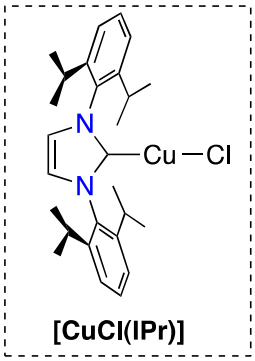

[CuCl(IPr)]

General conclusion and perspectives

This thesis deals with a series of new *N*-heterocyclic carbene ligands characterised by the presence of expanded 9-alkyl-9-fluorenyl substituents. Special focus has been put on the steric properties of these ligands, and their influence on catalytic reactions involving palladium and copper centres.

The introductory chapter gives a general overview of the beneficial impact of NHCs used in transition metal chemistry and organometallic catalysis.

In the first chapter, we have prepared a series of benzimidazolium salts disubstituted by large AF groups, starting from *ortho*-phenylenediamine. These were readily converted into PEPPSI palladium complexes. NMR and X-ray diffraction studies revealed that the flat fluorenylidene moiety orientates the alkyl groups towards the metal centre and because of its restricted rotational freedom makes the ligand bulkiness time independent. Thus, in these complexes the metal centre is permanently confined between the two alkyl groups, and thereby forms a monoligating clamp with the carbenic centre. The CH_2 groups close to the palladium ion give rise to anagostic (mainly electrostatic) C–H···Pd interactions. Catalytic tests revealed that the palladium complexes having 9-ethyl-9-fluorenyl groups are highly efficient in Suzuki–Miyaura cross-coupling reactions, their activity being equal or superior to the most commonly used PEPPSI catalysts, notably IPr, SIPr, and IMes.

This study was then extended (Chapter II) to analogues bearing two different AF groups ($Alkyl^1/Alkyl^2$ = Me/Et, Me/*n*-Pr, Me/*i*-Pr, Me/*n*-Bu, Me/Bn, Me/CH_2SMe). For their synthesis *N,N'*-bis(9*H*-fluoren-9-ylidene)benzene-1,2-diamine was succesively alkylated with two distinct nucleophiles. When reacted with $PdCl_2/K_2CO_3$, these benzimidazolium salts, except the one with the Me/CH_2SMe groups, were converted into the corresponding PEPPSI-type palladium complexes, the sulfur containing precursor leading to a ($S,C_{carbene},C_{alkyl}$) pincer complex resulting from metallation of the methyl group attached to the fluorenylidene moiety. It is likely that this metallation takes place after formation of a ($C_{carbene},S$) chelate, which positions the Me group of the 9-methyl-9-fluorenyl substituent trans to the sulfur atom, this strongly facilitating the CH activation process. Again NMR and X-ray diffraction studies revealed that the sulfur-free carbenes behave as clamp-like ligands, the resulting metal confinement arising from a combination of the orientational properties of the fluorenylidene moieties that push the alkyl groups towards the metal

centre and attractive anagostic interactions involving CH(fluorenyl) groups. The corresponding complexes were assessed in Suzuki–Miyaura cross-coupling reactions. Like their symmetrical analogues, they displayed high activity in the coupling of phenylboronic acid with *para*-tolyl chloride, but their performance remained slightly inferior to that of the related, symmetrical Et/Et complex described in Chapter I.

In Chapter III, we have described additional 9-ethyl-9-fluorenyl (EF)-substituted imidazolium and imidazolinium salts. They contain heterocyclic rings smaller than those of the previous chapters, and therefore enable rotation of the substituent about the N–C(EF) bond. The key intermediate of their syntheses is the new primary amine 9-ethyl-9-fluorenylamine, which was prepared in 75% yield. Both salts were converted into PEPPSI-type palladium complexes. Despite easy rotation of the EF moieties about the C-N bond in their cationic precursors, the carbene ligands of these Pd(II)-complexes both behave as rigid clamps in solution and in the solid state, anagostic CH_2···Pd interactions impeding the substituents dynamics. Such ligands have been termed "bimodal pincers" as they combine a strongly coordinating atom (in our case a carbenic C atom) and two other donor atoms (CH atoms) able to interact in a non-covalent manner with the complexed metal ion.

The imidazolylidene chlorosilver complex was also prepared. In this case, unlike in the above two palladium complexes, there was no indication for anagostic interactions between the CH_2 protons and the silver atom. In the solid state, however, this complex adopts a remarkable "open sandwich" structure, with the two alkylfluorenylidene planes η^2-bonded to the silver, this constituting a further bimodal pincer-type bonding mode of this ligand class.

The two palladium complexes were assessed in Suzuki-Miyaura cross-coupling reactions. Only the imidazolylidene complex displayed high activity towards unencumbered aryl chlorides, its efficiency being comparable to that of the previously reported benzimidazolylidene Et/Et analogue.

In chapter IV, an *N*-heterocyclic carbene substituted by two expanded EF groups was shown to bind an AuCl unit in an unusual manner, namely with the Au–X rod sitting out of the plane defined by the central imidazolium unit. As shown by X-ray studies and DFT calculations, the observed large pitch angle (21°) arises from an easy displacement of the gold(I) atom out of the carbene lone pair axis, combined with the stabilisation provided by weak CH···Au interactions involving aliphatic and aromatic H atoms of the EF

substituents. A general belief until now was that tilt angles in NHC complexes arise only from steric effects.

Chapter V concerns the synthesis of copper complexes bearing AF-substituted NHC ligands. These were tested in the hydrosylilation of functionalized and/or sterically demanding ketones and aldehydes. The runs, carried out with triethylsilane as hydride source, were best achieved with the imidazolylidene copper complex in which the two substituents can freely rotate about their corresponding N-C bonds. The remarkable stability of the active species, which surpasses that of previously reported CuCl(imidazol-2-ylidene) catalysts relies on the ability of the NHC to protect the copper centre during the catalytic cycle by forming sandwich-like intermediates, but also on its steric flexilbility enabling coordination of encumbered substrates. TONs up to 1000 were reached. These studies were undertaken with the aim of developing new, cost-effective catalysts, with the hope to move away from the expensive Rh- or Ru-catalyst, which are traditionally employed for these reactions.

Future work in this area may include:

- the development of chiral NHC ligands displaying embracing properties similar to those described in this thesis, anticipating that the presence of stereogenic centres in the N-substituents will result in high stereoselectivity.

- the use of the gold complexes described in chapter IV in catalytic reactions requiring specific steric control.

- the use of "sophisticated", unsymmetrical NHCs in olefin metathesis, this possibly enabling an increased stereocontrol of the resulting olefins.

Matthieu TECI

Chimie de coordination de carbènes *N*-hétérocycliques substitués par des groupements alkylfluorényles: interactions faibles, effets stériques, catalyse.

Résumé

Cette thèse porte sur l'étude de nouveaux carbènes *N*-hétérocycliques dont les atomes d'azote sont substitués par des groupes étendus alkylfluorényle (AF). Les caractéristiques principales de ces coordinats sont leur fort encombrement stérique, la modularité de ce dernier, et la proximité créée dans les complexes correspondants entre les groupes AF et le métal coordiné.

La première partie de ce travail décrit la synthèse et la caractérisation d'un ensemble de sels d'azolium, précurseurs de cette nouvelle famille de NHCs. Ces composés ont d'abord été utilisés pour la préparation de complexes de palladium de type "Pd-PEPPSI-NHC", complexes qui se sont avérés très efficaces en couplage de Suzuki-Miyaura entre acides arylboroniques et chlorures d'aryle *para*-substitués. Des études structurales et RMN ont montré que dans leur complexes, les NHC formés agissent comme des pinces bimodales, c'est-à-dire combinant une interaction covalente (la liaison M-Carbène) et deux interactions non-covalentes impliquant les groupes AF.

Dans certains complexes linéaires de l'or(I) et du cuivre (I), ces interactions faibles entre le métal et des liaisons C-H alentours ont permis la coordination non-optimale du centre métallique qui, à l'état solide, se retrouve hors de l'axe formé par le doublet non liant du carbène.

Enfin, un complexe de type CuCl(NHC) dont l'encombrement stérique est variable a été préparé. Il s'est avéré être un excellent catalyseur d'hydrosilylation d'aldéhydes et de cétones. A ce jour, il possède l'une des plus grandes activité et longévité (TONs jusqu'à 1000) pour ce type de complexe.

Summary

This thesis deals with a series of *N*-heterocyclic carbene ligands (NHCs) in which the N atoms bear expanded alkylfluorenyl (AF) substituents. Special focus has been put on the steric properties of these new ligands, as well as their influence on catalytic reactions involving Pd and Cu centres.

The first part of this work describes the synthesis of a series of AF-substituted azolium salts suitable for the preparation of palladium PEPPSI-NHC complexes. These turned out to be very active in Suzuki-Miyaura cross-coupling reactions between *para*-substituted aryl chlorides and arylboronic acids. Structural and NMR studies revealed that in all the complexes, the NHC ligand displays a "bimodal pincer" type behaviour, that is functions as a tridentate ligand bound to the metal through both covalent and non covalent bonds, the former involving the carbenic C atom, the latter C*H* atoms of the wingtips.

In the second part of the study, a series of linear [AuCl(NHC)] and [CuCl(NHC)] complexes were prepared. In some of them were observed weak CH•••M interactions involving the alkyl chains fixing the metal centre in a position below the NHC ring plane. This leads to an unusual coordination of the ligand able to freeze out the movement of the metal centre during its natural oscillation about the M-carbene axis.

In the last part of this thesis, one of the [CuCl(NHC)] complexes synthesised was shown to be highly efficient in the catalytic hydrosilylation of functionalised/sterically crowded aldehydes and ketones (TONs up to 1000). Its high stability was attributed to the variable encumbrance of the ligand.