Formation of Borane Adducts and Some Complexes Starting from N-Heterocyclic Carbenes

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(Dissertation)

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M. Liu, Jan C. Namyslo, Nieger, M., A. Schmidt, From betaines to anionic N-heterocyclic carbenes. Borane, gold, rhodium, and nickel complexes starting from an imidazoliumphenolate and its carbene tautomer. *Beilstein J. Org. Chem.* **2016**, *12*, 2673-2681.

M. Liu, M. Nieger, E. G. Hübner, A. Schmidt, Formation of N-Heterocyclic Carbenes by Tautomerization of Mesomeric Betaines: Cyclic-boron adducts and palladium complexes from 2-(imidazolium-1-yl)phenolates. *Chem. Eur. J.* **2016**, *22*, 5416-5424. (hot paper)

M. Liu, M. Nieger, A. Schmidt, Mesomeric betaine – N-heterocyclic carbene interconversions of 1,2,4-triazolium-phenolates. Sulfur, selenium, and borane adduct formation. *Chem. Commun.* **2015**, *51*, 477-479.

N. Pidlypnyi, S. Wolf, M. Liu, K. Rissanen, M. Nieger, A. Schmidt, N-Heterocyclic carbenes from ylides of indolyl-imidazolium, azaindolyl-imidazolium, and indolyl-triazolium salts, and their borane adducts. *Tetrahedron* **2014**, *70*, 8672-8680.

Weitere Veröffentlichung:

A. Schmidt, M. Liu, Recent advances in the chemistry of acridines. *Adv. Heterocycl. Chem.* **2015**, *115*, 288-353.

List of Abbreviations

abs	absolute
AcOH	acetic acid
AH	alternant hydrocarbon
*a*NHC	abnormal N-heterocyclic carbene
9-BBN	9-borabicyclo[3.3.1]nonane
Bn	benzyl
Bu	butyl
CCMB	cross conjugated mesomeric betaine
CD_3OD	deuterated methanol
CMB	conjugated mesomeric betaine
COD	1,5-cyclooctadiene
Dipp	2,6-diisopropylphenyl
DMF	dimethylformamide
DMSO	dimethylsulfoxide
EI-MS	electron impact mass spectrometry
Et	ethyl
GC-MC	gas chromatography mass spectrometry
HR	high resolution
Hz	Hertz
IAd	1,3-di(adamantyl)imidazol-2-ylidene
IR	infrared
J	coupling constant
m	multiplett
MB	mesomeric betaine
Mes	mesitylene
MS	mass spectrometry
mp	melting point
n	normal
NHC	*N*-heterocyclic Carbene
NMR	nuclear magnetic resonance

h	hour
PCCMB	pseudo-cross-conjugated mesomeric betaine
ppm	parts per million (NMR spectroscopy)
*r*NHC	remote N-heterocyclic carbene
t	triplet (NMR spectroscopy)
*t*Bu	*tert*-butyl
THF	tetrahydrofuran

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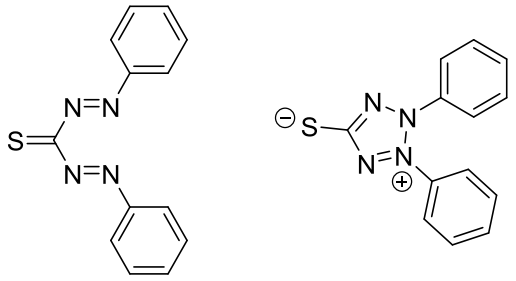
1 General introduction

1.1 Mesomeric betaines

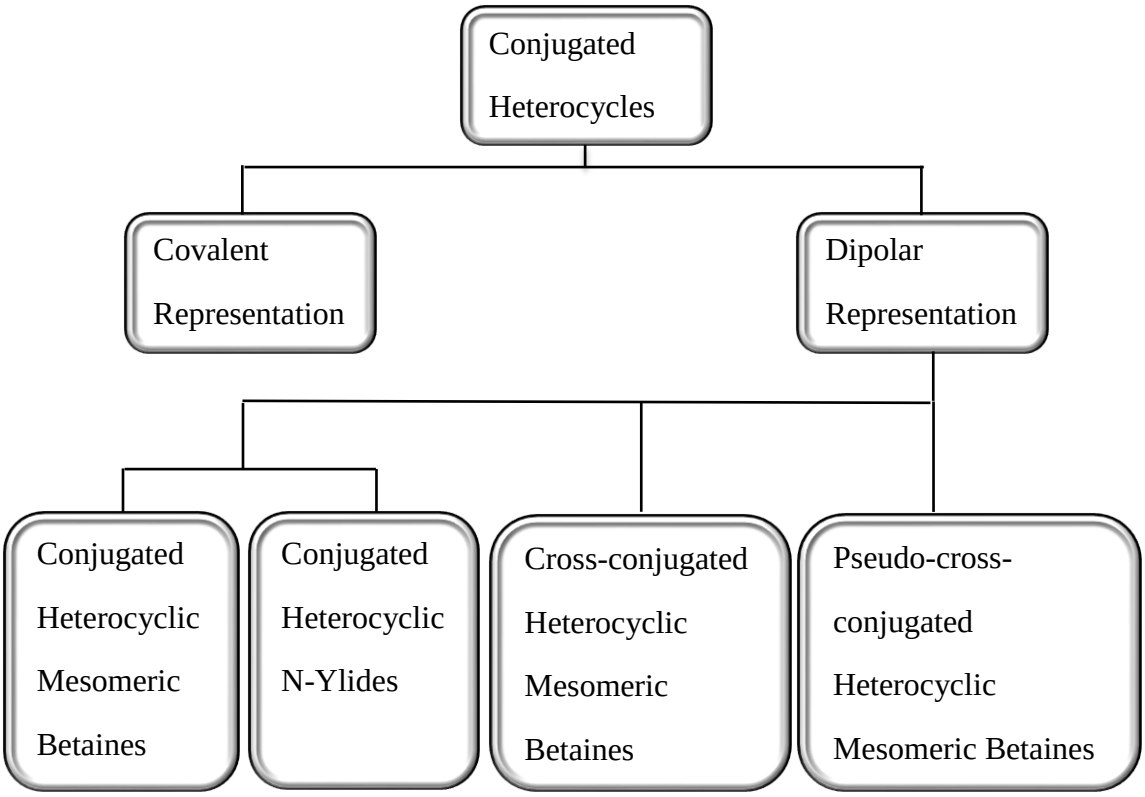
Mesomeric betaines are neutral conjugated molecules with delocalized positive and negative charges within a common π-electron system. They are divided into two types: (i) acyclic mesomeric betaines and (ii) heterocyclic mesomeric betaines.[1] The first heterocyclic mesomeric betaine **1B** was found by Fischer and Besthorn in 1882,[2] however, at that time instead of **1B** structure **1A** was assumed. In 1969 the structure has been corrected to **1B** (Scheme 1).[3]



1A **1B**

Scheme 1: First heterocyclic mesomeric betaine was unknowingly prepared by Fischer and Besthorn.

In 1985 a first comprehensive classification of mesomeric betaines was presented by Ollis, Stanford, and Ramsden. Based on structures and theoretically predictable connections mesomeric betaines were divided into four main classes[1](Scheme 2):



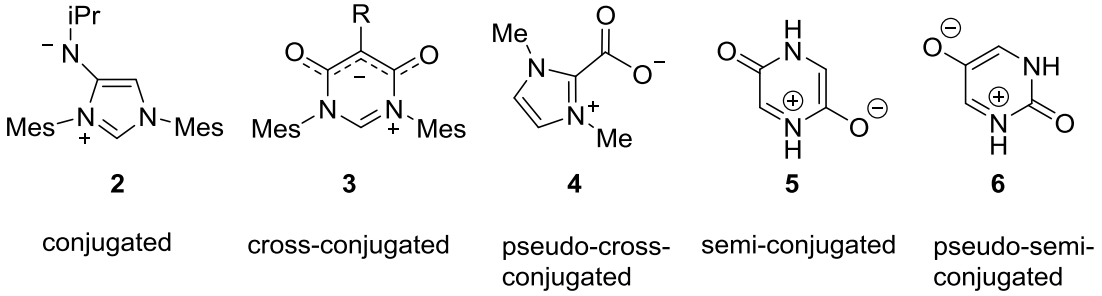
Scheme 2: Classification of mesomeric betaines according to a theory published in 1985.

The classification of heterocyclic mesomeric betaines was further expanded by Ramsden in 2013[4] and 2014[5]. Thereafter heterocyclic mesomeric betaines have been divided into five major classes.

The five major classes are:

1. conjugated heterocyclic mesomeric betaines (CMB),
2. cross-conjugated heterocyclic mesomeric betaines (CCMB),
3. pseudo-cross-conjugated heterocyclic mesomeric betaines (PCCMB),
4. semi-conjugated heterocyclic mesomeric betaines,
5. pseudo-semi-conjugated heterocyclic mesomeric betaines.

The five classes of HMBs are represented by structures **2 - 6** in Scheme 3. Imidazolium-4-aminide **2**,[6] pyrimidinium-4-olate **3**,[7,8] imidazolium-2-carboxylate **4**,[9-16] 5-oxo-4,5-dihydropyrazinium-2-olate **5**[5] and 2-oxo-2,3-dihydropyrimidinium-5-olate **6**[5] are examples of conjugated mesomeric betaines (CMB), cross-conjugated mesomeric betaines (CCMB), pseudo-cross-conjugated mesomeric betaines (PCCMB), semi-conjugated and pseudo-semi-conjugated mesomeric betaines, respectively.



Scheme 3: Examples of the five classes of heterocyclic mesomeric betaines (HMB).

In 2013 Ramsden has formulated the differentiation between CMBs and CCMBs according to a connectivity approach (Figure 1)[4]: CMBs are molecules with both alternant hydrocarbon (AH) fragments connected to one heteroatom at a starred position (i.e., two stars at the bottom of the connectivity matrix in structure **2**). On the other hand, in CCMB both heteroatoms (i.e., N^1 and N^2 between the positive and negative parts in structure **3**) are connected to one of the odd alternant hydrocarbon (AH) fragments at only inactive positions (i.e., only zeros in the connectivity matrix in structure **3**).

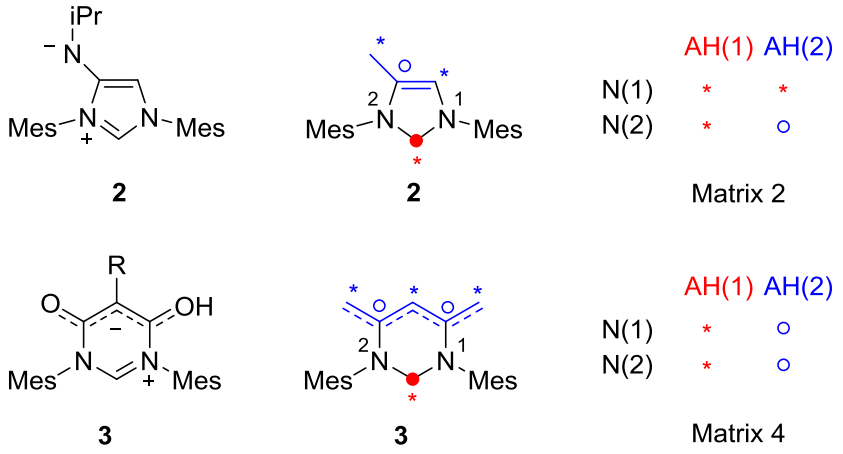
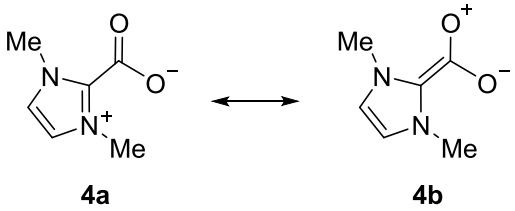


Figure 1: Connectivity matrices of CMB and CCMB.

CCMB are set apart from PCCMB in such a way that in the latter mentioned species positive and negative charges can be located in the same alternant fragments (e.g., **4a** and **4b**) (Scheme 4) when electron-sextet structures without internal octet stabilization are taken into consideration. These serve as marker to identify the class of compound, however, they do not contribute to the overall electronic structure of the molecule. Nevertheless, PCCMB have their own chemistry which differs considerably from those of CCMB and CCMB.



Scheme 4: Examples of pseudo-cross-conjugated heterocyclic mesomeric betaines (PCCMB).

Semi-conjugated and pseudo-semi-conjugated mesomeric were first mentioned in 2013 by Ramsden.[4] The existence of these two compound classes have been predicted on the basis of theoretical analyses of structure increments. They have very scarcely been examined to date and still await syntheses and examinations of their properties.

1.2 N-heterocyclic carbenes

The first stable nucleophilic carbene was isolated from (trimethylsilyl) [bis(diisopropyl-amino)phosphino]diazomethane by Bertrand et al. in 1988.[17] In 1991 the first *N*-heterocyclic carbene (NHC) 1,3-di(adamantyl)imidazol-2-ylidene (IAd, compound labelled **7**) was synthesized via deprotonation of 1,3-di-1-adamantylimidazolium chloride with sodium hydride by Arduengo et al. (Figure 2).[18] Since then, NHCs have attracted considerable interest, especially as ligands of catalysts.[19,20] Aside reactions with metals and metalloids in versatile approaches,[21-24] NHCs have proven to be useful in metal-complexes, *p*-block elements and as organocatalysts,[25] i.e. palladium complexes for coupling reaction catalysis.[26]

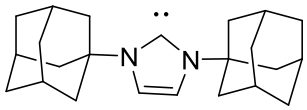


Figure 2: The first *N*-heterocyclic carbene **7**.

Based on two reviews by Albrecht[27] and Schmidt[28], *normal* NHC's, *abnormal* NHC's[29-35] and *remote* NHC's[27,36-40] conception and properties have been described. According to Albrecht's review, imidazol-2-ylide **A** is defined as a *normal* NHC (*n*NHC) due to neutral electron sextet structures (Figure 3) and so are carbenes **D**, **G**, and **K**.[27] As already mentioned the first example of *n*NHCs was prepared by Arduengo et al. in 1991.[41] Carbenes **B**, **C**, **E**, and **I** are defined as abnormal NHCs (*a*NHC) due to dipolar forms in the molecules that are not located in the same bond. The first example of *a*NHC was prepared in 2001.[31] The carbenes **E**, **F**, **H** and **I** belong to remote NHCs (*r*NHC), because there is no heteroatom located adjacent to the carbene carbon. The first example of *r*NHC was reported by the Raubenheimer group in 2006.[42]

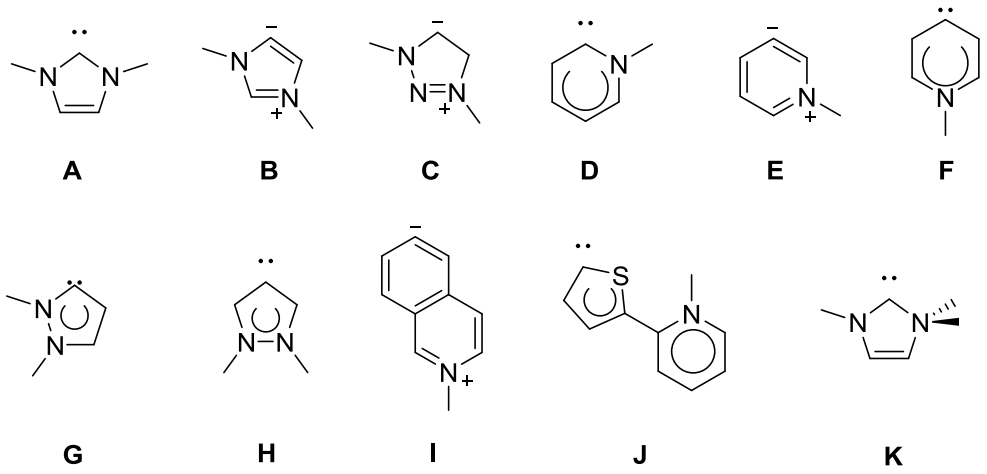


Figure 3: Examples of *N*-heterocyclic carbenes (*n*NHC, *a*NHC, *r*NHC).

Three different types of drawing complexes **9**-**11** were described recently (Figure 4). Actually, they are identical. In my dissertation I prefer using the formula **10**, because it emphasizes the aromatic character of the imidazol moiety. The first pyridinylidene-type *n*NHC and *r*NHC complexes of Ni(II) were reported in 2006.[43] The pyridinylidene-type *n*NHC complexes of gold and platinum were obtained in 1994 and 2004.[44,45] The first pyrazole-type *r*NHC **8** complexes of palladium(II) were reported by Huynh group in 2007 (Figure 4).[46] Recently new *r*NHC complexes were presented such as rhodium, gold and nickel.[37-39,47] *r*NHC complexes have a wide range of utilization i.e. as catalysts of C-C coupling reactions with complexes of palladium(II).[48] Other *n*NHC complexes have also been described. As example, copper(I) complexes of **9**[49] have served as starting materials for transition-metal complexes.[50] Furthermore silver, gold and rhodium complexes of **10** and **11** have been obtained in mono- and dimer forms.[51-58] Nickel complexes of **12** have been prepared by heating triazolium salts with anhydrous nickel chloride.[59] NHCs **11** and **13** were successfully used in reactions with metalloids (Al, Si) to give chelating complexes.[60,61] Some *n*NHC complexes have proven use as catalysts in coupling reactions of ArMgX with aryl chlorides, fluorides, and methyl ethers.[62] *n*NHC complexes also have applications.[63] The first *a*NHC complex of **14** was reported by the reaction pyridine substituted imidazolium salt with iridium compounds.[31] Some other *a*NHC complexes were also reported recently.[29,32,33,35,64-68]

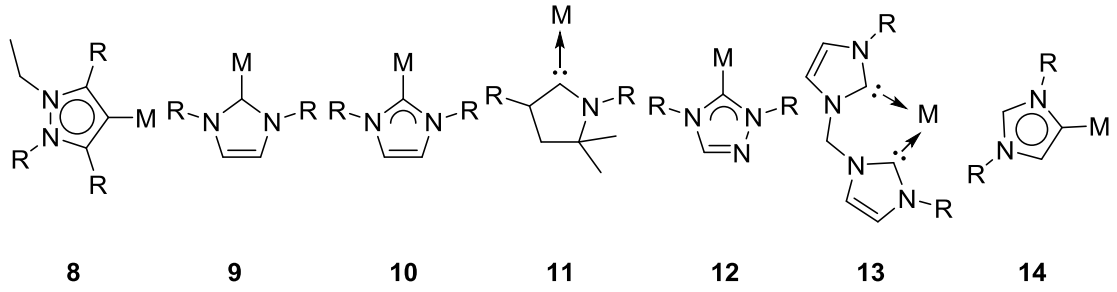


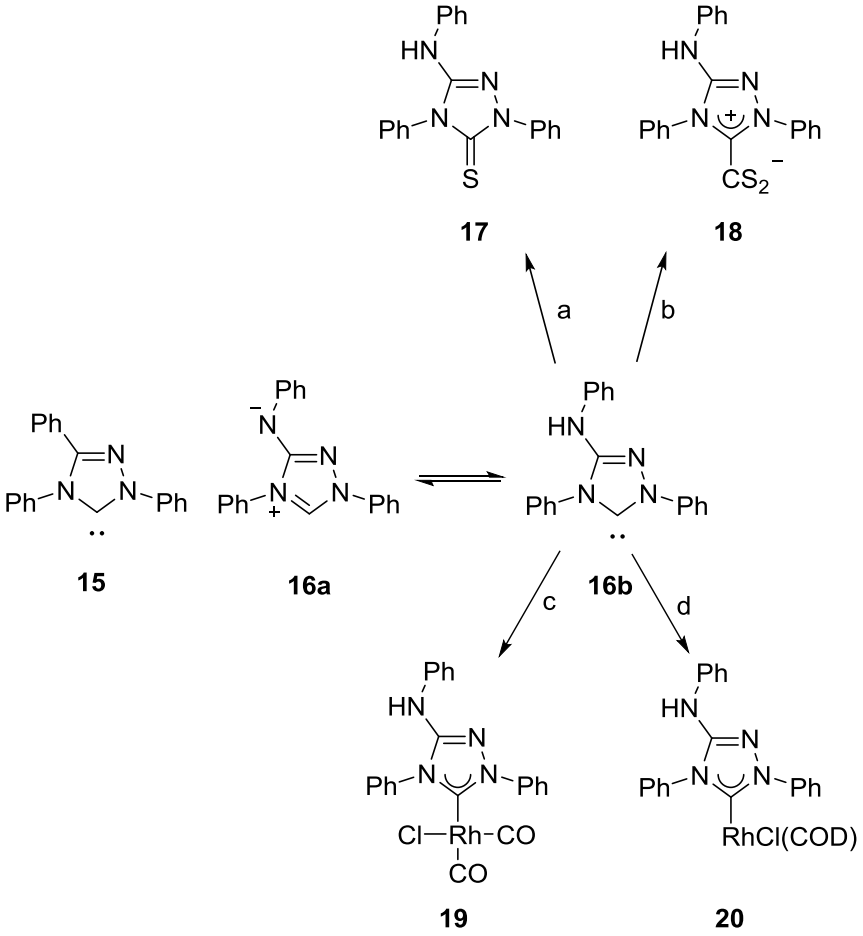
Figure 4: Examples of metal complexes of *N*-heterocyclic carbenes.

1.3 Area of overlap between mesomeric betaines and N-heterocyclic carbenes

According to the aforementioned classification published in 1985, mesomeric betaines have been divided into four major classes: CMBs, ylides, CCMBs, and PCCMBs. Three subclasses of *N*-heterocyclic carbenes have been mentioned before, *n*NHC, *a*NHC and *r*NHC. In the following sections, the area of overlap between mesomeric betaines and *N*-heterocyclic carbenes will be discussed.[69]

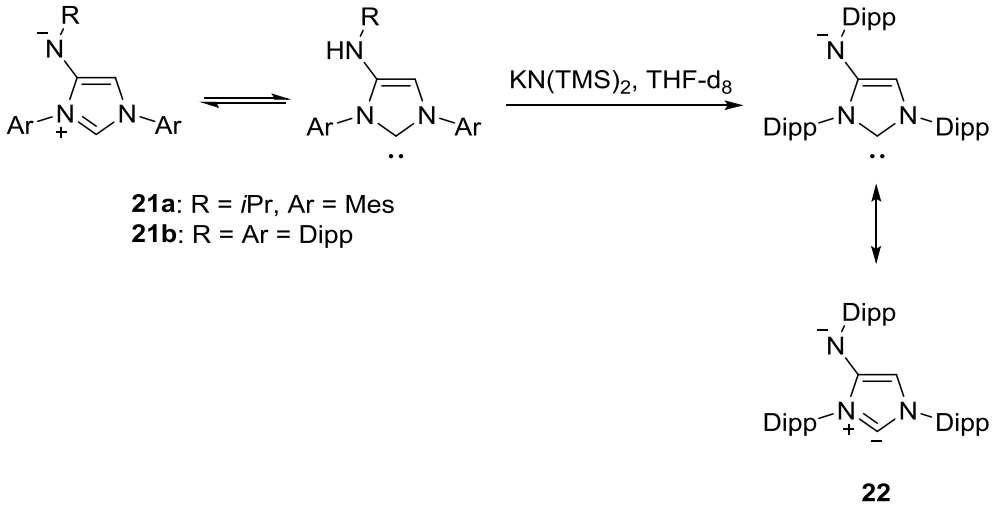
1.3.1 Interconversions of *normal* (*n*NHC) and anionic N-heterocyclic carbenes and mesomeric betaines (CMB)

After 1,2,4-triazol-5-ylidene **15**[70] was described, Nitron **16** has been reported to be in tautomeric equilibrium with its N-heterocyclic carbene which undergoes characteristic reactions (Scheme 5).[71,72] As an example, Nitron **16** is in equilibrium with its corresponding *N*-heterocyclic carbene [a *normal N*-heterocyclic carbene (*n*NHC)] and can generate the thione **17**, the triazolium-dithiocarboxylate **18** and the rhodium complexes **19**, **20**.[72] Product **18** was obtained by conversion of a tautomeric *normal N*-heterocyclic carbene to a pseudo-cross-conjugated mesomeric betaine (PCCMB).



Scheme 5: Examples of a tautomeric equilibrium of conjugated mesomeric betaine **16a** and its corresponding *normal* *N*-heterocyclic carbene (*n*NHC) **16b** and, additionally, known carbene trapping reactions. The trapping reactions were performed as follows: a) S_8, THF, room temperature; b) CS_2, THF, reflux; c) [{Rh(μ-Cl)$(CO)_2$}$_2$], dichloromethane, room temperature; d) [{Rh(μ-Cl)(COD)}$_2$], THF, room temperature.

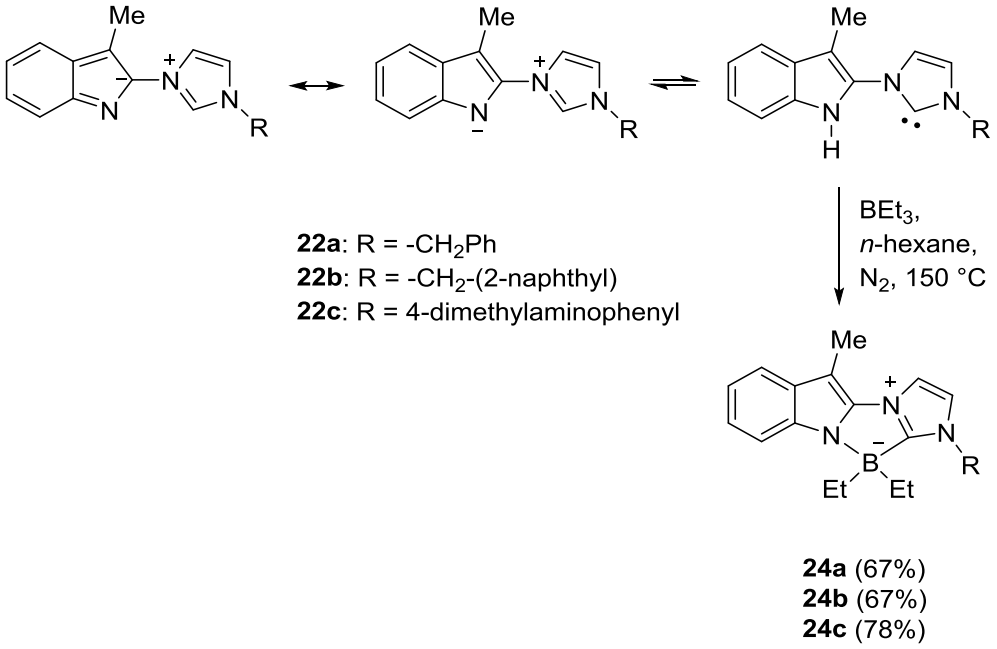
The conjugated mesomeric betaine **21a** is also in equilibrium with its normal *N*-heterocyclic carbene which can be trapped as a pseudo-cross-conjugated mesomeric betaine (PCCMB) with CS_2 (Scheme 6).[6] Additionally, the anionic *N*-heterocyclic carbene **22** was successfully obtained by deprotonation of **21b**.[73] The $C_{carbene}$ signal of **22** can be detected at δ = 202.3 ppm in the ^{13}C NMR spectrum.



Scheme 6: Formation of an anionic *N*-heterocyclic carbene.

1.3.2 Interconversions of *normal* N-heterocyclic carbenes (*n*NHC) and ylides

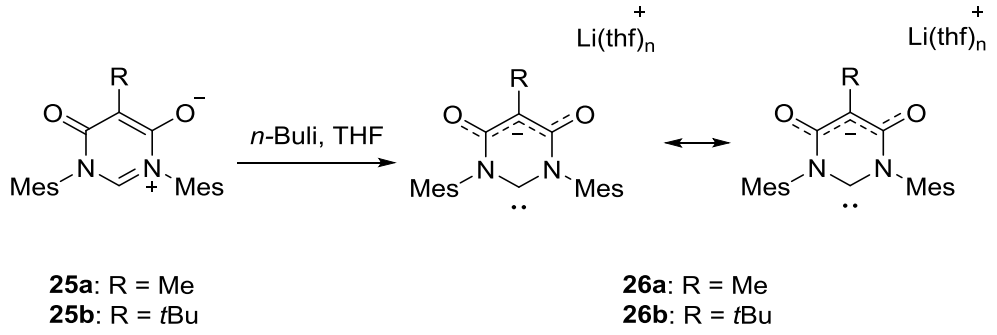
Not many samples of interconversions of *n*NHC and ylides are known. However, Schmidt et al. reported an example which is shown in Scheme 7.[74] The ylides **23a-c** are in tautomeric equilibrium with their normal *N*-heterocyclic carbenes which were trapped as borane adducts **24a-c** in satisfactory yields.



Scheme 7: Samples of interconversions of *normal N*-heterocyclic carbenes (*n*NHC) and ylides.

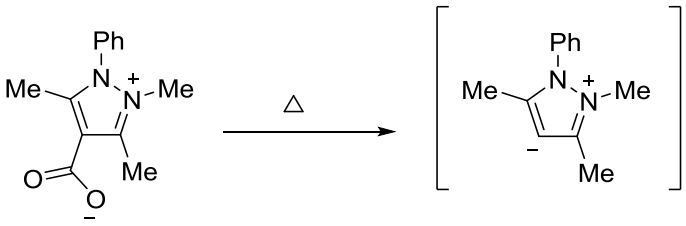
1.3.3 Interconversions of *normal*, *abnormal*, and *remote N*-heterocyclic carbenes (*n*NHC, *a*NHC, *r*NHC) and cross-conjugated heterocyclic mesomeric betaines (CCMB)

The anionic *N*-heterocyclic carbene **26a** was isolated by deprotonation of **25a** with *n*-BuLi or KHMDS in quantitative yields (Scheme 8).[7,8] The rhodium complexes were obtained by reaction of the carbenes with $[RhCl(1,5\text{-}COD)]_2$. The silver and iron complexes were both formed from mesomeric betaines with KHDMS and $CpFe(CO)_2I$ and $Ph_3PAgOTf$.



Scheme 8: Examples of interconversions of *normal N*-heterocyclic carbenes (*n*NHC) and cross-conjugated heterocyclic mesomeric betaines (CCMB).

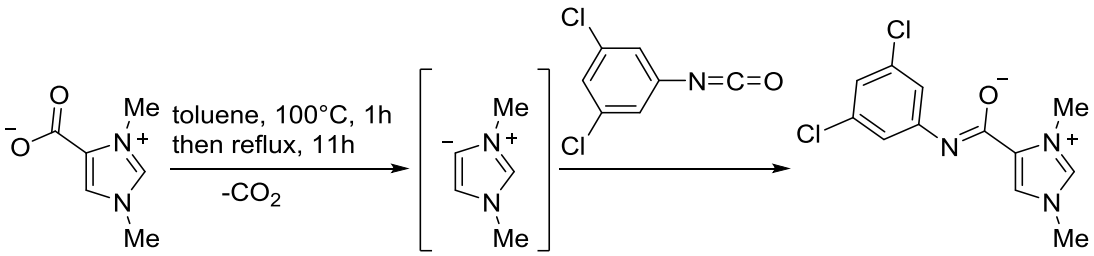
Deprotonation of the cross-conjugated heterocyclic mesomeric betaines (CCMB) **27** to the *remote N*-heterocyclic carbene **28** was possible under harsh conditions (Scheme 9).[75] The carbene **27** was detected as sodium and lithium adducts by mass spectrometry.



27 **28**

Scheme 9: Samples of interconversions of *remote N*-heterocyclic carbenes (*r*NHC) and cross-conjugated heterocyclic mesomeric betaines (CCMB).

The *abnormal N*-heterocyclic carbene **30**, generated by decarboxylation of betaine **29**, was observed in high resolution electrospray ionization mass spectrometry and reacted with 3,5-dichlorophenylisocyanate to form the betaine **31** (Scheme 10).[76]



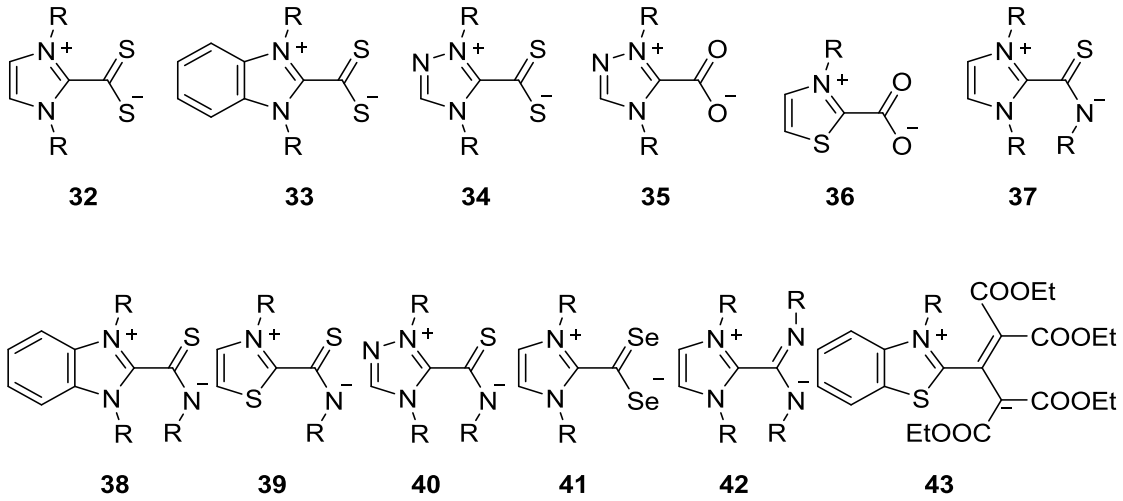
29 **30** **31**

Scheme 10: Example of an interconversion of an *abnormal N*-heterocyclic carbene (*r*NHC) and a cross-conjugated heterocyclic mesomeric betaine (CCMB).

1.3.4 Interconversions of *normal* N-heterocyclic carbenes (*n*NHC) and pseudo-cross-conjugated heterocyclic mesomeric betaines (PCCMB)

Interconversion of *normal N*-heterocyclic carbenes (*n*NHC) and pseudo-cross-conjugated heterocyclic mesomeric betaines (PCCMB) have a significant relevance due to its mild

conditions. Some betaine adducts of *N*-heterocyclic carbenes **32-43** were illustrated in a review in 2009 (Scheme 11).[77]



Scheme 11: Examples of pseudo-cross-conjugated heterocyclic mesomeric betaines (PCCMB) formed on trapping of *normal N*-heterocyclic carbenes (*n*NHC) with heterocumulenes.

1.4 Imidazole

As a planar five membered heterocyclic ring, numerous imidazole derivatives have been found as natural products.[78-81] Imidazole is known to have two tautomeric structures (Figure 5). Due to its amphoteric features imidazole can be used in numerous electrophilic and nucleophilic substitution reactions. Recent reports summarize various biological activities of imidazole derivatives which are applied as herbicides,[82] fungicides,[82] and therapeutic agents.[82-86]

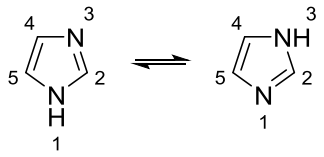
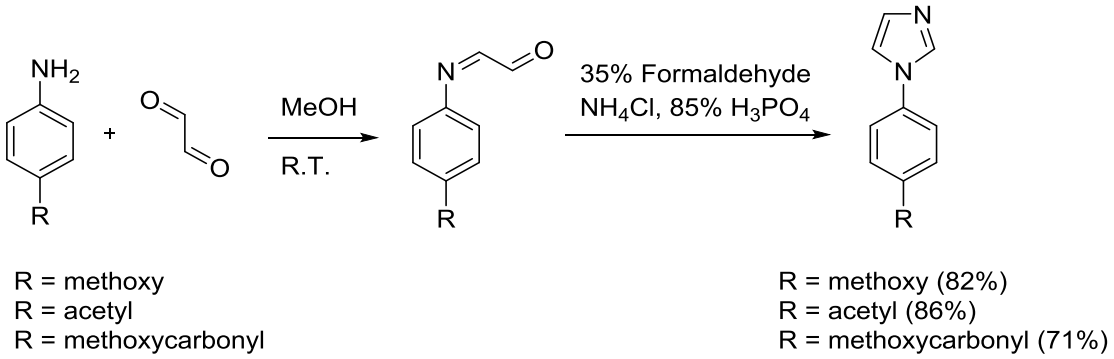


Figure 5: Imidazole tautomerism and numberings.

1-Arylimidazoles were first formed in 1956 by the reaction aryl amines with ammonia and glyoxal in yields of less than 1%.[87] Since then, various methods for syntheses of 1-arylimidazoles have been reported aiming to improve the yields.[78,88-90] The following scheme shows a two-step produce to yield a 1-aryl substituted imidazole (Scheme 12).



Scheme 12: Synthesis of 1-aryl substituted imidazole.

The application of imidazole derivatives in organometallic chemistry has attracted considerable interest. To mention just one example here, iridium(I) complexes of imidazole-NHC have been used as catalysts for hydrogenations.[91]

1.5 1,2,4-Triazole

Triazole is a five membered heterocyclic ring containing three nitrogen atoms. Two types are present in nature: 1,2,3-triazole and 1,2,4-triazole.[92] If the substituents of the two carbon atoms are hydrogens, each 1,2,3-triazole and 1,2,4-triazole has two tautomeric structures **44**/**45** and **46**/**47** (Figure 6).[93]

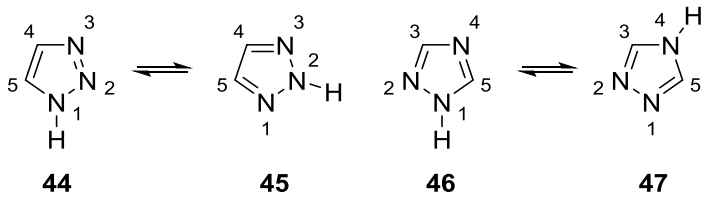


Figure 6: Isomeric triazoles and their tautomers.

In contrast, C3-substituted 1,2,4-triazoles have three tautomeric structures **48a**, **48b**, **48c** (Figure 7). The order of stability regarding these tautomeric structures decreases from **48a** to **48c** according to physical and theoretical studies.[94-96]

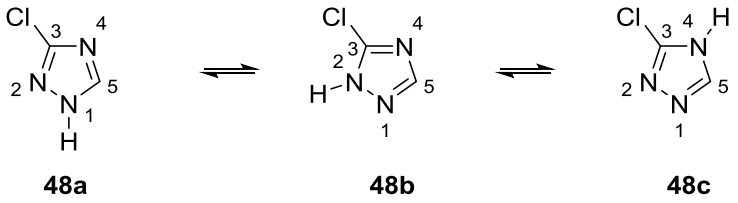
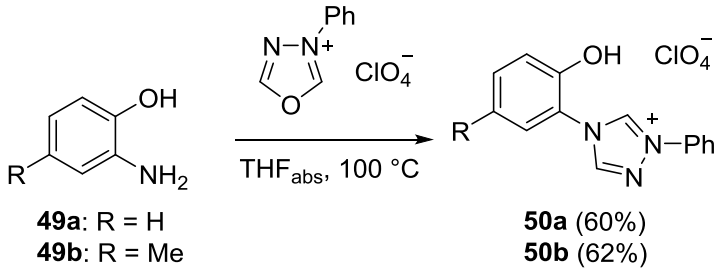


Figure 7: Three tautomeric forms of 3-chloro-1,2,4-triazoles.

1,2,4-Triazoles and their derivatives have proven to be useful in medicinal chemistry as anticancer,[97,98] antimicrobial,[99-102] antitubercular,[103] antiviral,[104,105] anticonvulsant,[106] antibacterial,[107-109] as well as anti-oxidant[103,108,110] activities have been found.

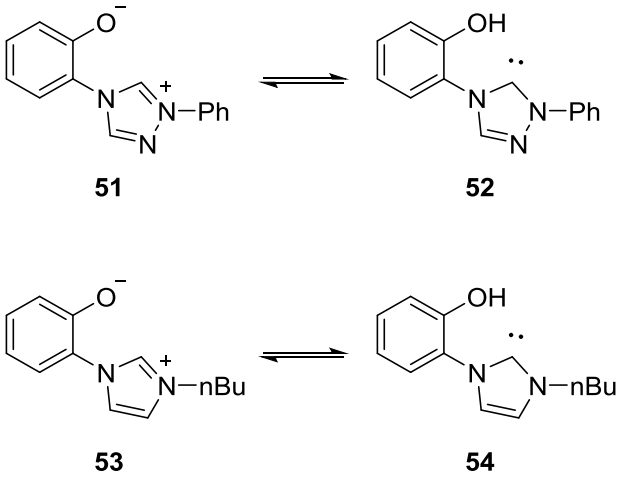
Ever since the first 1,2,4-triazole derivative was reported by Bladin in 1885,[111] methods for triazole-syntheses have been developed.[94,112-114] Scheme 13 shows an example in which the reaction of 2-aminophenol and its derivate **49a**,**b** with 3-phenyl-1,3,4-oxadiazolium salt yielded the triazolium salts **50a**,**b** in acceptable yields.[115]



Scheme 13: Synthesis of triazolium salts.

2 Motivation

The interesting area of overlap between the substance classes of mesomeric betaines and of *N*-heterocyclic carbenes in combination with the emerging field of the chemistry of anionic *N*-heterocyclic carbenes has been the motivation of this work. I will report on tautomeric equilibria of 1,2,4-triazolium-phenolate (**51**-**52**)[115] and 2-(imidazolium-1-yl)phenolate (**53**-**54**)[116] with their corresponding *N*-heterocyclic carbenes.



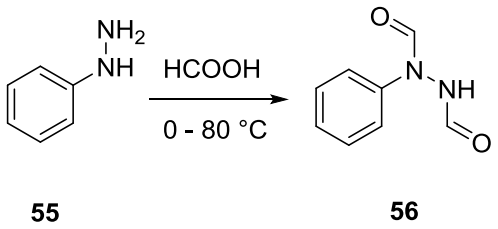
Scheme 14: Examples of equilibrium between mesomeric betaines and carbenes.

Trapping reactions of carbenes with sulfur and selenium will be reported. It has been the goal of this work to develop new adduct and complex formations for either species of the equilibria as well as of the anionic *N*-heterocyclic carbenes which derive thereof by deprotonation.

3 Results and discussion

3.1 Synthesis of 1,2,4-triazolium perchlorates

In order to prepare the starting mesomeric betaine **60aA**, **60bA** and **60cA**, a three-step procedure has been applied. First, phenyl hydrazine **55** was reacted with formic acid to give *N*,*N*'-diformyl-*N*-phenylhydrazine **56** in good yield[114] (Scheme 15).

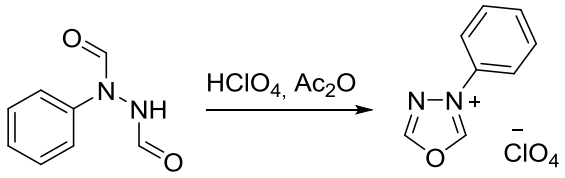


55 **56**

Scheme 15: Synthesis of *N*,*N*'-diformyl-*N*-phenylhydrazine **56**.

After cooling **55** to 0°C, formic acid was added and the reaction was left stirring at 80°C for 8 hours. The product was obtained by recrystallization.

N,*N*'-Diformyl-*N*-phenylhydrazine **56** was then treated with acetic anhydride and perchloric acid (70 %) to give 3-phenyl-1,3,4-oxadiazol-3-ium perchlorate **58** in 74 % yield[117] (Scheme 16).

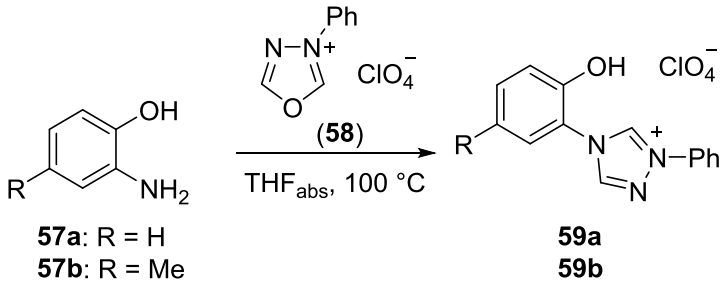


56 **58**

Scheme 16. Synthesis of 3-phenyl-1,3,4-oxadiazolium perchlorate **58**.

Due to its exothermic nature this reaction should be performed at low temperature (0°C). The target compound **58** is very hygroscopic and needs to be stored under inert conditions. Hence, structure analysis via NMR spectroscopy is difficult.

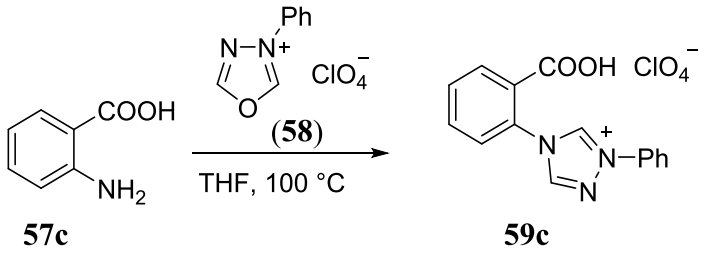
The reaction of 2-aminophenol **57a** and 2-amino-4-methylphenol **57b** with 3-phenyl-1,3,4-oxadiazolium salt **58** in anhydrous THF at 100 °C resulted in the formation of 1,2,4-triazolium-salts **59a** and **59b** in reasonable yields, respectively (Scheme 17).



Scheme 17: Synthesis of 1,2,4-triazolium salts **59a** and **59b**.

The compounds **59a**,**b** are stable on storage. The protons of the OH group in **59a** and **59b** appear at δ = 11.22 and 10.95 ppm in DMSO-d_6, respectively.

In analogy to the procedure shown in Scheme 17 the salt **59c** was prepared in 54 % yield (Scheme 18). The property of **59c** is similar to those of the salts **59a** and **59b**. The resonance frequency of the COOH proton of **59c** appeared at δ = 13.92 ppm in DMSO-d_6.



Scheme 18: Synthesis of 1,2,4-triazolium perchlorate **59c**.

The structure of **59b** was proven by X-ray structure analysis (Figure 8). Single crystals of **59b** were grown from a concentrated solution in ethanol. The dihedral angle for

C5-N4-C6-C7 is 56.24(19)° so that the phenyl and the triazolium rings are not planar in the crystal**.**

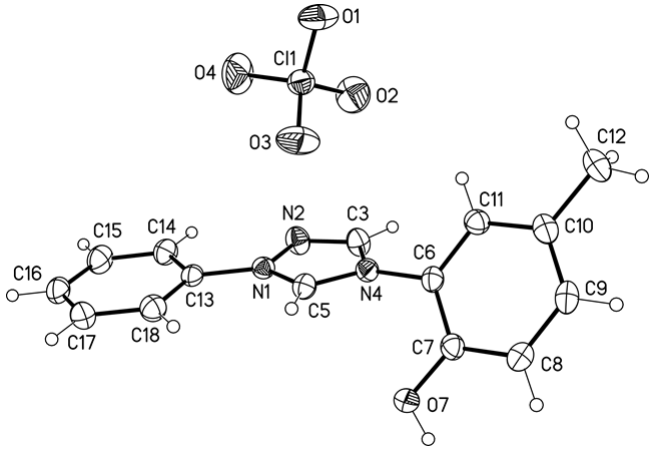
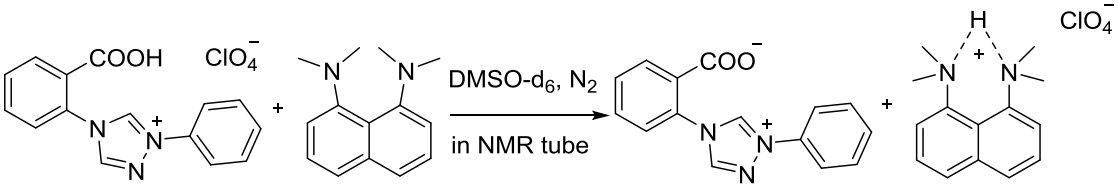


Figure 8. Molecular drawing of 1,2,4-triazoliumphenolate **59b**.

3.1.1 Synthesis of triazolium betaines

The deprotonation of the aforementioned triazolium salts was attempted by a base-screening in combination with NMR experiments. The deprotonation of salt **59c** with proton sponge (N^1, N^1, N^8, N^8-tetramethylnaphthalene-1,8-diamine) was examined in DMSO-d_6 applying different substrate-base ratios (Scheme 19). The ^{1}H NMR spectrum shows that the proton of the COOH group of **59c** at δ = 13.92 ppm disappeared gradually. Characteristically, the proton's signal of the captured proton of the base appeared at δ = 18.32 ppm (Figure 9), so that the titration could well be monitored.



59c N^1,N^1,N^8,N^8-tetramethylnaphthalene-1,8-diamine **60c**

Scheme 19: Synthesis of betaine **60c.**

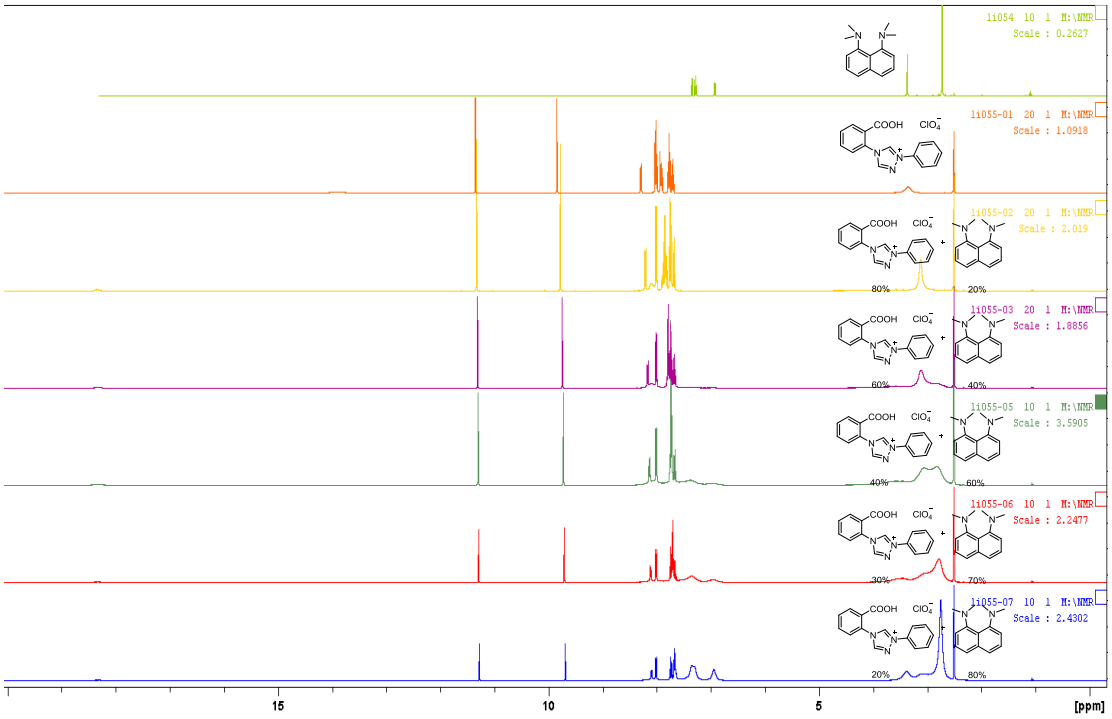
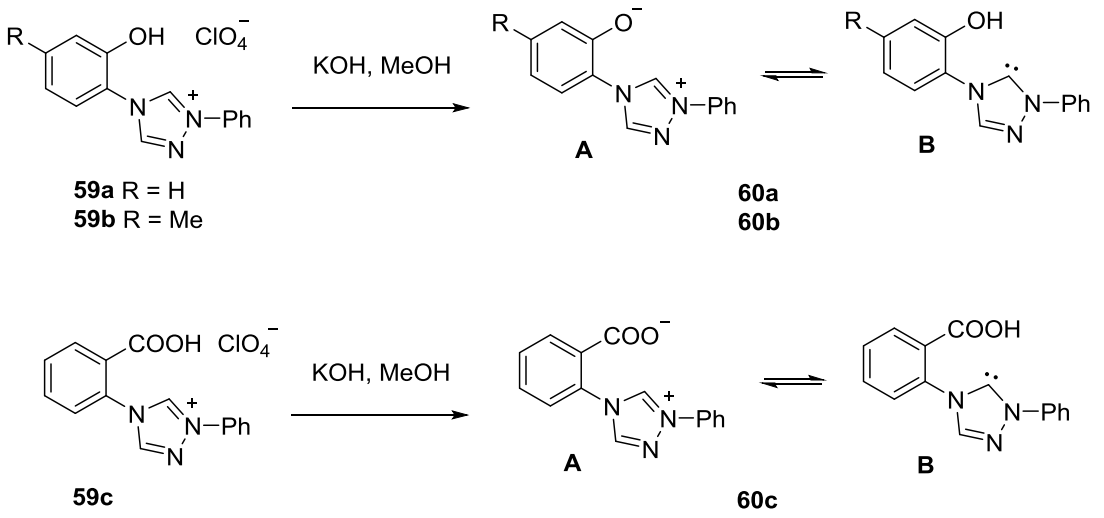


Figure 9: NMR-spectra of deprotonation with N^1, N^1, N^8, N^8-tetramethylnaphthalene-1,8-diamine.

The positive results of the NMR experiments inspired the deprotonation of **59c** in a lab scale. The deprotonations of **59a**,**b**,**c** with potassium hydroxide in methanol at room temperature were successfully carried out to generate the betaines **60a**,**b**,**c** in acceptable yields, respectively (Scheme 20). In contrast to the ^{1}H NMR spectra of the corresponding salts, the protons of the COOH and OH groups have disappeared and the proton resonance frequencies of 2-*H* of the triazolium ring shifted upfield and were finally detected at δ = 11.27/11.25/11.24 ppm as broad signals, respectively. The betaines **60a**,**b**,**c** are stable in methanol, but proved to be unstable in DMSO over a period of more than 12 hours.



Scheme 20: Synthesis of betaines **60a**,**b**,**c**.

Single crystals of **60b** were grown from a concentrated solution in ethanol and ethyl acetate so that an X-ray structure analysis was carried out (Figure 10). The analysis exhibits a network of *H*-bonded molecules with water of crystallization. The bond length between the atoms C5-H5 was found to be 95 pm, and between H5-O1W and C5-O1W bond distances of 203 pm and 297(4) pm were detected, respectively (crystallographic numberings). The oxygen O18 is surrounded by two additional molecules of water of crystallization via *H*-bondings (H···O/O-H···O: 188(2) pm/177(3)°, 192(2) pm/163(3)°). The dihedral angles for C5-H5···O1W, O1W-H1W1···O18^{i}, and O1W-H1W2···O18^{ii} are 172°, 177(3)°, and 163(3)°, respectively.

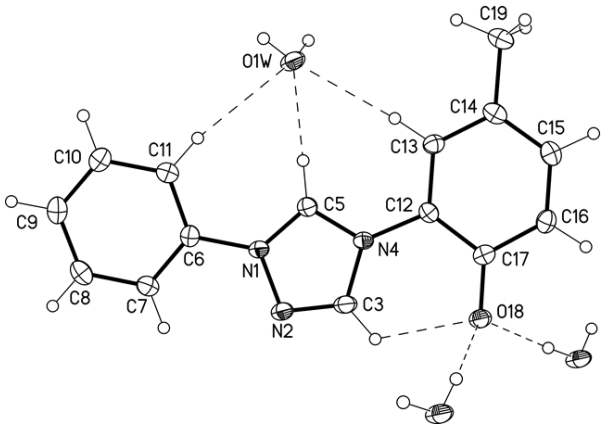
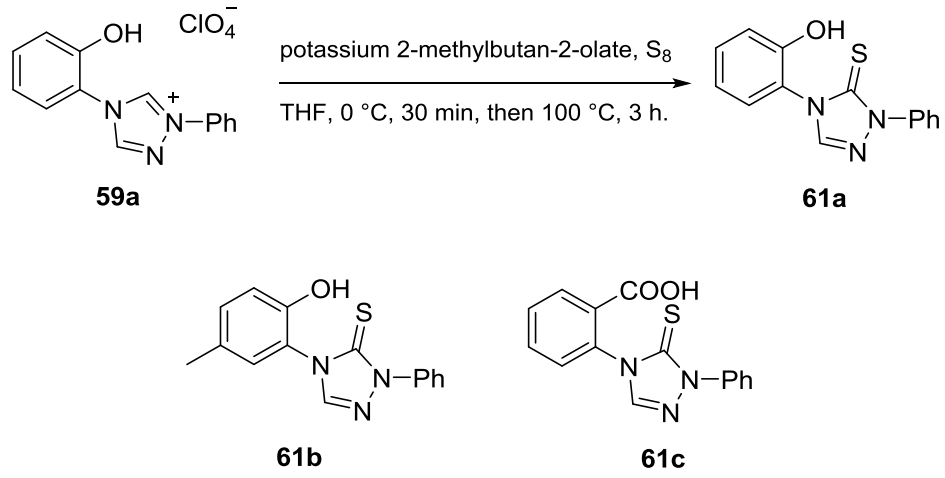


Figure 10: X-ray structure of triazolium betaine **60b**.

3.1.2 Reaction of triazolium salts/betaines with sulfur

The trapping of *N*-heterocyclic carbenes with elemental sulfur has proven to be an efficient synthetic tool to shift tautomeric equilibria between mesomeric betaines and *N*-heterocyclic carbenes toward the carbene side. In a first attempt trapping reactions with sulfur were performed to prove the existence of carbenes in equilibrium with triazolium salts and their betaines. Two methods have been applied.[74,118]

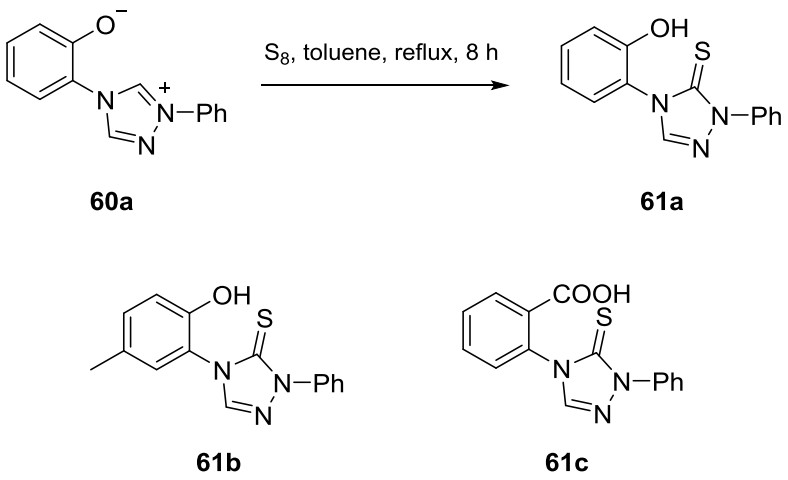
Method A: The triazolium salts were deprotonated with potassium 2-methylbutan-2-olate at 0 °C in anhydrous THF. Afterwards, elemental sulfur was added and stirred at 100 °C for 3 h. The products **61a,b,c** were obtained in reasonable yields (Scheme 21).



59a **61a** **61b** **61c**

Scheme 21: Synthesis of the thiones **61a**,**b**,**c**.

Method B: The betaines **60a**,**b**,**c** were refluxed with sulfur in dry toluene for 8 hours to produce **61a**,**b**,**c** (Scheme 22).



Scheme 22: Synthesis of the thiones **61a**,**b**,**c** by an alternative method.

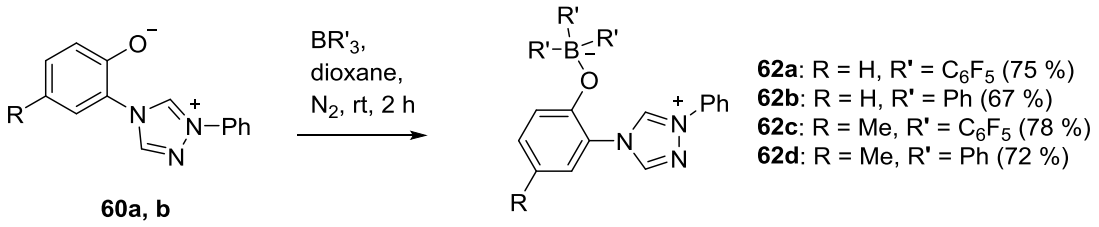
The former carbene atom of the thiones **61a,b,c** (the thiocarbonyl carbon atoms) were detected at δ = 168, 167 and 167 ppm, respectively.

3.1.3 Reaction of betaines with triphenylborane and tris(pentafluorophenyl)-borane

Recently, our group has found another trapping reaction of tautomeric *N*-heterocyclic carbenes. As a matter of fact, this trapping reaction can also be regarded as formal trapping reaction of the corresponding anionic *N*-heterocyclic carbenes. It's the reaction with triethylborane or triphenylborane which supplement the current research on *N*-heterocyclic carbene – borane adduct formations.[22] This new trapping reaction has also been successfully applied to the aforementioned betaine – carbene equilibria. Moreover, by variation of the substitution pattern of the borane it has been possible to trap the individual tautomers independently.

Thus, the betaines **60a**,**b** reacted with triphenylborane and tris(pentafluorophenyl) borane at room temperature to give the borane adducts **62a-d** in reasonable yields (Scheme 23). By means of X-ray structure and NMR spectra analysis we learned that the boron atom was exclusively connected with the olate group of the betaine tautomers. The resonance frequencies of the protons of **62a-d** appeared at δ = 11.02, 11.23, 11.00 and 11.20 ppm, respectively. The ^{11}B NMR spectra of **62a-d** showed the

borane atoms at δ = -3.30, -6.56, -4.46 and -6.57 ppm, respectively. The fluorine atoms of **62a**,**c** gave resonance frequencies at δ = -133.44, -159.07, -164.33 and -133.44, -159.14, -164.36 ppm in the ^{19}F NMR spectra.



Scheme 23: Synthesis of triazolium phenoxytriphenylborates **62a-d.**

Single crystals of **62c** were obtained from a saturated solution in DMSO. The X-ray structure of triazolium phenoxytriphenylborate **62c** shows that the three pentafluorophenyl rings are twisted. The bond length of O19-B20 was determined to be 150.30(19) pm. The dihedral angles for C5-N1-C6-C7, C5-N4-C12-C17, and C5-N4-C12-C13 are -120.8(3)°, 148.59(15)°, and -35.7(2)°, respectively (Figure 11).

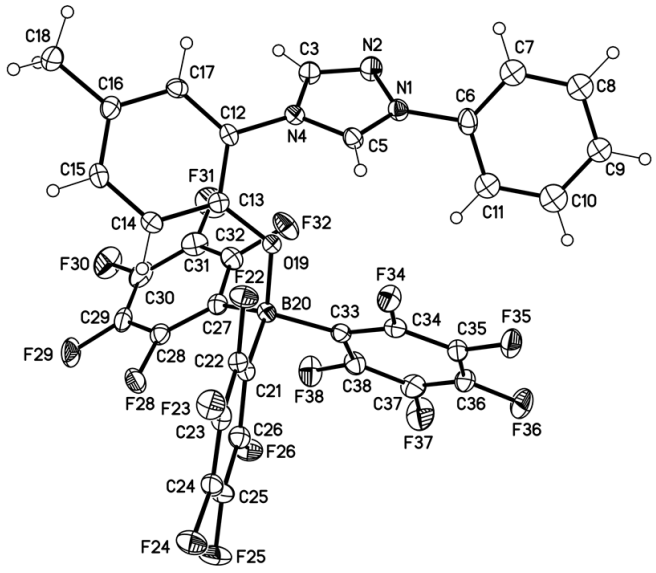
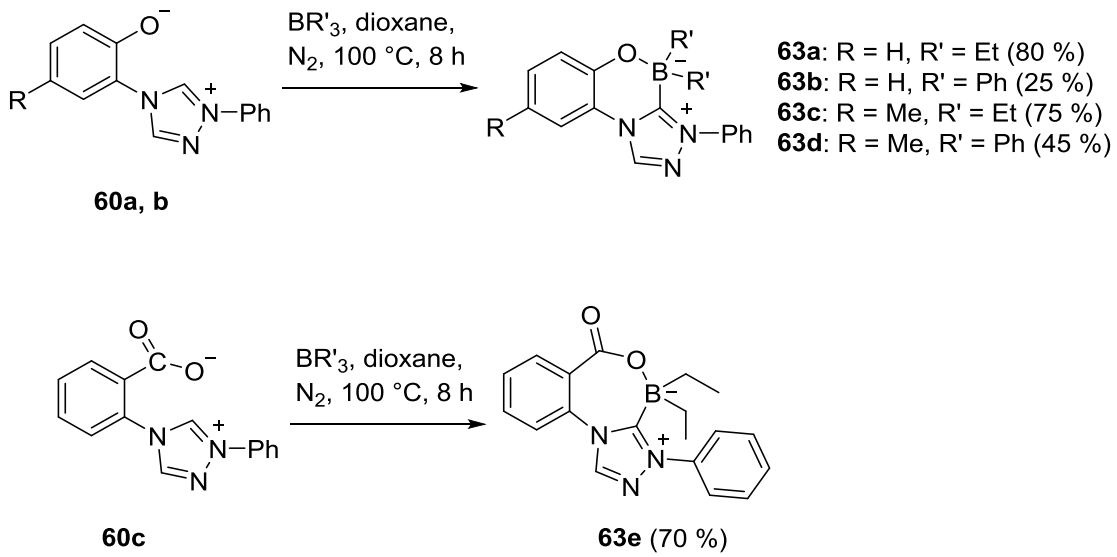


Figure 11: Molecular drawing of triazolium phenoxytriphenylborate **62c** according to a single crystal X-ray structure analysis.

3.1.4 Synthesis of 3-phenyl-4*H*-benzo[*e*][1,2,4]triazolo[3,4-*c*][1,4,2]oxazaborininium-4-ide

The betaines **60a**,**b** reacted with BEt_3 and BPh_3 at 100 °C in a bomb tube to give the products **63a-d** (Scheme 24). The new seven-membered ring **63e** obtained from betaine **60c** proved to be hygroscopic. These molecules are first representatives of new heterocyclic ring systems.



Scheme 24: Synthesis of 3-phenyl-4*H*-benzo[*e*][1,2,4]triazolo[3,4-*c*][1,4,2]oxazaborininium-4-ides **63a-d**.

By use of ^{1}H NMR spectroscopy on **63c** it became evident that the proton of the potential carbene carbon disappeared in parallel with the formation of resonance frequencies of two ethyl groups (Figure 12).

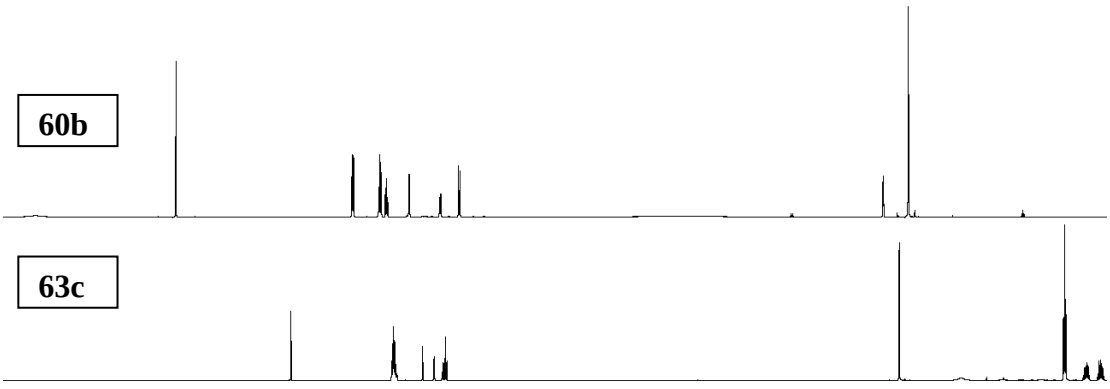


Figure 12: ^{1}H NMR spectrum of triazolium phenoxytriphenylborate **63c**.

Single crystals of **63a** were grown from a concentrated solution in ethanol. The X-ray structure of **63a** shows that two ligand molecules share one water molecule by *H*-bonding. Geometric parameters of the two molecules differ slightly. The bond lengths O1-B1, O101-B102, C3-B1, C103-B2 were determined to be 154.26(17) pm [154.27(19) pm] and 163.9(2) pm [164.2(2) pm] respectively. The B–$C_{carbene}$ bond length in imidazodiazaboroloindoles [165.2(2) pm] is longer compared to **63a**[74]. The dihedral angles for N5-N4-C18-C23, N105-N104-C118-C123, O1-B2-C3-N7 [O101-B102-C103-N107], C13-O1-B2-C3 [C113-O101-B102-C103 are 178(2)/162(2)°, 46.13(18)°, -42.7(2)°, -28.57(16) [24.48(17)°], 46.77(15)° [-46.84(16)°], respectively (Figure 13; crystallographic numberings).

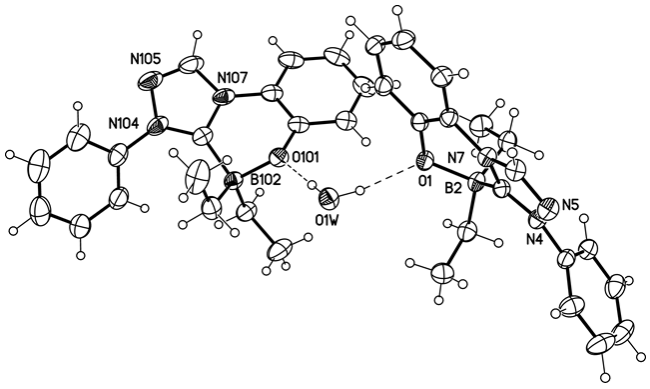
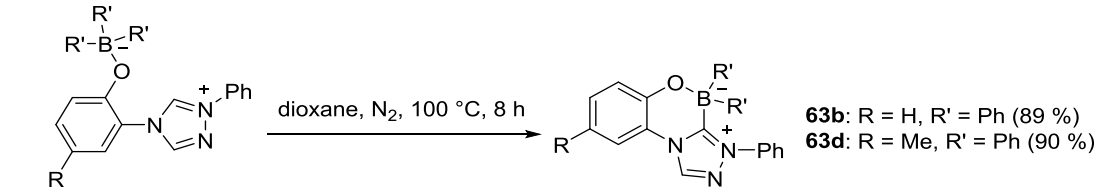


Figure 13: X-ray structure of triazolium phenoxytriphenylborate **63a**.

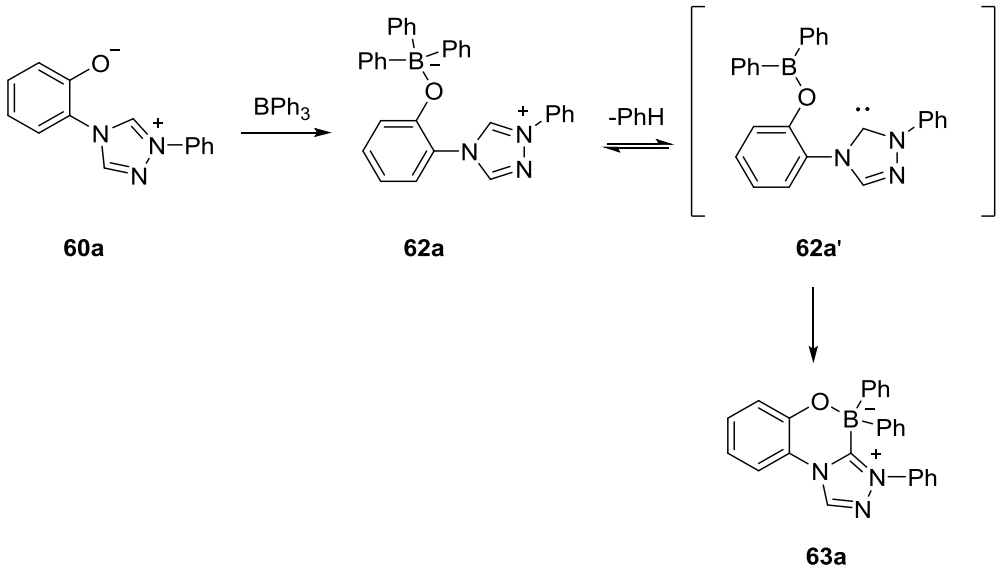
The products **63b**,**d** were obtained from triazolium phenoxytriphenylborates **62b**,**d** dissolved in dioxane by heating to 100 °C in a bomb tube. In contrast, **62a**,**c** could not be converted into the desired products probably due to steric hindrance (Scheme 25).



Scheme 25: Synthesis of 3-phenyl-4*H*-benzo[*e*][1,2,4]triazolo[3,4-*c*][1,4,2]oxazaborininium-4-ides **63b**,**d**.

In analogy to the above mentioned methods, we also investigated reactions of the betaines **60a**,**b** with BH_3, BBr_3, $B(OMe)_3$, and 9-BBN, respectively, However, the reactions did not yield the desired target molecules.

The following mechanism can be suggested in accordance to the two-step synthesis from betaine **60a** to 3-phenyl-4*H*-benzo[*e*][1,2,4]triazolo[3,4-*c*][1,4,2]oxazaborininium-4-ide **63a**: first, the phenyl oxygen attacks the triphenylborane to produce the intermediate **62a**. In a next step, formally the phenyl group of triphenylborane acts as a leaving group, deprotonating the carbene position under formation of benzene. Thus, intermediate carbene **62a**' is formed which is unstable and undergoes an intramolecular ring closure to give the carbene borane adduct **63a** (Scheme 26).

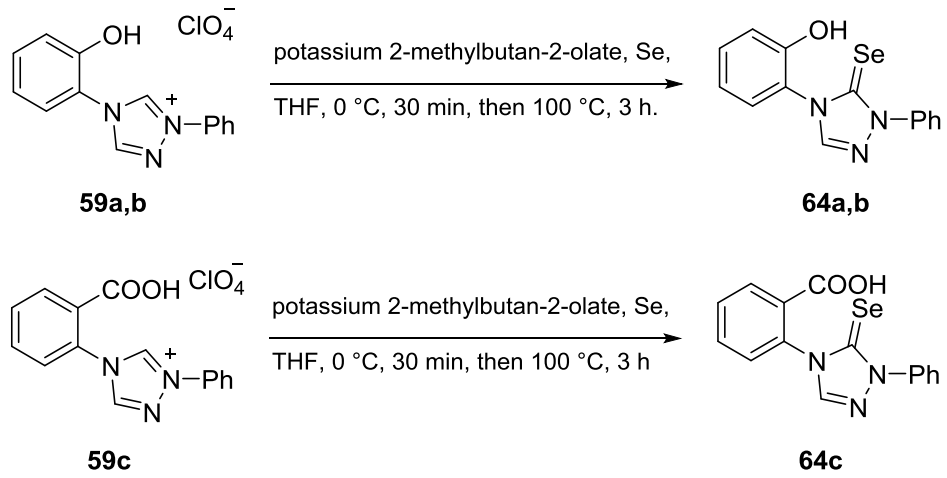


Scheme 26: Proposed mechanism of 3-phenyl-4*H*-benzo[*e*][1,2,4]triazolo[3,4-*c*] [1,4,2]oxazaborininium-4-ides **63a-d**.

3.1.5 Synthesis of triazoleselenones

Reactions of triazolium salts to triazoleselenones were also investigated. Therefore, triazolium salts **59a**,**b**,**c** were reacted with selenium and potassium 2-methylbutan-2-olate in dry THF at 0 °C. Afterwards, the reaction was refluxed at 100 °C for 3 h. This method yielded the products **64a**,**b**,**c** in reasonable yields (Scheme 27). The

selenocarbonyl carbon atoms of **64a**,**b**,**c** can be detected at δ = 161.3, 161.8 and 166.8 ppm by ^{13}CNMR spectroscopy in DMSO-d_6, respectively.

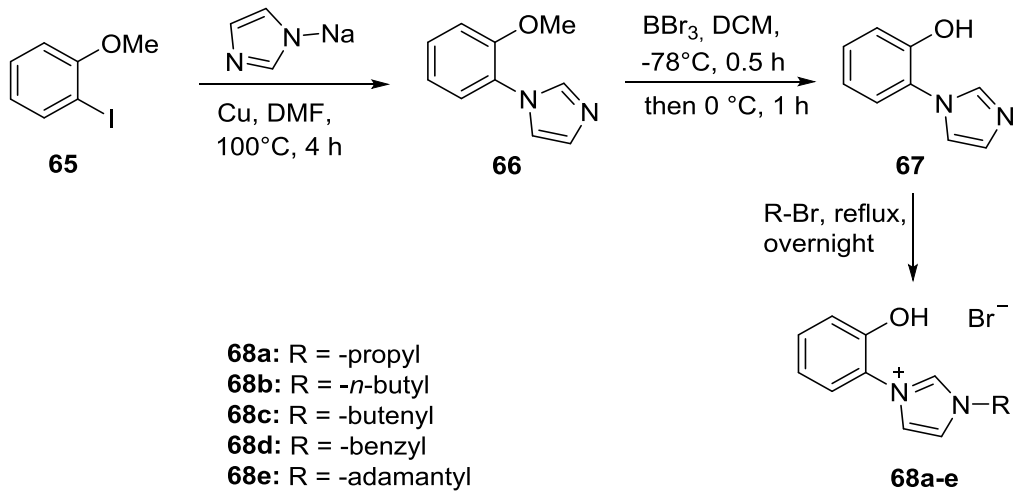


Scheme 27: Synthesis of triazoleselenones **64a**,**b**,**c**.

3.2 Synthesis of imidazolium salts and betaines

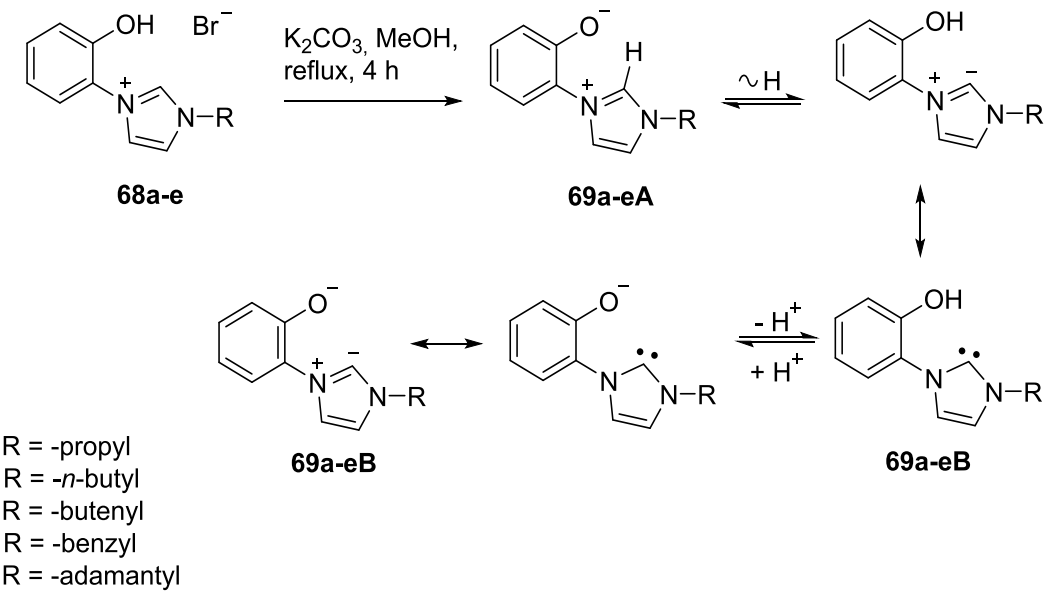
In analogy to our examinations concerning 1,2,4-triazolium-phenolates, syntheses of new ring systems starting from the corresponding imidazole derivatives were attempted. We began our investigations with the synthesis of 2-(imidazolium-1-yl)phenolates and performed some reactions to prove the equilibrium between betaine and carbene.

First, 2-iodoanisole **65** was coupled with sodium imidazolate in the presence of copper in dry DMF under an inert atmosphere to give the compound **66** (Scheme 28). The sodium imidazolate required can be easily synthesized in lab scale by reaction of imidazole and sodium hydride. Two methods for the deprotection of the OH group of the resulting ether are follows: a) application of BBr_3 at low temperatures and b) addition of 48 % HBr while refluxing. Both reaction pathways gave the phenol **67** in good yields[117,119]. Finally, refluxing **67** overnight with various bromoalkanes gave the salts **68a-e** in reasonable yields via nucleophilic substitution (Table 1).



Scheme 28: Synthesis of imidazolium salts **68a-e**.

Subsequently, the mesomeric betaines **69a-e** were obtained by deprotonating the salts **68a-e** with potassium carbonate in boiling methanol in good yields (Scheme 29) (Table 1). In contrast to the ^{1}H NMR spectra of the salts, the disappearance of the phenolic OH group and the broadened signal of the 2-position of the imidazolium moiety are diagnostic for betaine formation. In the positive mode of ESI mass spectrometry, betaine **69bA** can be detected as proton adduct (i.e. as reprotonated salt) and as sodium adduct ($[M + H]^+ = 217$, $[M + Na]^+ = 239$). The latter can be regarded as important hint for the proof of structure.



68a: R = -propyl
68b: R = -*n*-butyl
68c: R = -butenyl
68d: R = -benzyl
68e: R = -adamantyl

Scheme 29: Synthesis of imidazole carbenes **69a-e**.

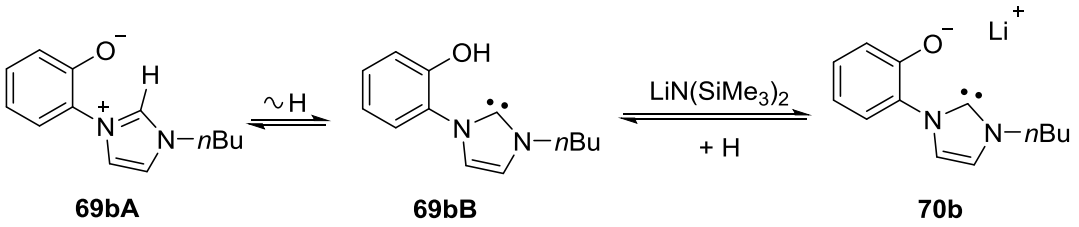
Table 1. Substitution patterns and yields of **68** and **69 (**Scheme **28** and **29)**

R	**68**/yields	**69**/yields
n-propyl	**68a:** 86 %	**69a:** 90 %
n-butyl	**68b:** 94 %	**69b:** 98 %
but-3-en-1-yl	**68c:** 90 %	**69c:** 91 %
benzyl	**68d:** 89 %	**69d:** 87 %
1-adamantyl	**68e:** 63 %	**69e:** 68 %

3.2.1 Deprotonation of betaine with base

We were delighted to see the anionic *N*-heterocyclic carbenes such as **70b** in the anion detection mode of the ESI mass spectrum, even under very mild measurement conditions (e. g. [**69b** - H]$^-$ = 215). Therefore, a base- and solvent-screening was performed to find best conditions for an NMR spectroscopic investigation. Finally, we found that treating the betaine **69b** with lithium bis(trimethylsilyl)amide in THF/pyridine yielded the *N*-heterocyclic carbene **70b** in quantitative yield. In the ^{13}C NMR spectrum the carbene carbon atom gives a resonance frequency at δ = 203 ppm in pyridine-d_5. NHC **70b** is very unstable and is reprotonated rapidly in

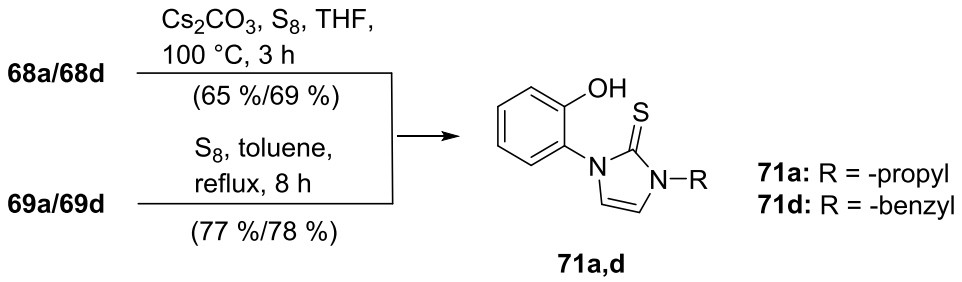
the carbene position in the presence of minute traces of water. Thus, it proved to be impossible to grow single crystals, even under vigorous exclusion of water.



Scheme 30: Formation of NHC **70b**.

3.2.2 Reaction of betaines with sulfur

Sulfur is believed to be an excellent reagent to trap the carbene tautomers, and therefore trapping reactions of the in-situ generated carbene of the imidazole salts **68a**,**d** as well as the betaines **69a**,**d** (Scheme 31) were attempted. The imidazole-2-thiones **71a**,**d** were indeed obtained in reasonable yields, respectively. The thione carbon resonance frequency of **71a,d** can be detected at δ = 162.5 and 163.5 ppm in DMSO-d_6 in the ^{13}C NMR spectra, respectively. Both protons of the OH group of **71a,d** give resonance frequencies at δ = 9.87 ppm in the same solvent in the ^{1}H NMR spectra. Formation of a tautomer under formation of a thiol group could thus be excluded.



Scheme 31: Synthesis of imidazole-2-thiones **71a,d**.

The structure of imidazole-2-thione **71d** was proven by X-ray structure analysis. After slow evaporation of a concentrated solution of **71d** in ethyl acetate, single crystals of **71d** were obtained. The crystal analysis illustrates that two independent molecules

share one unit (Figure 14). The thione tautomer is unambiguously present in the unit cell.

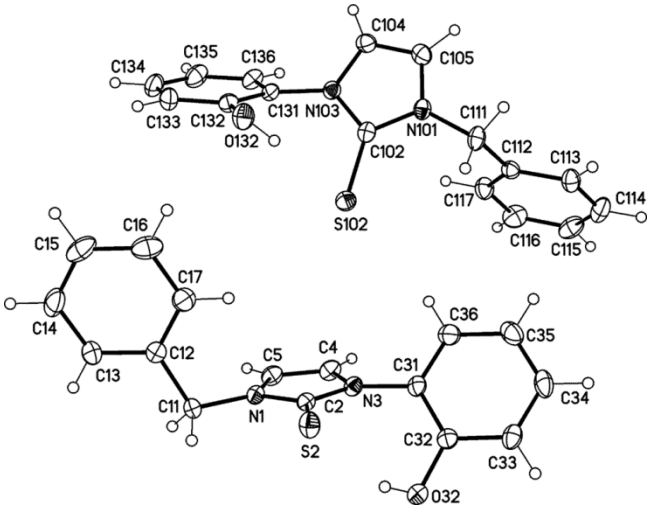
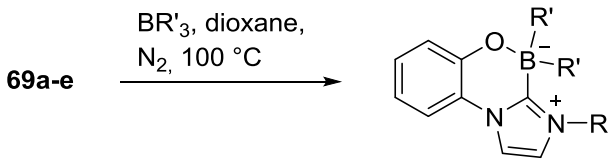


Figure 14: X-ray structure of imidazole-2-thione **71d**.

3.2.3 Reaction of imidazole betaines with borane compounds

Borane compounds as trapping reagents for carbenes have shown great popularity in the research fields of inorganic as well as organic chemistry. A review has appeared recently.[22] Reactions of betaines **69a-d** with triethylborane and triphenylborane yielded the 4,4-diethyl- or 4,4-diphenyl-4*H*-benzo[*e*]imidazo[2,1-*c*][1,4,2]oxazaborininium-4-ides **72a-d** and **73a-d** in good yields (Table 2), respectively (Scheme 33). The boron atom of **72/73a-d** can be detected between 0.94 ppm and -1.17 ppm in the ^{11}B NMR spectrum.



69a: R = -propyl
69b: R = -*n*-butyl
69c: R = -butenyl
69d: R = -benzyl
69e: R = -adamantyl

Scheme 33: Synthesis of borane adducts **72/73a-d**.

These derivatives are first representatives of a new heterocyclic ring system. The compounds **72e** and **73e**, however, were not formed probably due to steric hindrance.

Table 2: Substitution patterns and yields of **72** and **73** (Scheme 33)

R	R'	**72**/yields	**73**/yields
n-propyl	Et/Ph	**72a:** 94 %	**73a:** 93 %
n-butyl	Et/Ph	**72b:** 55 %	**73b:** 60 %
but-3-en-1-yl	Et/Ph	**72c:** 42 %	**73c:** 42 %
benzyl	Et/Ph	**72d:** 55 %	**73d:** 60 %

Single crystals of **73c** and **73d** were obtained from concentrated solutions in ethyl acetate, respectively. The X-ray analysis of **73c** shows the bond lengths of O1-B2 and B2-C3 to be 152.12(13) and 163.05(15) pm and the torsion angles of O1-B2-C3-N7, C3-N7-C8-C13, and B2-O1-C13-C8 were determined to be 15.05(13)°, -15.92(14)°, 29.58(14)°, respectively (Figure 16; crystallographic numberings).

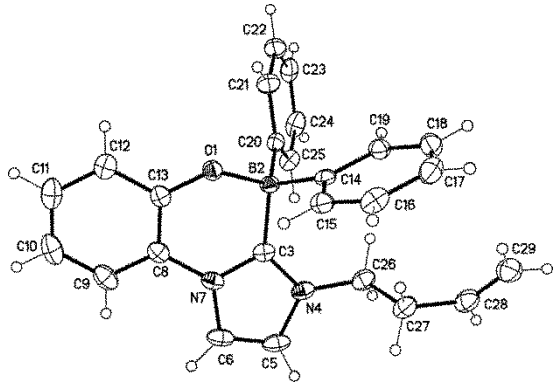


Figure 16: X-ray structure of boron adduct **73c**.

The X-ray structure of **74d** shows the four independent zwitterions in the asymmetric unit (Figure 17). In comparison to **73c**, the bond lengths of O1-B2 and B2-C3 are slightly longer. The torsion angles of O1-B2-C3-N7 were determined to be 33.0(2)°, 33.5(2)°, -30.9(2)°, and -28.9(3)°, respectively (Figure 18, crystallographic numberings).

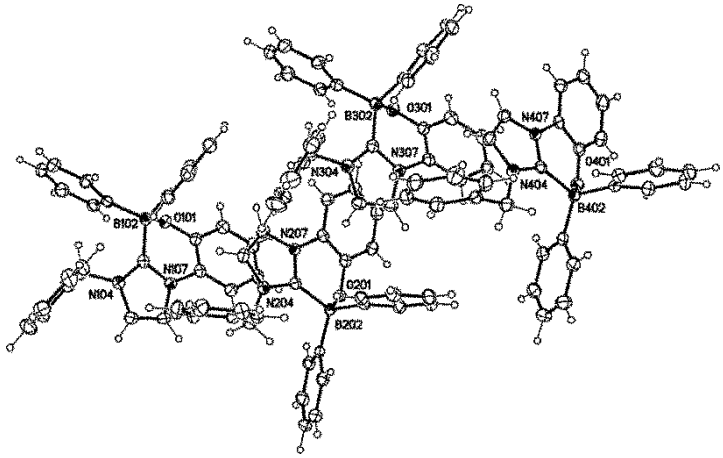


Figure 17: X-ray structure of four independent molecules in the asymmetric unit of **73d**.

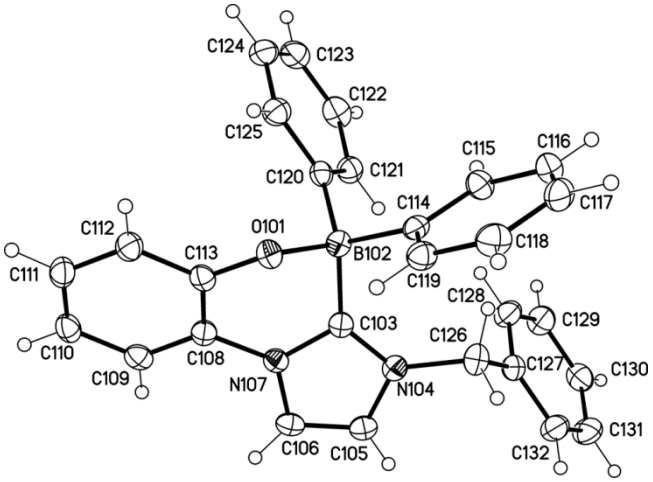
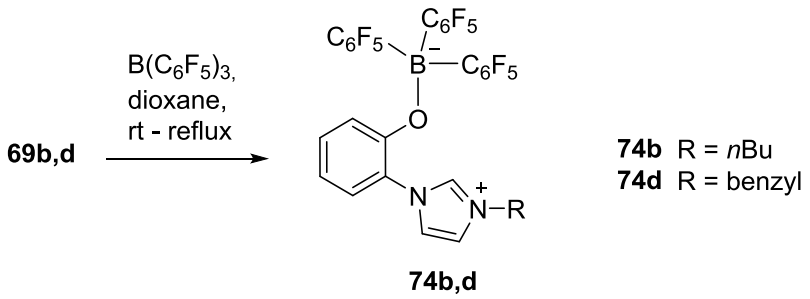


Figure 18: X-ray structure of one of the four independent molecules in the asymmetric unit of **73d**.

According to the above mentioned procedure, the mesomeric betaines **69b,d** can also be trapped with tris(pentafluorophenyl)borane to give the products **74b,d** in reasonable yields (Scheme 34). The boron atom is not connected to the carbene carbon, as evidenced from the spectroscopic analysis via 2D NMR spectra and X-ray single crystal structure analyses. The proton (H2) of the imidazolium ring was measured at δ = 9.22 and 9.41 ppm in DMSO-d_6, respectively. The boron atom of **74b,d** can be detected at δ = -3.45 and -3.47 ppm in the ^{11}B spectrum. The fluorine atom of **74b** shows resonance frequencies at δ = -133.91, -159.97 and -165.18 ppm in the ^{19}F NMR spectra.



Scheme 34: Synthesis of borane adducts **74b,d**.

Single crystals of the ring system **74b** were prepared by slow evaporation a concentrated solution in ethyl acetate. The X-ray structure shows two different

conformers in one unit (Figure 19). The bond lengths B1-O1 were detected to be 149.60(15) and 148.68(16) pm, respectively. The torsion angles between the imidazole and the phenol ring for C2-C7-N8-C9 were 125.71(13) and -48.39(17)°, respectively.

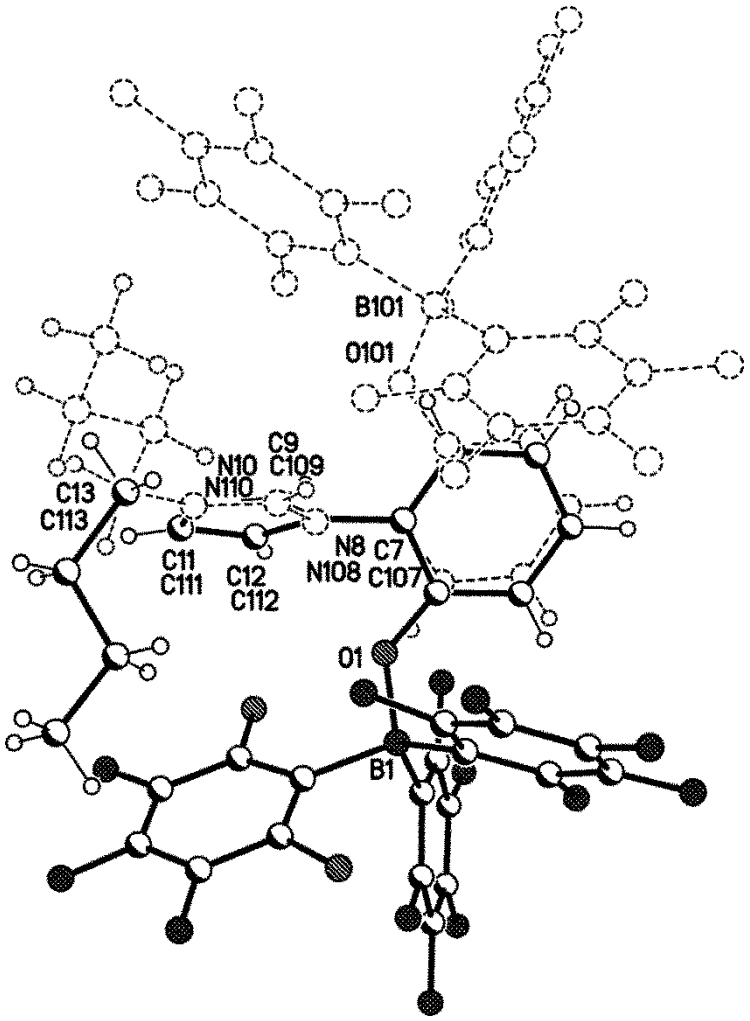
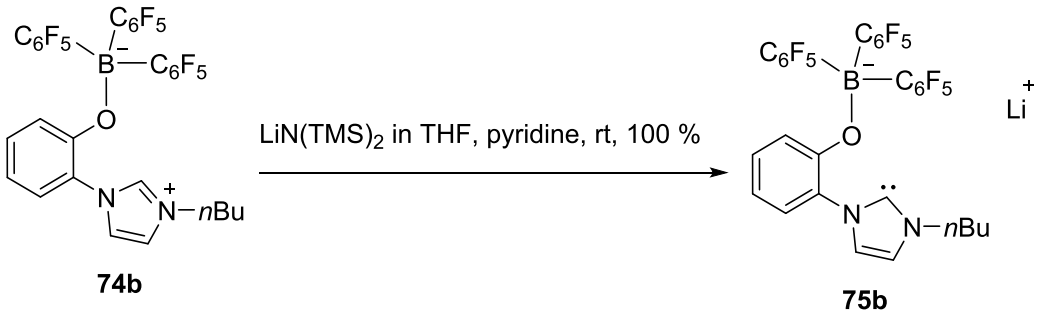


Figure 19: X-ray structure of two dependent molecules **74b**.

3.2.4 Deprotonation of borane compound 74b with base

The anionic *N*-heterocyclic carbene **75b** can be generated by the reaction of the betaine **74b** with lithium bis(trimethylsilyl)amide in THF/pyridine in quantitative yield (Scheme 35). The carbene carbon atom was detected at δ = 197.9 ppm in pyridine-d_5. The boron and fluorine atom resonance frequencies appear at δ = -3.40 ppm

and -132.82, 161.55, -165.96 - -166.09 ppm in pyridine-d_5, respectively. Growing single crystals of **75b** were unsuccessful due to hydrolysis.

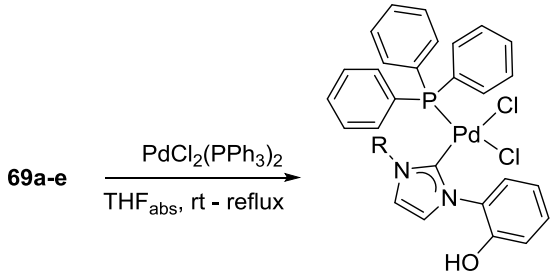


74b **75b**

Scheme 35: Synthesis of lithium (2-(1-butyl-1*H*-imidazolium-2-id-3-yl)phenoxy)tris(hexafluorophenyl)-borate.

3.2.5 Reaction of imidazole betaines with palladium complexes

In an attempt to trap carbenes the synthesis of complexes of palladium, rhodium, nickel and gold were envisaged. The palladium complexes **76a**,**b**,**d** were prepared by refluxing the betaines **69a-e** with *trans*-dichlorobis(triphenylphosphine)palladium(II) in dry THF (Scheme 32). The complex **76c** proved to be inseparable from the mixture of compounds due to very similar polarities. The corresponding complex **76e** was not obtained due to steric hindrance of the 1-adamantyl group. The analysis of the 2D NMR spectra and the crystal structure shows that **76a**,**b**,**d** are monomers and that the palladium atom is not connected to the oxygen atom in all of them. In summary, we have found a trapping method for the carbene of the betaine/carbene tautomeric equilibrium. The carbene atoms of **76a**,**b**,**d** give resonance frequencies at δ = 158.3, 158.3 and 159.4 ppm in ^{13}C NMR spectra, respectively.



69a: R = -propyl
69b: R = -*n*-butyl
69c: R = -butenyl
69d: R = -benzyl
69e: R = -adamantyl

76a (76 %)
76b (84 %)
76c (mixture)
76d (75 %)
76e (0 %)

Scheme 32: Synthesis of palladium complexes of the carbene tautomer.

Single crystals of **76d** were grown from a concentrated solution in methanol. Spectroscopic data as well as the results of the single crystal X-ray analysis prove that the phenol ring is not involved in the complex formation (Figure 15). A Cl/Br disorder in the ratio of 90:10 was found. The torsion angle between the phenol and imidazole rings was determined to be 55.3(2)°. The dihedral angle Cl1-Pd1-C2-N3 was found to be 90.1(2)°. The bond length Pd1-C2 is 199.89(16)°pm (crystallographic numberings).

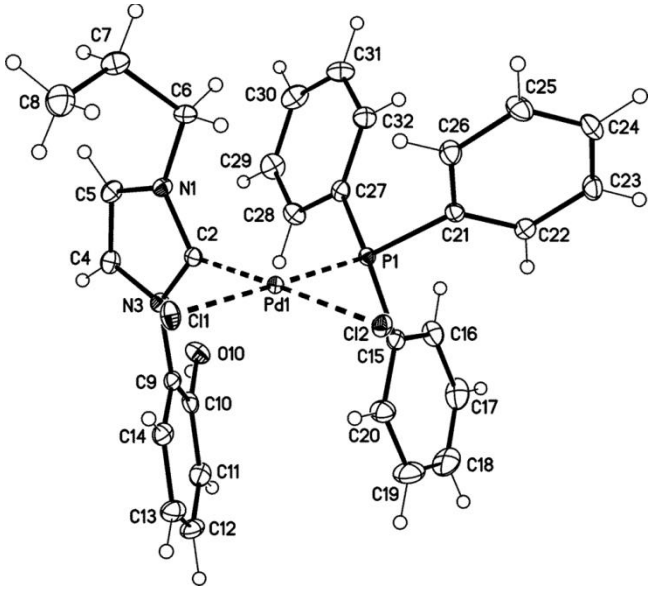


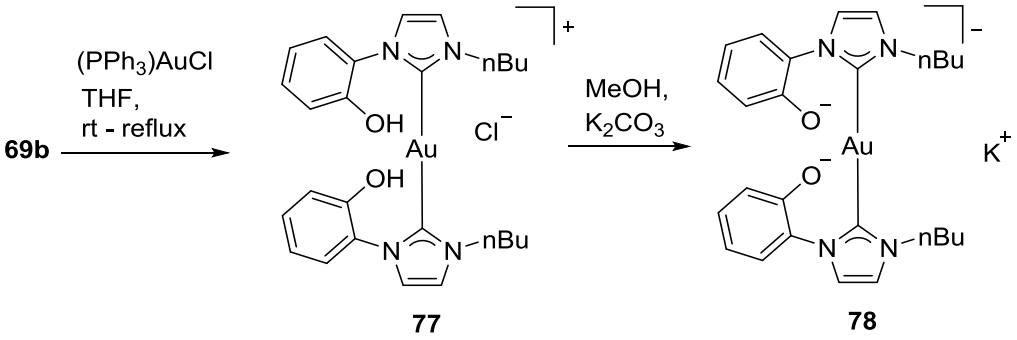
Figure 15: X-ray structure of imidazole-2-thione **76d**.

3.2.6 Reaction of imidazole betaines with gold complexes

Recently, NHC−Au(I) complexes as one of the most interesting areas of NHC-based catalysis have been reported.[53,120-122] Thus we will report on the synthesis and structural characterization of Au(I) complex of the imidazole carbenes described here.

As previously mentioned, the gold complex **77** was prepared by refluxing the *N*-heterocyclic carbene tautomer **69bB** with chloro(triphenylphosphine) gold(I) in dry THF under an inert atmosphere (Scheme 36). The target molecule was obtained in good yield. The complex **77** shows the peak at *m/z* = 629 in the ESI mass spectrum and the OH group was found clearly at δ = 10.34 ppm in DMSO-d_6 in the ^{1}H NMR spectra. The carbene carbon atom gives a resonance frequency at δ = 183.9 ppm in comparison to δ = 135.7 ppm from the betaine **69b**.

The anionic complex **78** was prepared through the reaction of the gold complex **77** with potassium carbonate in methanol. Compound **78** shows the molecular peak at *m/z* = 627 in the negative mode of the ESI mass spectra.



Scheme 36: Synthesis of the gold complexes **77** and **78**.

Single crystals of **77** were obtained from a concentrated solution in methanol (Figure 20). The crystal analysis proved that in the elemental cell two molecules are connected *via* one chloride anion which forms hydrogen bonds to two OH groups. The X-ray structure shows a Cl/Br disorder of 4:1. The bond length Au1-C2 is 202.11(15) pm and the dihedral angle C2-Au(I)-C2A was found to be 177.35(8)°. The imidazole and the phenol rings are twisted by -119.84(16)° (C5-N1-C6-N7).

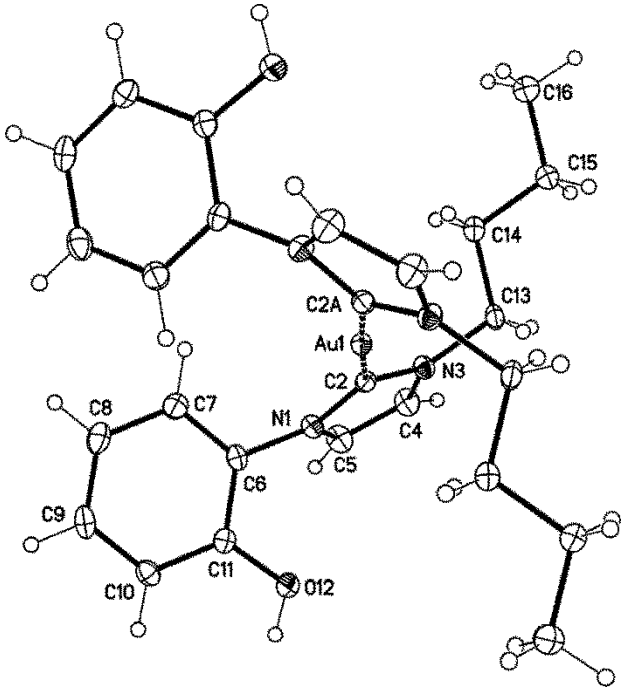
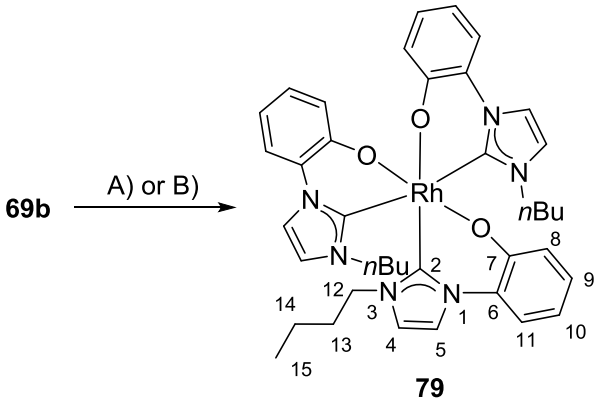


Figure 20: X-ray structure of gold complex **77**.

3.2.7 Reaction of imidazole betaines with rhodium complexes

Rhodium *N*-heterocyclic carbene (NHC) complexes[123-126] have attracted considerable attention, especially as catalysts.[127-138] We found that the mesomeric betaine **69b** can be trapped as a rhodium complex **79** by refluxing **21bA/B** with chloro(1,5-cyclooctadiene)rhodium(I) dimer in dry THF in good yield or with bis(triphenylphosphine) rhodium(I) carbonyl chloride in dry toluene at reflux temperature in good yield (Scheme 37). The carbene carbon atom of compound **79** can be detected at $\delta = 173.5$, 171.0 and 164.4 ppm, and the coupling values with rhodium in the ^{13}C NMR spectrum were 35.6 Hz, 35.6 Hz, and 48.5 Hz, respectively, probably due to the larger bond length in axial position.



A) $[RhCl(COD)]_2$, THF, rt - reflux; B) $[RhCl(PPh_3)_2(CO)]$, toluene, reflux

Scheme 37: Synthesis of rhodium complex **79**.

At 298 K, the six protons at 12, 12' and 12"-H show four non-equivalent signals at 3.5 - 4.3 ppm and the corresponding integrals are 1:1:3:1. The general trend of the protons' behaviour on warming is a shifting. At 378 K, the protons have two non-equivalent signals in the ratio of 2:4. The heating was stopped at 378 K due to protection of the NMR instrument, then cooled to 298 K. The last ^{1}H NMR spectrum is the same as in the beginning (Figure 21). This presumably means that the magnetic environment of 12, 12' and 12"-H change to identity with elevation of temperature.

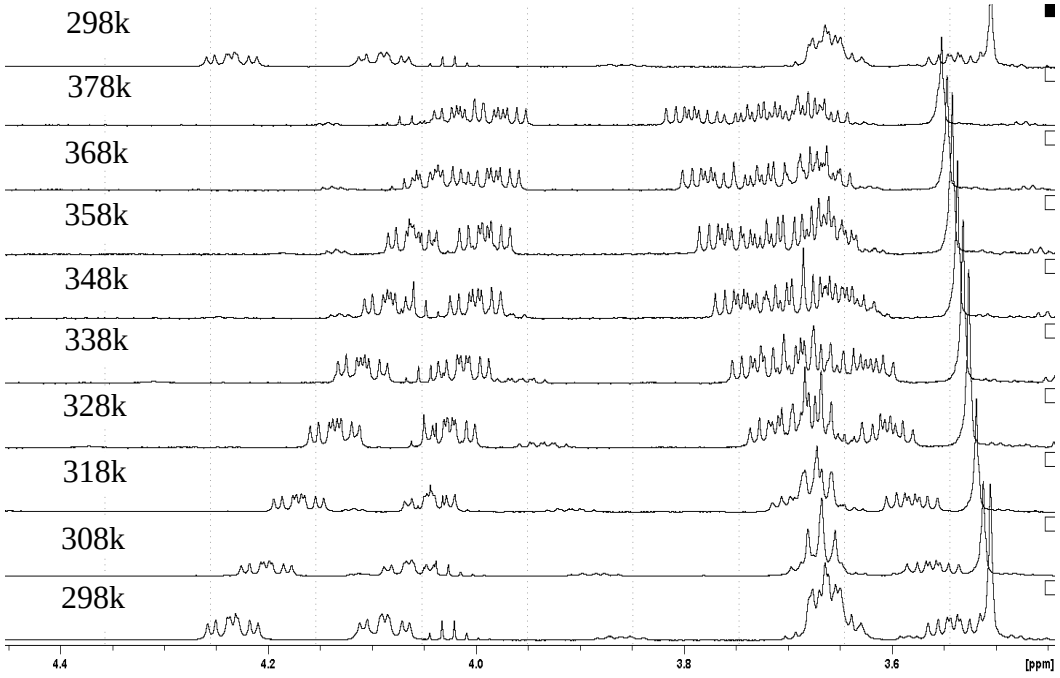


Figure 21: ^{1}H NMR spectra (600 MHz) of rhodium complex **79** in DMSO-d_6 with increasing temperature.

Single crystals of **79** were obtained by slow evaporation of a concentrated solution in a mixture of ethyl acetate and methanol. The single crystal proved that three anionic *N*-heterocyclic carbenes **70b** as ligands are connected to rhodium (Figure 22). The *n*-butyl group connected to N25 is disordered. The bond lengths between the rhodium atom and the carbene carbon atoms (C1, C21 and C41, crystallographic numberings) were found at 196.6(2), 204.7(2) and 204.4(2) pm, respectively. The bond lengths of Rh-O15 and Rh-O35 were 202.49(14) pm and 202.44 (14) pm, respectively, which is shorter than the distance [209.98(15) pm] between Rh and O55. The dihedral angles for C1-N2-C10-C15, C21-N22-C30-C35, and C41-N42-C50-C55 were 26.371(5)°, 18.939(5)°, and -33.008(5)°, respectively.

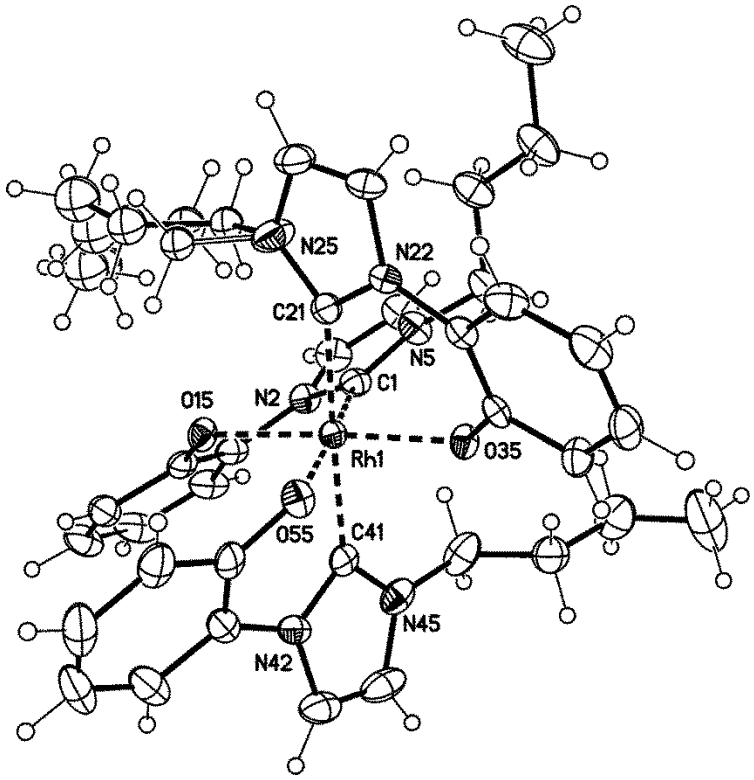
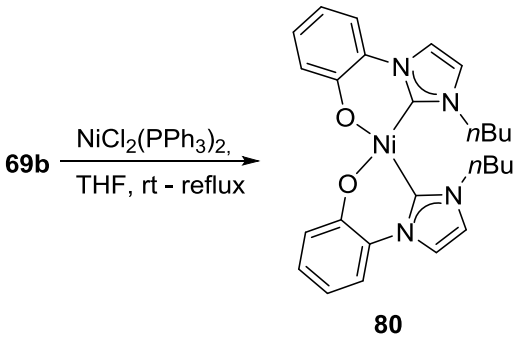


Figure 22: X-ray structure of rhodium complex **79**.

3.2.8 Reaction of imidazole betaines with nickel complexes

Nickel complexes[139-142] as catalysts[143-155] have been examined, because they are less expensive than catalysts of other metals. We found that refluxing the carbene **69b** with bis(triphenylphosphine)nickel(II) in dry THF yielded the nickel complex **80** in good

yield. The electrospray ionization mass spectrum shows the molecular peak at *m/z* = 511 which corresponds to the complex **80** as sodium adduct $[Ni(\mathbf{69})_2+Na]^+$ (Scheme 38).



Scheme 38: Synthesis of nickel complex **80**.

Single crystals of **80** were obtained by slow evaporation of a concentrated solution in a mixture of ethyl acetate and methanol (Figure 23). The X-ray analysis shows two dimer nickel complexes connected by hydrogen bonds with two molecules of water. The bond length of Ni-$C_{carbene}$ was detected to be 184.06(19) pm and 184.82(19) pm and the bond length between the nickel and the oxygen atom were 187.60(13) pm and 190.11(13) pm, respectively.

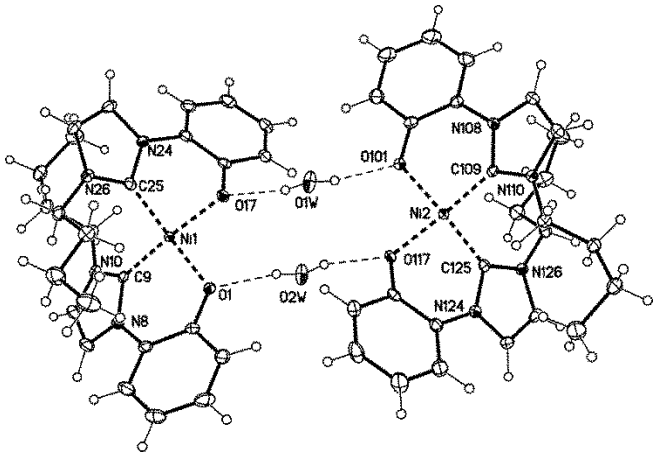
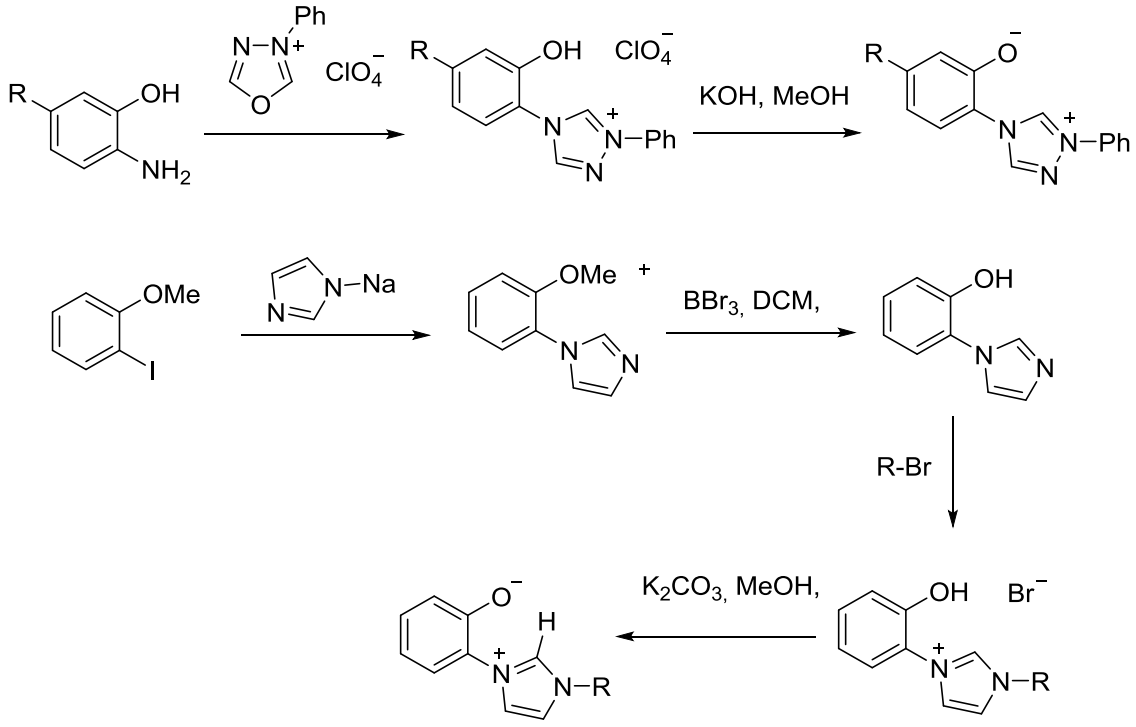


Figure 23: X-ray structure of nickel complex **80**

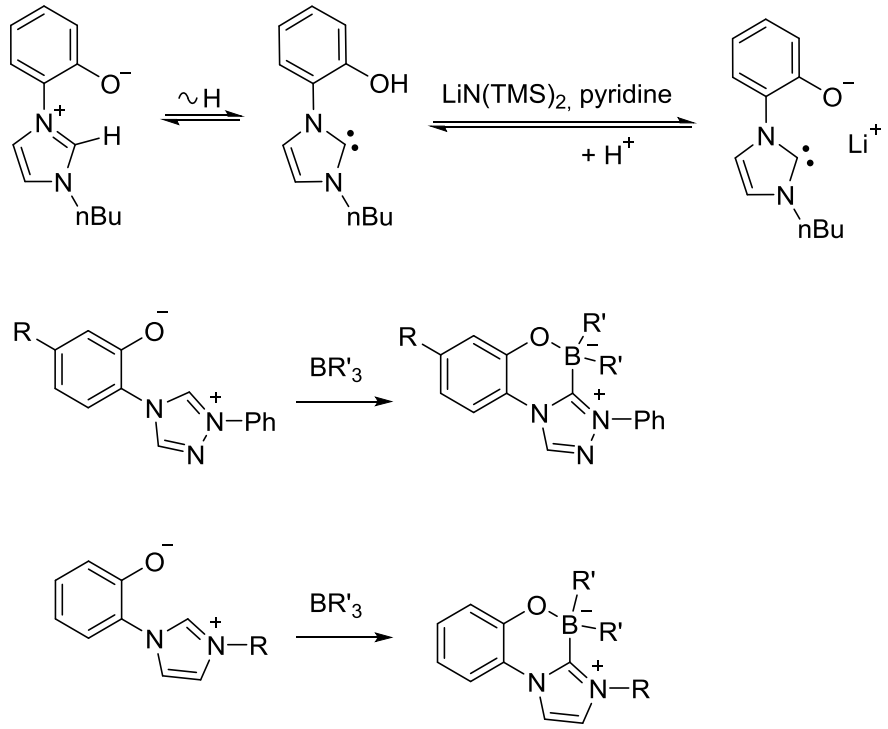
4 Summary and conclusion

Here we reported the design and synthesis of 1,2,4-triazolium and imidazolium salts which are substituted *via* N1 by an *ortho*-phenol ring, respectively. Treatment of the salts with potassium hydroxide and potassium carbonate resulted in the formation of 1,2,4-triazolium-phenolates and imidazolium-phenolates which belong to the substance class of heterocyclic mesomeric betaines. As a proof of the existence of a tautomeric equilibrium between mesomeric betaines and *N*-heterocyclic carbenes, trapping reactions were carried out. Thus, thione formation can be regarded as typical trapping reaction of *N*-heterocyclic carbenes. They were formed by treatment of the salts with potassium 2-methylbutan-2-olate and caesium carbonate or other bases and sulfur in THF.

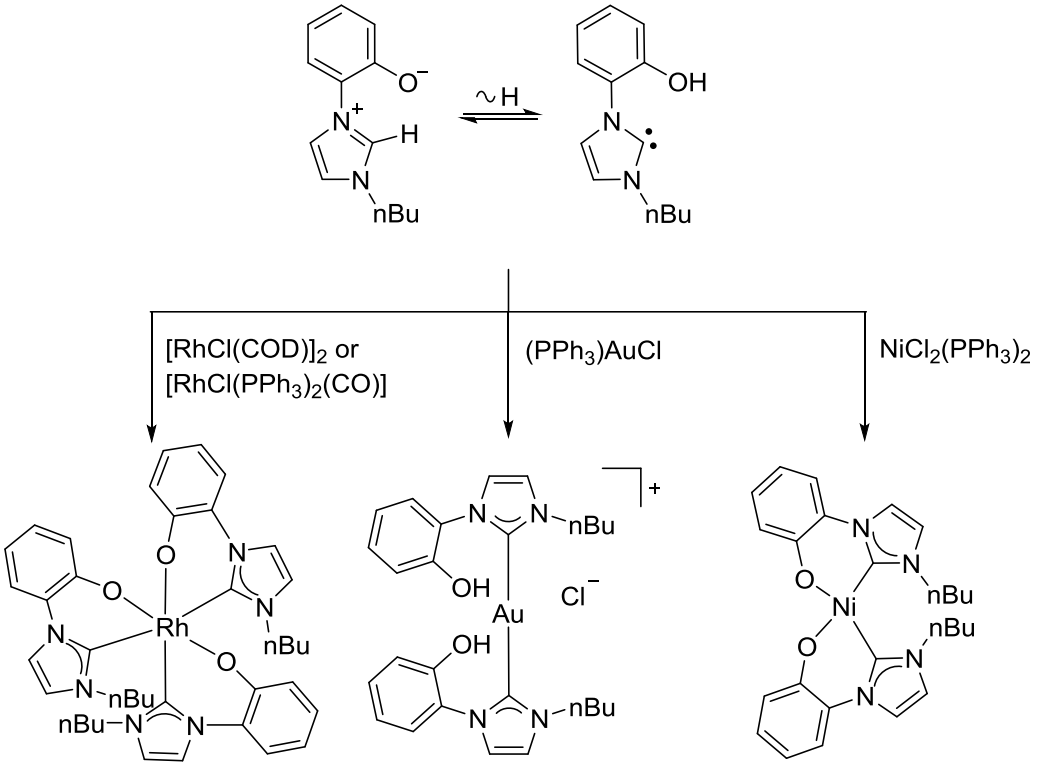


Next, the formation of anionic *N*-heterocyclic carbenes from 1,2,4-triazolium-phenolates and imidazolium-phenolates and their carbene tautomers were investigated. It was found that the anionic *N*-heterocyclic carbene can be generated in quantitative yield starting from imidazolium-phenolate and lithium bis(trimethylsilyl)amide as base in THF/pyridine. The reaction with triethylborane or

triphenylborane gave first representatives of new heterocyclic systems, 3-phenyl-4*H*-benzo[*e*][1,2,4]triazolo[3,4-*c*][1,4,2]oxazaborininium-4-ides and 4,4-diethyl- or 4,4-diphenyl-4*H*-benzo[e]imidazo[2,1-*c*][1,4,2]oxazaborininium-4-ides which are formal trapping products of the aforementioned anionic *N*-heterocyclic carbene.



Last, we focused our interest on complexes of palladium, rhodium, gold, and nickel. The carbene tautomers can be trapped as palladium and gold adducts, whereas the formation of nickel and rhodium complexes from solution in THF and toluene are formal trapping products of the anionic *N*-heterocyclic carbene. Several X-ray structures have been carried out.


O⁻
N⁺
H
N
nBu
∼H
OH
N
N
nBu
[RhCl(COD)]2 or
[RhCl(PPh3)2(CO)]
(PPh3)AuCl
NiCl2(PPh3)2
O
N
Rh
nBu
Au
Cl⁻
Ni

5 Experimental section

5.1 General considerations

All reactions were carried out under an inert atmosphere. Anhydrous solvents such as THF, DMF, diethylether, toluene, dioxane were dried according to standard procedures before usage. All chemicals were purchased and used without further purification.

Melting points: Melting points are uncorrected and were determined in an apparatus according to Dr. Tottoli (Büchi).

FT-IR-spectra: FT-IR spectra were obtained on a *Bruker Alpha* T in the range of 400 to 4000 cm^{-1}.

^{1}H NMR-spectra: ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz.

^{11}B NMR-spectra: ^{11}B NMR spectra were recorded at 128 MHz or 193 MHz.

^{19}F NMR-spectra: ^{19}F NMR spectra were recorded at 376 MHz or 565 MHz.

^{13}C NMR-spectra: ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Signal orientations in DEPT experiments were described as follows: o = no signal; + = up (CH, CH_3); - = down (CH_2).

Mass spectra: The mass spectra were measured with a *Varian 320 MS Triple Quad GC/MS/MS* with a *Varian 450-GC*.

ESIMS-spectra: The electrospray ionization mass spectra (ESI-MS) were measured with an *Agilent LCMSD series HP 1100 with APIES* at fragmentor voltages as indicated. Samples were sprayed from MeOH at 4000 V capillary voltage and fragmentor voltages of 30 V, unless otherwise noted.

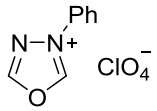
HR-ESI-MS: High resolution ESI-MS were measured at the Institute of Organic Chemistry, Leibniz University, Hannover.

Column Chromatography: The reactions were traced by thin layer chromatography with silica gel 60 (F_{254}, company MERCK). For the detection of substances was used light at either 254 nm or 366 nm generated by a mercury lamp. The preparative column chromatography was conducted through silica gel 60 (230-400 mesh) of the company MERCK.

X-ray: The x-ray measurements were examined by Dr. Martin Nieger of the Department of Chemistry at the University of Helsinki, Finland.

5.2 General procedure for the synthesis of triazolium salts and mesomeric betaines

3-Phenyl-1,3,4-oxadiazolium perchlorate 58[1]

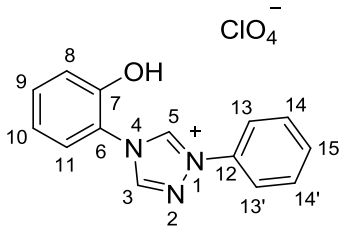


A sample of 0.893 g (5.44 mmol) of *N*, *N'*-diformyl-*N*-phenylhydrazine was treated with 5.2 mL (54.4 mmol) of acetic anhydride under an atmosphere of nitrogen. The mixture was cooled to 0 °C. Afterwards 0.37 mL (6.5 mmol) of perchloric acid (70%) was added dropwise with a syringe, causing a precipitate to appear. The reaction was stirred one more hour at room temperature and 20 mL of anhydrous diethyl ether was added into the mixture. The precipitate was filtered off under an inert atmosphere and washed with Et_2O three times.

Yield: 0.994 g (74%) of a colorless solid.

This compound is hygroscopic and was continuously kept under an inert atmosphere.

4-(2-Hydroxyphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate 59a



A sample of 0.450 g (4.12 mmol) of 2-aminophenol was reacted with 1.016 g (4.12 mmol) of 3-phenyl-1,3,4-oxadiazolium perchlorate in 20 mL of anhydrous THF at 100 °C under an inert atmosphere overnight. The solution was evaporated and the residue was treated with 20 mL of diethyl ether. The solid was filtered off and dried *in vacuo*.

Yield: 0.833 g (60%) of a yellowish solid.

Mp: 154 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.27 (s, 1 H, 5-H), 11.21 (s, 1 H, OH), 9.83 (s, 1 H, 3-H), 8.04 8.01 (m, 2 H, 13/13'-H), 7.76 7.66 (m, 4 H, 14/14'/15/11-H), 7.52 (ddd, J_1 = 1.6 Hz, J_2 = 7.6 Hz, J_3 = 8.2 Hz, 1 H, 9-H), 7.22 (dd, J_1 = 1.1 Hz, J_2 = 8.2 Hz, 1 H, 8-H), 7.13 (ddd, J_1 = 1.1 Hz, J_2 = 7.6 Hz, J_3 = 7.9 H, 1 H, 10-H) ppm.

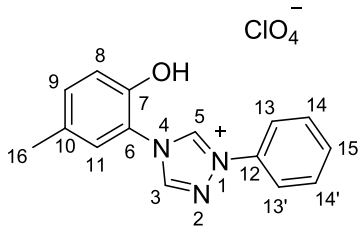
^{13}C NMR (100 MHz, DMSO-d_6): δ = 150.6 (o, C-7), 145.1 (+, C-3), 141.4 (+, C-5), 134.9 (o, C-12), 132.3 (+, C-9), 130.7 (+, C-15), 130.2 (+, C-14/C-14'), 125.9 (+, C-11), 120.9 (+, C-13/C-13'), 119.8 (+, C-10), 119.4 (o, C-6), 117.2 (+, C-8) ppm.

IR (ATR): $\bar{\nu}$ = 3167, 1565, 1338, 1093, 1074, 1034, 999, 773, 755, 741, 639, 551, 499, 468 cm^{-1}.

MS (ESI, 10 V): m/z (%) = 436.0 (100) $[M+2ClO_4]^-$.

HR ESI-MS: calcd for $C_{14}H_{12}N_3O^+$ 238.0980. Found 238.0975.

4-(2-Hydroxy-5-methylphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate 59b



A sample of 0.530 g (4.30 mmol) of 2-amino-4-methylphenol was reacted with 1.060 g (4.30 mmol) of 3-phenyl-1,3,4-oxadiazolium perchlorate in 20 mL of anhydrous THF at 100 °C under an inert atmosphere overnight. Then the reaction mixture was evaporated and the residue was treated with 20 mL of diethyl ether. The resulting solid was filtered off and dried *in vacuo.*

Yield: 0.935 g (62%) of a yellowish solid.

Mp: 156 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.25 (s, 1 H, 5-H), 10.95 (s, 1 H, OH), 9.81 (s, 1 H, 3-H), 8.03 - 8.01 (m, 2 H, 13/13'-H), 7.76 - 7.72 (m, 2 H, 14/14'-H), 7.69 – 7.65 (m, 1 H, 15-H), 7.54 (d, J = 1.6 Hz, 1 H, 11-H), 7.32 (dd, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1 H, 9-H), 7.11 (d, J = 8.4 Hz, 1 H, 8-H), 2.33 (s, 3 H, 16-H) ppm.

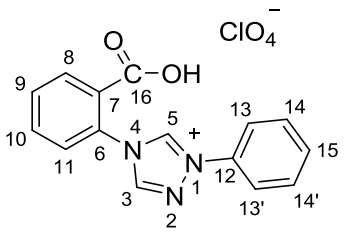
^{13}C NMR (100 MHz, DMSO-d_6): δ = 148.2 (o, C-7), 145.0 (+, C-3), 141.3 (+, C-5), 134.9 (o, C-12), 132.6 (+, C-9), 130.7 (+, C-15), 130.2 (+, C-14/C-14'), 128.9 (o, C-10), 125.8 (+, C-11), 120.9 (+, C-13/C-13'), 118.9 (o, C-6), 117.1 (+, C-8), 19.8 (+, C-16) ppm.

IR (ATR): $\bar{\nu}$ = 3241, 1567, 1522, 1289, 1268, 1144, 1123, 1108, 1095, 1046, 759, 666, 620, 475 cm^{-1}.

MS (ESI, 10 V): *m/z* (%) = 450.0 (100) $[M^+ + 2ClO_4]^-$.

HR ESI-MS: calcd for $C_{15}H_{14}N_3O^+$ 252.1137. Found 252.1137.

4-(2-Carboxyphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate 59c



A sample of 0.589 g (4.30 mmol) of 2-aminobenzoic acid was reacted with 1.060 g (4.30 mmol) of 3-phenyl-1,3,4-oxadiazolium perchlorate in 20 mL of anhydrous THF at 100 °C under an inert atmosphere overnight. The solvent was evaporated and the residue was treated with 20 mL of diethyl ether. The solid was filtered off and dried *in vacuo.*

Yield: 848 mg (54 %) of white solid.

Mp: 110 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.9 (s, 1 H, COOH), 11.35 (s, 1 H, 5-H), 9.84 (s, 1 H, 3-H), 8.29 (dd, J_1 = 1.4 Hz, J_2 = 7.7 Hz, 1 H, 8-H), 8.03 - 7.98 (m, 3 H, 10/13/13'-H), 7.94 - 7.88 (m, 2 H, 9/15-H), 7.79 - 7.74 (m, 2H, 14/14'-H), 7.71 - 7.67 (m, 1 H, 11-H) ppm.

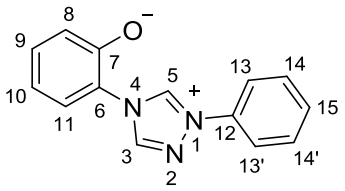
^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.8 (o, C-16), 146.0 (+, C-3), 142.2 (+, C-5), 134.6 (o, C-12), 134.1 (+, C-10), 132.1 (+, C-8), 132.1 (+, C-9), 131.2 (o, C-6), 130.9 (+, C-11), 130.4 (+, C-14/14'), 128.6 (+, C-15), 126.7 (o, C-7), 120.5 (+, C-13/13') ppm.

IR (ATR): 3134, 1706, 1564, 1121, 1097, 1079, 1038, 981, 764, 756, 667, 619 cm^{-1}.

MS (ESI, 30V): m/z = 266.1 $[M]^+$.

HR ESI-MS: calcd for $C_{15}H_{12}N_3O_2$ 266.0931. Found 266.0930.

2-(1-Phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate 60a



A sample of 0.338 g (1.00 mmol) of 4-(2-hydroxyphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate was deprotonated with 1.2 equivalents of KOH in 10 mL of methanol at 0 °C. After precipitation, the solid was filtered off. The organic solution was evaporated and then the resulting solid was dried *in vacuo.*

Yield: 0.206 g (87%) of a yellow solid.

Mp: 155 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.26 (s, 1 H, 5-H), 9.82 (s, 1 H, 3-H), 8.02 - 7.99 (m, 2 H, 13/13'-H), 7.74 - 7.70 (m, 2 H, 14/14'-H), 7.67 - 7.62 (overlapped signals, 2 H, 15/11-H), 7.37 (ddd, J_1 = 1.7 Hz, J_2 = 7.7 Hz, J_3 = 8.4 Hz, 1 H, 9-H), 7.09 (dd, J_1 = 1.1 Hz, J_2 = 8.4 Hz, 1 H, 8-H), 6.87 (ddd, J_1 = 1.1 Hz, J_2 = 7.7 Hz, J_3 = 7.9 Hz, 1 H, 10-H) ppm.

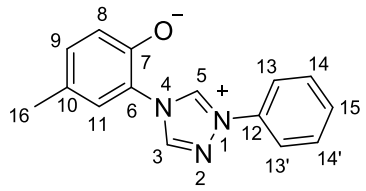
^{13}C NMR (100 MHz, DMSO-d_6): δ= 154.4 (o, C-7), 144.9 (+, C-3), 140.9 (+, C-5), 134.9 (o, C-12), 131.8 (+, C-9), 130.5 (+, C-15), 130.2 (+, C-14/C-14'), 125.1 (+, C-11), 120.8 (+, C-13/C-13'), 119.8 (o, C-6), 118.4 (+, C-8), 116.5 (+, C-10) ppm.

IR (ATR): $\tilde{\nu}$ = 2902, 1592, 1564, 1479, 1450,1334, 1327, 1270, 977, 848, 746, 733, 629, 477, 458 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 238.1 (100) $[M+H]^+$.

HR ESI-MS: calcd for $C_{14}H_{13}N_3O^+$ 238.0980. Found 238.0984.

4-Methyl-2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate 60b



A sample of 0.351 g (1.00 mmol) of 4-(2-hydroxy-5-methylphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate was deprotonated with 1.2 equivalents of KOH in 10 mL of MeOH at 0 °C. After precipitation, the solid was filtered off. The organic solution was evaporated and then the resulting solid was dried *in vacuo.*

Yield: 0.153 g (61%) of a yellow solid.

Mp: 188°C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 11.26 (s, 1 H, 5-H), 9.81(s, 1 H, 3-H), 7.99 - 7.97 (m, 2 H, 13/13'-H), 7.71 7.68 (m, 2 H, 14/14'-H), 7.65 – 7.62 (m, 1 H, 15-H), 7.40 (d, *J* = 1.8 Hz, 1 H, 11-H), 7.08 (dd, J_1 = 1.8 Hz, J_2 = 8.5 Hz, 1 H, 9-H), 6.88 (d, *J* = 8.5 Hz, 1 H, 8-H), 2.24 (s, 3 H, 16-H) ppm.

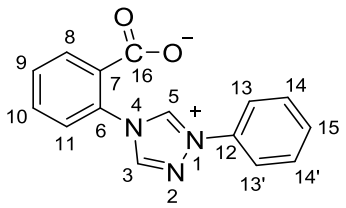
^{13}C NMR (150 MHz, DMSO-d_6): δ = 153.5 (o, C-7), 144.7 (+, C-3), 140.4 (+, C-5), 135.0 (o, C-12), 132.2 (+, C-9), 130.5 (+, C-15), 130.1 (+, C-14/C-14'), 124.5 (+, C-11), 120.7 (+, C-13/C-13'), 119.4 (o, C-6), 118.8 (+, C-8), 19.8 (+, C-16) ppm.

IR (ATR): $\tilde{\nu}$ = 3136, 1569, 1275, 1100, 1082, 1047, 988, 872, 757, 665, 629, 619, 455 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 252.1 (100) $[M+H]^-$.

HR ESI-MS: calcd for $C_{15}H_{15}N_3O^+$ 252.1137. Found 252.1129.

2-(1-Phenyl-4*H*-1,2,4-triazolium-4-yl)benzoate 60c



A sample of 0.351 g (1.00 mmol) of 4-(2-carboxyphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate was deprotonated with 1.2 equivalents of KOH in 10 mL of MeOH at 0 °C. After precipitation, the solid was filtered off. The organic solution was evaporated and then the resulting solid was dried *in vacuo.*

Yield: 151 mg (57 %) of white solid.

Mp: 213 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 11.24 (s, 1 H, 5-H), 9.65 (s, 1 H, 3-H), 8.07 - 8.05 (m, 1 H, 15-H), 8.02 - 7.99 (m, 2H, 13/13'-H), 7.75 - 7.71 (m, 2 H, 14/14'-H), 7.67 - 7.57 (m, 4 H, 8/9/10/11-H) ppm.

^{13}C NMR (151 MHz, DMSO-d_6): δ = 165.0 (o, C-16), 146.3 (+, C-3), 142.7 (+, C-5), 137.7 (o, C-7), 135.4 (o, C-12), 132.0 (+, C-9), 131.2 (+, C-15), 130.9 (+, C-14/C-14'), 130.8 (+, C-11), 130.7 (o, C-6), 129.7 (+, C-13/C-13'), 126.6 (+, C-8), 120.9 (+, C-10) ppm.

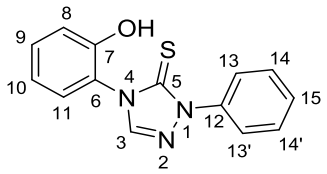
IR (ATR): 1615, 1602, 1564, 1367, 828, 754, 710, 683, 669, 643, 550 cm^{-1}.

MS (ESI, 30V): m/z = 266.1 $[M+H]^+$.

HR ESI-MS: calcd for $C_{15}H_{12}N_3O_2$ 266.0929. Found 266.0930.

5.3 General procedure for the synthesis of thiones, selenium and boron adducts

4-(2-Hydroxyphenyl)-2-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione 61a



Method A: To 0.169 g (0.50 mmol) of 4-(2-hydroxyphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate and 0.019 g (0.60 mmol) of sulfur was added 0.55 mmol of potassium 2-methylbutan-2-olate in 10 mL of dry THF at 0 °C under an inert atmosphere. Afterwards the reaction was stirred 30 min at room temperature and heated at 100 °C for 3 h. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.079 g (59%) of a yellow solid.

Mp: 182 °C.

Method B: A sample of 0.119 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate and 0.032 g (1.00 mmol) of sulfur were refluxed in 10 mL of dry toluene for 8 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.135 g (50 %).

Mp: 182 °C.

^{1}H NMR (400 MHz, CD_3OD): δ = 8.43 (s, 1 H, 3-H), 8.04 - 8.01 (m, 2 H, 13/13'-H), 7.56 - 7.51 (m, 2 H, 14/14'-H), 7.46 - 7.42 (overlapped signals, 2 H, 15/11-H), 7.37 (ddd, J_1 = 1.7 Hz, J_2 = 7.5 Hz, J_3 = 8.3 Hz, 1 H, 9-H), 7.07 (dd, J_1 = 1.2 Hz, J_2 = 8.3 Hz, 1 H, 8-H), 7.01 (ddd, J_1 = 1.2 Hz, J_2 = 7.5 Hz, J_3 = 7.9 Hz, 1 H, 10-H) ppm.

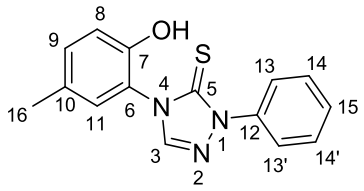
^{13}C NMR (100 MHz, CD_3OD): δ = 168.1 (o, C-5), 154.0 (o, C-7), 143.5 (+, C-3), 139.9 (o, C-12), 132.2 (+, C-9), 130.4 (+, C-15), 129.8 (+, C-14/C-14'), 129.3 (+, C-11), 125.6 (+, C-13/C-13'), 123.1 (o, C-6), 120.8 (+, C-8), 118.0 (+, C-10) ppm.

IR (ATR): $\bar{\nu}$ = 3080, 1598, 1541, 1499, 1467, 1403, 1324, 1295, 1160, 961, 748, 715, 574 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 292.0 (100) $[M+Na]^+$.

HR ESI-MS: calcd for $C_{14}H_{12}N_3OS^+$ 270.0701. Found 270.0704.

4-(2-Hydroxy-5-methylphenyl)-2-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione 61b



Method A: To 0.176 g (0.50 mmol) of 4-(2-hydroxy-5-methylphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate and 0.019 mg (0.6 mmol) of sulfur was added 0.55 mmol of potassium-2-methylbutan-2-olate in 10 mL of dry THF at 0 °C under an inert atmosphere. Afterwards the reaction was stirred for 30 min at room temperature and then heated at 100 °C for 3 h. The solvent was evaporated and the product was separated by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.112 g (79%) of a yellow solid.

Mp: 177 °C.

Method B: A sample of 0.126 g (0.50 mmol) of 4-methyl-2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate and 0.032 mg (1.00 mmol) of sulfur were refluxed in 10 mL of dry toluene for 8 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.085 g (60%) of a yellow solid.

Mp: 177 °C.

^{1}H NMR (400 MHz, CD_3OD): δ = 8.391 (s, 1 H, 3-H), 8.01 - 7.99 (m, 2 H, 13/13'-H), 7.53 - 7.50 (m, 2 H, 14/14'-H), 7.46 – 7.42 (m, 1 H, 15-H), 7.23 (d, *J* =1.9 Hz, 1 H, 11-H), 7.17 (dd, J_1 = 1.9 Hz, J_2 = 8.5 Hz, 1 H, 9-H), 6.94 (d, *J* = 8.5 Hz, 1 H, 8-H) ppm.

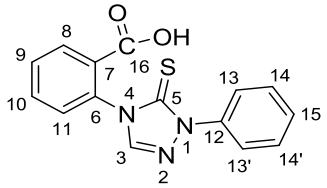
^{13}C NMR (100 MHz, CD_3OD): δ = 167.2 (o, C-5), 150.8 (o, C-7), 142.7 (+, C-3), 139.1 (o, C-12), 131.9 (+, C-9), 129.7 (o, C-10), 129.5 (+, C-15), 129.0 (+, C-14/C-14'), 128.5 (+, C-11), 124.8 (+, C-13/ C-13'), 121.9 (o, C-6), 117.1 (+, C-8), 19.6 (+, C-16) ppm.

IR (ATR): $\bar{\nu}$ = 3145, 1542, 1517, 1501, 1400, 1311, 1288, 1261, 1183, 967, 807, 759, 692, 578, 548 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 306.0 (100) $[M+Na]^+$.

HR ESI-MS: calcd for $C_{15}H_{14}N_3OS^+$ 284.0858. Found 284.0860.

2-(1-Phenyl-5-thioxo-1,5-dihydro-4*H*-1,2,4-triazol-4-yl)benzoic acid 61c



To 0.183 g (0.50 mmol) of 4-(2-carboxyphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate and 0.019 g (0.6 mmol) of sulfur was added 0.55 mmol of potassium 2-methylbutan-2-olate in 10 mL of dry THF at 0 °C under an inert atmosphere. Afterwards the reaction was stirred over a period of 30 min at room temperature and finally heated at 100 °C for 3 h. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 85 mg (57 %) of yellow solid.

Mp: 115 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.63 (s, 1 H, 3-H), 8.10 - 8.07 (m, 2 H, 13/13'), 7.91 - 7.89 (m, 1 H, 8-H), 7.56 - 7.52 (m, 2 H, 14/14'-H), 7.46 - 7.35 (m, 4 H, 9/10/11/15-H) ppm.

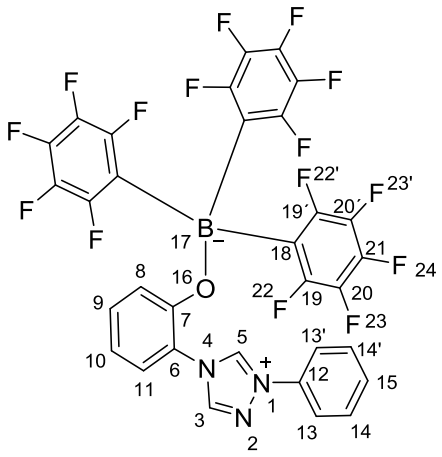
^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.9 (o, C-16), 165.7 (o, C-5), 143.5 (+, C-3), 139.2 (o, C-7), 138.5 (o, C-12), 132.2 (o, C-6), 130.6 (+, C-8), 128.8 (+, C-10), 128.7 (+, C-11), 128.6 (+, C-14/14'), 128.1 (+, C-9), 127.4 (+, C-15), 123.4 (+, C-13/13') ppm.

IR (ATR): 1595, 1565, 1392, 1373, 1342, 1309, 958, 755, 696, 689, 640, 576 cm^{-1}.

MS (ESI, 50V): m/z = 298.0 $[M+H]^+$.

HR ESI-MS: $C_{15}H_{12}N_3O_2S$ required 298.0647. Found 298.0650.

Tris(perfluorophenyl)(2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenoxy)borate 62a



A sample of 0.119 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl) phenolate was reacted with 0.512 mg (1.0 mmol) of tris(pentafluorophenyl)borane in 10 mL of dry dioxane at room temperature for 2 h in a bomb tube under an inert atmosphere. The solvent was then evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.281 g (75%) of a colorless solid.

Mp: 260 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 11.02 (s, 1 H, 5-H), 9.51 (s, 1 H, 3-H), 7.92 - 7.91 (m, 2 H, 13/13'-H), 7.73 - 7.66 (overlapped signals, 4 H, 14/14'/15/11-H), 7.29 (ddd, J_1 = 1.7 Hz, J_2 = 7.6 Hz, J_3 = 8.5 Hz, 1 H, 9-H), 6.93 (ddd, J_1 = 1.0 Hz, J_2 = 7.6 Hz, , J_3 = 7.8 Hz, 1 H, 10-H), 6.62 (dd, J_1 = 1.0 Hz, J_2 = 8.4 Hz, 1 H, 8-H) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.7 (o, C-7), 148.0 (o, C19), 146.4 (o, C-19'), 145.3 (+, C-3), 141.3 (+, C-5), 139.0 - 137.4 (C-21), 136.8 - 136.6 (C-20), 135.2 - 135.0 (C-20'), 134.6 (o, C-12), 131.5 (+, C-9), 130.8 (+, C-15), 130.3 (+, C-14/C-14'), 125.1 (+, C-11), 122.5 (o, C-6), 121.6 (o, C-18), 120.4 (+, C-13/C-13'), 118.0 (+, C-10), 117.3 (+, C-8) ppm.

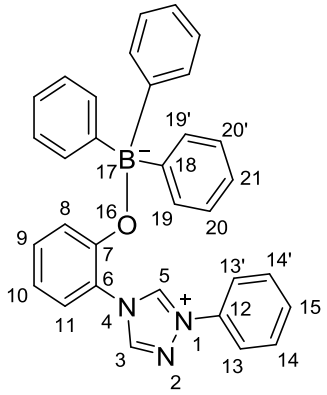
^{11}B NMR (DMSO-d_6, 193 MHz, $B(OMe)_3$): δ = -3.30 ppm.

^{19}F NMR (DMSO-d_6, 376 MHz, Cl_3CF): δ = -133.44 (d, J = 22.37 Hz, 6 F, FC-22/FC-22'), 159.07 (t, J = 21.51 Hz, 3F, FC-24), -164.33 (t, J = 19.51 Hz, 6 F, FC-23/FC-23') ppm.

IR (ATR): $\bar{\nu}$ = 3150, 1565, 1512, 1483, 1277, 1087, 975, 965, 929, 764, 749, 690, 669, 549 cm^{-1}.

GC-MS: 237.0 (100) [M-$B(C_6F_5)_3$].

Triphenyl(2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenoxy)borate 62b



A sample of 0.119 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate was reacted with 0.242 g (1.00 mmol) of triphenylborane solution in dioxane in 5 mL of dry dioxane at room temperature in a bomb tube for 2 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.321 g (67%) of a colorless solid.

Mp: 158 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 11.23 (s, 1 H, 5-H), 9.81 (s, 1 H, 3-H), 7.98 - 7.96 (m, 2 H, 13/13'-H), 7.74 - 7.71 (m, 2 H, 14/14'-H), 7.69 – 7.66 (m, 1 H, 15-H), 7.58 (dd, J_1= 1.7 Hz, J_2 = 7.9 Hz, 1 H, 11-H), 7.29 (dd, J_1 = 1.3 Hz, J_2 = 8.0 Hz, 6 H, 19/19'-H), 6.97 - 6.94 (overlapped signals, 7 H, 20/20´/9-H), 6.86 (m, 3 H, 21-H), 6.67 (td, J_1 = 1.2 Hz, J_2 = 7.9 Hz, 1 H, 10-H), 6.62 (dd, J_1 = 1.2 Hz, J_2 = 8.5 Hz, 1 H, 8-H) ppm.

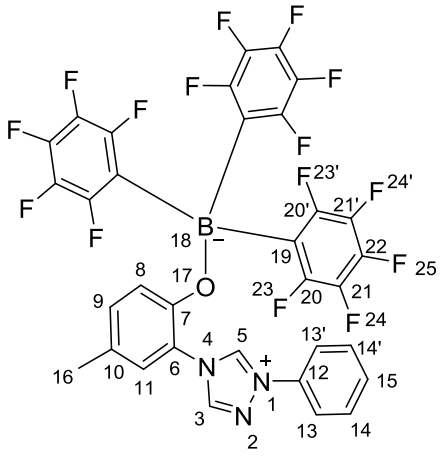
^{13}C NMR (150 MHz, DMSO-d_6): δ = 157.2 (o, C-18), 155.4 (o, C-7), 145.2 (+, C-3), 141.2 (+, C-5), 134.9 (o, C-12), 133.0 (+, C-19/C-19'), 130.6 (+, C-15), 130.2 (+, C-14/C-14'), 126.0 (+, C-20/C-20'), 125.8 (+, C-9), 123.9 (+, C-11), 123.1 (+, C-21), 121.8 (o, C-6), 121.3 (+, C-8), 120.8 (+, C-13/C-13'), 115.0 (+, C-10) ppm.

^{11}B NMR (DMSO-d_6, 193 MHz, $B(OMe)_3$): δ = -6.56 ppm.

IR (ATR): $\bar{\nu}$ = 1601, 1557, 1497, 1311, 1115, 827, 806, 702, 684, 667, 612 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 238.1 (100) $[M\text{-}B(C_6H_5)_3+H]^+$.

(4-Methyl-2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenoxy)tris(perfluorophenyl) borate 62c



A sample of 0.126 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate was reacted with 0.512 g (1.00 mmol) of tris(pentafluorophenyl)borane in 10 mL of dry dioxane at room temperature for 2 h in a bomb tube under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.298 g (78%) of a colorless solid.

Mp: 281 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 11.00 (s, 1 H, 5-H), 9.49 (s, 1 H, 3-H), 7.92 - 7.91 (m, 2 H, 13/13'-H), 7.72 - 7.69 (m, 2 H, 14/14'-H), 7.67 – 7.64 (m, 1 H, 15-H), 7.53 (d, J = 2.0 Hz, 1 H, 11-H), 7.08 (dd, J_1 = 2.0 Hz, J_2 = 8.8 Hz, 2 H, 9-H), 6.55 (d, J = 8.8 Hz, 1 H, 8-H) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 150.7 (o, C-7), 148.5 (o, C-20), 146.9 (o, C-20'), 145.6 (+, C-3), 141.5 (+, C-5), 139.5 - 137.9 (o, C-22), 137.3 - 137.1 (o, C-21), 135.7 - 135.4 (o, C-21'), 135.1 (o, C-12), 132.3 (+, C-9), 131.2 (+, C-15), 130.7 (+, C-14/C-14'), 127.4 (o, C-10), 125.5 (+, C-11), 122.4 (o, C-6), 122.1 (o, C-19), 120.9 (+, C-13/C-13'), 117.7 (+, C-8), 20.2 (+, C-16) ppm.

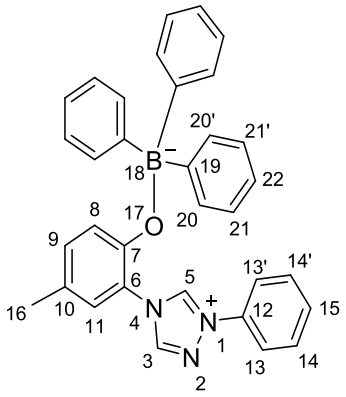
^{11}B NMR (DMSO-d_6, 193 MHz, $BF_3 \cdot Et_2O$): δ = -4.46 ppm.

^{19}F NMR (DMSO-d_6, 376 MHz, Cl_3CF): δ = -133.44 (d, *J* = 22.64 Hz, 6 F, FC-23 /FC-23'), -159.14 (t, *J* = 21.47 Hz, 3F, FC-25), -164.36 (t, *J* = 20.08 Hz, 6 F, FC-24/FC-24') ppm.

IR (ATR): $\bar{\nu}$ = 3163, 1514, 1457, 1277, 1089, 975, 965, 949, 941, 929, 916, 767, 759, 753, 667 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 252.1 (100) $[M\text{-}B(C_6F_5)_3+H]^+$.

(4-Methyl-2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenoxy)triphenylborate 62d



A sample of 0.126 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate was reacted with 0.242 g (1.0 mmol) of triphenylborane solution in dioxane in 5 mL of anhydrous dioxane at room temperature in a bomb tube for 2 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.355 g (72%) of a colorless solid.

Mp: 148 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 11.20 (s, 1 H, 5-H), 9.79 (s, 1 H, 3-H), 7.95 (d, *J* = 7.9 Hz, 2 H, 13/13'-H), 7.73 - 7.71 (m, 2 H, 14/14'-H), 7.68 – 7.65 (m, 1 H, 15-H), 7.40 (d, *J* = 1.83 Hz, 1 H, 11-H), 7.28 (dd, J_1= 1.1 Hz, *J* = 7.1 Hz, 6 H, 20/20'-H), 6.95 (t, *J* = 7.1 Hz, 6 H, 21/21'-H), 6.86 (m, 3 H, 22-H), 6.77 (dd, 1 H, J_1 = 1.8 Hz, J_2 = 8.7 Hz, 9-H), 6.53(d, *J* = 8.7 Hz, 1 H, 8-H), 2.18 (s, 3 H, 16-H) ppm.

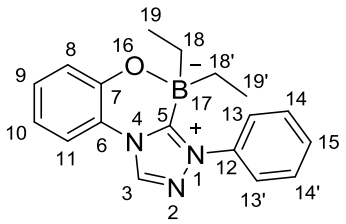
^{13}C NMR (150 MHz, DMSO-d_6): δ = 157.4 (o, C-19), 156.0 (o, C-7), 144.9 (+, C-3), 140.8 (+, C-5), 134.9 (o, C-12), 133.0 (+, C-20/C-20'), 130.7 (+, C-9), 130.6 (+, C-15), 130.2 (+, C-14/C-14'), 125.9 (+, C-21/C-21'), 123.8 (o, C-10), 123.6 (+, C-11), 123.0 (+, C-22), 121.3 (o, C-6), 121.2 (+, C-8), 120.7 (+, C-13/C-13'), 19.7 (+, C-16) ppm.

^{11}B NMR (DMSO-d_6, 193 MHz, $BF_3 \cdot Et_2O$): δ = -6.57 ppm.

IR (ATR): $\bar{\nu}$ = 3120, 1566, 1520, 1292, 1284, 1094, 1072, 870, 845, 752, 699, 684, 666, 621, 482 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 252.1 (100) $[M\text{-}B(C_6H_5)_3+H]^+$.

4,4-Diethyl-3-phenyl-4*H*-benzo[*e*][1,2,4]triazolo[3,4-*c*][1,4,2]oxazaborininium-4-ide 63a



A sample of 0.119 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate was reacted with 0.460 g (5.00 mmol) of triethylborane solution in dioxane in 5 mL of anhydrous dioxane at 100 °C in a bomb tube for 8 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.122 g (80%) of a colorless solid.

Mp: 143 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (s, 1 H, 3-H), 7.60 - 7.52 (m, 5 H, 13/13'/14/14'/15-H), 7.33 (dd, J_1 = 1.7 Hz, J_2 = 7.8 Hz, 1 H, 11-H), 7.24 (ddd, J_1 = 1.7 Hz, J_2 = 7.6 Hz, J_3 = 8.3 Hz, 1 H, 9-H), 7.12 (dd, J_1 = 1.3 Hz, J_2 = 8.3 Hz, 1 H, 8-H), 6.81 (ddd, J_1 = 1.3 Hz, J_2 = 7.6 Hz, J_3 = 7.8 Hz, 1 H, 10-H), 0.63 (t, J = 7.7 Hz,

6 H, 19/19'-H), 0.47 - 0.37 (overlapped signals, 2 H, 18/18'-H), 0.30 - 0.21 (overlapped signals, 2 H, 18/18'-H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.2 (o, C-7), 137.4 (o, C-12), 136.1 (+, C-13), 130.5 (+, C-15), 130.1 (+, C-9), 129.2 (+, C-13/C-13'), 125.5 (+, C-14/C-14'), 121.3 (o, C-6), 121.2 (+, C-8), 117.0 (+, C-10), 115.9 (+, C-11), 14.6 (-, C-18/C-18'), 9.9 (+, C-19/C-19') ppm.

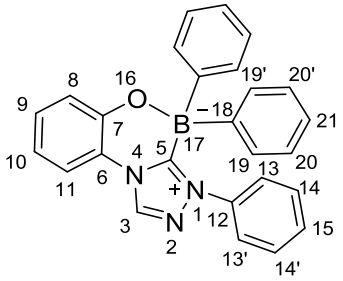
^{11}B NMR ($CDCl_3$, 193 MHz, $BF_3 \cdot Et_2O$): δ = -1.97 ppm.

IR (ATR): $\bar{\nu}$ = 2864, 1506, 1460, 1306, 1292, 1146, 1036, 978, 883, 816, 750, 688, 659 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 238.1 (100) $[M+Na]^+$.

HR ESI-MS: calcd for $C_{18}H_{21}N_3OB^+$ 306.1778. Found 306.1775.

3,4,4-Triphenyl-4*H*-benzo[*e*][1,2,4]triazolo[3,4-*c*][1,4,2]oxazaborininium-4-ide 63b



Method A: A sample of 0.119 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate was reacted with 0.242 g (1.00 mmol) of triphenylborane in 5 mL of anhydrous dioxane at 100 °C in a bomb tube for 8 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.050 g (25%) of a colorless solid.

Mp: 86 °C.

Method B: A sample of 0.240 g (0.50 mmol) triphenyl(2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenoxy) borate was stirred in 10 mL of dry dioxane at 100 °C for 8 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.178 g (89%).

Mp: 86 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.68 (s, 1 H, 3-H), 7.34 (d, J = 7.9 Hz, 1 H, 11-H), 7.30 - 7.27 (m, 1 H, 15-H), 7.25 - 7.24 (m, 2 H, 9/10-H), 7.18 (dd, J_1 = 2.0 Hz, J_2 = 7.7 Hz, 4 H, 19/19'-H), 7.15 - 7.12 (m, 2 H, 14/14'-H), 7.11 - 7.05 (m, 8 H, 13/13'/20/20'/21-H), 6.84 - 6.82 (m, 1 H, 8-H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.1 (o, C-7), 136.4 (o, C-12), 136.0 (+, C-3), 133.2 (+, C-19/C-19'), 130.3 (+, C-9), 129.6 (+, C-15), 128.6 (+, C-13/C-13'), 127.1 (+, C-20/C-20'), 125.9 (+, C-21), 125.5 (+, C-14/C-14'), 121.8 (+, C-10), 121.5 (o, C-6), 118.2 (+, C-8), 116.1 (+, C-11) ppm.

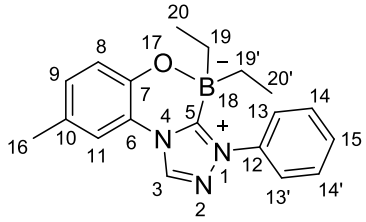
^{11}B NMR ($CDCl_3$, 193 MHz, $BF_3 \cdot Et_2O$): δ = -0.08 ppm.

IR (ATR): $\bar{\nu}$ = 3042, 1530, 1305,1279, 1181, 979, 926, 898, 739, 701, 688, 660, 650 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 424.1 (100) $[M+Na]^+$.

HR ESI-MS: calcd for $C_{26}H_{20}N_3OBNa^+$ 424.1597. Found 424.1598.

4,4-Diethyl-3-phenyl-4*H*-benzo[*e*][1,2,4]triazolo[3,4-*c*][1,4,2]oxazaborininium-4-ide 63c



A sample of 0.126 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate was reacted with 0.460 g (5.00 mmol) of triethylborane in 5 mL of anhydrous dioxane at 100 °C in a bomb tube for 8 h under an atmosphere of nitrogen. The solvent was then evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.120 g (75%) of a colorless solid.

Mp: 114 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.62 (s, 1 H, 3-H), 7.58 - 7.52 (m, 5 H, 13/13'/14/14'/15-H), 7.14 (d, *J* = 1.6 Hz, 1 H, 11-H), 7.05 (ddd, J_1 = 0.4 Hz, J_2 = 1.6 Hz, J_3 = 8.3 Hz, 1 H, 9-H), 7.02 (d, *J* = 8.3 Hz, 1 H, 8-H), 2.33 (s, 3 H, 16-H), 0.63 (t, *J* = 7.7 Hz, 6 H, 20/20'-H), 0.43 - 0.37 (overlapped signals, 2 H, 19/19'-H), 0.28 - 0.22 (overlapped signals, 2 H, 19/19'-H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.0 (o, C-5), 150.8 (o, C-7), 137.4 (o, C-12), 136.0 (+, C-3), 130.8 (+, C-9), 130.4 (+, C-15), 129.2 (+, C-13/C-13'), 126.5 (o, C-10), 125.5 (+, C-14/C-14'), 120.9 (o, C-6), 120.9 (+, C-8), 116.2(+, C-11), 20.6 (+, C-16), 14.5 (-, C-19/C-19'), 9.9 (+, C-20/C-20') ppm.

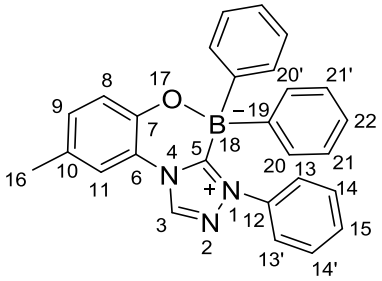
^{11}B NMR ($CDCl_3$, 193 MHz, $BF_3{\cdot}Et_2O$): δ = -0.98 ppm.

IR (ATR): $\bar{\nu}$ = 2864, 1513, 1456, 1305, 1117, 913, 897, 868, 821, 763, 689, 661 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 342.1 (100) $[M+Na]^+$.

HR ESI-MS: calcd for $C_{19}H_{22}N_3OBNa^+$ 342.1754. Found 342.1758.

8-Methyl-3,4,4-triphenyl-4*H*-benzo[*e*][1,2,4]triazolo[3,4-*c*][1,4,2]oxazaborininium-4-ide 63d



Method A: A sample of 0.126 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate was reacted with 0.242 g (1.0 mmol) of triphenylborane solution (in dioxane) in 5 mL of anhydrous dioxane at 100 °C in a bomb tube for 8 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.093 g (45%) of a colorless solid.

Mp: 182 °C.

Method B: A sample of 0.247 g (0.50 mmol) of (4-methyl-2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenoxy)triphenylborate was stirred in 10 mL of dry dioxane at 100 °C for 8 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.187 g (90%) of a colorless solid.

Mp: 182 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.65 (s, 1 H, 3-H), 7.28 – 7.26 (m, 1 H, 15-H), 7.18 (dd, J_1 = 0.9 Hz, J_2 = 7.2 Hz, 4 H, 20/20'-H), 7.14 - 7.10 (m, 6 H, 13/13'/14/14'/11/8-H), 7.09 - 7.04 (m, 7 H, 21/21'/22/9-H), 2.29 (s, 3 H, 16-H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 149.7 (o, C-19), 148.3 (o, C-7), 136.4 (o, C-12), 136.0 (+, C-3), 133.2 (+, C-20/C-20'), 130.0 (+, C-9), 129.6 (+, C-15), 128.6 (+, C-13/C-13'), 127.7 (o, C-10), 127.1 (+, C-21/C-21'), 125.9 (+, C-22), 125.4 (+, C-14/C-14'), 121.4 (+, C-8), 121.1 (o, C-6), 116.3 (+, C-11), 20.6 (+, C-16) ppm.

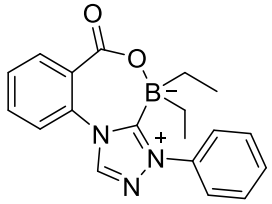
^{11}B NMR ($CDCl_3$, 193 MHz, $BF_3 \cdot Et_2O$): δ = -0.80 ppm.

IR (ATR): $\bar{\nu}$ = 1511, 1301, 1177, 1145, 927, 907, 872, 823, 739, 689, 660 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 438.1 (100) $[M+Na]^+$.

HR ESI-MS: calcd for $C_{27}H_{22}N_3OBNa^+$ 438.1754. Found 438.1758.

4,4-Diethyl-6-oxo-3-phenyl-4*H*,6*H*-benzo[e][1,2,4]triazolo[3,4-c][1,4,2] oxazaborepinium-4-ide 63e



A sample of 0.133 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)benzoate was reacted with 0.460 g (5.00 mmol) of triethylborane in 5 mL of anhydrous dioxane at 100 °C in a bomb tube for 8 h under an atmosphere of nitrogen. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

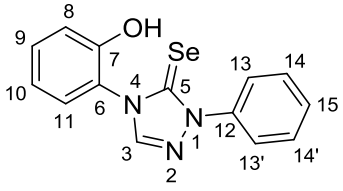
Yield: 0.167 g (18%) of a white solid.

This compound is hygroscopic and was continuously kept under an inert atmosphere.

MS (ESI, 30V): m/z = 356.1 $[M+Na]^+$.

HR ESI-MS: $C_{19}H_{21}N_3O_2B_1$ required 334.1728. Found 334.1727.

4-(2-Hydroxyphenyl)-2-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-selenone 64a



To 0.169 g (0.50 mmol) of 4-(2-hydroxyphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate and 0.047 mg (0.60 mmol) of selenium was added 0.55 mmol of potassium 2-methylbutan-2-olate in 10 mL of dry THF at 0 °C under a nitrogen atmosphere. Afterwards the reaction was stirred at room temperature for 30 min and then heated at 100 °C for 3 h. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.079 g (50%) of a yellow solid.

Mp: 168 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ =10.32 (s, 1H, OH), 9.02 (s, 1 H, 3-H), 8.04 - 8.02 (m, 2 H, 13/13'-H), 7.60 - 7.56 (m, 2 H, 14/14'-H), 7.52 - 7.45 (overlapped signals, 2 H, 15/11-H), 7.38 (ddd, J_1 = 1.6 Hz, J_2 = 7.5 Hz, J_3 = 8.2 Hz, 1 H, 9-H), 7.09 (dd, J_1 = 1.1 Hz, J_2 = 8.2 Hz, 1 H, 8-H), 6.98 (ddd, J_1 = 1.1 Hz, J_2 = 7.5 Hz, J_3 = 7.8 Hz, 1 H, 10-H) ppm.

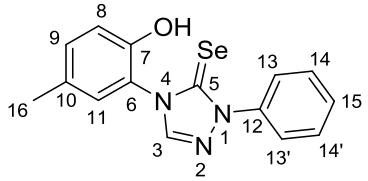
^{13}C NMR (100 MHz, DMSO-d_6): δ = 161.3 (o, C-5), 152.6 (o, C-7), 144.4 (+, C-3), 138.6 (o, C-12), 131.0 (+, C-9), 129.7 (+, C-15), 128.8 (+, C-14/C-14'), 128.5 (+, C-11), 124.8 (+, C-13/C-13'), 122.2 (o, C-6), 119.0 (+, C-8), 116.8 (+, C-10) ppm.

IR (ATR): $\bar{\nu}$ = 3069, 1694, 1598, 1500, 1457, 1409,1322, 1316, 1303, 962, 747, 692, 684, 549, 498 cm^{-1}.

MS (ESI, 10 V): m/z (%) = 316.0 (100) [M-H]$^-$.

HR ESI-MS: calcd for $C_{14}H_{13}N_3OSe^+$ 318.0146. Found 318.0147.

4-(2-Hydroxy-5-methylphenyl)-2-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-selenone 64b



To 0.176 g (0.50 mmol) of 4-(2-hydroxy-5-methylphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate and 0.047 mg (0.60 mmol) of selenium was added 0.55 mmol of potassium 2-methylbutan-2-olate in 10 mL of dry THF at 0 °C under a nitrogen atmosphere. Afterwards the reaction was stirred at room temperature for 30 min and then heated at 100 °C for 3 h. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.089 g (54%) of a yellow solid.

Mp: 137 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.02 (s, 1 H, OH), 8.98 (s, 1 H, 3-H), 8.02 - 8.00 (m, 2 H, 13/13'-H), 7.59 - 7.56 (m, 2 H, 14/14'-H), 7.51 – 7.48 (m, 1 H, 15-H), 7.25 (d, J =1.9 Hz, 1 H, 11-H), 7.18 (ddd, J_1 = 0.5 Hz, J_2 = 1.9 Hz, J_3 = 8.3 Hz, 1 H, 9-H), 6.97 (d, J = 8.3 Hz, 1 H, 8-H), 2.26 (s, 3 H, 16-H) ppm.

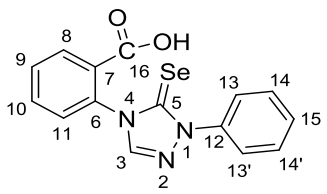
^{13}C NMR (150 MHz, DMSO-d_6): δ = 161.8 (o, C-5), 150.7 (o, C-7), 144.9 (+, C-3), 139.1 (o, C-12), 132.0 (+, C-9), 130.1 (+, C-11), 129.3 (+, C-14/C-14'), 129.0 (+, C-15), 128.3 (o, C-10), 125.3 (+, C-13/C-13'), 122.3 (o, C-6), 117.1 (+, C-8), 20.3 (+, C-16) ppm.

IR (ATR): $\tilde{\nu}$ = 3067, 1694, 1516, 1500, 1405, 1309, 1273, 1181, 965, 811, 760, 693, 486 cm^{-1}.

MS (ESI, 10 V): m/z (%) = 330.0 (100) [M-H]$^-$.

HR ESI-MS: $C_{15}H_{12}N_3OSe$ required 330.0146. Found 330.0149.

2-(1-Phenyl-5-selenoxo-1,5-dihydro-4*H*-1,2,4-triazol-4-yl)benzoic acid 64c



To 0.183 g (0.50 mmol) of 4-(2-carboxyphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate and 0.047 mg (0.60 mmol) of selenium was added 0.55 mmol of potassium 2-methylbutan-2-olate in 10 mL of dry THF at 0 °C under an inert atmosphere. Afterwards, the reaction was stirred at room temperature for 30 min and then heated at 100 °C for 3 h. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 91 mg (53 %) of a yellow solid.

Mp: 191 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.78 (s, 1H, 3-H), 8.07 - 8.05 (m, 2H, 13/13´-H), 7.94 - 7.92 (m, 1 H, 8-H), 7.57 - 7.52 (m, 2H, 14/14´-H), 7.48 - 7.37 (m, 4H, 9/10/11/15-H) ppm.

^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.8 (o, C-16), 160.4 (o, C5), 145.2 (+, C-3), 139.2 (o, C-7), 138.8 (o, C-12), 133.2 (o, C-6), 130.8 (+, C-8), 129.1 (+, C-10), 128.8 (+, C-11), 128.6 (+, C-14/14´), 128.0 (+, C-9), 128.0 (+, C-15), 124.6 (+, C-13/13´) ppm.

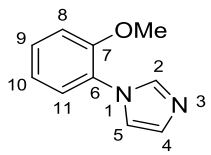
IR (ATR): 1594, 1565, 1498, 1381, 1370, 1325, 1307, 1290, 960, 753, 672, 643, 625, 536 cm^{-1}.

MS (ESI, 30V): m/z = 344.0 $[M-H]^-$.

HR ESI-MS: $C_{15}H_{10}N_3O_2Se$ required 343.9937. Found 343.9938.

5.4 General procedure for the synthesis of imidazolium salts and mesomeric betaines

1-(2-Methoxyphenyl)-1*H*-imidazole 66[2]



A sample of 0.234 g (1.00 mmol) of 2-iodoanisole was reacted with 0.090 g (1.00 mmol) of the sodium imidazolate salt in the presence of 0.006 g (0.10 mmol) of copper powder in 0.2 mL of anhydrous DMF at 150 °C for 4 h under an inert atmosphere. After the reaction cooled down, the mixture was diluted with $CHCl_3$ (1.5 mL) and water (0.5 mL), stirred for 1 h, and filtered. Afterwards the organic phase was washed with water, dried over anhydrous K_2CO_3, and evaporated to yield the crude product which was purified by column chromatography (methanol/CH_2Cl_2).

Yield: 0.082 g (47%) of a yellow solid.

Mp: 53 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.76 (dd, +J_1 = 0.8 Hz, J_2 = 1.2 Hz, 1 H, 2-H), 7.34 (ddd, J_1 = 1.7 Hz, J_2 = 7.5 Hz, J_3 = 8.0 Hz, 1 H, 9-H), 7.26 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1 H, 11-H), 7.19 (dd, J_1 = 0.8 Hz, J_2 = 1.2 Hz, 1 H, 5-H), 7.15 (dd, J_1 = 0.8 Hz, J_2 = 1.2 Hz, 1 H, 4-H), 7.05 - 7.00 (overlapped signals, 2 H, 10-H/8-H), 3.82 (s, 3 H, -OCH_3) ppm.

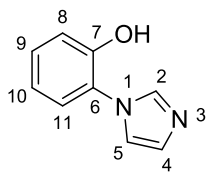
^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.5 (o, C-7), 137.7 (+, C-2), 128.8 (+, C-9), 128.8 (+, C-5), 126.5 (o, C-6), 125.4 (+, C-11), 120.9 (+, C-4), 120.2 (+, C-10), 112.3 (+, C-8), 55.7 (+, -OCH_3) ppm.

IR (ATR): ϑ = 1597, 1512, 1506, 1495, 1464, 1455, 1314, 1296, 1285, 1279, 1062, 1021, 905, 769, 744, 660 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 197.0 (100) $[M+Na]^+$.

HR ESI-MS: calcd for $C_{10}H_{11}N_2O^+$ 175.0871. Found 175.0868.

2-(1*H*-Imidazol-1-yl)phenol 67[2]



A sample of 0.174 g (1.00 mmol) of 1-(2-methoxyphenyl)-1*H*-imidazole was reacted with 0.377 g (1.50 mmol) BBr_3 in 2 mL of anhydrous CH_2Cl_2 at -78 °C under an inert atmosphere. After 30 min, the mixture was stirred for 1 more hour at 0 °C. The excess BBr_3 was quenched by adding MeOH. The product was purified by column chromatography (methanol/CH_2Cl_2 = 5 : 95 v/v).

Yield: 0.141 g (88%) of a white solid.

Mp: 218 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.28 (dd, J_1 = 0.8 Hz, J_2 = 1.2 Hz, 1 H, 2-H), 7.87 (dd, J_1 = 0.8 Hz, J_2 = 1.2 Hz, 1 H, 5-H), 7.73 (dd, J_1 = 0.8 Hz, J_2 = 1.2 Hz, 1 H, 4-H), 7.52 (dd, J_1 = 0.4 Hz, J_2 = 7.5 Hz, 1 H, 11-H), 7.41 (ddd, J_1 = 0.4 Hz, J_2 = 7.5 Hz, J_3 = 7.8 Hz,1 H, 9-H), 7.11 (dd, J_1 = 0.4 Hz, J_2 = 7.5 Hz, 1 H, 8-H), 7.05 (ddd, J_1 = 0.4 Hz, J_2 = 7.5 Hz, J_3 = 7.8 Hz, 1 H, 10-H) ppm.

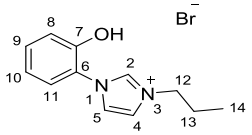
^{13}C NMR (150 MHz, $CDCl_3$): δ = 150.7 (o, C-7), 136.2 (+, C-2), 131.3 (+, C-9), 125.5 (+, C-11), 123.3 (+, C-5), 122.5 (o, C-6), 120.1 (+, C-10), 119.5 (+, C-4), 116.8 (+, C-8) ppm.

IR (ATR): ϑ̃ = 3128, 1586, 1515, 1448, 1283, 1246, 1231, 1100, 1033, 962, 934, 832, 744, 655, 484 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 161.0 (100) $[M+H]^+$.

HR ESI-MS: calcd for $C_9H_9N_2O^+$ 161.0715. Found 161.0714.

1-(2-Hydroxyphenyl)-3-propyl-1*H*-imidazolium bromide 68a



A sample of 0.160 g (1.00 mmol) of 2-(1*H*-imidazol-1-yl)phenol and 0.91 mL (10.00 mmol) of 1-bromopropane was refluxed in a bomb tube overnight under an inert atmosphere. After cooling down to room temperature, the excess

1-bromopropane was taken out by a pipette. The product was purified by column chromatography (Methanol/CH_2Cl_2).

Yield: 0.243 g (86%) of a colorless liquid.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.89 (d, *J* = 2.0 Hz, 1 H, 5-H), 7.85 (d, *J* = 2.0 Hz, 1 H, 4-H), 7.53 (dd, J_1 = 1.6 Hz, J_2 = 7.9 Hz, 1 H, 11-H), 7.42 (ddd, J_1 = 1.6 Hz, J_2 = 7.6 Hz, J_3 = 8.3 Hz, 1 H, 9-H), 7.13 (dd, J_1 = 1.2 Hz, J_2 = 8.3 Hz, 1 H, 8-H), 7.05 (ddd, J_1 = 1.2 Hz, J_2 = 7.6 Hz, J_3 = 7.9 Hz, 1 H, 10-H), 4.33 (t, *J* = 7.2 Hz, 2 H, 12-H), 2.04 - 1.98 (m, 2 H, 13-H), 1.03 (t, *J* = 7.4 Hz, 3 H, 14-H) ppm.

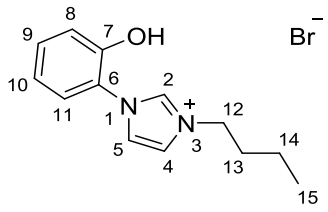
^{13}C NMR (150 MHz, CD_3OD): δ = 150.8 (o, C-7), 136.6 (+, C-2), 131.3 (+, C-9), 125.2 (+, C-11), 123.4 (+, C-5), 122.5 (o, C-6), 121.9 (+, C-4), 119.9 (+, C-10), 116.8 (+, C-8), 51.2 (-, C-12), 23.1 (-, C-13), 9.5 (+, C-14) ppm.

IR (ATR): ϑ = 3039, 1551, 1507, 1460, 1275, 1219, 1187, 1112, 828, 753, 649, 624 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 203.1 (100) $[M]^+$.

HR ESI-MS: calcd for $C_{12}H_{15}N_2O^+$.203.1184 Found 203.1180.

3-Butyl-1-(2-hydroxyphenyl)-1*H*-imidazolium bromide 68b



A sample of 0.160 g (1.00 mmol) of 2-(1*H*-imidazol-1-yl)phenol and 1.07 mL (10.00 mmol) of 1-bromobutane was refluxed in a bomb tube at reflux temperature overnight under an inert atmosphere. After cooling down to room temperature, the excess 1-bromopropane was removed by a pipette. The product was purified by column chromatography (methanol/CH_2Cl_2).

Yield: 0.278 g (94%) of a yellow liquid.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.84 (s, 1 H, -OH), 9.62 (dd, J_1 = 1.7 Hz, J_2 = 2.1 Hz, 1 H, 2-H), 8.06 (dd, J_1 = 1.7 Hz, J_2 = 2.1 Hz, 1 H, 5-H), 8.02 (dd, J_1 = 1.7 Hz, J_2 = 2.1 Hz, 1 H, 4-H), 7.54 (dd, J_1 = 1.6 Hz, J_2 = 7.8 Hz, 1 H, 11-H), 7.41 (ddd, J_1 = 1.6 Hz, J_2 = 7.9 Hz, J_3 =8.5 Hz, 1 H, 9-H), 7.18 (dd, J_1 = 1.2 Hz, J_2 = 7.9 Hz, 1 H, 8-H), 7.02 (ddd, J_1 = 1.2 Hz, J_2 = 7.8 Hz, J_3 = 8.5 Hz, 1 H, 10-H), 4.29 (t, J = 7.2 Hz, 2 H, 12-H), 1.88 - 1.83 (m, 2 H, 13-H), 1.34 - 1.28 (m, 2 H, 14-H), 0.92 (t, J = 7.4 Hz, 3 H, 15-H) ppm.

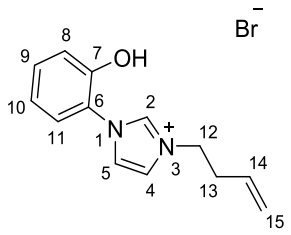
^{13}C NMR (150 MHz, DMSO-d_6): δ= 150.6 (o, C-7), 136.9 (+, C-2), 131.2 (+, C-9), 125.9 (+, C-11), 123.5 (+, C-5), 122.3 (o, C-6), 122.2 (+, C-4), 119.7 (+, C-10), 117.1 (+, C-8), 48.9 (-, C-12), 31.2 (-, C-13), 18.8 (-, C-14), 13.3 (+, C-15) ppm.

IR (ATR): ϑ̃ = 2960, 1551, 1505, 1458, 1379, 1273, 1229, 1188, 1117, 1067, 827, 762, 750, 641, 623, 477 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 217.1 (100) $[M+H]^+$.

HR ESI-MS: calcd for $C_{13}H_{17}N_2O^+$ 217.1341. Found 217.1339.

3-(But-3-en-1-yl)-1-(2-hydroxyphenyl)-1*H*-imidazolium bromide 68c



A sample of 0.160 g (1.00 mmol) of 2-(1*H*-imidazol-1-yl)phenol and 1.02 mL (10.0 mmol) of 4-bromobut-1-ene was refluxed in a bomb tube at reflux overnight under an inert atmosphere. After cooling down to room temperature, the excess 1-bromopropane was removed by a pipette. The product was purified by column chromatography (methanol/CH_2Cl_2).

Yield: 0.265 g (90%) of a yellow liquid.

^{1}H NMR (600 MHz, CD_3OD): δ = 9.38 (dd, J_1 = 1.6 Hz, J_2 = 2.1 Hz, 1 H, 2-H), 7.88 (dd, J_1 = 1.6 Hz, J_2 = 2.1 Hz,, 1 H, 5-H), 7.84 (dd, J_1 = 1.6 Hz, J_2 = 2.1 Hz, 1 H, 4-H), 7.50 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1 H, 11-H), 7.40 (ddd, J_1 = 1.6 Hz, J_2 = 7.9 Hz, J_3 =8.5 Hz, 1 H, 9-H), 7.12 (dd, J_1 = 1.2 Hz, J_2 = 7.9 Hz, 1 H, 8-H), 7.05 (ddd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, J_3 = 8.5 Hz, 1 H, 10-H), 5.90 - 5.84 (m, 1 H, 14-H), 5.15 - 5.12 (m, 2 H, 15-H), 4.44 (t, J = 6.8 Hz, 2 H, 12-H), 2.74 - 2.70 (m, 2 H, 13-H) ppm.

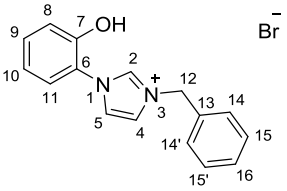
^{13}C NMR (150 MHz, CD_3OD): δ= 150.7 (o, C-7), 136.9 (+, C-2), 132.7 (+, C-14), 131.3 (+, C-9), 125.1 (+, C-11), 123.4 (+, C-5), 122.4 (o, C-6), 122.0 (+, C-4), 118.2 (-, C-15), 116.8 (+, C-8), 49.0 (-, C-12), 33.9 (-, C-13) ppm.

IR (ATR): ϑ = 3030, 1553, 1508, 1465, 1277, 1232, 1188, 1113, 1074, 928, 829, 752, 741, 646 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 215.1 (100) $[M]^+$.

HR ESI-MS: calcd for $C_{13}H_{15}N_2O^+$ 215.1184. Found 215.1183.

3-Benzyl-1-(2-hydroxyphenyl)-1*H*-imidazolium bromide 68d



A sample of 0.160 g (1.00 mmol) of 2-(1*H*-imidazol-1-yl)phenol and 1.02 mL (10.0 mmol) of 1-bromobenzyl was refluxed in a bomb tube at reflux temperature overnight under an inert atmosphere. After cooling down to room temperature, the excess 1-bromopropane was removed by a pipette. The product was purified by column chromatography (methanol/CH_2Cl_2).

Yield: 0.294 g (89 %) of a yellow solid.

Mp: 137°C.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.89 (d, *J* = 2.1 Hz, 1 H, 5-H), 7.76 (d, *J* = 2.1 Hz, 1 H, 4-H), 7.52 - 7.39 (overlap, 7 H, 9/11/14/14'/15/15'/16-H), 7.11 (dd, J_1 = 1.2 Hz, J_2 = 8.3 Hz, 1 H, 8-H), 7.03 (ddd, J_1 = 1.2 Hz, J_2 = 7.5 Hz, J_3 = 8.0 Hz, 1 H, 10-H), 5.55 (s, 2 H, 12-H) ppm.

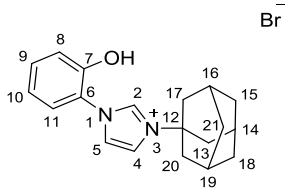
^{13}C NMR (150 MHz, CD_3OD): δ = 151.0 (o, C-7), 136.6 (+, C-2), 133.8 (o, C-13), 131.3 (+, C-9), 129.1 (+, C-14/14'), 129.0 (+, C-15/15'), 128.3 (+, C-16), 125.0 (+, C-11), 123.7 (+, C-5), 122.5 (o, C-6), 121.8 (+, C-4), 119.7 (+, C-10), 117.0 (+, C-8), 52.9 (-, C-12) ppm.

IR (ATR): ϑ = 3061, 1554, 1508, 1462, 1456, 1438, 1279, 1227, 1185, 1111, 1076, 815, 761, 719, 691, 653, 636 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 251.1 (100) $[M]^+$.

HR-ESI-MS: calcd for $C_{16}H_{15}N_2O^+$ 251.1184. Found 251.1187.

3-(Adamantan-1-yl)-1-(2-hydroxyphenyl)-1*H*-imidazolium bromide 68e



A sample of 0.160 g (1.00 mmol) of 2-(1*H*-imidazol-1-yl)phenol and 1.02 mL (10.0 mmol) of 1-bromoadamantane was heated at reflux temperature in a bomb tube overnight under an inert atmosphere. After cooling down to room temperature, the excess 1-bromopropane was removed by a pipette. The product was purified by column chromatography (methanol/CH_2Cl_2).

Yield: 0.236 g (63 %) of a white solid.

Mp: 106 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.56 (dd, J_1 = 1.7 Hz, J_2 = 2.0 Hz, 1 H, 2-H), δ = 8.26 (dd, J_1 = 1.7 Hz, J_2 = 2.0 Hz, 1 H, 5-H), 8.10 (dd, J_1 = 1.7 Hz, J_2 = 2.0 Hz,

1 H, 4-H), 7.56 (dd, J_1 = 1.6 Hz, J_2 = 7.9 Hz, 1 H, 11-H), 7.38 (ddd, J_1 = 1.6 Hz, J_2 = 7.8 Hz, J_3 =8.5 Hz, 1 H, 9-H), 7.15 (dd, J_1 = 1.2 Hz, J_2 = 7.8 Hz, 1 H, 8-H), 6.96 (ddd, J_1 = 1.2 Hz, J_2 = 7.9 Hz, J_3 = 8.5 Hz, 1 H, 10-H), 2.23 (t, J = 2.4 Hz, 3 H, 14/16/19-H), 2.20 (d, J = 2.8 Hz, 6 H, 13/17/20-H), 1.74 (t, J = 2.8 Hz, 6 H, 15/18/21-H) ppm.

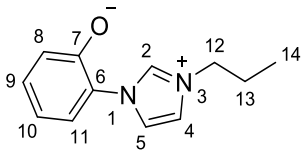
^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.3 (o, C-7), 135.0 (+, C-2), 131.6 (+, C-9), 126.6 (+, C-11), 124.4 (+, C-4), 123.1 (o, C-6), 119.6 (+, C-5), 119.2 (+, C-10), 117.8 (+, C-8), 60.2 (o, C-12), 42.0 (-, C-13/17/20), 35.3 (-, C-15/18/21), 29.4 (+, C-14/16/19) ppm.

IR (ATR): ϑ = 2906, 1539, 1463, 1456, 1276, 1174, 1114, 1103, 1083, 825, 751, 657, 644, 634 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 295.2 (100) $[M]^+$.

HR ESI-MS: calcd for $C_{19}H_{23}N_2O^+$ 295.1810. Found 295.1810.

2-(3-Propyl-1*H*-imidazolium-1-yl)phenolate 69a



A sample of 0.282 g (1.00 mmol) of 1-(2-hydroxyphenyl)-3-propyl-1*H*-imidazolium bromide was refluxed to deprotonate with 0.691 g (5.00 mmol) of K_2CO_3 in 10 mL methanol 4 h. Potassium carbonate was filtered off and the solvent was evaporated. The product was purified by column chromatography (methanol/CH_2Cl_2).

Yield: 0.181 g (90%) of a gray solid.

Mp: 164 °C.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.73 (d, J = 2.0 Hz, 1 H, 5-H), 7.67 (d, J = 2.0 Hz, 1 H, 4-H), 7.19 (dd, J_1 = 1.8 Hz, J_2 = 7.8 Hz, 1 H, 11-H), 7.14 (ddd, J_1 = 1.8 Hz, J_2 = 7.2 Hz, J_3 =8.3 Hz, 1 H, 9-H), 6.84 (dd, J_1 = 1.3 Hz, J_2 = 8.3 Hz, 1 H, 8-H), 6.49

(ddd, J_1 = 1.3 Hz, J_2 = 7.2 Hz, J_3 = 7.8 Hz, 1 H, 10-H), 4.23 (t, J = 7.2 Hz, 2 H, 12-H), 2.01 - 1.95 (m, 2 H, 13-H), 1.03 (t, J = 7.4 Hz, 3 H, 14-H) ppm.

^{13}C NMR (150 MHz, CD_3OD): δ = 161.2 (o, C-7), 135.8 (o, C-2), 130.6 (+, C-9), 124.5 (o, C-6), 123.7 (+, C-11), 123.0 (+, C-5), 121.7 (+, C-8), 121.1 (+, C-4), 112.6 (+, C-10), 50.9 (-, C-12), 23.1 (-, C-13), 9.6 (+, C-14) ppm.

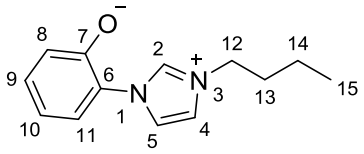
IR (ATR): ϑ = 3041, 1592, 1532, 1478, 1453, 1339, 1171, 1141, 1133, 1122, 1110, 1102, 836, 744, 726, 645, 625 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 203.1 (100) $[M]^+$.

MS (ESI, 75 V): m/z (%) = 201.1 (100) $[M-H]^-$.

HR ESI-MS: calcd for $C_{12}H_{15}N_2O^+$ 203.1184. Found 203.1185.

2-(3-Butyl-1*H*-imidazolium-1-yl)phenolate 69b



A sample of 0.296 g (1.00 mmol) of 3-butyl-1-(2-hydroxyphenyl)-1*H*-imidazolium bromide was refluxed with 0.691 g (5.00 mmol) of K_2CO_3 in 10 mL of methanol over a period of 4 h. The excess potassium carbonate was filtered off and the solvent was evaporated. The product was purified by column chromatography (methanol/CH_2Cl_2).

Yield: 0.212 g (98%) of a white solid.

Mp: 142 °C.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.73 (d, J = 2.0 Hz, 1 H, 5-H), 7.69 (d, J = 2.0 Hz, 1 H, 4-H), 7.20 (dd, J_1 = 1.7 Hz, J_2 = 7.9 Hz, 1 H, 11-H), 7.15 (ddd, J_1 = 1.7 Hz, J_2 = 7.3 Hz, J_3 = 8.4 Hz, 1 H, 9-H), 6.84 (dd, J_1 = 1.4 Hz, J_2 = 8.4 Hz, 1 H, 8-H), 6.51 (ddd, J_1 = 1.4 Hz, J_2 = 7.3 Hz, J_3 = 7.9 Hz, 1 H, 10-H), 4.28 (t, J = 7.4 Hz, 2 H, 12-H),

1.96 - 1.91 (m, 2 H, 13-H), 1.48 - 1.42 (m, 2 H, 14-H), 1.02 (t, *J* = 7.4 Hz, 3 H, 15-H) ppm.

^{13}C NMR (150 MHz, CD_3OD): δ = 161.0 (o, C-7), 135.7 (+, C-2), 130.6 (+, C-9), 124.5 (o, C-6), 123.8 (+, C-11), 123.0 (+, C-5), 121.7 (+, C-8), 121.1 (+, C-4), 112.8 (+, C-10), 49.2 (-, C-12), 31.7 (-, C-13), 19.1 (-, C-14), 12.4 (+, C-15) ppm.

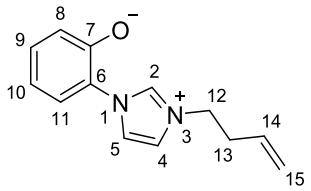
IR (ATR): ϑ = 2931, 1553, 1436, 1336, 1198, 1113, 1104, 1074, 866, 836, 745, 733, 619, 545, 526, 472 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 217.1 (100) $[M+H]^+$.

MS (ESI, 75 V): m/z (%) = 215.1 (100) $[M-H]^-$.

HR ESI-MS: calcd for $C_{13}H_{17}N_2O^+$ 217.1341. Found 217.1340.

2-(3-(But-3-en-1-yl)-1*H*-imidazolium-1-yl)phenolate 69c



A sample of 0.294 g (1.00 mmol) of 3-(but-3-en-1-yl)-1-(2-hydroxyphenyl)-1*H*-imidazolium bromide was refluxed with 0.691 g (5.00 mmol) of K_2CO_3 in 10 mL of methanol for 4 h. Potassium carbonate was filtered off and the solvent was evaporated. The product was purified by column chromatography (methanol/CH_2Cl_2).

Yield: 0.195 g (91%) of a white solid.

Mp: 142 °C.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.81 (d, *J* = 2.0 Hz, 1 H, 5-H), 7.76 (d, *J* = 2.0 Hz, 1 H, 4-H), 7.34 (dd, J_1 = 1.7 Hz, J_2 = 7.9 Hz, 1 H, 11-H), 7.27 (ddd, J_1 = 1.7 Hz, J_2 = 7.4 Hz, J_3 =8.3 Hz, 1 H, 9-H), 6.98 (dd, J_1 = 1.3 Hz, J_2 = 8.3 Hz, 1 H, 8-H), 6.78 (ddd, J_1 = 1.3 Hz, J_2 = 7.4 Hz, J_3 = 7.9 Hz, 1 H, 10-H), 5.91 - 5.84 (m, 1 H, 14-H),

5.16 - 5.13 (m, 2 H, 15-H), 4.39 (t, *J* = 6.9 Hz, 2 H, 12-H), 2.73 - 2.69 (m, 2 H, 13-H) ppm.

^{13}C NMR (150 MHz, CD_3OD): δ= 157.2 (o, C-7), 134.2 (+, C-14), 132.3 (+, C-9), 125.7 (+, C-11), 124.8 (+, C-5), 123.0 (+, C-4), 120.6 (+, C-8), 119.5 (-, C-15), 117.7 (+, C-10), 50.2 (-, C-12), 35.3 (-, C-13) ppm.

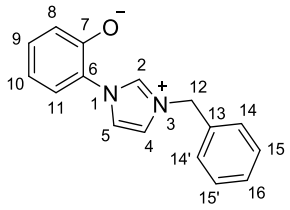
IR (ATR): ϑ̃ = 3053, 1553, 1542, 1184, 1111, 1063, 983, 953, 833, 822, 756, 749, 630, 575, 543, 527, 487 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 215.1 (100) $[M+H]^+$.

MS (ESI, 75 V): m/z (%) = 213.1 (100) $[M-H]^-$.

HR ESI-MS: calcd for $C_{13}H_{15}N_2O^+$ 215.1184. Found 215.1181.

2-(3-Benzyl-1*H*-imidazolium-1-yl)phenolate 69d



A sample of 0.330 g (1.00 mmol) of 3-benzyl-1-(2-hydroxyphenyl)-1*H*-imidazolium bromide was refluxed with 0.691 g (5.00 mmol) of K_2CO_3 in 10 mL of methanol over a period of 4 h. Excess potassium carbonate was filtered off and the solvent was evaporated. The product was purified by column chromatography (methanol/CH_2Cl_2).

Yield: 0.218 g (87%) of a white solid.

Mp: 178 °C.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.74 (d, *J* = 2.0 Hz, 1 H, 5-H), 7.60 (d, *J* = 2.0 Hz, 1 H, 4-H), 7.49 - 7.40 (m, 5 H, 14/14'/15/15'/16-H), 7.20 (dd, J_1 = 1.7 Hz, J_2 = 7.9 Hz, 1 H, 11-H), 7.14 (ddd, J_1 = 1.7 Hz, J_2 = 7.2 Hz, J_3 = 8.4 Hz, 1 H, 9-H), 6.84 (dd,

J_1 = 1.3 Hz, J_2 = 8.4 Hz, 1 H, 8-H), 6.51 (ddd, J_1 = 1.3 Hz, J_2 = 7.2 Hz, J_3 = 7.9 Hz, 1 H, 10-H), 5.46 (s, 2 H, 12-H) ppm.

^{13}C NMR (150 MHz, CD_3OD): δ = 160.9 (o, C-7), 135.9 (+, C-2), 134.0 (o, C-13), 130.7 (+, C-9), 129.0 (+, C-15/15'), 128.9 (+, C-16), 128.3 (+, C-14/14'), 124.4 (o, C-6), 123.6 (+, C-11), 123.2 (+, C-5), 121.7 (+, C-8), 121.0 (+, C-4), 112.8 (+, C-10), 52.7 (-, C-12) ppm.

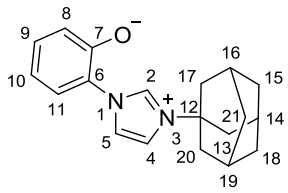
IR (ATR): ϑ = 3019, 1596, 1541, 1475, 1452, 1339, 1327, 1280, 1150, 1128, 1099, 837, 774, 720, 691, 656, 647, 455 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 251.1 (100) $[M+H]^+$.

MS (ESI, 75 V): m/z (%) = 249.1 (100) $[M-H]^-$.

HR ESI-MS: calcd for $C_{16}H_{15}N_2O^+$ 251.1184. Found 251.1184.

2-(3-(Adamantan-1-yl)-1*H*-imidazolium-1-yl)phenolate 69e



A sample of 0.374 g (1.00 mmol) of 3-(adamantan-1-yl)-1-(2-hydroxyphenyl)-1*H*-imidazolium bromide was refluxed with 0.691 g (5.00 mmol) of K_2CO_3 in 10 mL of methanol over a period of 4 h. Excess potassium carbonate was then filtered off and the solvent was evaporated. The product was purified by column chromatography (methanol/CH_2Cl_2).

Yield: 0.200 g (68%) of a white solid.

Mp: 210 °C.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.92 (d, J_1 = 2.1 Hz, 1 H, 5-H), 7.74 (d, J_1 = 2.1 Hz, 1 H, 4-H), 7.23 (dd, J_1 = 1.7 Hz, J_2 = 7.8 Hz, 1 H, 11-H), 7.17 (ddd, J_1 = 1.7 Hz,

J_2 = 7.3 Hz, J_3 =8.3 Hz, 1 H, 9-H), 6.87 (dd, J_1 = 1.3 Hz, J_2 = 8.3 Hz, 1 H, 8-H), 6.56 (ddd, J_1 = 1.3 Hz, J_2 = 7.3 Hz, J_3 = 7.8 Hz, 1 H, 10-H), 2.30 (t, J = 2.4 Hz, 3 H, 14/16/19-H), 2.20 (d, J = 2.9 Hz, 6 H, 13/17/20-H), 1.86 (t, J = 2.8 Hz, 6 H, 15/18/21-H) ppm.

^{13}C NMR (150 MHz, CD_3OD): δ = 160.2 (o, C-7), 133.5 (+, C-2), 130.6 (+, C-9), 124.5 (o, C-6), 124.1 (+, C-11), 123.0 (+, C-4), 121.2 (+, C-8), 118.0 (+, C-5), 113.4 (+, C-10), 59.6 (o, C-12), 42.0 (-, C-13/17/20), 35.1 (-, C-15/18/21), 29.6(+, C-14/16/19) ppm.

IR (ATR): ϑ = 2910, 1539, 1476, 1455, 1342, 1176, 1101, 844, 838, 767, 744, 730, 657 cm^{-1}.

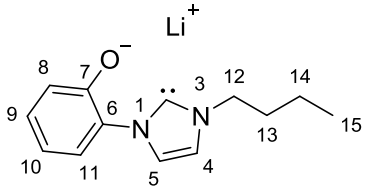
MS (ESI, 30 V): m/z (%) = 295.1 (100) $[M+H]^+$.

MS (ESI, 75 V): m/z (%) = 293.2 (100) $[M-H]^-$.

HR ESI-MS: calcd for $C_{19}H_{23}N_2O^+$ 295.1810. Found 295.1810.

5.5 General procedure for the synthesis of carbenes, thiones and boron-adducts

Lithium 2-(3-butyl-1*H*-imidazol-2-ylidene-1-yl)phenolate 70



A sample of 0.020 g (0.09 mmol) of 2-(3-butyl-1*H*-imidazolium-1-yl)phenolate was deprotonated with 0.10 mL of lithium bis(trimethylsilyl)amide (1.0 M solution in THF) in 0.7 mL of pyridine at room temperature 30 minutes. The title compound was characterized by NMR spectroscopy under an atomosphere of nitrogen and reacted with water to reconstitute the betaine **69A/B** in quantitative yield.

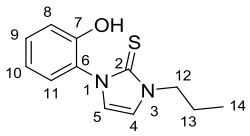
Yield: 0.020 g (100%).

^{1}H NMR (600 MHz, pyridine-d_5): δ = 7.44 (d, J = 0.8 Hz, 1 H, 5-H), 7.40 (dd, J_1 = 1.0 Hz, J_2 = 7.6 Hz, 1 H, 11-H), 7.12 - 7.16 (m, 2 H, 9/8-H), 7.05 (d, J = 0.8 Hz, 1 H, 4-H), 6.59 (ddd, J_1 = 0.9 Hz, J_2 = 7.3 Hz, J_3 = 7.6 Hz, 1 H, 10-H), 3.94 (t, J = 7.0 Hz, 2 H, 12-H), 1.6ß - 1.62 (m, 2 H, 13-H), 1.19 - 1.15 (m, 2 H, 14-H), 0.75 (t, J = 7.3 Hz, 3 H, 15-H) ppm.

^{13}C NMR (150 MHz, pyridine-d_5): δ = 203.1 (o, C-2), 162.2 (o, C-7), 131.0 (o, C-6), 127.2 (+, C-9), 123.0 (+, C-8), 122.7 (+, C-11), 119.5 (+, C-5), 118.5 (+, C-4), 111.2 (+, C-10), 50.7 (-, C-12), 33.5 (-, C-13), 19.8 (-, C-14), 13.5 (+, C-15) ppm.

MS (ESI, 50 V): m/z (%) = 215.1 (100) $[M-Li]^-$.

1-(2-Hydroxyphenyl)-3-propyl-1,3-dihydro-2*H*-imidazole-2-thione 71b



Method A: A mixture of 0.101 g (0.50 mmol) of 1-(2-hydroxyphenyl)-3-propyl-1*H*-imidazolium bromide, 19.2 mg (0.6 mmol) of sulfur and 0.326 g (1.00 mmol) of Cs_2CO_3 in 10 mL of dry THF was stirred at reflux for 4 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.076 g (65%) of a white solid.

Mp: 115 °C.

Method B: A sample of 0.101 g (0.5 mmol) of 2-(3-propyl-1*H*-imidazolium-1-yl) was reacted with 0.032 mg (1.00 mmol) of sulfur in 10 ml of dry toluene at reflux temperature for 8 h. The solvent was then evaporated and the crude product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.090 g (77 %) of a white solid.

Mp: 115 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.87 (s, 1H, -OH), 7.24 - 7.28 (m, 3 H, 5/9/11-H), 7.11 (d, J = 2.4 Hz, 1 H, 4-H), 7.00 (dd, J_1 = 1.2 Hz, J_2 = 8.7 Hz, 1 H, 8-H), 6.89 (ddd, J_1 = 1.4 Hz, J_2 = 7.5 Hz, J_3 = 8.2 Hz, 1 H, 10-H), 3.97 (t, J = 7.3 Hz, 2 H, 12-H), 1.72 - 1.78 (m, 2 H, 13-H), 6.90 (t, J = 7.4 Hz, 3 H, 14-H) ppm.

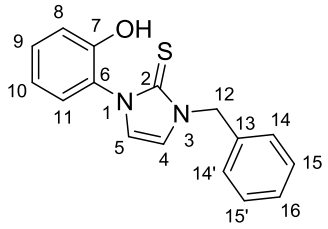
^{13}C NMR (150 MHz, DMSO-d_6): δ = 162.6 (o, C-2), 152.8 (o, C-7), 130.1 (+, C-9), 129.8 (+, C-11), 126.1 (o, C-6), 119.8 (+, C-4), 119.4 (+, C-11), 128.2 (+, C-5), 117.4 (+, C-8), 49.1 (-, C-12), 22.1 (-, C-13), 11.4 (-, C-14) ppm.

IR (ATR): ϑ = 2964, 1456, 1425, 1397, 1382, 1362, 1272, 1246, 1208, 1143, 1127, 826, 768, 724, 673, 539, 520 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 235.1 (100) $[M+H]^+$.

HR ESI-MS: calcd for $C_{12}H_{15}N_2OS^+$ 235.0905. Found 235.0909.

1-Benzyl-3-(2-hydroxyphenyl)-1, 3-dihydro-2*H*-imidazole-2-thione 71d



Method A: A mixture of 0.165 g (0.50 mmol) of 3-benzyl-1-(2-hydroxyphenyl)-1*H*-imidazolium bromide, 19.2 mg (0.6 mmol) of sulfur and 0.326 g (1.00 mmol) of Cs_2CO_3 in 10 mL of dry THF was stirred at reflux for 4 h under a nitrogen atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.097 g (69%) of a white solid.

Mp: 168 °C.

Method B: A sample of 0.125 g (0.5 mmol) of 2-(3-benzyl-1*H*-imidazolium-1-yl)phenolate and 0.032 mg (1.00 mmol) of sulfur was refluxed in 10 ml of dry toluene

under an inert atmosphere for 8 h. The solvent was evaporated and the product was obtained by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.110 g (78 %) of a white solid.

Mp: 168 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.87 (s, 1 H, -OH), 7.41 - 7.36 (overlap, 4 H, 14//14'15/15'-H), 7.33 - 7.30 (overlap, 2 H, 11/16-H), 7.28 - 7.25 (overlap, 2 H, 5/9-H), 7.14 (d, J = 2.5 Hz, 1 H, 4-H), 7.01 (dd, J_1 = 1.3 Hz, J_2 = 8.2 Hz, 1 H, 8-H), 6.90 (ddd, J_1 = 1.3 Hz, J_2 = 7.5 Hz, J_3 = 7.7 Hz, 1 H, 10-H), 5.28 (s, 2 H, 12-H) ppm.

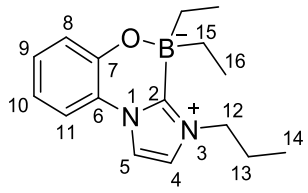
^{13}C NMR (150 MHz, DMSO-d_6): δ = 163.5 (o, C-2), 152.9 (o, C-7), 137.5 (o, C-13), 130.2 (+, C-9), 129.9 (+, C-11), 129.0 (+, C-15/15'), 128.4 (+, C-14/'), 128.1 (+, C-16), 126.1 (o, C-6), 120.3 (+, C-4), 119.4 (+, C-10), 118.1 (+, C-5), 117.3 (+, C-8), 50.4 (-, C-12) ppm.

IR (ATR): ϑ = 3031, 1496, 1399, 1362, 1318, 1287, 1254, 1229, 764, 752, 724, 717, 692, 677, 664, 585, 482 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 283.1 (100) $[M+H]^+$.

HR ESI-MS: calcd for $C_{16}H_{15}N_2OS^+$ 283.0905. Found 283.0906.

4,4Diethyl-3-propyl-4*H*-benzo[*e*]imidazo[2,1-*c*][1,4,2]oxazaborininium-4-ide 72a



A sample of 0.101 g (0.50 mmol) of 2-(3-propyl-1*H*-imidazolium-1-yl)phenolate was reacted with 0.460 g (5.00 mmol) of triethylborane solution in dioxane in 5 mL of anhydrous dioxane at 100 °C in a bomb tube for 8 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.130 g (94%) of a colorless liquid.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.94 (d, *J* = 2.1 Hz, 1 H, 5-H), 7.46 - 7.45 (overlap, 2 H, 4/11-H), 7.08 (ddd, J_1 =1.6 Hz, J_2 = 7.4 Hz, J_3 = 8.2 Hz, 1 H, 9-H), 6.90 (dd, J_1 =1,3 Hz, J_2 = 8.2 Hz, 1 H, 8-H) , 6.74 (ddd, J_1 = 1.3 Hz, J_2 = 7.4 Hz, J_3 = 8.0 Hz, 1 H, 10-H), 4.06 (t, J_1 = 7.7 Hz, 2 H, 12-H), 1.93 - 1.86 (m, 2 H, 13-H), 1.01 (t, *J* = 7.4 Hz, 3 H, 14-H), 0.07 (t, *J* = 7.7 Hz, 6 H, 16-H), 0.53 - 0.44 (m, 4 H, 15-H) ppm.

^{13}C NMR (150 MHz, CD_3OD): δ = 164.0 (o, C-2), 152.0 (o, C-7), 127.8 (+, C-9), 123.5 (o, C-6), 120.9 (o, C-4), 118.9 (+, C-8), 116.7 (+, C-10), 115.8 (+, C-11), 114.5 (+, C-5), 49.3 (-, C-12), 23.3 (-, C-13), 16.0 (-, C-15), 9.9 (+, C-14), 9.2 (+, C-17) ppm.

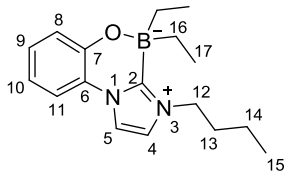
^{11}B NMR (CD_3OD, 193 MHz, $B(OMe)_3$): δ = 0.94 ppm.

IR (ATR): ϑ̃ = 2934, 2899, 2860, 1609, 1503, 1457, 1428, 1272, 1138, 1050, 901, 825, 745 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 271.0 (100) $[M+H]^+$.

HR ESI-MS: calcd for $C_{16}H_{24}N_2OB^+$ 271.1982. Found 271.1985.

3-Butyl-4,4-diethyl-4*H*-benzo[*e*]imidazo[2,1-*c*][1,4,2]oxazaborininium-4-ide 72b



A sample of 0.108 g (0.50 mmol) of 2-(3-butyl-1*H*-imidazolium-1-yl)phenolate was reacted with 0.460 g (5.00 mmol) of triethylborane solution in dioxane in 5 mL of anhydrous dioxane at 100 °C in a bomb tube for 8 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.078 g (55%) of a yellow liquid.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.95 (d, *J* = 2.1 Hz, 1 H, 5-H), 7.47 (d, *J* = 2.1 Hz, 1 H, 4-H), 7.46 (dd, J_1 =1,4 Hz, J_2 = 8.0 Hz, 1 H, 11-H), 7.08 (ddd, J_1 =1.4 Hz, J_2 = 7.4 Hz, J_3 = 8.2 Hz, 1 H, 9-H), 6.90 (dd, J_1 =1,4 Hz, J_2 = 8.2 Hz, 1 H, 8-H), 6.74 (ddd, J_1 = 1.4 Hz, J_2 = 7.4 Hz, J_3 = 8.0 Hz, 1 H, 10-H), 4.10 (tt, J_1 = 1.6 Hz, J_2 = 7.9 Hz, 2 H, 12-H), 1.88 - 1.83 (overlapped signals, 2 H, 13-H), 1.48 - 1.41 (overlapped signals, 2 H, 14-H), 1.01 (t, *J* = 7.4 Hz, 3 H, 15-H), 0.67 (t, *J* = 7.7 Hz, 6 H, 17-H), 0.53 - 0.44 (m, 4 H, 16-H) ppm.

^{13}C NMR (150 MHz,CD_3OD): δ = 163.8 (o, C-2), 152.0 (o, C-7), 127.8 (+, C-9), 123.5 (o, C-6), 120.9 (o, C-4), 118.9 (+, C-8), 116.7 (+, C-10), 115.8 (+, C-11), 114.5 (+, C-5), 47.5 (-, C-12), 32.1 (-, C-13), 19.5 (-, C-14), 16.1 (-, C-16), 12.6 (+, C-15), 9.2 (+, C-17) ppm.

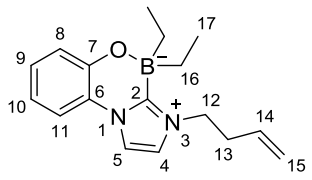
^{11}B NMR (CD_3OD, 193 MHz, $BF_3{\cdot}Et_2O$): δ = -0.99 ppm.

IR (ATR): ϑ = 2932, 2860, 1608, 1503, 1456, 1310, 1046, 895, 825, 744 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 285.1 (100) $[M+H]^+$.

HR ESI-MS: calcd for $C_{17}H_{26}N_2OB^+$ 285.2138. Found 285.2143.

3-(But-3-en-1-yl)-4,4-diethyl-4*H*-benzo[*e*]imidazo[2,1-*c*][1,4,2]oxazaborininium-4-ide 72c



A sample of 0.107 g (0.50 mmol) of 2-(3-(but-3-en-1-yl)-1*H*-imidazolium-1-yl)phenolate was reacted with 0.460 g (5.00 mmol) of triethylborane solution in dioxane in 5 mL of anhydrous dioxane at 100 °C in a bomb tube for 8 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.059 g (42%) of a colorless liquid.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.93 (d, *J* = 2.2 Hz, 1 H, 5-H), 7.44 - 4.46 (overlap, 2 H, 4/11-H), 7.08 (ddd, J_1 = 1.6 Hz, J_2 = 7.3 Hz, J_3 =8.2 Hz, 1 H, 9-H), 6.91 (dd, J_1 = 1.4 Hz, J_2 = 8.2 Hz, 1 H, 8-H), 6.74 (ddd, J_1 = 1.4 Hz, J_2 = 7.3 Hz, J_3 = 8.0 Hz, 1 H, 10-H), 5.89 - 5.82 (m, 1 H, 14-H), 5.17 - 5.10 (m, 2 H, 15-H), 4.18 (t, *J* = 7.4 Hz, 2 H, 12-H), 2.64 - 2.60 (m, 2 H, 13-H), 0.67 (t, *J* = 7.7 Hz, 6 H, 17-H), 0.54 - 0.44 (m, 4 H, 16-H) ppm.

^{13}C NMR (150 MHz, CD_3OD): δ = 164.0 (o, C-2), 152.0 (o, C-7), 133.5 (+, C-14), 127.8 (+, C-9), 123.5 (o, C-6), 121.1 (+, C-4), 118.9 (+, C-8), 117.3 (-, C-15), 116.7 (+, C-10), 115.8 (+, C-11), 114.4 (+, C-5), 47.1 (-, C-12), 34.2 (-, C-13), 16.0 (-, C-16), 9.2 (+, C-17) ppm.

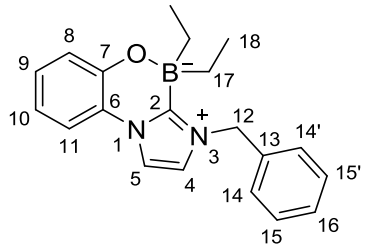
^{11}B NMR (CD_3OD, 193 MHz, $B(OMe)_3$): δ = -0.91 ppm.

IR (ATR): ϑ = 2859, 1608, 1503, 1452, 1428, 1312, 1139, 1054, 899, 825, 746 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 283.2 (100) $[M+H]^+$.

HR ESI-MS: calcd for $C_{17}H_{24}N_2OB^+$ 283.1982. Found 283.1980.

3-Benzyl-4,4-diethyl-4*H*-benzo[*e*]imidazo[2,1-*c*][1,4,2]oxazaborininium-4-ide 72d



A sample of 0.125 g (0.50 mmol) of 2-(3-benzyl-1*H*-imidazolium-1-yl)phenolate was reacted with 0.460 g (5.00 mmol) of triethylborane solution in dioxane in 5mL at 100 °C in a bomb tube for 8 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.087 g (55%) of a colorless liquid.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.96 (d, *J* = 2.1 Hz, 1 H, 5-H), 7.47 (dd, J_1 = 1.5 Hz, J_2 = 8.0 Hz, 1 H, 11-H), 7.41 - 7.38 (m, 2 H, 15/15'-H), 7.37 - 7.34 (m, 1 H, 16-H), 7.29 - 7.27 (m, 2 H, 14/14'-H), 7.21 (d, *J* = 2.1 Hz, 1 H, 4-H), 7.10 (ddd, J_1 = 1.5 Hz, J_2 = 7.4 Hz, J_3 = 8.2 Hz, 1 H, 9-H), 6.93 (dd, J_1 = 1.3 Hz, J_2 = 8.2 Hz, 2 H, 8-H), 6.75 (ddd, J_1 = 1.3 Hz, J_2 = 7.4 Hz, J_3 = 8.0 Hz, 1 H, 10-H), 5.33 (s, 2 H, 12-H), 0.69 (t, *J* = 7.6 Hz, 6 H, 20-H), 0.51 (q, *J* = 7.6, 4 H, 19-H) ppm.

^{13}C NMR (150 MHz, CD_3OD): δ = 164.7 (o, C-2), 152.1 (o, C-7), 135.3 (o, C-13), 128.7 (+, C-15/15'), 128.1 (+, C-16), 127.9 (+, C-9), 127.5 (+, C-14/14'), 123.4 (o, C-6), 121.3 (+, C-4), 119.0 (+, C-8), 116.8 (+, C-10), 115.9 (+, C-11), 114.8 (+, C-5), 51.2 (-, C-12), 15.9 (-, C-19), 9.2 (+, C-20) ppm.

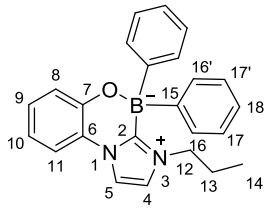
^{11}B NMR (CD_3OD, 193 MHz, $B(OMe)_3$): δ = -1.00 ppm.

IR (ATR): ϑ = 2859, 1501, 1455, 1441, 1311, 1144, 1050, 893, 824, 744, 713, 694 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 341.1 (100) $[M+Na]^+$.

HR ESI-MS: calcd for $C_{20}H_{24}N_2OB^+$ 319.1982. Found 319.1981.

4,4-Diphenyl-3-propyl-4*H*-benzo[*e*]imidazo[2,1-*c*][1,4,2]oxazaborininium-4-ide 73a



A sample of 0.101 g (0.50 mmol) of 2-(3-propyl-1*H*-imidazolium-1-yl)phenolate was reacted with 0.242 g (1.0 mmol) of triphenylborane solution in dioxane in 5 mL of anhydrous dioxane at 100 °C in a bomb tube for 8 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.340 g (93%) of a white solid.

Mp: 178 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.32 (d, *J* = 2.1 Hz, 1 H, 5-H), 7.78 (d, *J* = 2.1 Hz, 1 H, 4-H), 7.66 (dd, J_1 = 1.5 Hz, J_2 = 8.4 Hz, 1 H, 11-H), 7.18 - 7.07 (m, 11 H, 9/16/16'/17/17'/18-H), 6.97 (dd, J_1 = 1.3 Hz, J_2 = 8.4 Hz, 1 H, 8-H), 6.77 (ddd, J_1 = 1.3 Hz, J_2 = 8.0 Hz, J_3 = 8.4 Hz, 1 H, 10-H), 3.70 (t, *J* = 7.9 Hz, 2 H, 12-H), 1.30 - 1.23 (m, 2 H, 13-H), 0.43 (t, *J* = 7.3 Hz, 3 H, 14-H) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ= 159.6 (o, C-2), 151.8 (o, C-7), 151.5 (o, C-15), 133.3 (+, C-17/17'), 128.7 (+, C-9), 127.4 (+, C-16/16'), 125.9 (+, C-18), 124.6 (o, C-6), 122.8 (+, C-4), 120.5 (+, C-8), 118.0 (+, C-10), 117.4 (+, C-11), 116.2 (+, C-5), 49.9 (-, C-12), 23.3 (-, C-13), 10.8 (+, C-14) ppm.

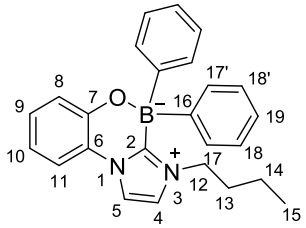
^{11}B NMR (DMSO-d_6, 193 MHz, $B(OMe)_3$): δ = -0.96 ppm.

IR (ATR): ϑ̃ = 1603, 1503, 1441, 1367, 1345, 1300, 1265, 1166, 1141, 933, 736, 701, 687, 578 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 389.1 (100) $[M+Na]^+$.

HR ESI-MS: calcd for $C_{24}H_{24}N_2OB^+$ 367.1982. Found 367.1982.

3-Butyl-4,4-diphenyl-4*H*-benzo[*e*]imidazo[2,1-*c*][1,4,2]oxazaborininium-4-ide 73b



A sample of 0.108 g (0.50 mmol) of 2-(3-butyl-1*H*-imidazolium-1-yl)phenolate was reacted with 0.242 g (1.0 mmol) of triphenylborane solution in dioxane in 5 mL of anhydrous dioxane at 100 °C in a bomb tube for 8 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.114 g (60%) of a white solid.

Mp: 170 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.32 (d, *J* = 2.1 Hz, 1 H, 5-H), 7.78 (d, *J* = 2.1 Hz, 1 H, 4-H), 7.66 (dd, J_1 = 1.5 Hz, J_2 = 8.0 Hz, 1 H, 11-H), 7.17 - 7.07 (m, 11 H, 9/17/17'/18/18'/19-H), 6.97 (dd, J_1 = 1.4 Hz, J_2 = 8.2 Hz, 1 H, 8-H), 6.77 (ddd, J_1 = 1.4 Hz, J_2 = 7.4 Hz, J_3 = 8.0 Hz, 1 H, 10-H), 3.73 (tt, J_1 = 2.0 Hz, J_2 = 8.1 Hz, 2 H, 12-H), 1.24 - 1.19 (overlapped signals, 2 H, 13-H), 1.87 - 0.81 (overlapped signals, 2 H, 14-H), 0.59 (t, *J* = 7.3 Hz, 3 H, 15-H) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ= 159.6 (o, C-2), 151.8 (o, C-7), 151.5 (o, C-16), 133.3 (+, C-18/18'), 128.7 (+, C-9), 127.4 (+, C-17/17'), 125.9 (+, C-19), 124.6 (o, C-6), 122.9 (+, C-4), 120.4 (+, C-8), 117.9 (+, C-10), 117.4 (+, C-11), 116.2 (+, C-5), 48.4 (-, C-12), 31.9 (-, C-13), 19.5 (-, C-14), 13.7 (+, C-15) ppm.

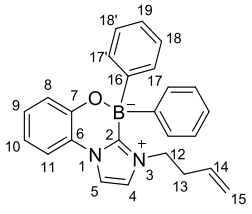
^{11}B NMR (DMSO-d_6, 193 MHz, $B(OMe)_3$): δ = -0.81 ppm.

IR (ATR): ῡ = 1503, 1302, 1287, 1168, 1141, 937, 922, 899, 738, 724, 699 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 403.1 (100) $[M+Na]^+$.

HR ESI-MS: calcd for $C_{25}H_{26}N_2OB^+$ 381.2138. Found 381.2137.

3-(But-3-en-1-yl)-4,4-diphenyl-4*H*-benzo[*e*]imidazo[2,1-*c*][1,4,2]oxazaborininium-4-ide 73c



A sample of 0.107 g (0.50 mmol) of 2-(3-(but-3-en-1-yl)-1*H*-imidazolium-1-yl)phenolate was reacted with 0.242 g (1.0 mmol) of triphenylborane solution in dioxane in 5 mL of anhydrous dioxane at 100 °C in a

bomb tube for 8 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.079 g (42%) of a white solid.

Mp: 187 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.32 (d, *J* = 2.1 Hz, 1 H, 5-H), 7.79 (d, *J* = 2.1 Hz, 1 H, 4-H), 7.66 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1 H, 11-H), 7.18 - 7.07 (m, 11 H, 9/17/17'/18/18'/19-H), 6.97 (dd, J_1 = 1.3 Hz, J_2 = 8.2 Hz, 1 H, 8-H), 6.77 (ddd, J_1 = 1.3 Hz, J_2 = 7.4 Hz, *J3* = 8.0 Hz, 1 H, 10-H), 5.32 - 5.25 (m, 1 H, 14-H), 4.89 - 4.74 (m, 2 H, 15-H), 3.82 (t, *J* = 7.7 Hz, 2 H, 12-H), 2.00 - 1.97 (m, 2 H, 13-H) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ= 160.0 (o, C-2), 151.8 (o, C-7), 151.4 (o, C-16), 134.0 (+, C-14), 133.3 (+, C-18/18'), 128.7 (+, C-9), 127.4 (+, C-17/17'), 126.0 (+, C-19), 124.5 (o, C-6), 123.0 (+, C-4), 120.4 (+, C-8), 118.2 (-, C-15), 118.0 (+, C-10), 117.4 (+, C-11), 116.1 (+, C-5), 47.7 (-, C-12), 33.9 (-, C-13) ppm.

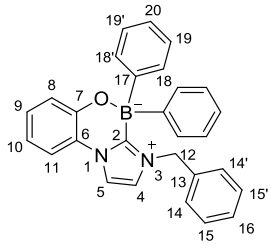
^{11}B NMR (DMSO-d_6, 193 MHz, $B(OMe)_3$): δ = -1.17 ppm.

IR (ATR): ῡ = 1608, 1502, 1428, 1300, 1289, 1169, 1140, 923, 903, 873, 743, 736, 722, 704, 592 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 401.1 (100) $[M+Na]^+$.

HR ESI-MS: calcd for $C_{25}H_{24}N_2OB^+$ 379.1982. Found 379.1982.

3-Benzyl-4,4-diphenyl-4*H*-benzo[*e*]imidazo[2,1-*c*][1,4,2]oxazaborininium-4-ide 73d



A sample of 0.125 g (0.50 mmol) of 2-(3-benzyl-1*H*-imidazolium-1-yl)phenolate was reacted with 0.242 g (1.0 mmol) of triphenylborane solution in dioxane in 5 mL of anhydrous dioxane at 100 °C in a bomb tube for 8 h under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate/petroleum ether).

Yield: 0.124 g (60%) of a white solid.

Mp: 88 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.35 (d, *J* = 2.1 Hz, 1 H, 5-H), 7.69 (dd, J_1 = 1.5 Hz, J_2 = 8.4 Hz, 1 H, 11-H), 7.58 (d, *J* = 2.1 Hz, 1 H, 4-H), 7.27 - 7.22 (m, 3 H, 15/15'/16-H), 7.20 (dd, J_1 = 1.4 Hz, J_2 = 8.0 Hz, 4 H, 18/18'-H), 7.15 - 7.10 (overlap, 5 H, 9/19/19'-H), 7.07 - 7.05 (m, 2 H, 20-H), 7.01 (dd, J_1 = 1.3 Hz, J_2 = 8.2 Hz, 2 H, 14/14'-H), 6.78 (ddd, J_1 = 1.3 Hz, J_2 = 8.0 Hz, J_3 = 8.4 Hz, 1 H, 10-H), 5.04 (s, 2 H, 12-H) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 160.2 (o, C-2), 151.8 (o, C-7), 151.3 (o, C-17), 135.3 (o, C-13), 133.4 (+, C-18/18'), 129.0 (+, C-15/15'), 128.8 (+, C-9), 128.6 (+, C-16), 128.4 (+, C-14/14'), 127.4 (+, C-19/19'), 126.0 (+, C-20), 124.5 (o, C-6), 123.0 (+, C-4), 120.5 (+, C-8), 118.0 (+, C-10), 117.6 (+, C-11), 116.7 (+, C-5), 51.2 (-, C-12) ppm.

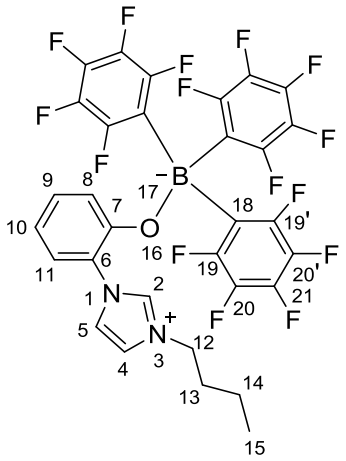
^{11}B NMR (DMSO-d_6, 193 MHz, $BF_3 \cdot Et_2O$): δ = -0.73 ppm.

IR (ATR): ῡ = 1500, 1429, 1302, 1289, 1262, 1173, 1146, 924, 904, 879, 740, 724, 700, 650 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 415.2 (100) $[M+H]^+$.

HR ESI-MS: calcd for $C_{28}H_{24}N_2OB^+$ 415.1982. Found 415.198.

(2-(3-Butyl-1*H*-imidazolium-1-yl)phenoxy)tris(perfluorophenyl)borate 74b



A sample of 0.108 g (0.50 mmol) of 2-(3-butyl-1*H*-imidazolium-1-yl)phenolate and 0.152 mg (1.00 mmol) of tris(pentafluorophenyl)borane were refluxed in 10 mL of dry dioxane for 4 h in a bomb tube under an inert atmosphere. The solvent was evaporated and the product was purified by column chromatography (ethyl acetate).

Yield: 0.155 g (43%) of a colorless solid.

Mp: 230 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.22 (dd, J_1 = 1.4 Hz, J_2 = 1.5 Hz, 1 H, 2-H), 7.90 (dd, J_1 = 1.4 Hz, J_2 = 1.5 Hz, 1 H, 4-H), 7.82 (dd, J_1 = 1.4 Hz, J_2 = 1.5 Hz, 1 H, 5-H), 7.43 (dd, J_1 = 2.3 Hz, J_2 = 9.8 Hz, 1 H, 11-H), 7.17 (ddd, J_1 = 2.3 Hz, J_2 = 7.4 Hz, J_3 = 8.4 Hz, 3 H, 9-H), 6.81 (ddd, J_1 = 1.0 Hz, J_2 = 7.4 Hz, J_3 = 9.8 Hz, 1 H, 10-H), 6.60 (dd, J_1 = 1.0 Hz, J_2 = 8.4 Hz, 1 H, 8-H), 4.18 (t, J = 10.8 Hz, 2 H, 12-H), 1.72 - 1.64 (overlapped, 2 H, 13-H), 1.22 - 1.13 (overlapped, 2 H, 14-H), 0.84 (t, J = 11.0 Hz, 3 H, 15-H) ppm.

^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.5 (o, C-7), 147.2 (o, d, $^{1}J_{C,F}$ = 242.1 Hz, C-20/20'), 138.2 (o, d, $^{1}J_{C,F}$ = 230.3 Hz, C-21), 136.3 (+, C-2), 135.8 (o, d, $^{1}J_{C,F}$ = 235.5 Hz, C-19/19'), 130.2 (+, C-9), 125.4 (o, C-6), 125.0 (+, C-11), 123.5 (+, C-5), 121.8 (o, C-4), 122.2 - 121.3 (o, C-18), 117.7 (+, C-10), 117.4 (+, C-8), 48.7 (-,C-12), 31.4 (-, C-13), 18.6 (-, C-14), 13.0 (+, C-15) ppm.

^{11}B NMR (DMSO-d_6, 128 MHz, external reference): δ = -3.45 ppm.

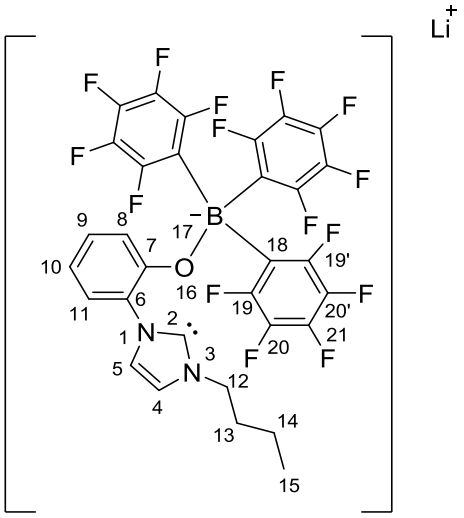
^{19}F NMR (DMSO-d_6, 565 MHz, Cl_3CF) δ = -133.91 (d, $^3J_{F,F}$ = 21.5 Hz, 6 F, 19/19'-H), -159.97 (t, $^3J_{F,F}$ = 21.5 Hz, 3 F, 21-F), -165.18 (dd, overlapped, $^3J_{F,F}$ = 21.5 Hz, 6 F, 20/20'-F) ppm.

IR (ATR): ϑ̃ = 1511, 1498, 1456, 1304, 1277, 1262, 1079, 1038, 974, 965, 945, 936, 802, 768, 762, 755, 733, 691, 673, 667, 654, 649 cm^{-1}.

MS (ESI, 50 V): m/z (%) = 727.0 (100) $[M-H]^-$.

HR ESI-MS: calcd for $C_{31}H_{15}N_2OF_{15}B$ 727.1038. Found 727.1038.

Lithium (2-(3-butyl-2λ^2-imidazol-1(3*H*)-yl)phenoxy)tris(perfluorophenyl)borate 75



A sample of 0.024 g (0.03 mmol) of tris(pentafluorophenyl)borane was deprotonated with 0.04 mL (0.03 mmol) of lithium bis(trimethylsilyl) amide solution (1.0 m in THF) in 0.7 mL pyridine. The reaction was stirred for 30 minutes at room temperature. The solvent was evaporated *in vacuo* and gave the target compound.

Yield: 0.024 g (100%).

^{1}H NMR (600 MHz, pyridine-d_5): δ = 7.78 (d, *J* = 1.7 Hz, 1 H, 4-H), 7.34 (dd, J_1 = 1.4 Hz, J_2 = 7.6 Hz, 1 H, 11-H), 7.10 (d, *J* = 1.7 Hz, 1 H, 5-H), 6.95 - 6.91 (m,

2H, 8/9-H), 6.32 (ddd, J_1 = 1.7 Hz, J_2 = 6.7 Hz, J_3 = 7.6 Hz, 3 H, 10-H), 3.99 (t, J = 7.6 Hz, 2 H, 12-H), 1.12 - 1.08 (m, 2 H, 14-H), 0.72 (t, J = 7.4 Hz,3 H, 15-H) ppm.

^{13}C NMR (150 MHz, pyridine-d_5): δ = 197.9 (o, C-2), 154.1 (o, C-7), 148.4 (o, d, $^1J_{C,F}$ = 245.8 Hz, C-19/19'), 138.6 (o, d, $^1J_{C,F}$ = 247.3 Hz, C-21), 136.7 (o, d, $^1J_{C,F}$ = 269.2 Hz, C-20/20'), 132.4 (o, C-6), 127.6 (+, C-8/9), 126.8 (+, C-11), 123.7 (+, C-4), 117.8 (+, C-5), 117.3 (+, C-8/9), 116.7 (+, C-10), 50.2 (-,C-12), 33.7 (-, C-13), 19.8 (-, C-14), 13.4 (+, C-15) ppm.

^{11}B NMR (pyridine-d_5, 193 MHz, $B(OMe)_3$): δ = -3.40 ppm.

^{19}F NMR (pyridine-d_5, 377 MHz, Cl_3CF) δ = -132.82 (d, $^3J_{F,F}$ = 19.2 Hz, 6 F, 19/19'-H), -161.55 (t, $^3J_{F,F}$ = 20.2 Hz, 3 F, 21-F), -165.96- -166.09 (m, 6 F, 20/20'-F) ppm.

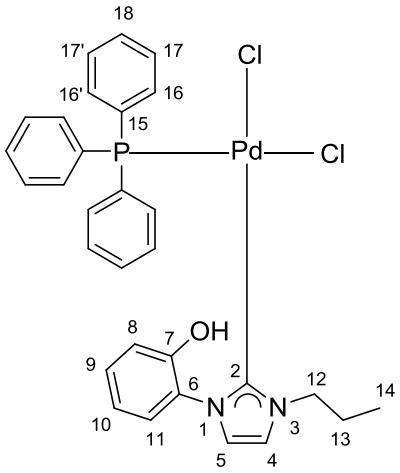
IR (ATR): ϑ = 1511, 1498, 1456, 1304, 1277, 1262, 1079, 1038, 974, 965, 945, 936, 802, 768, 762, 755, 733, 691, 673, 667, 654, 649 cm^{-1}.

MS (ESI, 50 V): m/z (%) = 727.0 (100) $[M-H]^-$.

HR ESI-MS: calcd for $C_{31}H_{15}N_2OF_{15}B$ 727.1038. Found 727.1038.

5.6 General procedure for the synthesis of complexes

(cis)-Chloro-(*N*-(hydroxyphenyl)-1-propylimidazole)-chloro-triphenylphosphine-palladium(II) 76a



A sample of 0.09 g (0.43 mmol) of 2-(3-propyl-1*H*-imidazolium-1-yl)phenolate was reacted with 0.30 g (0.43 mmol) of trans-dichlorobis-(triphenylphosphine)palladium(II) in 5 mL of anhydrous THF at boiling temperature under an inert atmosphere overnight. The precipitated was filtered off, washed with THF and dried *in vacuo*.

Yield: 0.21 g (76%) of a white solid.

Mp: 265 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.99 (s, 1 H, -OH), 8.67 (dd, J_1 = 1.0 Hz, J_2 = 8.0 Hz, 1 H, 5-H), 7.48 - 7.46 (m, 3 H, 18-H), 7.43 (d, J = 1.9 Hz, 1 H, 8-H), 7.34 - 7.25 (m, 14 H, 9/11/16/16'/17/17'-H), 7.07 (ddd, J_1 = 0.9 Hz, J_2 = 7.8 Hz, J_3 = 8.2 Hz, 1 H, 10-H), 6.80 (d, J_1 = 1.0 Hz, J_2 = 8.0 Hz, 1 H, 4-H), 4.24 - 4.19 (m, 1 H, 12-H), 3.69 - 3.64 (m, 1 H, 12-H), 1.94 - 1.86 (m, 1 H, 13-H), 1.61 - 1.52 (m, 1 H, 13-H), 0.90 (t, J = 7.3 Hz, 14-H) ppm.

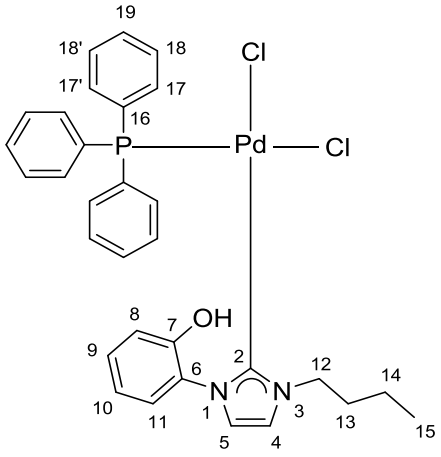
^{13}C NMR (150 MHz, DMSO-d_6): δ = 158.3 (o, C-2), 151.2 (o, C-7), 134.0 (+, C-16/16'), 131.2 (+, C-18), 130.4 - 130.6 (o, C-15), 130.3 (+, C-9), 128.9 (+, C-5), 128.7 - 128.8 (+, C-17/17'), 125.9 (o, C-6), 125.8 (+, C-8), 121.7 (+, C-11), 119.2 (+, C-10), 117.1 (+, C-4), 52.5 (-, C-12), 22.6 (-, C-13), 11.5 (+, C-14) ppm.

IR (ATR): ϑ = 3279, 1511, 1435, 1427, 1286, 1098, 769, 709, 689, 683, 533, 510, 497 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 605.1 (100) $[M]^+$.

HR ESI-MS: calcd for $C_{30}H_{29}N_2O_1Cl_1Pd_1P_1^+$ 605.0741. Found 605.0739.

(cis-)-Chloro-(*N*-(hydroxyphenyl)-1-butylimidazole)-chloro-triphenyl phosphine-palladium(II) 76b



A sample of 0.09 g (0.43 mmol) of 2-(3-butyl-1*H*-imidazolium-1-yl)phenolate and 0.30 g (0.43 mmol) of trans-dichlorobis-(triphenylphosphine)palladium(II) were refluxed in 5 mL of anhydrous THF under an inert atmosphere overnight. The precipitated was filtered off, washed with THF and dried *in vacuo*.

Yield: 0.24g (84%) of a white solid.

Mp: 286 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.95 (s, 1H, -OH), 8.63 (dd, J_1 = 1.1 Hz, J_2 = 8.0 Hz, 1 H, 5-H), 7.46 - 7.43 (m, 3 H, 19-H), 7.40 (d, J = 2.0 Hz, 1 H, 8-H), 7.31 - 7.27 (m, 8 H, 9/11/18/18'-H), 7.214- 7.21 (m, 6 H, 17/17'-H), 7.05 (ddd, J_1 = 1.1 Hz, J_2 = 7.9 Hz, J_3 = 8.5 Hz, 1 H, 10-H), 6.75 (dd, J_1 = 1.1, J_2 = 8.0, 1 H, 4-H), 4.21- 4.16 (m, 1 H, 12-H), 3.78 - 3.73 (m, 1 H, 12-H), 1.84 - 1.77 (m, 1 H, 13-H),

1.46 - 1.39 (m, 1 H, 13-H), 1.34 - 1.28 (overlap, 2 H, 14-H), 0.88 (t, *J* = 7.3, 3 H, 15-H) ppm.

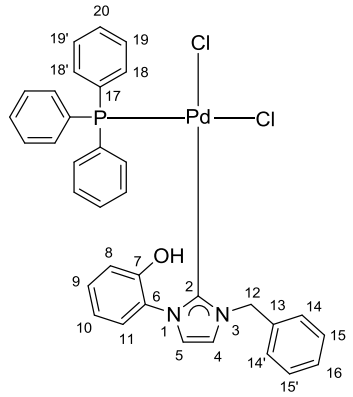
^{13}C NMR (150 MHz, DMSO-d_6): δ = 158.3 (o, C-2), 151.2 (o, C-7), 134.0 (+, C-17/17'), 131.2 (+, C-19), 130.4 - 130.3 (o, C-16), 130.1 (+, C-9), 128.9 (+, C-5), 128.78- 128.7 (+, C-18/18'), 125.9 (o, C-6), 125.8 (+, C-8), 121.7 (+, C-11), 119.2 (+, C-10), 117.1 (+, C-4), 50.8 (-, C-12), 31.1 (-, C-13), 19.9 (-, C-14), 14.0 (+, C-15) ppm.

IR (ATR): ϑ = 3282, 1511, 1436, 1427, 1289, 1098, 770, 756, 693, 688, 682, 534, 509, 498 cm^{-1}.

MS (ESI, 20 V): m/z (%) = 619.0 (100) $[M]^+$.

HR ESI-MS: decomposed.

(cis-)-Chloro-(*N*-(hydroxyphenyl)-1-benzylimidazole)-chloro-triphenylphosphine-palladium(II) 76d



A sample of 0.11 g (0.43 mmol) of 2-(3-benzyl-1*H*-imidazolium-1-yl)phenolate and 0.30 g (0.43 mmol) of trans-dichlorobis-(triphenylphosphine)palladium(II) were refluxed in 5 mL of anhydrous THF under an inert atmosphere overnight. The precipitated was filtered off, washed with THF and dried *in vacuo*.

Yield: 0.22 g (75%) of a white solid.

Mp: 241 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.95 (s, 1H, -OH), 8.66 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1 H, 5-H), 7.47 - 7.44 (overlapped signals, 3 H, 20-H), 7.41 - 7.40 (overlapped signals, 2-H, 14/14'-H), 7.37 (d, 14 H, J = 2.0 Hz, 8-H), 7.33 - 7.26 (m, 10 H, 9/15/15'/16/19/19'-H), 7.18 - 7.21 (m, 6 H, 18/18'-H), 7.08 (ddd, J_1 = 1.6 Hz, J_2 = 7.9 Hz, J_3 = 8.6 Hz, 10-H), 6.94 (d, J = 1.6 Hz, 1 H, 11-H), 6.80 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1 H, 4-H), 6.82 (d, J = 14.3 Hz, 1H, 12-H), 4.72 (d, J = 14.3 Hz, 1 H, 12-H) ppm.

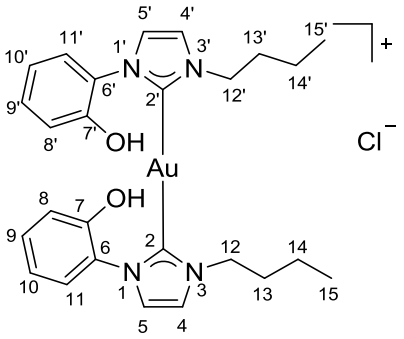
^{13}C NMR (150 MHz, DMSO-d_6): δ = 159.4 (o, C-2), 151.3 (o, C-7), 135.3 (o, C-17), 134.0 - 134.1 (+, C-18/18'), 131.2 (+, C-20), 130.4 (+, C-9), 130.0 (o, C-13), 129.6 (+, C-14/14'), 129.0 (+, C-15/15'), 128.8 (+, C-1919'), 128.8 (+, C-5), 128.7 (+, C-16), 126.3 (+, C-8), 125.8 (o, C-6), 121.5 (+, C-11), 119.3 (+, C-10), 117.1 (+, C-4), 54.3 (-, C-12) ppm.

IR (ATR): ϑ = 3276, 1510, 1422, 1363, 1285, 1238, 1098, 1092, 769, 684, 661, 535, 530, 508, 498 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 654.0 (100) $[M]^+$.

HR ESI-MS: calcd for $C_{34}H_{30}N_2O_1Cl_1Pd_1P_1^+$ 654.0819. Found 654.0819.

Mono(bis(3-butyl-1-(2-hydroxyphenyl)-1*H*-imidazolium-2-yl)gold) monochloride 77



A sample of 0.43 g (0.20 mmol) of 2-(3-butyl-1*H*-imidazolium-1-yl)phenolate was reacted with 0.05 g (0.10 mmol) of chloro(triphenylphosphine)gold(I) in 5 mL of

anhydrous THF at reflux temperature under an atmosphere of nitrogen overnight. The solid was filtered off, washed with THF and dried *in vacuo*.

Yield: 0.40g (60%) of a yellow solid.

Mp: 242 °C.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.39 (d, *J* = 2.0 Hz, 2 H, 4/4'-H), 7.37 (dd, J_1 = 1.6 Hz, J_2 = 7.7 Hz, 2 H, 11/11'-H), 7.38 - 7.33 (overlapped signals, 4 H, 5/5'/9/9'-H), 7.01 (dd, J_1 = 1.3 Hz, J_2 = 8.2 Hz, 2 H, 8/8'-H), 6.93 (ddd, J_1 = 1.3 Hz, J_2 = 7.5 Hz, J_3 = 7.7 Hz, 2 H, 10/10'-H), 4.01 (t, *J* = 7.1 Hz, 4 H, 12/12'-H), 1.71 - 1.66 (m, 4 H, 13/13'-H), 1.22 - 1.15 (m, 4 H, 14/14'-H), 0.88 (t, *J* = 7.3 Hz, 6 H, 15/15'-H) ppm.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.34 (s_{broad}, 2 H, OH), 7.62 (d, *J* = 1.9 Hz, 2 H, 2/2'-H), 7.57 (d, *J* = 1.9 Hz, 2 H, 3/3'-H), 7.38 (dd, J_1 = 1.7 Hz, J_2 = 7.8 Hz, 2 H, 11/11'-H), 7.34 (ddd, J_1 = 1.7 Hz, J_2 = 7.6 Hz, J_3 = 8.2 Hz, 2 H, 9/9'-H), 7.06 (dd, J_1 = 1.3 Hz, J_2 = 8.2 Hz, 2 H, 8/8'-H), 6.93 (ddd, J_1 = 1.3 Hz, J_2 = 7.6 Hz, J_3 = 7.8 Hz, 2 H, 10/10'-H), 3.96 (t, *J* = 7.0 Hz, 4 H, 12/12'-H), 1.64 - 1.59 (m, 4 H, 13/13'-H), 1.11 - 1.05 (m, 4 H, 14/14'-H), 0.81 (t, *J* = 7.3 Hz, 6 H, 15/15'-H) ppm.

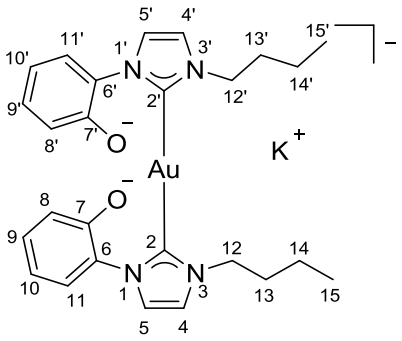
^{13}C NMR (150 MHz, CD_3OD): δ =183.9 (o, C-2/2'), 152.5 (o, C-7/7'), 130.3 (+, C-9/9'), 128.1 (+, C-11/11'), 126.8 (o, C-6/6'), 123.8 (+, C-5/5'), 120.7 (+, C-4/4'), 119.1 (+, C-10/10'), 116.5 (+, C-8/8'), 50.4 (-, C-12/12'), 32.9 (-, C-13/13'), 19.2 (-, C-14/14'), 13.6 (+, C-15/15') ppm.

IR (ATR): ϑ̃ = 2956, 1598, 1509, 1463, 1455, 1285, 1241, 829, 766, 752, 734, 687 cm^{-1}.

MS (ESI, 5 V): m/z (%) = 629.1 (100) M^+.

HR ESI-MS: calcd for $C_{26}H_{32}N_4O_2Au^+$ 629.2192. Found 629.2191.

Potassium mono(bis(3-butyl-1-(2-phenolate)-1*H*-imidazolium-2-yl)gold) 78



A sample of 0.066 g (0.10 mmol) of mono(bis(3-butyl-1-(2-hydroxyphenyl)-1*H*-imidazolium-2-yl)gold) monochloride was deprotonated with 0.014 g (0.10 mmol) of K_2CO_3 in 5 mL methanol. The solution was stirred for 30 minutes under ultrasonic irradiation and evaporated to give a colorless solid.

Yield: 0.066 g (100%).

Mp: 240 °C.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.34 (d, J = 1.8 Hz, 2 H, 4/4'-H), 7.23 - 7.21 (overlapped signals, 4 H, 4/4'-H and 11/11'-H), 7.08 (ddd, J_1 = 1.86 Hz, J_2 = 7.3 Hz, J_3 = 8.3 Hz, 2 H, 9/9'-H), 6.80 (dd, J_1 = 1.2 Hz, J_2 = 8.3 Hz, 2 H, 8/8'-H), 6.43 (ddd, J_1 = 1.2 Hz, J_2 = 7.3 Hz, J_3 = 7.5 Hz, 2 H, 10/10'-H), 4.00 (t, J = 7.1 Hz, 4 H, 12/12'-H), 1.70 - 1.65 (m, 4 H, 13/13'-H), 1.26 - 1.19 (m, 4 H, 14/14'-H), 0.88 (t, J = 7.3 Hz, 6 H, 15/15'-H) ppm.

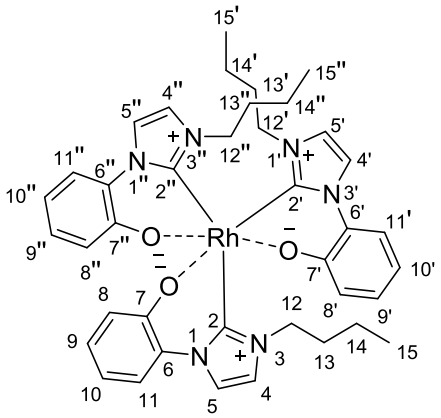
^{13}C NMR (150 MHz, CD_3OD): δ = 183.5 (o, 2/2'-C), 162.5 (o, 7-C), 160.1 (o, 7'-C), 129.5 (+, 9/9'-C), 129.2 (o, 6/6'-C), 127.4 (+, 11/11'-H), 124.1 (+, 5/5'-C), 121.2 (+, 8/8'-H), 119.7 (+, 4/4'-C), 111.9 (+, 10/10'-C), 50.2 (-, 12/12'-C), 33.1 (-, 13/13'-C), 19.3 (-, 14/14'-C), 12.7 (+, 15/15'-C) ppm.

IR (ATR): ϑ̃ = 3157, 2958, 1637, 1591, 1483, 1447, 1311, 1246, 1076, 1061, 844, 748, 701, 566 cm^{-1}.

MS (ESI, 50 V): m/z (%) = 627.2 (100) $[M-K]^-$.

HR ESI-MS: calcd for $C_{26}H_{32}N_4O_2Au^+$ 629.2191. Found 629.2191.

Tris(3-butyl-1-(2-oxidophenyl)-1*H*-imidazolium-2-yl)rhodium 79



Method A: A sample of 0.16 g (0.72 mmol) of 2-(3-butyl-1*H*-imidazolium-1-yl)phenolate and 0.06 g (0.12 mmol) of chloro(1,5-cyclooctadiene)rhodium(I) dimer were refluxed in 5 mL of anhydrous toluene under an inert atmosphere overnight. The solid was filtered off, washed with THF and dried *in vacuo*.

Yield: 0.09g (50%) of a yellow solid.

Mp: 280 °C.

Method B: A sample of 0.16 g (0.72 mmol) of 2-(3-butyl-1*H*-imidazolium-1-yl)phenolate and 0.17 g (0.24 mmol) of bis(triphenylphosphine)rhodium(I) carbonyl chloride were refluxed in 5 mL of anhydrous toluene under an inert atmosphere overnight. The solid was filtered off, washed with THF and dried *in vacuo*.

Yield: 0.09g (50%) of a yellow solid.

Mp: 280 °C.

^{1}H NMR (600 MHz, CD_3OD): δ = 8.00 (d, *J* = 2.2 Hz, 1 H, 5-H), 7.82 (d, *J* = 2.2 Hz, 1 H, 5'-H), 7.52 dd, J_1 = 1.5 Hz, J_2 = 8.2 Hz, 1 H, 11-H), 7.44 (d, *J* = 2.2 Hz, 1 H, 4-H), 7.39 (d, *J* = 2.0 Hz, 1 H, 4'-H), 7.29 (d, *J* = 2.2 Hz, 1 H, 5"-H), 7.12 (d,

J = 2.0 Hz, 1 H, 5'-H), 7.11 (dd, J_1 = 1.5 Hz, J_2 = 8.2 Hz, 1 H, 11'-H), 7.05 (dd, J_1 = 1.4 Hz, J_2 = 8.1 Hz, 1 H, 11''-H), 6.97 - 6.93 (m, 2 H, 8/9-H), 6.80 (ddd, J_1 = 1.5 Hz, J_2 = 7.0 Hz, J_3 = 8.2 Hz, 1 H, 9'-H), 6.72 (dd, J_1 = 1.5 Hz, J_2 = 8.3 Hz, 1 H, 8'-H), 6.64 - 6.60 (overlapped signals, 2 H, 9''/10-H), 6.57 (ddd, J_1 = 1.5 Hz, J_2 = 7.0 Hz, J_3 = 8.3 Hz, 1 H, 10'-H), 6.41 (ddd, J_1 = 1.4 Hz, J_2 = 7.3 Hz, J_3 = 8.1 Hz, 1 H , 10''-H), 5.81 (dd, J_1 = 1.3 Hz, J_2 = 8.1 Hz, 1 H, 8''-H), 4.33 (ddd, J_1 = 4.8 Hz, J_2 = 11.8 Hz, J_3 = 16.7 Hz, 1 H, 12-H), 4.49 (ddd, J_1 = 4.8 Hz, J_2 = 11.8 Hz, J_3 = 16.7 Hz, 1 H, 12-H), 3.78 (t, J = 8.5 Hz, 2 H, 12'-H), 3.78 - 3.64 (m, 2 H, 12''-H), 1.70 - 1.64 (m, 1 H, 13-H), 1.62-1.56 (m, 1 H, 13-H), 1.53 - 1.45 (m, 1 H, 13'-H), 1.37 - 1.30 (m, 1 H, 13'-H), 1.27 - 1.18 (m, 1 H, 14-H), 1.08 - 0.89 (m, 8 H, 13''/14/ 2 x 14'/14''/15-H), 0.88 - 0.82 (m, 1 H, 14''-H), 0.79 - 0.72 (m, 1 H, 13''-H), 0.68 (t, J = 7.3 Hz, 3 H, 15'-H), 0.63 (t, J = 7.4 Hz, 3 H, 15''-H) ppm.

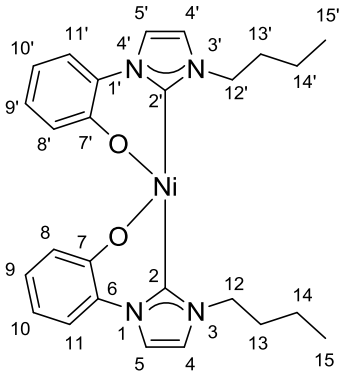
^{13}C NMR (150 MHz, CD_3OD): δ = 173.5 (o, d, $^1J_{C,Rh}$ = 35.6 Hz, C-2), 171.0 (o, d, $^1J_{C,Rh}$ = 35.6 Hz, C-2'), 164.4 (o, d, $^1J_{C,Rh}$ = 48.5 Hz, C-2''), 160.2 (o, C-7), 159.8(o, C-7'), 157.3 (o, C-7''), 130.5 (o, C-6), 129.8 (o, C-6'), 128.2 (o, C-6''), 126.6 (+, C-9), 126.1 (+, C-9'), 125.9 (+, C-9''), 123.4 (+, C-8), 122.9 (+, C-4), 122.7 (+, C-8'), 122.2 (+, C-4'), 121.3 (+, C-8''), 120.8 (+, C-4''), 120.7 (+, C-11), 119.6 (+, C-11'), 118.7 (+, C-11''), 118.4 (+, C-5), 118.4 (+, C-5'), 117.8 (+, C-5''), 115.1 (+, C-10), 114.1 (+, C-10'), 113.6 (+, C-10''), 48.7/48.3/48.2 (-, C-12/12'/12''), 32.5/32.3/32.0 (-, C-13/13'/13''), 20.0/19.7/19.7 (-, C-14/14'/14''), 12.9/12.4/12.4 (+, C-15/15'/15') ppm.

IR (ATR): ϑ = 2955, 1590, 1419, 1374, 1302, 1268, 1122, 950, 850, 742, 716, 698, 690, 683, 657 cm^{-1}.

MS (ESI, 30 V): m/z (%) = 749.2 (100) $[M+H]^+$.

HR ESI-MS: calcd for $C_{39}H_{46}N_6O_3Rh^+$ 749.2686. Found 749.2685.

Bis(3-butyl-1-(2-oxidophenyl)-1*H*-imidazolium-2-yl)nickel 80



A sample of 0.15 g (0.70 mmol) of 2-(3-butyl-1*H*-imidazolium-1-yl)phenolate and 0.23 g (0.35 mmol) of bis(triphenylphosphine)nickel(II) dichloride were refluxed in 5 mL of anhydrous toluene under an inert atmosphere overnight. The solid was filtered off, washed with THF and dried *in vacuo*.

Yield: 0.09 g (45%) of a yellow solid.

Mp: 153 °C.

^{1}H NMR (600 MHz, CD_3OD): δ = 7.67 (d, J = 2.0 Hz, 2 H, 4/4'-H), 7.44 (dd, J_1 = 1.3 Hz, J_2 = 7.5 Hz, 2 H, 11/11'-H), 7.36 (d, J = 2.0 Hz, 2 H, 5/5'-H), 7.11 (dd, J_1 = 1.9 Hz, J_2 = 8.2 Hz, 2 H, 8/8'-H), 7.08 (ddd, J_1 = 1.3 Hz, J_2 = 8.2 Hz, J_3 = 8.9 Hz, 2 H, 9/9'-H), 6.72 (ddd, J_1 = 1.9 Hz, J_2 = 7.5 Hz, J_3 = 8.9 Hz, 2 H, 10/10'-H), 3.68 - 3.63 (m, 2 H, 12/12'-H), 3.06 - 3.01 (m, 2 H, 12/12'-H), 2.42 - 2.35 (m, 2 H, 13/13'-H), 1.84 - 1.76 (m, 2 H, 13/13'-H), 1.27 - 1.21 (m, 4 H, 14/14'-H), 0.77 (t, J_1 = 7.4 Hz, 6 H, 15/15'-H) ppm.

^{13}C NMR (600 MHz, CD_3OD): δ = 156.8 (o, C-7/7'), 156.2 (o, C-2/2'), 128.8 (o, C-6/6'), 127.4 (+, C-9/9'), 124.2 (+, C-5/5'), 120.9 (+, C-8/8'), 118.4 (+, C-11/11'), 118.3 (+, C-4/4'), 115.1 (+, C-10/10'), 49.8 (+, C-12/12'), 33.4 (+, C-13/13'), 19.5 (+, C-14/14'), 12.3 (+, C-15/15') ppm.

IR (ATR): ϑ = 2958, 2929, 2872, 1593, 1487, 1457, 1417, 1395, 1300, 1273, 1235, 1154, 952, 840, 742, 724, 681 cm^{-1}.

MS (ESI, 5 V): m/z (%) = 511.0 (100) $[M+Na]^+$.

HR-ESI-MS: calcd for $C_{26}H_{31}N_4O_2Ni^+$ 489.1800. Found 489.1800.

6 X-ray analysis data

6.1 Crystal structure determination of 4-(2-Hydroxy-5-methylphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate 59b

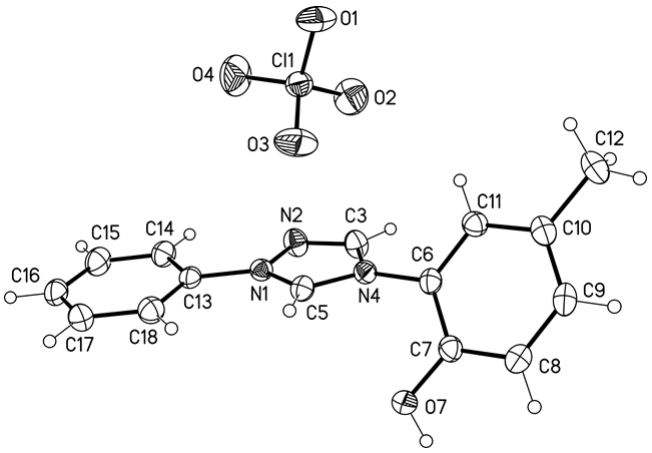


Figure 24. X-ray structure of molecules **59b**.

Table 3: Crystallography data and refinement details for **59b**.

$C_{15}H_{14}N_3O{\cdot}ClO_4$	Z = 2
M_r = 351.74	F(000) = 364
Triclinic, $P\bar{1}$	D_x = 1.542 Mg m^{-3}
a = 6.0904 (5) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å
b = 7.6950 (5) Å	Cell parameters from 3383 reflections
c = 16.3916 (13) Å	θ = 2.6–29.6°
α = 83.899 (6)°	μ = 0.28 mm^{-1}
β = 82.995 (7)°	T = 173 K
γ = 87.213 (6)°	Blocks, colourless
V = 757.65 (10) Å^3	0.50 × 0.25 × 0.15 mm
Refinement on F2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map

R[F2 > 2σ(F2)] = 0.038	H atoms treated by a mixture of independent and constrained refinement
wR(F2) = 0.106	w = 1/[σ2(Fo2) + (0.0538P)2 + 0.1867P] where P = (Fo2 + 2Fc2)/3
S = 1.04	(Δ/σ)max < 0.001
3750 reflections	Δ⟩max = 0.32 e Å-3
222 parameters	Δ⟩min = -0.42 e Å-3
1 restraint	Extinction correction: SHELXL, Fc*=kFc[1+0.001xFc2λ3/sin(2θ)]-1/4
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.082 (5)

Table 4: Bond length (pm) data for **59b**.

Cl1—O3	1.4218 (13)	C9—C10	1.392 (2)
Cl1—O4	1.4250 (13)	C9—H9	0.9500
Cl1—O2	1.4333 (13)	C10—C11	1.391 (2)
Cl1—O1	1.4487 (12)	C10—C12	1.506 (2)
N1—C5	1.3194 (18)	C11—H11	0.9500
N1—N2	1.3683 (17)	C12—H12A	0.9800
N1—C13	1.4410 (17)	C12—H12B	0.9800
N2—C3	1.3001 (19)	C12—H12C	0.9800
C3—N4	1.3610 (19)	C13—C18	1.377 (2)
C3—H3	0.9500	C13—C14	1.384 (2)
N4—C5	1.3332 (18)	C14—C15	1.388 (2)
N4—C6	1.4399 (17)	C14—H14	0.9500
C5—H5	0.9500	C15—C16	1.380 (2)
C6—C11	1.388 (2)	C15—H15	0.9500
C6—C7	1.389 (2)	C16—C17	1.380 (2)
C7—O7	1.3651 (17)	C16—H16	0.9500
C7—C8	1.388 (2)	C17—C18	1.393 (2)

O7—H7	0.830 (15)	C17—H17	0.9500
C8—C9	1.387 (2)	C18—H18	0.9500
C8—H8	0.9500		
O3—Cl1—O4	110.69 (9)	C10—C9—H9	119.0
O3—Cl1—O2	109.44 (9)	C11—C10—C9	117.83 (14)
O4—Cl1—O2	109.92 (9)	C11—C10—C12	121.11 (15)
O3—Cl1—O1	108.88 (8)	C9—C10—C12	121.06 (14)
O4—Cl1—O1	109.16 (9)	C6—C11—C10	120.05 (14)
O2—Cl1—O1	108.72 (8)	C6—C11—H11	120.0
C5—N1—N2	110.99 (11)	C10—C11—H11	120.0
C5—N1—C13	128.99 (12)	C10—C12—H12A	109.5
N2—N1—C13	120.01 (11)	C10—C12—H12B	109.5
C3—N2—N1	103.89 (12)	H12A—C12—H12B	109.5
N2—C3—N4	111.80 (13)	C10—C12—H12C	109.5
N2—C3—H3	124.1	H12A—C12—H12C	109.5
N4—C3—H3	124.1	H12B—C12—H12C	109.5
C5—N4—C3	106.11 (12)	C18—C13—C14	122.18 (13)
C5—N4—C6	127.52 (12)	C18—C13—N1	120.04 (13)
C3—N4—C6	126.34 (12)	C14—C13—N1	117.78 (13)
N1—C5—N4	107.20 (13)	C13—C14—C15	118.27 (15)
N1—C5—H5	126.4	C13—C14—H14	120.9
N4—C5—H5	126.4	C15—C14—H14	120.9
C11—C6—C7	121.95 (13)	C16—C15—C14	120.78 (15)
C11—C6—N4	119.14 (13)	C16—C15—H15	119.6
C7—C6—N4	118.89 (12)	C14—C15—H15	119.6
O7—C7—C8	123.49 (14)	C15—C16—C17	119.83 (14)
O7—C7—C6	118.44 (12)	C15—C16—H16	120.1
C8—C7—C6	118.07 (13)	C17—C16—H16	120.1
C7—O7—H7	109.5 (15)	C16—C17—C18	120.58 (16)

C9—C8—C7	120.07 (14)	C16—C17—H17	119.7
C9—C8—H8	120.0	C18—C17—H17	119.7
C7—C8—H8	120.0	C13—C18—C17	118.37 (15)
C8—C9—C10	121.97 (13)	C13—C18—H18	120.8
C8—C9—H9	119.0	C17—C18—H18	120.8
C5—N1—N2—C3	0.11 (16)	C7—C8—C9—C10	-0.2 (2)
C13—N1—N2—C3	-178.91 (12)	C8—C9—C10—C11	1.7 (2)
N1—N2—C3—N4	0.23 (17)	C8—C9—C10—C12	-178.36 (13)
N2—C3—N4—C5	-0.47 (17)	C7—C6—C11—C10	-1.2 (2)
N2—C3—N4—C6	-178.55 (13)	N4—C6—C11—C10	-179.46 (12)
N2—N1—C5—N4	-0.40 (16)	C9—C10—C11—C6	-1.0 (2)
C13—N1—C5—N4	178.51 (12)	C12—C10—C11—C6	179.04 (13)
C3—N4—C5—N1	0.51 (15)	C5—N1—C13—C18	-2.0 (2)
C6—N4—C5—N1	178.56 (12)	N2—N1—C13—C18	176.87 (13)
C5—N4—C6—C11	-125.40 (15)	C5—N1—C13—C14	179.11 (14)
C3—N4—C6—C11	52.28 (19)	N2—N1—C13—C14	-2.07 (18)
C5—N4—C6—C7	56.24 (19)	C18—C13—C14—C15	0.3 (2)
C3—N4—C6—C7	-126.08 (16)	N1—C13—C14—C15	179.24 (13)
C11—C6—C7—O7	-177.97 (12)	C13—C14—C15—C16	-0.4 (2)
N4—C6—C7—O7	0.34 (19)	C14—C15—C16—C17	0.4 (2)
C11—C6—C7—C8	2.6 (2)	C15—C16—C17—C18	-0.2 (2)
N4—C6—C7—C8	-179.05 (12)	C14—C13—C18—C17	-0.2 (2)
O7—C7—C8—C9	178.71 (13)	N1—C13—C18—C17	-179.06 (13)
C6—C7—C8—C9	-1.9 (2)	C16—C17—C18—C13	0.1 (2)

Table 5: Selected hydrogen-bond lengths (pm) and bond angles (°) for **59b**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

C3—H3···O7^{i}	0.95	2.33	3.2629 (19)	169
C5—H5···O2^{ii}	0.95	2.28	3.196 (2)	162
O7—H7···O1^{iii}	0.83 (2)	1.91 (2)	2.7289 (17)	168 (2)

6.2 Crystal structure determination of 4-methyl-2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate hydrate 60b

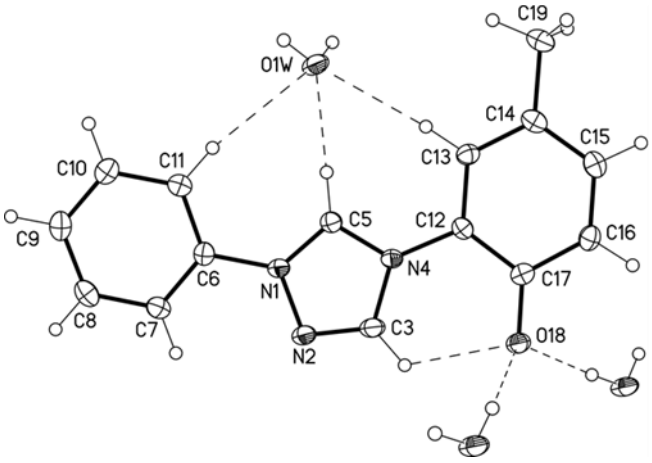


Figure 24. X-ray structure of molecule **60b**.

Table 6: Crystallography data and refinement details for **60b**.

$C_{15}H_{13}N_3O{\cdot}H_2O$	$F(000)$ = 568
M_r = 269.30	D_x = 1.377 Mg m^{-3}
Monoclinic, *Cc (no.9)*	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 19.9626 (9) Å	Cell parameters from 85 reflections
b = 4.6037 (2) Å	θ = 2.5–25.0°
c = 15.3349 (6) Å	μ = 0.09 mm^{-1}
β = 112.829 (5)°	T = 123 K
V = 1298.91 (11) Å^3	Blocks, yellow
Z = 4	0.60 × 0.30 × 0.25 mm
Refinement on F2	Secondary atom site location: difference Fourier map

Least-squares matrix: full	Hydrogen site location: difference Fourier map
R[F2 > 2σ(F2)] = 0.029	H atoms treated by a mixture of independent and constrained refinement
wR(F2) = 0.070	w = 1/[σ2(Fo2) + (0.0381P)2 + 0.4096P] where P = (Fo2 + 2Fc2)/3
S = 1.04	(Δ/σ)max < 0.001
2901 reflections	Δ⟩max = 0.16 e Å-3
188 parameters	Δ⟩min = -0.21 e Å-3
5 restraints	Absolute structure: Flack x determined using 1299 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons and Flack (2004), Acta Cryst. A60, s61). Determination of absolute structure using Bayesian statistics on Bijvoet differences (Hooft, Straver and Spek, 2008): Hooft's y = -0.1(4) (PLATON: Spek, 2009).
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: 0.0 (4)

Table 7: Bond length (pm) data for **60b**.

N1—C5	1.325 (2)	C10—H10	0.9500
N1—N2	1.372 (2)	C11—H11	0.9500
N1—C6	1.435 (2)	C12—C13	1.394 (3)
N2—C3	1.306 (3)	C12—C17	1.416 (3)
C3—N4	1.376 (2)	C13—C14	1.386 (3)
C3—H3	0.9500	C13—H13	0.9500
N4—C5	1.339 (2)	C14—C15	1.394 (3)
N4—C12	1.447 (2)	C14—C19	1.510 (3)
C5—H5	0.9500	C15—C16	1.381 (3)
C6—C11	1.384 (3)	C15—H15	0.9500
C6—C7	1.387 (3)	C16—C17	1.423 (3)
C7—C8	1.387 (3)	C16—H16	0.9500
C7—H7	0.9500	C17—O18	1.304 (2)
C8—C9	1.388 (3)	C19—H19A	0.9800

C8—H8	0.9500	C19—H19B	0.9800
C9—C10	1.389 (3)	C19—H19C	0.9800
C9—H9	0.9500	O1W—H1W1	0.85 (2)
C10—C11	1.389 (3)	O1W—H1W2	0.85 (2)
C5—N1—N2	111.36 (15)	C6—C11—C10	119.02 (18)
C5—N1—C6	127.42 (16)	C6—C11—H11	120.5
N2—N1—C6	121.22 (15)	C10—C11—H11	120.5
C3—N2—N1	103.74 (15)	C13—C12—C17	123.34 (17)
N2—C3—N4	111.87 (17)	C13—C12—N4	117.40 (17)
N2—C3—H3	124.1	C17—C12—N4	119.25 (16)
N4—C3—H3	124.1	C14—C13—C12	120.77 (18)
C5—N4—C3	105.75 (15)	C14—C13—H13	119.6
C5—N4—C12	125.34 (15)	C12—C13—H13	119.6
C3—N4—C12	128.91 (16)	C13—C14—C15	117.50 (18)
N1—C5—N4	107.29 (16)	C13—C14—C19	121.05 (19)
N1—C5—H5	126.4	C15—C14—C19	121.44 (18)
N4—C5—H5	126.4	C16—C15—C14	121.90 (18)
C11—C6—C7	121.73 (18)	C16—C15—H15	119.1
C11—C6—N1	119.16 (16)	C14—C15—H15	119.1
C7—C6—N1	119.10 (16)	C15—C16—C17	122.47 (17)
C8—C7—C6	118.59 (19)	C15—C16—H16	118.8
C8—C7—H7	120.7	C17—C16—H16	118.8
C6—C7—H7	120.7	O18—C17—C12	124.04 (17)
C7—C8—C9	120.59 (19)	O18—C17—C16	121.94 (16)
C7—C8—H8	119.7	C12—C17—C16	114.01 (16)
C9—C8—H8	119.7	C14—C19—H19A	109.5
C8—C9—C10	119.94 (19)	C14—C19—H19B	109.5
C8—C9—H9	120.0	H19A—C19—H19B	109.5
C10—C9—H9	120.0	C14—C19—H19C	109.5

C11—C10—C9	120.12 (19)	H19A—C19—H19C	109.5
C11—C10—H10	119.9	H19B—C19—H19C	109.5
C9—C10—H10	119.9	H1W1—O1W—H1W2	112 (2)
C5—N1—N2—C3	0.0 (2)	N1—C6—C11—C10	179.47 (17)
C6—N1—N2—C3	-179.73 (16)	C9—C10—C11—C6	1.0 (3)
N1—N2—C3—N4	0.0 (2)	C5—N4—C12—C13	-5.4 (3)
N2—C3—N4—C5	0.0 (2)	C3—N4—C12—C13	173.52 (18)
N2—C3—N4—C12	-179.06 (17)	C5—N4—C12—C17	173.72 (18)
N2—N1—C5—N4	0.1 (2)	C3—N4—C12—C17	-7.4 (3)
C6—N1—C5—N4	179.72 (15)	C17—C12—C13—C14	0.6 (3)
C3—N4—C5—N1	0.0 (2)	N4—C12—C13—C14	179.72 (17)
C12—N4—C5—N1	179.08 (15)	C12—C13—C14—C15	0.3 (3)
C5—N1—C6—C11	-4.9 (3)	C12—C13—C14—C19	-178.95 (19)
N2—N1—C6—C11	174.70 (18)	C13—C14—C15—C16	-1.1 (3)
C5—N1—C6—C7	175.18 (19)	C19—C14—C15—C16	178.19 (19)
N2—N1—C6—C7	-5.2 (2)	C14—C15—C16—C17	0.9 (3)
C11—C6—C7—C8	0.0 (3)	C13—C12—C17—O18	179.98 (17)
N1—C6—C7—C8	179.90 (17)	N4—C12—C17—O18	0.9 (3)
C6—C7—C8—C9	0.3 (3)	C13—C12—C17—C16	-0.8 (3)
C7—C8—C9—C10	0.1 (3)	N4—C12—C17—C16	-179.88 (16)
C8—C9—C10—C11	-0.7 (3)	C15—C16—C17—O18	179.28 (18)
C7—C6—C11—C10	-0.6 (3)	C15—C16—C17—C12	0.0 (3)

Table 8: Selected hydrogen-bond lengths (pm) and bond angles (°) for **60b**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O18	0.95	2.19	2.765 (2)	118
C5—H5···O1*W*	0.95	2.03	2.974 (2)	172
C11—H11···O1*W*	0.95	2.49	3.405 (2)	161
C13—H13···O1*W*	0.95	2.38	3.324 (2)	175

O1*W*—H1*W*1···O18^{i}	0.85 (2)	1.88 (2)	2.733 (2)	177 (3)
O1*W*—H1*W*2···O18^{ii}	0.85 (2)	1.92 (2)	2.744 (2)	163 (3)

6.3 Crystal structure determination of (4-methyl-2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenoxy)-tris-(perfluorophenyl)-borate 62c

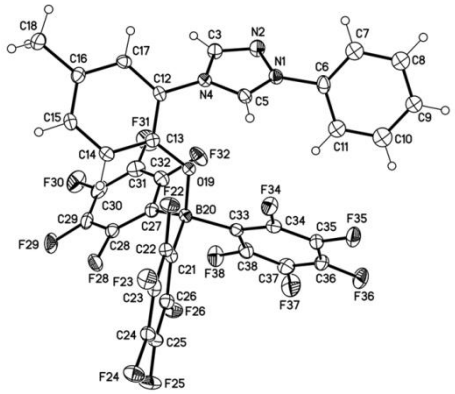


Figure 25. X-ray structure of molecule **62c**.

Table 9: Crystallography data and refinement details for **62c**.

$C_{33}H_{13}BF_{15}N_3O$	Z = 2
M_r = 763.27	F(000) = 760
Triclinic, *P*-1 (no.2)	D_x = 1.715 Mg m^{-3}
a = 11.777 (1) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å
b = 12.266 (1) Å	Cell parameters from 127 reflections
c = 12.551 (1) Å	θ = 2.5–25.0°
α = 76.40 (1)°	μ = 0.17 mm^{-1}
β = 64.72 (1)°	T = 123 K
γ = 64.59 (1)°	Blocks, colourless
V = 1477.8 (3) Å^3	0.60 × 0.40 × 0.35 mm
Refinement on F2	Primary atom site location: structure-invariant direct methods

Least-squares matrix: full	Secondary atom site location: difference Fourier map
R[F2 > 2□(F2)] = 0.038	Hydrogen site location: inferred from neighbouring sites
wR(F2) = 0.096	H-atom parameters constrained
S = 1.03	w = 1/[σ2(Fo2) + (0.0371P)2 + 1.0253P] where P = (Fo2 + 2Fc2)/3
6759 reflections	(Δ/σ)max < 0.001
474 parameters	Δ⟩max = 0.61 e Å-3
132 restraints	Δ⟩min = -0.38 e Å-3

Table 10: Bond length (pm) data for **62c**.

N1—C5	1.3160 (19)	C17—H17	0.9500
N1—N2	1.3734 (18)	C18—H18A	0.9800
N1—C6	1.436 (2)	C18—H18B	0.9800
N2—C3	1.301 (2)	C18—H18C	0.9800
C3—N4	1.3717 (19)	O19—B20	1.5030 (19)
C3—H3	0.9500	B20—C27	1.645 (2)
N4—C5	1.3372 (19)	B20—C21	1.645 (2)
N4—C12	1.4387 (18)	B20—C33	1.651 (2)
C5—H5	0.9500	C21—C22	1.382 (2)
C6—C11'	1.327 (4)	C21—C26	1.391 (2)
C6—C7	1.354 (3)	C22—F22	1.3547 (17)
C6—C7'	1.413 (4)	C22—C23	1.385 (2)
C6—C11	1.429 (3)	C23—F23	1.3442 (17)
C7—C8	1.391 (4)	C23—C24	1.372 (2)
C7—H7	0.9500	C24—F24	1.3431 (17)
C8—C9	1.375 (4)	C24—C25	1.381 (2)
C8—H8	0.9500	C25—F25	1.3442 (18)
C9—C10	1.374 (4)	C25—C26	1.378 (2)

C9—H9	0.9500	C26—F26	1.3549 (17)
C10—C11	1.388 (3)	C27—C28	1.381 (2)
C10—H10	0.9500	C27—C32	1.396 (2)
C11—H11	0.9500	C28—F28	1.3513 (18)
C7'—C8'	1.376 (5)	C28—C29	1.384 (2)
C7'—H7'	0.9500	C29—F29	1.3464 (19)
C8'—C9'	1.381 (5)	C29—C30	1.371 (3)
C8'—H8'	0.9500	C30—F30	1.3446 (19)
C9'—C10'	1.403 (5)	C30—C31	1.371 (3)
C9'—H9'	0.9500	C31—F31	1.343 (2)
C10'—C11'	1.390 (5)	C31—C32	1.377 (2)
C10'—H10'	0.9500	C32—F32	1.3548 (19)
C11'—H11'	0.9500	C33—C34	1.388 (2)
C12—C17	1.391 (2)	C33—C38	1.392 (2)
C12—C13	1.400 (2)	C34—F34	1.3571 (17)
C13—O19	1.3444 (17)	C34—C35	1.380 (2)
C13—C14	1.399 (2)	C35—F35	1.3453 (18)
C14—C15	1.388 (2)	C35—C36	1.379 (2)
C14—H14	0.9500	C36—F36	1.3393 (18)
C15—C16	1.396 (2)	C36—C37	1.372 (3)
C15—H15	0.9500	C37—F37	1.3465 (19)
C16—C17	1.392 (2)	C37—C38	1.382 (2)
C16—C18	1.509 (2)	C38—F38	1.3476 (19)
C5—N1—N2	111.78 (13)	C16—C18—H18A	109.5
C5—N1—C6	127.50 (13)	C16—C18—H18B	109.5
N2—N1—C6	120.66 (12)	H18A—C18—H18B	109.5
C3—N2—N1	103.29 (12)	C16—C18—H18C	109.5
N2—C3—N4	112.06 (13)	H18A—C18—H18C	109.5
N2—C3—H3	124.0	H18B—C18—H18C	109.5

N4—C3—H3	124.0	C13—O19—B20	122.19 (11)
C5—N4—C3	105.85 (12)	O19—B20—C27	105.73 (12)
C5—N4—C12	127.03 (13)	O19—B20—C21	112.06 (12)
C3—N4—C12	127.00 (13)	C27—B20—C21	115.78 (12)
N1—C5—N4	107.02 (13)	O19—B20—C33	106.62 (12)
N1—C5—H5	126.5	C27—B20—C33	112.84 (12)
N4—C5—H5	126.5	C21—B20—C33	103.60 (12)
C11'—C6—C7'	122.9 (3)	C22—C21—C26	113.45 (13)
C7—C6—C11	121.0 (2)	C22—C21—B20	125.33 (13)
C11'—C6—N1	120.9 (2)	C26—C21—B20	121.01 (13)
C7—C6—N1	122.36 (19)	F22—C22—C21	121.16 (13)
C7'—C6—N1	115.2 (2)	F22—C22—C23	114.48 (13)
C11—C6—N1	116.51 (16)	C21—C22—C23	124.33 (14)
C6—C7—C8	119.4 (3)	F23—C23—C24	120.25 (14)
C6—C7—H7	120.3	F23—C23—C22	120.31 (14)
C8—C7—H7	120.3	C24—C23—C22	119.39 (14)
C9—C8—C7	120.7 (3)	F24—C24—C23	120.30 (14)
C9—C8—H8	119.7	F24—C24—C25	120.59 (14)
C7—C8—H8	119.7	C23—C24—C25	119.11 (14)
C10—C9—C8	120.3 (3)	F25—C25—C26	121.04 (15)
C10—C9—H9	119.8	F25—C25—C24	119.77 (14)
C8—C9—H9	119.8	C26—C25—C24	119.19 (14)
C9—C10—C11	120.6 (3)	F26—C26—C25	116.42 (13)
C9—C10—H10	119.7	F26—C26—C21	119.18 (13)
C11—C10—H10	119.7	C25—C26—C21	124.40 (14)
C10—C11—C6	117.9 (2)	C28—C27—C32	113.39 (14)
C10—C11—H11	121.0	C28—C27—B20	128.06 (14)
C6—C11—H11	121.0	C32—C27—B20	118.18 (13)
C8'—C7'—C6	118.0 (4)	F28—C28—C27	121.38 (14)

C8'—C7'—H7'	121.0	F28—C28—C29	114.87 (14)
C6—C7'—H7'	121.0	C27—C28—C29	123.73 (15)
C7'—C8'—C9'	119.9 (5)	F29—C29—C30	120.06 (15)
C7'—C8'—H8'	120.1	F29—C29—C28	119.92 (16)
C9'—C8'—H8'	120.1	C30—C29—C28	120.01 (15)
C8'—C9'—C10'	120.2 (4)	F30—C30—C31	120.42 (17)
C8'—C9'—H9'	119.9	F30—C30—C29	120.39 (16)
C10'—C9'—H9'	119.9	C31—C30—C29	119.15 (15)
C11'—C10'—C9'	119.3 (4)	F31—C31—C30	119.88 (16)
C11'—C10'—H10'	120.3	F31—C31—C32	121.10 (16)
C9'—C10'—H10'	120.3	C30—C31—C32	119.01 (16)
C6—C11'—C10'	119.0 (4)	F32—C32—C31	116.07 (15)
C6—C11'—H11'	120.5	F32—C32—C27	119.24 (14)
C10'—C11'—H11'	120.5	C31—C32—C27	124.69 (15)
C17—C12—C13	122.58 (13)	C34—C33—C38	113.34 (14)
C17—C12—N4	119.32 (13)	C34—C33—B20	120.43 (13)
C13—C12—N4	117.95 (13)	C38—C33—B20	125.70 (13)
O19—C13—C14	124.95 (13)	F34—C34—C35	115.59 (13)
O19—C13—C12	118.31 (13)	F34—C34—C33	119.53 (13)
C14—C13—C12	116.74 (13)	C35—C34—C33	124.86 (14)
C15—C14—C13	120.69 (14)	F35—C35—C36	119.78 (14)
C15—C14—H14	119.7	F35—C35—C34	121.04 (14)
C13—C14—H14	119.7	C36—C35—C34	119.18 (15)
C14—C15—C16	122.15 (14)	F36—C36—C37	120.65 (15)
C14—C15—H15	118.9	F36—C36—C35	120.71 (15)
C16—C15—H15	118.9	C37—C36—C35	118.64 (14)
C17—C16—C15	117.58 (14)	F37—C37—C36	119.52 (15)
C17—C16—C18	121.27 (14)	F37—C37—C38	120.09 (16)
C15—C16—C18	121.14 (14)	C36—C37—C38	120.39 (15)

C12—C17—C16	120.19 (14)	F38—C38—C37	115.65 (14)
C12—C17—H17	119.9	F38—C38—C33	120.75 (14)
C16—C17—H17	119.9	C37—C38—C33	123.58 (15)
C5—N1—N2—C3	-0.43 (17)	F23—C23—C24—F24	0.4 (2)
C6—N1—N2—C3	176.95 (14)	C22—C23—C24—F24	-176.97 (13)
N1—N2—C3—N4	0.28 (17)	F23—C23—C24—C25	179.83 (14)
N2—C3—N4—C5	-0.05 (18)	C22—C23—C24—C25	2.5 (2)
N2—C3—N4—C12	-176.29 (14)	F24—C24—C25—F25	-1.5 (2)
N2—N1—C5—N4	0.42 (17)	C23—C24—C25—F25	179.07 (14)
C6—N1—C5—N4	-176.75 (14)	F24—C24—C25—C26	177.97 (14)
C3—N4—C5—N1	-0.22 (16)	C23—C24—C25—C26	-1.5 (2)
C12—N4—C5—N1	176.02 (13)	F25—C25—C26—F26	-1.6 (2)
C5—N1—C6—C11'	34.2 (4)	C24—C25—C26—F26	178.94 (14)
N2—N1—C6—C11'	-142.7 (4)	F25—C25—C26—C21	177.64 (14)
C5—N1—C6—C7	-120.8 (3)	C24—C25—C26—C21	-1.8 (2)
N2—N1—C6—C7	62.3 (3)	C22—C21—C26—F26	-177.06 (13)
C5—N1—C6—C7'	-134.7 (3)	B20—C21—C26—F26	-2.0 (2)
N2—N1—C6—C7'	48.3 (3)	C22—C21—C26—C25	3.7 (2)
C5—N1—C6—C11	63.0 (3)	B20—C21—C26—C25	178.70 (15)
N2—N1—C6—C11	-114.0 (2)	O19—B20—C27—C28	-118.98 (16)
C11'—C6—C7—C8	24.4 (5)	C21—B20—C27—C28	5.7 (2)
C7'—C6—C7—C8	-115.4 (13)	C33—B20—C27—C28	124.84 (16)
C11—C6—C7—C8	-2.6 (5)	O19—B20—C27—C32	53.51 (17)
N1—C6—C7—C8	-178.7 (3)	C21—B20—C27—C32	178.21 (13)
C6—C7—C8—C9	0.6 (5)	C33—B20—C27—C32	-62.66 (17)
C7—C8—C9—C10	0.5 (5)	C32—C27—C28—F28	-177.20 (13)
C8—C9—C10—C11	0.5 (5)	B20—C27—C28—F28	-4.4 (2)
C9—C10—C11—C6	-2.4 (5)	C32—C27—C28—C29	1.0 (2)
C11'—C6—C11—C10	-73.5 (6)	B20—C27—C28—C29	173.76 (14)

C7—C6—C11—C10	3.5 (4)	F28—C28—C29—F29	-4.8 (2)
C7'—C6—C11—C10	19.6 (5)	C27—C28—C29—F29	176.90 (14)
N1—C6—C11—C10	179.8 (2)	F28—C28—C29—C30	176.39 (14)
C11'—C6—C7'—C8'	5.4 (7)	C27—C28—C29—C30	-1.9 (2)
C7—C6—C7'—C8'	50.6 (11)	F29—C29—C30—F30	0.5 (2)
C11—C6—C7'—C8'	-25.4 (7)	C28—C29—C30—F30	179.26 (14)
N1—C6—C7'—C8'	174.1 (4)	F29—C29—C30—C31	-177.52 (15)
C6—C7'—C8'—C9'	-1.7 (8)	C28—C29—C30—C31	1.3 (2)
C7'—C8'—C9'—C10'	2.3 (9)	F30—C30—C31—F31	1.0 (3)
C8'—C9'—C10'—C11'	-6.2 (9)	C29—C30—C31—F31	178.98 (15)
C7—C6—C11'—C10'	-20.2 (7)	F30—C30—C31—C32	-177.88 (15)
C7'—C6—C11'—C10'	-9.3 (7)	C29—C30—C31—C32	0.1 (3)
C11—C6—C11'—C10'	95.2 (8)	F31—C31—C32—F32	0.8 (2)
N1—C6—C11'—C10'	-177.4 (4)	C30—C31—C32—F32	179.67 (15)
C9'—C10'—C11'—C6	9.6 (9)	F31—C31—C32—C27	-179.90 (15)
C5—N4—C12—C17	148.59 (15)	C30—C31—C32—C27	-1.0 (3)
C3—N4—C12—C17	-35.9 (2)	C28—C27—C32—F32	179.77 (13)
C5—N4—C12—C13	-35.7 (2)	B20—C27—C32—F32	6.2 (2)
C3—N4—C12—C13	139.77 (15)	C28—C27—C32—C31	0.5 (2)
C17—C12—C13—O19	178.38 (13)	B20—C27—C32—C31	-173.07 (15)
N4—C12—C13—O19	2.82 (19)	O19—B20—C33—C34	49.32 (17)
C17—C12—C13—C14	-1.0 (2)	C27—B20—C33—C34	164.97 (13)
N4—C12—C13—C14	-176.58 (13)	C21—B20—C33—C34	-69.07 (16)
O19—C13—C14—C15	-177.17 (14)	O19—B20—C33—C38	-139.60 (15)
C12—C13—C14—C15	2.2 (2)	C27—B20—C33—C38	-24.0 (2)
C13—C14—C15—C16	-1.3 (2)	C21—B20—C33—C38	102.01 (16)
C14—C15—C16—C17	-0.9 (2)	C38—C33—C34—F34	-177.99 (13)
C14—C15—C16—C18	178.16 (15)	B20—C33—C34—F34	-5.9 (2)
C13—C12—C17—C16	-1.1 (2)	C38—C33—C34—C35	0.3 (2)

N4—C12—C17—C16	174.37 (13)	B20—C33—C34—C35	172.42 (14)
C15—C16—C17—C12	2.1 (2)	F34—C34—C35—F35	-2.1 (2)
C18—C16—C17—C12	-177.00 (14)	C33—C34—C35—F35	179.58 (14)
C14—C13—O19—B20	37.2 (2)	F34—C34—C35—C36	177.26 (14)
C12—C13—O19—B20	-142.12 (13)	C33—C34—C35—C36	-1.1 (2)
C13—O19—B20—C27	38.44 (16)	F35—C35—C36—F36	0.8 (2)
C13—O19—B20—C21	-88.55 (15)	C34—C35—C36—F36	-178.53 (15)
C13—O19—B20—C33	158.77 (12)	F35—C35—C36—C37	179.99 (15)
O19—B20—C21—C22	-4.9 (2)	C34—C35—C36—C37	0.7 (2)
C27—B20—C21—C22	-126.30 (15)	F36—C36—C37—F37	0.3 (3)
C33—B20—C21—C22	109.62 (15)	C35—C36—C37—F37	-178.90 (15)
O19—B20—C21—C26	-179.33 (13)	F36—C36—C37—C38	179.67 (15)
C27—B20—C21—C26	59.30 (18)	C35—C36—C37—C38	0.5 (3)
C33—B20—C21—C26	-64.78 (17)	F37—C37—C38—F38	-0.8 (2)
C26—C21—C22—F22	179.18 (13)	C36—C37—C38—F38	179.83 (15)
B20—C21—C22—F22	4.4 (2)	F37—C37—C38—C33	178.04 (15)
C26—C21—C22—C23	-2.6 (2)	C36—C37—C38—C33	-1.3 (3)
B20—C21—C22—C23	-177.36 (14)	C34—C33—C38—F38	179.68 (14)
F22—C22—C23—F23	0.7 (2)	B20—C33—C38—F38	8.1 (2)
C21—C22—C23—F23	-177.69 (13)	C34—C33—C38—C37	0.9 (2)
F22—C22—C23—C24	177.97 (13)	B20—C33—C38—C37	-170.71 (15)
C21—C22—C23—C24	-0.4 (2)		

Table 11: Selected hydrogen-bond lengths (pm) and bond angles (°) for **62c**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···F23^{i}	0.95	2.54	3.0499 (18)	114
C3—H3···F30^{ii}	0.95	2.46	3.3280 (19)	151
C5—H5···F34	0.95	2.62	3.4544 (18)	147
C7—H7···F29^{iii}	0.95	2.45	3.391 (4)	171

C7′—H7′···F29^{iii}	0.95	2.42	3.265 (5)	148

6.4 Crystal structure determination of 4,4-di-ethyl-3-phenyl-4*H*-benzo[*e*][1,2,4] triazolo[3,4-*c*][1,4,2]oxaza-borininium-4-ide 63a

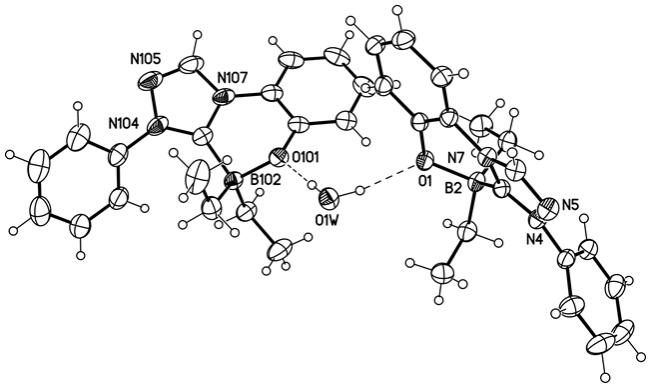


Figure 26. X-ray structure of molecule **63a**.

Table 12: Crystallography data and refinement details for **63a**.

$C_{18}H_{20}BN_3O·0.5(H_2O)$	Z = 4
M_r = 314.19	F(000) = 668
Triclinic, *P*-1 (no.2)	D_x = 1.245 Mg m^{-3}
a = 9.0122 (4) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å
b = 11.1230 (5) Å	Cell parameters from 5167 reflections
c = 17.8748 (9) Å	θ = 2.5–29.9°
α = 72.078 (4)°	μ = 0.08 mm^{-1}
β = 87.907 (4)°	T = 173 K
γ = 79.532 (4)°	Plates, colourless
V = 1676.14 (14) Å^3	0.32 × 0.16 × 0.12 mm
Refinement on F2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
R[F2 > 2□(F2)] = 0.047	H atoms treated by a mixture of independent and

	constrained refinement
wR(F2) = 0.116	w = 1/[σ2(Fo2) + (0.0394P)2 + 0.4454P] where P = (Fo2 + 2Fc2)/3
S = 1.03	(Δ/σ)max < 0.001
7704 reflections	Δ⟩max = 0.29 e Å-3
433 parameters	Δ⟩min = -0.16 e Å-3
0 restraints	Extinction correction: SHELXL, Fc*=kFc[1+0.001xFc2λ3/sin(2θ)]-1/4
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0072 (9)

Table 13: Bond length (pm) data for **63a**.

O1—C13	1.3520 (16)	O101—B102	1.5427 (19)
O1—B2	1.5426 (17)	B102—C116	1.603 (2)
B2—C14	1.606 (2)	B102—C114	1.618 (2)
B2—C16	1.627 (2)	B102—C103	1.642 (2)
B2—C3	1.639 (2)	C103—N104	1.3418 (18)
C3—N4	1.3364 (17)	C103—N107	1.356 (2)
C3—N7	1.3590 (17)	N104—N105	1.3840 (19)
N4—N5	1.3849 (16)	N104—C118	1.435 (2)
N4—C18	1.4348 (17)	N105—C106	1.292 (2)
N5—C6	1.2966 (18)	C106—N107	1.366 (2)
C6—N7	1.3689 (18)	C106—H106	0.9500
C6—H6	0.9500	N107—C108	1.427 (2)
N7—C8	1.4298 (17)	C108—C109	1.384 (2)
C8—C9	1.3897 (19)	C108—C113	1.394 (2)
C8—C13	1.393 (2)	C109—C110	1.379 (2)
C9—C10	1.385 (2)	C109—H109	0.9500
C9—H9	0.9500	C110—C111	1.383 (2)
C10—C11	1.384 (2)	C110—H110	0.9500

C10—H10	0.9500	C111—C112	1.389 (2)
C11—C12	1.385 (2)	C111—H111	0.9500
C11—H11	0.9500	C112—C113	1.393 (2)
C12—C13	1.3926 (19)	C112—H112	0.9500
C12—H12	0.9500	C114—C115	1.534 (2)
C14—C15	1.531 (2)	C114—H11A	0.9900
C14—H14A	0.9900	C114—H11B	0.9900
C14—H14B	0.9900	C115—H11C	0.9800
C15—H15A	0.9800	C115—H11D	0.9800
C15—H15B	0.9800	C115—H11E	0.9800
C15—H15C	0.9800	C116—C117	1.524 (3)
C16—C17	1.522 (2)	C116—H11F	0.9900
C16—H16A	0.9900	C116—H11G	0.9900
C16—H16B	0.9900	C117—H11H	0.9800
C17—H17A	0.9800	C117—H11I	0.9800
C17—H17B	0.9800	C117—H11J	0.9800
C17—H17C	0.9800	C118—C119	1.376 (2)
C18—C19	1.379 (2)	C118—C123	1.380 (2)
C18—C23	1.382 (2)	C119—C120	1.384 (3)
C19—C20	1.391 (2)	C119—H119	0.9500
C19—H19	0.9500	C120—C121	1.379 (3)
C20—C21	1.374 (3)	C120—H120	0.9500
C20—H20	0.9500	C121—C122	1.380 (3)
C21—C22	1.380 (3)	C121—H121	0.9500
C21—H21	0.9500	C122—C123	1.381 (3)
C22—C23	1.387 (2)	C122—H122	0.9500
C22—H22	0.9500	C123—H123	0.9500
C23—H23	0.9500	O1W—H1W1	0.89 (2)
O101—C113	1.3435 (17)	O1W—H1W2	0.94 (2)

C13—O1—B2	119.55 (10)	O101—B102—C116	105.31 (12)
O1—B2—C14	106.04 (11)	O101—B102—C114	108.14 (12)
O1—B2—C16	108.60 (12)	C116—B102—C114	116.20 (14)
C14—B2—C16	115.62 (12)	O101—B102—C103	102.24 (11)
O1—B2—C3	102.34 (10)	C116—B102—C103	112.81 (13)
C14—B2—C3	114.55 (12)	C114—B102—C103	110.90 (12)
C16—B2—C3	108.66 (11)	N104—C103—N107	103.62 (13)
N4—C3—N7	103.40 (12)	N104—C103—B102	136.30 (14)
N4—C3—B2	136.47 (12)	N107—C103—B102	119.87 (12)
N7—C3—B2	120.11 (11)	C103—N104—N105	112.76 (14)
C3—N4—N5	113.28 (11)	C103—N104—C118	128.91 (13)
C3—N4—C18	128.98 (12)	N105—N104—C118	118.32 (12)
N5—N4—C18	117.74 (11)	C106—N105—N104	103.69 (13)
C6—N5—N4	103.50 (11)	N105—C106—N107	111.44 (16)
N5—C6—N7	111.16 (12)	N105—C106—H106	124.3
N5—C6—H6	124.4	N107—C106—H106	124.3
N7—C6—H6	124.4	C103—N107—C106	108.46 (14)
C3—N7—C6	108.65 (11)	C103—N107—C108	122.55 (12)
C3—N7—C8	122.60 (12)	C106—N107—C108	128.98 (14)
C6—N7—C8	128.75 (12)	C109—C108—C113	121.95 (15)
C9—C8—C13	121.86 (13)	C109—C108—N107	121.44 (14)
C9—C8—N7	121.12 (13)	C113—C108—N107	116.60 (13)
C13—C8—N7	117.02 (12)	C110—C109—C108	119.45 (16)
C10—C9—C8	118.93 (14)	C110—C109—H109	120.3
C10—C9—H9	120.5	C108—C109—H109	120.3
C8—C9—H9	120.5	C109—C110—C111	119.64 (16)
C11—C10—C9	120.05 (14)	C109—C110—H110	120.2
C11—C10—H10	120.0	C111—C110—H110	120.2
C9—C10—H10	120.0	C110—C111—C112	120.83 (16)

C10—C11—C12	120.64 (14)	C110—C111—H111	119.6
C10—C11—H11	119.7	C112—C111—H111	119.6
C12—C11—H11	119.7	C111—C112—C113	120.27 (15)
C11—C12—C13	120.37 (14)	C111—C112—H112	119.9
C11—C12—H12	119.8	C113—C112—H112	119.9
C13—C12—H12	119.8	O101—C113—C112	121.27 (13)
O1—C13—C12	120.38 (13)	O101—C113—C108	120.82 (13)
O1—C13—C8	121.41 (12)	C112—C113—C108	117.85 (14)
C12—C13—C8	118.14 (13)	C115—C114—B102	112.38 (14)
C15—C14—B2	116.81 (13)	C115—C114—H11A	109.1
C15—C14—H14A	108.1	B102—C114—H11A	109.1
B2—C14—H14A	108.1	C115—C114—H11B	109.1
C15—C14—H14B	108.1	B102—C114—H11B	109.1
B2—C14—H14B	108.1	H11A—C114—H11B	107.9
H14A—C14—H14B	107.3	C114—C115—H11C	109.5
C14—C15—H15A	109.5	C114—C115—H11D	109.5
C14—C15—H15B	109.5	H11C—C115—H11D	109.5
H15A—C15—H15B	109.5	C114—C115—H11E	109.5
C14—C15—H15C	109.5	H11C—C115—H11E	109.5
H15A—C15—H15C	109.5	H11D—C115—H11E	109.5
H15B—C15—H15C	109.5	C117—C116—B102	115.97 (15)
C17—C16—B2	112.13 (12)	C117—C116—H11F	108.3
C17—C16—H16A	109.2	B102—C116—H11F	108.3
B2—C16—H16A	109.2	C117—C116—H11G	108.3
C17—C16—H16B	109.2	B102—C116—H11G	108.3
B2—C16—H16B	109.2	H11F—C116—H11G	107.4
H16A—C16—H16B	107.9	C116—C117—H11H	109.5
C16—C17—H17A	109.5	C116—C117—H11I	109.5
C16—C17—H17B	109.5	H11H—C117—H11I	109.5

H17A—C17—H17B	109.5	C116—C117—H11J	109.5
C16—C17—H17C	109.5	H11H—C117—H11J	109.5
H17A—C17—H17C	109.5	H11I—C117—H11J	109.5
H17B—C17—H17C	109.5	C119—C118—C123	121.57 (17)
C19—C18—C23	121.70 (13)	C119—C118—N104	119.87 (14)
C19—C18—N4	119.99 (13)	C123—C118—N104	118.53 (16)
C23—C18—N4	118.27 (13)	C118—C119—C120	119.01 (16)
C18—C19—C20	118.64 (15)	C118—C119—H119	120.5
C18—C19—H19	120.7	C120—C119—H119	120.5
C20—C19—H19	120.7	C121—C120—C119	120.19 (19)
C21—C20—C19	120.19 (16)	C121—C120—H120	119.9
C21—C20—H20	119.9	C119—C120—H120	119.9
C19—C20—H20	119.9	C120—C121—C122	119.92 (19)
C20—C21—C22	120.66 (15)	C120—C121—H121	120.0
C20—C21—H21	119.7	C122—C121—H121	120.0
C22—C21—H21	119.7	C121—C122—C123	120.58 (18)
C21—C22—C23	119.87 (16)	C121—C122—H122	119.7
C21—C22—H22	120.1	C123—C122—H122	119.7
C23—C22—H22	120.1	C118—C123—C122	118.68 (19)
C18—C23—C22	118.95 (16)	C118—C123—H123	120.7
C18—C23—H23	120.5	C122—C123—H123	120.7
C22—C23—H23	120.5	H1W1—O1W—H1W2	104.5 (18)
C113—O101—B102	120.02 (11)		
C13—O1—B2—C14	167.13 (12)	C113—O101—B102—C116	-164.91 (12)
C13—O1—B2—C16	-68.01 (15)	C113—O101—B102—C114	70.24 (16)
C13—O1—B2—C3	46.77 (15)	C113—O101—B102—C103	-46.84 (16)
O1—B2—C3—N4	153.36 (15)	O101—B102—C103—N104	-149.13 (17)
C14—B2—C3—N4	39.1 (2)	C116—B102—C103—N104	-36.5 (2)
C16—B2—C3—N4	-91.90 (19)	C114—B102—C103—N104	95.8 (2)

O1—B2—C3—N7	-28.57 (16)	O101—B102—C103—N107	24.48 (17)
C14—B2—C3—N7	-142.83 (12)	C116—B102—C103—N107	137.08 (15)
C16—B2—C3—N7	86.17 (14)	C114—B102—C103—N107	-90.60 (16)
N7—C3—N4—N5	0.49 (15)	N107—C103—N104—N105	-1.69 (17)
B2—C3—N4—N5	178.77 (14)	B102—C103—N104—N105	172.61 (16)
N7—C3—N4—C18	-179.81 (12)	N107—C103—N104—C118	177.50 (15)
B2—C3—N4—C18	-1.5 (3)	B102—C103—N104—C118	-8.2 (3)
C3—N4—N5—C6	-0.01 (15)	C103—N104—N105—C106	0.6 (2)
C18—N4—N5—C6	-179.75 (12)	C118—N104—N105—C106	-178.65 (15)
N4—N5—C6—N7	-0.49 (15)	N104—N105—C106—N107	0.7 (2)
N4—C3—N7—C6	-0.76 (14)	N104—C103—N107—C106	2.04 (17)
B2—C3—N7—C6	-179.39 (12)	B102—C103—N107—C106	-173.42 (14)
N4—C3—N7—C8	179.56 (11)	N104—C103—N107—C108	-178.24 (13)
B2—C3—N7—C8	0.93 (19)	B102—C103—N107—C108	6.3 (2)
N5—C6—N7—C3	0.82 (16)	N105—C106—N107—C103	-1.8 (2)
N5—C6—N7—C8	-179.53 (13)	N105—C106—N107—C108	178.48 (16)
C3—N7—C8—C9	-165.59 (13)	C103—N107—C108—C109	159.85 (15)
C6—N7—C8—C9	14.8 (2)	C106—N107—C108—C109	-20.5 (3)
C3—N7—C8—C13	15.10 (19)	C103—N107—C108—C113	-21.4 (2)
C6—N7—C8—C13	-164.51 (13)	C106—N107—C108—C113	158.21 (16)
C13—C8—C9—C10	-0.1 (2)	C113—C108—C109—C110	-1.1 (2)
N7—C8—C9—C10	-179.33 (13)	N107—C108—C109—C110	177.52 (15)
C8—C9—C10—C11	-0.6 (2)	C108—C109—C110—C111	1.0 (3)
C9—C10—C11—C12	0.5 (2)	C109—C110—C111—C112	-0.6 (3)
C10—C11—C12—C13	0.1 (2)	C110—C111—C112—C113	0.4 (2)
B2—O1—C13—C12	145.13 (13)	B102—O101—C113—C112	-144.40 (14)
B2—O1—C13—C8	-37.98 (18)	B102—O101—C113—C108	38.58 (19)
C11—C12—C13—O1	176.26 (13)	C111—C112—C113—O101	-177.58 (14)
C11—C12—C13—C8	-0.7 (2)	C111—C112—C113—C108	-0.5 (2)

C9—C8—C13—O1	-176.27 (12)	C109—C108—C113—O101	177.97 (14)
N7—C8—C13—O1	3.04 (19)	N107—C108—C113—O101	-0.7 (2)
C9—C8—C13—C12	0.7 (2)	C109—C108—C113—C112	0.8 (2)
N7—C8—C13—C12	-179.99 (12)	N107—C108—C113—C112	-177.85 (13)
O1—B2—C14—C15	-65.85 (16)	O101—B102—C114—C115	61.83 (17)
C16—B2—C14—C15	173.75 (13)	C116—B102—C114—C115	-56.26 (19)
C3—B2—C14—C15	46.22 (17)	C103—B102—C114—C115	173.17 (14)
O1—B2—C16—C17	-55.58 (16)	O101—B102—C116—C117	60.44 (17)
C14—B2—C16—C17	63.42 (17)	C114—B102—C116—C117	-179.93 (13)
C3—B2—C16—C17	-166.17 (12)	C103—B102—C116—C117	-50.26 (19)
C3—N4—C18—C19	48.6 (2)	C103—N104—C118—C119	-44.0 (2)
N5—N4—C18—C19	-131.69 (14)	N105—N104—C118—C119	135.19 (17)
C3—N4—C18—C23	-133.56 (16)	C103—N104—C118—C123	138.20 (18)
N5—N4—C18—C23	46.13 (18)	N105—N104—C118—C123	-42.7 (2)
C23—C18—C19—C20	0.3 (2)	C123—C118—C119—C120	-2.5 (3)
N4—C18—C19—C20	177.99 (13)	N104—C118—C119—C120	179.74 (16)
C18—C19—C20—C21	-0.9 (2)	C118—C119—C120—C121	0.9 (3)
C19—C20—C21—C22	1.1 (3)	C119—C120—C121—C122	1.2 (3)
C20—C21—C22—C23	-0.7 (3)	C120—C121—C122—C123	-1.8 (3)
C19—C18—C23—C22	0.2 (2)	C119—C118—C123—C122	1.9 (3)
N4—C18—C23—C22	-177.62 (14)	N104—C118—C123—C122	179.72 (16)
C21—C22—C23—C18	0.1 (3)	C121—C122—C123—C118	0.2 (3)

Table 14: Selected hydrogen-bond lengths (pm) and bond angles (°) for **63a**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···O1*W*^{i}	0.95	2.24	3.1840 (18)	177
C9—H9···O1*W*^{i}	0.95	2.65	3.531 (2)	155
O1*W*—H1*W*1···O1	0.89 (2)	1.95 (2)	2.8163 (15)	162.4 (19)
O1*W*—	0.94 (2)	1.88 (2)	2.8266 (15)	178 (2)

H1*W*2···O101				

6.5 Crystal structure determination of 1-benzyl-3-(2-hydroxyphenyl)-1,3-dihydro-2*H*-imidazole-2-thione 71d

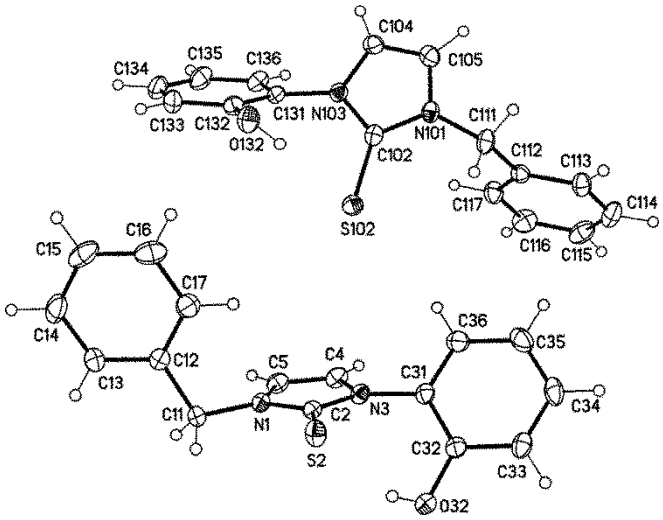


Figure 27. X-ray structure of molecule **71d**.

Table 15: Crystallography data and refinement details for **71d**.

$C_{16}H_{14}N_2OS$	Z = 4
M_r = 282.35	F(000) = 592
Triclinic, *P*-1 (no.2)	D_x = 1.358 Mg m^{-3}
a = 10.3745 (6) Å	Cu $K\alpha$ radiation, λ = 1.54178 Å
b = 11.7318 (7) Å	Cell parameters from 9915 reflections
c = 12.1148 (8) Å	θ = 4.0–72.1°
α = 107.263 (2)°	μ = 2.05 mm^{-1}
β = 90.585 (2)°	T = 123 K
γ = 100.511 (2)°	Blocks, colourless
V = 1381.20 (15) Å^3	0.20 × 0.12 × 0.08 mm
Refinement on F2	Secondary atom site location: difference Fourier map

Least-squares matrix: full	Hydrogen site location: difference Fourier map
R[F2 > 2σ(F2)] = 0.033	H atoms treated by a mixture of independent and constrained refinement
wR(F2) = 0.086	w = 1/[σ2(Fo2) + (0.0381P)2 + 0.6956P] where P = (Fo2 + 2Fc2)/3
S = 1.04	(Δ/σ)max = 0.001
5351 reflections	Δ⟩max = 0.27 e Å-3
368 parameters	Δ⟩min = -0.21 e Å-3
2 restraints	Extinction correction: SHELXL, Fc*=kFc[1+0.001xFc2λ3/sin(2θ)]-1/4
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0011 (2)

Table 16: Bond length (pm) data for **71d**.

N1—C2	1.3579 (18)	N101—C102	1.3581 (18)
N1—C5	1.3841 (18)	N101—C105	1.381 (2)
N1—C11	1.4581 (17)	N101—C111	1.4640 (18)
C2—N3	1.3696 (18)	C102—N103	1.3677 (19)
C2—S2	1.6922 (14)	C102—S102	1.6931 (15)
N3—C4	1.3947 (18)	N103—C104	1.3915 (18)
N3—C31	1.4333 (18)	N103—C131	1.4372 (18)
C4—C5	1.343 (2)	C104—C105	1.344 (2)
C4—H4	0.9500	C104—H104	0.9500
C5—H5	0.9500	C105—H105	0.9500
C11—C12	1.509 (2)	C111—C112	1.512 (2)
C11—H11A	0.9900	C111—H11C	0.9900
C11—H11B	0.9900	C111—H11D	0.9900
C12—C17	1.382 (2)	C112—C117	1.388 (2)
C12—C13	1.393 (2)	C112—C113	1.393 (2)
C13—C14	1.387 (2)	C113—C114	1.389 (2)
C13—H13	0.9500	C113—H113	0.9500

C14—C15	1.382 (3)	C114—C115	1.386 (2)
C14—H14	0.9500	C114—H114	0.9500
C15—C16	1.387 (3)	C115—C116	1.385 (2)
C15—H15	0.9500	C115—H115	0.9500
C16—C17	1.388 (2)	C116—C117	1.391 (2)
C16—H16	0.9500	C116—H116	0.9500
C17—H17	0.9500	C117—H117	0.9500
C31—C36	1.390 (2)	C131—C136	1.393 (2)
C31—C32	1.398 (2)	C131—C132	1.397 (2)
C32—O32	1.3646 (18)	C132—O132	1.3681 (18)
C32—C33	1.395 (2)	C132—C133	1.393 (2)
O32—H32	0.833 (15)	O132—H132	0.846 (15)
C33—C34	1.378 (2)	C133—C134	1.383 (2)
C33—H33	0.9500	C133—H133	0.9500
C34—C35	1.386 (3)	C134—C135	1.389 (3)
C34—H34	0.9500	C134—H134	0.9500
C35—C36	1.388 (2)	C135—C136	1.385 (2)
C35—H35	0.9500	C135—H135	0.9500
C36—H36	0.9500	C136—H136	0.9500
C2—N1—C5	110.38 (12)	C102—N101—C105	110.26 (12)
C2—N1—C11	125.09 (12)	C102—N101—C111	125.29 (13)
C5—N1—C11	124.51 (12)	C105—N101—C111	124.41 (12)
N1—C2—N3	105.42 (12)	N101—C102—N103	105.60 (12)
N1—C2—S2	126.94 (11)	N101—C102—S102	126.65 (11)
N3—C2—S2	127.62 (11)	N103—C102—S102	127.74 (11)
C2—N3—C4	109.55 (12)	C102—N103—C104	109.42 (12)
C2—N3—C31	126.76 (12)	C102—N103—C131	127.76 (12)
C4—N3—C31	123.68 (12)	C104—N103—C131	122.82 (12)
C5—C4—N3	107.25 (12)	C105—C104—N103	107.35 (13)

C5—C4—H4	126.4	C105—C104—H104	126.3
N3—C4—H4	126.4	N103—C104—H104	126.3
C4—C5—N1	107.39 (12)	C104—C105—N101	107.37 (13)
C4—C5—H5	126.3	C104—C105—H105	126.3
N1—C5—H5	126.3	N101—C105—H105	126.3
N1—C11—C12	113.99 (12)	N101—C111—C112	114.34 (11)
N1—C11—H11A	108.8	N101—C111—H11C	108.7
C12—C11—H11A	108.8	C112—C111—H11C	108.7
N1—C11—H11B	108.8	N101—C111—H11D	108.7
C12—C11—H11B	108.8	C112—C111—H11D	108.7
H11A—C11—H11B	107.6	H11C—C111—H11D	107.6
C17—C12—C13	118.79 (14)	C117—C112—C113	118.73 (14)
C17—C12—C11	122.68 (13)	C117—C112—C111	122.69 (13)
C13—C12—C11	118.52 (13)	C113—C112—C111	118.56 (13)
C14—C13—C12	120.60 (15)	C114—C113—C112	120.49 (14)
C14—C13—H13	119.7	C114—C113—H113	119.8
C12—C13—H13	119.7	C112—C113—H113	119.8
C15—C14—C13	120.33 (16)	C115—C114—C113	120.38 (15)
C15—C14—H14	119.8	C115—C114—H114	119.8
C13—C14—H14	119.8	C113—C114—H114	119.8
C14—C15—C16	119.27 (16)	C116—C115—C114	119.46 (15)
C14—C15—H15	120.4	C116—C115—H115	120.3
C16—C15—H15	120.4	C114—C115—H115	120.3
C15—C16—C17	120.39 (16)	C115—C116—C117	120.11 (15)
C15—C16—H16	119.8	C115—C116—H116	119.9
C17—C16—H16	119.8	C117—C116—H116	119.9
C12—C17—C16	120.60 (15)	C112—C117—C116	120.80 (14)
C12—C17—H17	119.7	C112—C117—H117	119.6
C16—C17—H17	119.7	C116—C117—H117	119.6

C36—C31—C32	120.42 (14)	C136—C131—C132	120.30 (13)
C36—C31—N3	118.40 (13)	C136—C131—N103	118.08 (13)
C32—C31—N3	121.09 (13)	C132—C131—N103	121.46 (13)
O32—C32—C33	118.29 (14)	O132—C132—C133	118.24 (13)
O32—C32—C31	122.94 (13)	O132—C132—C131	123.16 (13)
C33—C32—C31	118.72 (14)	C133—C132—C131	118.57 (14)
C32—O32—H32	107.9 (15)	C132—O132—H132	108.5 (14)
C34—C33—C32	120.62 (15)	C134—C133—C132	121.10 (15)
C34—C33—H33	119.7	C134—C133—H133	119.5
C32—C33—H33	119.7	C132—C133—H133	119.5
C33—C34—C35	120.52 (14)	C133—C134—C135	120.09 (15)
C33—C34—H34	119.7	C133—C134—H134	120.0
C35—C34—H34	119.7	C135—C134—H134	120.0
C34—C35—C36	119.68 (15)	C136—C135—C134	119.56 (15)
C34—C35—H35	120.2	C136—C135—H135	120.2
C36—C35—H35	120.2	C134—C135—H135	120.2
C35—C36—C31	120.02 (15)	C135—C136—C131	120.38 (14)
C35—C36—H36	120.0	C135—C136—H136	119.8
C31—C36—H36	120.0	C131—C136—H136	119.8
C5—N1—C2—N3	-0.64 (16)	C105—N101—C102—N103	-0.80 (15)
C11—N1—C2—N3	177.69 (13)	C111—N101—C102—N103	177.06 (12)
C5—N1—C2—S2	177.79 (11)	C105—N101—C102—S102	178.12 (11)
C11—N1—C2—S2	-3.9 (2)	C111—N101—C102—S102	-4.0 (2)
N1—C2—N3—C4	0.85 (16)	N101—C102—N103—C104	1.02 (15)
S2—C2—N3—C4	-177.57 (11)	S102—C102—N103—C104	-177.88 (11)
N1—C2—N3—C31	179.86 (13)	N101—C102—N103—C131	-178.31 (12)
S2—C2—N3—C31	1.4 (2)	S102—C102—N103—C131	2.8 (2)
C2—N3—C4—C5	-0.76 (17)	C102—N103—C104—C105	-0.88 (16)
C31—N3—C4—C5	-179.81 (13)	C131—N103—C104—C105	178.50 (12)

N3—C4—C5—N1	0.34 (17)	N103—C104—C105—N101	0.36 (16)
C2—N1—C5—C4	0.19 (17)	C102—N101—C105—C104	0.28 (16)
C11—N1—C5—C4	-178.16 (13)	C111—N101—C105—C104	-177.60 (13)
C2—N1—C11—C12	96.49 (16)	C102—N101—C111—C112	98.20 (16)
C5—N1—C11—C12	-85.41 (17)	C105—N101—C111—C112	-84.23 (17)
N1—C11—C12—C17	-27.35 (19)	N101—C111—C112—C117	-24.1 (2)
N1—C11—C12—C13	154.21 (13)	N101—C111—C112—C113	157.42 (13)
C17—C12—C13—C14	-1.5 (2)	C117—C112—C113—C114	-1.2 (2)
C11—C12—C13—C14	177.01 (14)	C111—C112—C113—C114	177.31 (14)
C12—C13—C14—C15	0.3 (2)	C112—C113—C114—C115	0.1 (3)
C13—C14—C15—C16	1.1 (2)	C113—C114—C115—C116	1.0 (3)
C14—C15—C16—C17	-1.2 (2)	C114—C115—C116—C117	-1.1 (3)
C13—C12—C17—C16	1.3 (2)	C113—C112—C117—C116	1.1 (2)
C11—C12—C17—C16	-177.10 (14)	C111—C112—C117—C116	-177.28 (15)
C15—C16—C17—C12	0.0 (2)	C115—C116—C117—C112	0.0 (3)
C2—N3—C31—C36	-129.40 (16)	C102—N103—C131—C136	-131.27 (15)
C4—N3—C31—C36	49.5 (2)	C104—N103—C131—C136	49.47 (19)
C2—N3—C31—C32	54.0 (2)	C102—N103—C131—C132	53.4 (2)
C4—N3—C31—C32	-127.09 (15)	C104—N103—C131—C132	-125.86 (15)
C36—C31—C32—O32	-175.95 (13)	C136—C131—C132—O132	-178.90 (14)
N3—C31—C32—O32	0.6 (2)	N103—C131—C132—O132	-3.7 (2)
C36—C31—C32—C33	1.6 (2)	C136—C131—C132—C133	-0.9 (2)
N3—C31—C32—C33	178.06 (12)	N103—C131—C132—C133	174.30 (14)
O32—C32—C33—C34	176.45 (13)	O132—C132—C133—C134	178.51 (15)
C31—C32—C33—C34	-1.2 (2)	C131—C132—C133—C134	0.4 (2)
C32—C33—C34—C35	0.0 (2)	C132—C133—C134—C135	0.4 (3)
C33—C34—C35—C36	0.8 (2)	C133—C134—C135—C136	-0.8 (3)
C34—C35—C36—C31	-0.4 (2)	C134—C135—C136—C131	0.3 (3)
C32—C31—C36—C35	-0.8 (2)	C132—C131—C136—C135	0.6 (2)

N3—C31—C36—C35	-177.40 (13)	N103—C131—C136—C135	-174.80 (14)

Table 17: Selected hydrogen-bond lengths (pm) and bond angles (°) for **71d**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11*B*···S102^{i}	0.99	3.02	3.8863 (15)	147
O32—H32···S2	0.83 (2)	2.29 (2)	3.0698 (12)	157 (2)
C33—H33···O32^{ii}	0.95	2.66	3.3798 (19)	133
C36—H36···S102	0.95	2.95	3.7654 (17)	144
O132—H132···S102	0.85 (2)	2.25 (2)	3.0556 (12)	160 (2)
C136—H136···S2^{iii}	0.95	3.02	3.8501 (16)	147

6.6 Crystal structure determination of 3-(but-3-en-1-yl)-4,4-diphenyl-4*H*-benzo[*e*]imidazo-[2,1-*c*][1,4,2]oxazaborininium-4-ide 73c

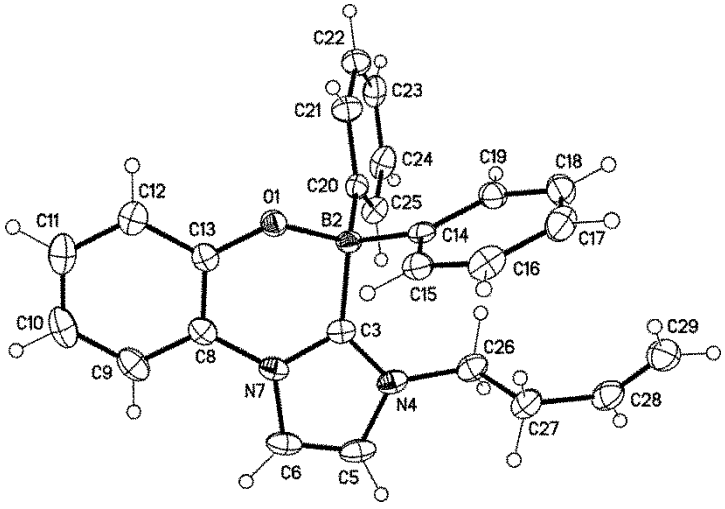


Figure 29: X-ray structure of molecule **73c**.

Table 21: Crystallography data and refinement details for **73c**.

$C_{25}H_{23}BN_2O$	$F(000)$ = 800
M_r = 378.26	D_x = 1.253 Mg m^{-3}

Monoclinic, $P2_1/c$ *(no.14)*	Cu $K\alpha$ radiation, λ = 1.54178 Å
a = 7.6873 (4) Å	Cell parameters from 9874 reflections
b = 16.0148 (7) Å	θ = 4.0–72.1°
c = 16.4645 (8) Å	μ = 0.59 mm^{-1}
β = 98.441 (1)°	T = 123 K
V = 2005.00 (17) $Å^3$	Blocks, colourless
Z = 4	0.36 × 0.28 × 0.20 mm
Refinement on F2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
R[F2 > 2σ(F2)] = 0.035	H-atom parameters constrained
wR(F2) = 0.089	w = 1/[σ2(Fo2) + (0.0372P)2 + 0.7526P] where P = (Fo2 + 2Fc2)/3
S = 1.04	(Δ/σ)max = 0.001
3946 reflections	Δ⟩max = 0.33 e Å-3
263 parameters	Δ⟩min = -0.18 e Å-3
0 restraints	Extinction correction: SHELXL, Fc*=kFc[1+0.001xFc2λ3/sin(2θ)]-1/4
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0024 (2)

Table 22: Bond length (pm) data for **73c**.

O1—C13	1.3405 (13)	C16—C17	1.3846 (18)
O1—B2	1.5212 (13)	C16—H16	0.9500
B2—C20	1.6238 (15)	C17—C18	1.3826 (19)
B2—C14	1.6269 (15)	C17—H17	0.9500
B2—C3	1.6305 (15)	C18—C19	1.3929 (16)
C3—N4	1.3451 (14)	C18—H18	0.9500
C3—N7	1.3501 (14)	C19—H19	0.9500
N4—C5	1.3872 (14)	C20—C25	1.3982 (16)

N4—C26	1.4677 (15)	C20—C21	1.4006 (15)
C5—C6	1.3378 (18)	C21—C22	1.3894 (16)
C5—H5	0.9500	C21—H21	0.9500
C6—N7	1.3880 (14)	C22—C23	1.3826 (18)
C6—H6	0.9500	C22—H22	0.9500
N7—C8	1.4224 (14)	C23—C24	1.3816 (18)
C8—C9	1.3889 (15)	C23—H23	0.9500
C8—C13	1.4017 (15)	C24—C25	1.3959 (16)
C9—C10	1.3832 (19)	C24—H24	0.9500
C9—H9	0.9500	C25—H25	0.9500
C10—C11	1.3851 (19)	C26—C27	1.5255 (16)
C10—H10	0.9500	C26—H26A	0.9900
C11—C12	1.3877 (17)	C26—H26B	0.9900
C11—H11	0.9500	C27—C28	1.5009 (16)
C12—C13	1.3958 (16)	C27—H27A	0.9900
C12—H12	0.9500	C27—H27B	0.9900
C14—C19	1.3971 (15)	C28—C29	1.3069 (19)
C14—C15	1.4028 (15)	C28—H28	0.9500
C15—C16	1.3915 (16)	C29—H29A	0.9500
C15—H15	0.9500	C29—H29B	0.9500
C13—O1—B2	122.04 (8)	C17—C16—H16	119.9
O1—B2—C20	110.61 (8)	C15—C16—H16	119.9
O1—B2—C14	105.74 (8)	C18—C17—C16	119.31 (11)
C20—B2—C14	113.07 (8)	C18—C17—H17	120.3
O1—B2—C3	105.37 (8)	C16—C17—H17	120.3
C20—B2—C3	112.22 (9)	C17—C18—C19	120.26 (11)
C14—B2—C3	109.35 (8)	C17—C18—H18	119.9
N4—C3—N7	105.69 (9)	C19—C18—H18	119.9
N4—C3—B2	132.60 (9)	C18—C19—C14	121.92 (11)

N7—C3—B2	121.60 (9)	C18—C19—H19	119.0
C3—N4—C5	110.06 (9)	C14—C19—H19	119.0
C3—N4—C26	126.20 (9)	C25—C20—C21	116.07 (10)
C5—N4—C26	123.74 (9)	C25—C20—B2	125.38 (10)
C6—C5—N4	107.32 (10)	C21—C20—B2	118.51 (9)
C6—C5—H5	126.3	C22—C21—C20	122.28 (11)
N4—C5—H5	126.3	C22—C21—H21	118.9
C5—C6—N7	106.64 (10)	C20—C21—H21	118.9
C5—C6—H6	126.7	C23—C22—C21	120.13 (11)
N7—C6—H6	126.7	C23—C22—H22	119.9
C3—N7—C6	110.28 (9)	C21—C22—H22	119.9
C3—N7—C8	121.94 (9)	C24—C23—C22	119.32 (11)
C6—N7—C8	127.70 (9)	C24—C23—H23	120.3
C9—C8—C13	121.40 (11)	C22—C23—H23	120.3
C9—C8—N7	121.05 (10)	C23—C24—C25	120.08 (11)
C13—C8—N7	117.55 (9)	C23—C24—H24	120.0
C10—C9—C8	119.99 (12)	C25—C24—H24	120.0
C10—C9—H9	120.0	C24—C25—C20	122.10 (11)
C8—C9—H9	120.0	C24—C25—H25	118.9
C9—C10—C11	119.43 (11)	C20—C25—H25	118.9
C9—C10—H10	120.3	N4—C26—C27	112.05 (9)
C11—C10—H10	120.3	N4—C26—H26A	109.2
C10—C11—C12	120.66 (11)	C27—C26—H26A	109.2
C10—C11—H11	119.7	N4—C26—H26B	109.2
C12—C11—H11	119.7	C27—C26—H26B	109.2
C11—C12—C13	120.91 (11)	H26A—C26—H26B	107.9
C11—C12—H12	119.5	C28—C27—C26	110.48 (10)
C13—C12—H12	119.5	C28—C27—H27A	109.6
O1—C13—C12	120.00 (10)	C26—C27—H27A	109.6

O1—C13—C8	122.36 (10)	C28—C27—H27B	109.6
C12—C13—C8	117.59 (10)	C26—C27—H27B	109.6
C19—C14—C15	116.44 (10)	H27A—C27—H27B	108.1
C19—C14—B2	123.36 (9)	C29—C28—C27	125.05 (12)
C15—C14—B2	120.16 (9)	C29—C28—H28	117.5
C16—C15—C14	121.96 (10)	C27—C28—H28	117.5
C16—C15—H15	119.0	C28—C29—H29A	120.0
C14—C15—H15	119.0	C28—C29—H29B	120.0
C17—C16—C15	120.10 (11)	H29A—C29—H29B	120.0
C13—O1—B2—C20	88.27 (11)	N7—C8—C13—O1	-2.36 (15)
C13—O1—B2—C14	-148.98 (9)	C9—C8—C13—C12	0.73 (16)
C13—O1—B2—C3	-33.23 (12)	N7—C8—C13—C12	-179.73 (9)
O1—B2—C3—N4	-160.71 (10)	O1—B2—C14—C19	-137.58 (10)
C20—B2—C3—N4	78.84 (14)	C20—B2—C14—C19	-16.41 (14)
C14—B2—C3—N4	-47.46 (15)	C3—B2—C14—C19	109.41 (11)
O1—B2—C3—N7	15.05 (13)	O1—B2—C14—C15	44.45 (12)
C20—B2—C3—N7	-105.39 (11)	C20—B2—C14—C15	165.62 (9)
C14—B2—C3—N7	128.30 (10)	C3—B2—C14—C15	-68.56 (12)
N7—C3—N4—C5	-1.15 (12)	C19—C14—C15—C16	-0.90 (15)
B2—C3—N4—C5	175.11 (10)	B2—C14—C15—C16	177.20 (9)
N7—C3—N4—C26	178.87 (9)	C14—C15—C16—C17	0.24 (17)
B2—C3—N4—C26	-4.88 (18)	C15—C16—C17—C18	0.35 (17)
C3—N4—C5—C6	0.72 (12)	C16—C17—C18—C19	-0.24 (17)
C26—N4—C5—C6	-179.29 (10)	C17—C18—C19—C14	-0.48 (17)
N4—C5—C6—N7	0.01 (12)	C15—C14—C19—C18	1.02 (15)
N4—C3—N7—C6	1.16 (11)	B2—C14—C19—C18	-177.02 (10)
B2—C3—N7—C6	-175.61 (9)	O1—B2—C20—C25	-134.07 (10)
N4—C3—N7—C8	-175.67 (9)	C14—B2—C20—C25	107.55 (11)
B2—C3—N7—C8	7.57 (14)	C3—B2—C20—C25	-16.71 (14)

C5—C6—N7—C3	-0.73 (12)	O1—B2—C20—C21	48.39 (13)
C5—C6—N7—C8	175.86 (10)	C14—B2—C20—C21	-69.99 (12)
C3—N7—C8—C9	163.63 (10)	C3—B2—C20—C21	165.75 (9)
C6—N7—C8—C9	-12.60 (16)	C25—C20—C21—C22	-1.06 (16)
C3—N7—C8—C13	-15.92 (14)	B2—C20—C21—C22	176.70 (10)
C6—N7—C8—C13	167.85 (10)	C20—C21—C22—C23	0.39 (18)
C13—C8—C9—C10	-1.70 (17)	C21—C22—C23—C24	0.53 (17)
N7—C8—C9—C10	178.77 (10)	C22—C23—C24—C25	-0.73 (17)
C8—C9—C10—C11	1.29 (18)	C23—C24—C25—C20	0.02 (17)
C9—C10—C11—C12	0.04 (18)	C21—C20—C25—C24	0.86 (16)
C10—C11—C12—C13	-1.01 (18)	B2—C20—C25—C24	-176.73 (10)
B2—O1—C13—C12	-153.11 (10)	C3—N4—C26—C27	104.38 (12)
B2—O1—C13—C8	29.58 (14)	C5—N4—C26—C27	-75.61 (13)
C11—C12—C13—O1	-176.82 (10)	N4—C26—C27—C28	173.40 (9)
C11—C12—C13—C8	0.62 (16)	C26—C27—C28—C29	115.73 (14)
C9—C8—C13—O1	178.10 (10)		

6.7 Crystal structure determination of 3-benzyl-4,4-diphenyl-4*H*-benzo[*e*]imidazo[2,1-*c*][1,4,2]-oxazaborininium-4-ide 73d

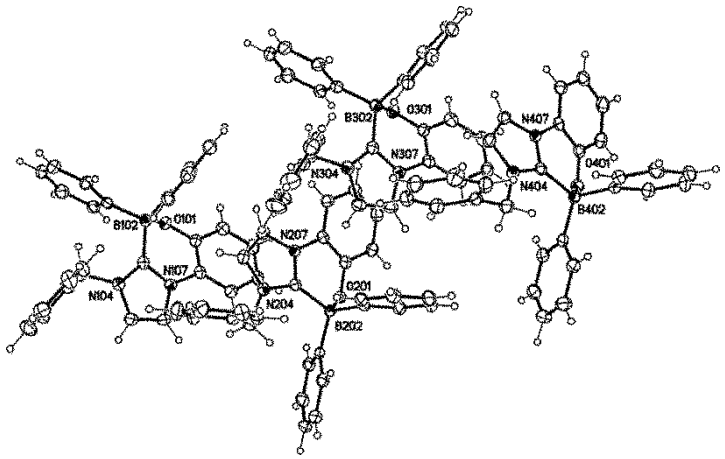


Figure 30: X-ray structure of molecule **73d**.

Table 23: Crystallography data and refinement details for **73d**.

$C_{28}H_{23}BN_2O$	Z = 8
M_r = 414.29	F(000) = 1744
Triclinic, P-1 (no.2)	D_x = 1.292 Mg m^{-3}
a = 12.3677 (5) Å	Cu $K\alpha$ radiation, λ = 1.54178 Å
b = 19.3760 (7) Å	Cell parameters from 9791 reflections
c = 20.5182 (7) Å	θ = 2.7–72.3°
α = 61.922 (1)°	μ = 0.61 mm^{-1}
β = 85.248 (2)°	T = 123 K
γ = 79.142 (2)°	Plates, colourless
V = 4260.5 (3) Å^3	0.35 × 0.15 × 0.05 mm
Refinement on F2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
R[F2 > 2σ(F2)] = 0.052	H-atom parameters constrained
wR(F2) = 0.143	w = 1/[σ2(Fo2) + (0.0551P)2 + 3.323P] where P = (Fo2 + 2Fc2)/3
S = 1.08	(Δ/σ)max < 0.001
16701 reflections	Δ⟩max = 0.32 e Å-3
1155 parameters	Δ⟩min = -0.26 e Å-3
0 restraints	Extinction correction: SHELXL, Fc*=kFc[1+0.001xFc2λ3/sin(2θ)]-1/4
Primary atom site location: dual	Extinction coefficient: 0.00076 (7)

Table 24: Bond length (pm) data for **73d**.

O101—C113	1.343 (3)	O301—C313	1.341 (3)
O101—B102	1.502 (3)	O301—B302	1.507 (3)
B102—C114	1.621 (3)	B302—C320	1.616 (3)
B102—C120	1.635 (3)	B302—C314	1.635 (3)
B102—C103	1.651 (3)	B302—C303	1.648 (3)

C103—N107	1.351 (3)	C303—N304	1.351 (3)
C103—N104	1.353 (3)	C303—N307	1.352 (3)
N104—C105	1.379 (3)	N304—C305	1.382 (3)
N104—C126	1.472 (3)	N304—C326	1.476 (3)
C105—C106	1.344 (3)	C305—C306	1.341 (3)
C105—H105	0.9500	C305—H305	0.9500
C106—N107	1.387 (3)	C306—N307	1.383 (3)
C106—H106	0.9500	C306—H306	0.9500
N107—C108	1.430 (3)	N307—C308	1.426 (3)
C108—C109	1.384 (3)	C308—C309	1.382 (3)
C108—C113	1.404 (3)	C308—C313	1.410 (3)
C109—C110	1.388 (3)	C309—C310	1.387 (4)
C109—H109	0.9500	C309—H309	0.9500
C110—C111	1.398 (4)	C310—C311	1.394 (4)
C110—H110	0.9500	C310—H310	0.9500
C111—C112	1.384 (4)	C311—C312	1.388 (4)
C111—H111	0.9500	C311—H311	0.9500
C112—C113	1.395 (3)	C312—C313	1.399 (3)
C112—H112	0.9500	C312—H312	0.9500
C114—C115	1.396 (3)	C314—C315	1.397 (3)
C114—C119	1.398 (3)	C314—C319	1.405 (3)
C115—C116	1.390 (3)	C315—C316	1.392 (3)
C115—H115	0.9500	C315—H315	0.9500
C116—C117	1.388 (4)	C316—C317	1.387 (4)
C116—H116	0.9500	C316—H316	0.9500
C117—C118	1.380 (4)	C317—C318	1.385 (4)
C117—H117	0.9500	C317—H317	0.9500
C118—C119	1.392 (3)	C318—C319	1.388 (4)
C118—H118	0.9500	C318—H318	0.9500

C119—H119	0.9500	C319—H319	0.9500
C120—C121	1.398 (3)	C320—C325	1.393 (3)
C120—C125	1.406 (3)	C320—C321	1.402 (3)
C121—C122	1.393 (3)	C321—C322	1.388 (3)
C121—H121	0.9500	C321—H321	0.9500
C122—C123	1.387 (4)	C322—C323	1.384 (4)
C122—H122	0.9500	C322—H322	0.9500
C123—C124	1.387 (4)	C323—C324	1.384 (4)
C123—H123	0.9500	C323—H323	0.9500
C124—C125	1.391 (4)	C324—C325	1.391 (3)
C124—H124	0.9500	C324—H324	0.9500
C125—H125	0.9500	C325—H325	0.9500
C126—C127	1.509 (3)	C326—C327	1.509 (3)
C126—H12A	0.9900	C326—H32A	0.9900
C126—H12B	0.9900	C326—H32B	0.9900
C127—C132	1.389 (3)	C327—C328	1.388 (4)
C127—C128	1.392 (3)	C327—C332	1.394 (3)
C128—C129	1.385 (4)	C328—C329	1.382 (4)
C128—H128	0.9500	C328—H328	0.9500
C129—C130	1.382 (4)	C329—C330	1.381 (4)
C129—H129	0.9500	C329—H329	0.9500
C130—C131	1.381 (4)	C330—C331	1.376 (4)
C130—H130	0.9500	C330—H330	0.9500
C131—C132	1.395 (4)	C331—C332	1.397 (4)
C131—H131	0.9500	C331—H331	0.9500
C132—H132	0.9500	C332—H332	0.9500
O201—C213	1.344 (3)	O401—C413	1.347 (3)
O201—B202	1.513 (3)	O401—B402	1.510 (3)
B202—C214	1.618 (3)	B402—C414	1.621 (3)

B202—C220	1.629 (3)	B402—C420	1.626 (3)
B202—C203	1.642 (3)	B402—C403	1.636 (3)
C203—N204	1.347 (3)	C403—N404	1.347 (3)
C203—N207	1.357 (3)	C403—N407	1.354 (3)
N204—C205	1.382 (3)	N404—C405	1.388 (3)
N204—C226	1.477 (3)	N404—C426	1.490 (3)
C205—C206	1.351 (4)	C405—C406	1.350 (3)
C205—H205	0.9500	C405—H405	0.9500
C206—N207	1.380 (3)	C406—N407	1.377 (3)
C206—H206	0.9500	C406—H406	0.9500
N207—C208	1.430 (3)	N407—C408	1.426 (3)
C208—C209	1.388 (3)	C408—C409	1.388 (3)
C208—C213	1.400 (3)	C408—C413	1.402 (3)
C209—C210	1.391 (3)	C409—C410	1.389 (3)
C209—H209	0.9500	C409—H409	0.9500
C210—C211	1.383 (4)	C410—C411	1.381 (4)
C210—H210	0.9500	C410—H410	0.9500
C211—C212	1.387 (4)	C411—C412	1.385 (4)
C211—H211	0.9500	C411—H411	0.9500
C212—C213	1.394 (3)	C412—C413	1.397 (3)
C212—H212	0.9500	C412—H412	0.9500
C214—C219	1.398 (3)	C414—C419	1.398 (3)
C214—C215	1.400 (3)	C414—C415	1.403 (3)
C215—C216	1.389 (3)	C415—C416	1.393 (4)
C215—H215	0.9500	C415—H415	0.9500
C216—C217	1.385 (4)	C416—C417	1.386 (4)
C216—H216	0.9500	C416—H416	0.9500
C217—C218	1.395 (4)	C417—C418	1.383 (4)
C217—H217	0.9500	C417—H417	0.9500

C218—C219	1.386 (4)	C418—C419	1.385 (4)
C218—H218	0.9500	C418—H418	0.9500
C219—H219	0.9500	C419—H419	0.9500
C220—C221	1.393 (3)	C420—C421	1.395 (4)
C220—C225	1.402 (3)	C420—C425	1.397 (3)
C221—C222	1.394 (3)	C421—C422	1.396 (3)
C221—H221	0.9500	C421—H421	0.9500
C222—C223	1.386 (4)	C422—C423	1.384 (4)
C222—H222	0.9500	C422—H422	0.9500
C223—C224	1.384 (4)	C423—C424	1.380 (4)
C223—H223	0.9500	C423—H423	0.9500
C224—C225	1.394 (3)	C424—C425	1.393 (4)
C224—H224	0.9500	C424—H424	0.9500
C225—H225	0.9500	C425—H425	0.9500
C226—C227	1.504 (3)	C426—C427	1.498 (3)
C226—H22A	0.9900	C426—H42A	0.9900
C226—H22B	0.9900	C426—H42B	0.9900
C227—C232	1.386 (3)	C427—C432	1.385 (3)
C227—C228	1.389 (3)	C427—C428	1.390 (3)
C228—C229	1.379 (4)	C428—C429	1.382 (3)
C228—H228	0.9500	C428—H428	0.9500
C229—C230	1.382 (4)	C429—C430	1.379 (4)
C229—H229	0.9500	C429—H429	0.9500
C230—C231	1.384 (4)	C430—C431	1.391 (4)
C230—H230	0.9500	C430—H430	0.9500
C231—C232	1.389 (4)	C431—C432	1.384 (4)
C231—H231	0.9500	C431—H431	0.9500
C232—H232	0.9500	C432—H432	0.9500
C113—O101—B102	116.93 (17)	C313—O301—B302	116.05 (18)

O101—B102—C114	106.36 (18)	O301—B302—C320	106.89 (19)
O101—B102—C120	109.46 (18)	O301—B302—C314	109.15 (18)
C114—B102—C120	112.28 (19)	C320—B302—C314	112.62 (19)
O101—B102—C103	103.12 (18)	O301—B302—C303	103.28 (18)
C114—B102—C103	113.89 (18)	C320—B302—C303	113.43 (19)
C120—B102—C103	111.13 (18)	C314—B302—C303	110.88 (19)
N107—C103—N104	105.1 (2)	N304—C303—N307	105.0 (2)
N107—C103—B102	118.93 (19)	N304—C303—B302	136.6 (2)
N104—C103—B102	135.9 (2)	N307—C303—B302	118.3 (2)
C103—N104—C105	110.4 (2)	C303—N304—C305	110.4 (2)
C103—N104—C126	126.2 (2)	C303—N304—C326	127.1 (2)
C105—N104—C126	122.8 (2)	C305—N304—C326	122.2 (2)
C106—C105—N104	107.4 (2)	C306—C305—N304	107.2 (2)
C106—C105—H105	126.3	C306—C305—H305	126.4
N104—C105—H105	126.3	N304—C305—H305	126.4
C105—C106—N107	106.4 (2)	C305—C306—N307	106.6 (2)
C105—C106—H106	126.8	C305—C306—H306	126.7
N107—C106—H106	126.8	N307—C306—H306	126.7
C103—N107—C106	110.70 (19)	C303—N307—C306	110.77 (19)
C103—N107—C108	121.32 (19)	C303—N307—C308	121.3 (2)
C106—N107—C108	127.9 (2)	C306—N307—C308	127.8 (2)
C109—C108—C113	121.6 (2)	C309—C308—C313	121.6 (2)
C109—C108—N107	121.5 (2)	C309—C308—N307	121.6 (2)
C113—C108—N107	116.9 (2)	C313—C308—N307	116.8 (2)
C108—C109—C110	119.4 (2)	C308—C309—C310	119.6 (2)
C108—C109—H109	120.3	C308—C309—H309	120.2
C110—C109—H109	120.3	C310—C309—H309	120.2
C109—C110—C111	119.7 (2)	C309—C310—C311	119.6 (2)
C109—C110—H110	120.2	C309—C310—H310	120.2

C111—C110—H110	120.2	C311—C310—H310	120.2
C112—C111—C110	120.7 (2)	C312—C311—C310	121.0 (2)
C112—C111—H111	119.6	C312—C311—H311	119.5
C110—C111—H111	119.6	C310—C311—H311	119.5
C111—C112—C113	120.1 (2)	C311—C312—C313	119.9 (2)
C111—C112—H112	119.9	C311—C312—H312	120.0
C113—C112—H112	119.9	C313—C312—H312	120.0
O101—C113—C112	119.7 (2)	O301—C313—C312	120.4 (2)
O101—C113—C108	121.8 (2)	O301—C313—C308	121.4 (2)
C112—C113—C108	118.5 (2)	C312—C313—C308	118.2 (2)
C115—C114—C119	116.8 (2)	C315—C314—C319	116.7 (2)
C115—C114—B102	122.8 (2)	C315—C314—B302	125.2 (2)
C119—C114—B102	120.4 (2)	C319—C314—B302	118.1 (2)
C116—C115—C114	121.8 (2)	C316—C315—C314	121.7 (2)
C116—C115—H115	119.1	C316—C315—H315	119.1
C114—C115—H115	119.1	C314—C315—H315	119.1
C117—C116—C115	120.2 (2)	C317—C316—C315	120.1 (2)
C117—C116—H116	119.9	C317—C316—H316	120.0
C115—C116—H116	119.9	C315—C316—H316	120.0
C118—C117—C116	119.1 (2)	C318—C317—C316	119.7 (2)
C118—C117—H117	120.4	C318—C317—H317	120.2
C116—C117—H117	120.4	C316—C317—H317	120.2
C117—C118—C119	120.3 (2)	C317—C318—C319	119.8 (2)
C117—C118—H118	119.8	C317—C318—H318	120.1
C119—C118—H118	119.8	C319—C318—H318	120.1
C118—C119—C114	121.7 (2)	C318—C319—C314	122.0 (2)
C118—C119—H119	119.1	C318—C319—H319	119.0
C114—C119—H119	119.1	C314—C319—H319	119.0
C121—C120—C125	116.6 (2)	C325—C320—C321	116.5 (2)

C121—C120—B102	124.9 (2)	C325—C320—B302	122.7 (2)
C125—C120—B102	118.5 (2)	C321—C320—B302	120.7 (2)
C122—C121—C120	122.2 (2)	C322—C321—C320	121.8 (2)
C122—C121—H121	118.9	C322—C321—H321	119.1
C120—C121—H121	118.9	C320—C321—H321	119.1
C123—C122—C121	119.7 (2)	C323—C322—C321	120.3 (2)
C123—C122—H122	120.1	C323—C322—H322	119.9
C121—C122—H122	120.1	C321—C322—H322	119.9
C122—C123—C124	119.6 (2)	C324—C323—C322	119.3 (2)
C122—C123—H123	120.2	C324—C323—H323	120.4
C124—C123—H123	120.2	C322—C323—H323	120.4
C123—C124—C125	120.2 (2)	C323—C324—C325	120.0 (2)
C123—C124—H124	119.9	C323—C324—H324	120.0
C125—C124—H124	119.9	C325—C324—H324	120.0
C124—C125—C120	121.7 (2)	C324—C325—C320	122.1 (2)
C124—C125—H125	119.2	C324—C325—H325	118.9
C120—C125—H125	119.2	C320—C325—H325	118.9
N104—C126—C127	112.91 (19)	N304—C326—C327	112.26 (19)
N104—C126—H12A	109.0	N304—C326—H32A	109.2
C127—C126—H12A	109.0	C327—C326—H32A	109.2
N104—C126—H12B	109.0	N304—C326—H32B	109.2
C127—C126—H12B	109.0	C327—C326—H32B	109.2
H12A—C126—H12B	107.8	H32A—C326—H32B	107.9
C132—C127—C128	118.9 (2)	C328—C327—C332	118.8 (2)
C132—C127—C126	121.2 (2)	C328—C327—C326	120.1 (2)
C128—C127—C126	119.8 (2)	C332—C327—C326	121.2 (2)
C129—C128—C127	120.6 (2)	C329—C328—C327	120.7 (2)
C129—C128—H128	119.7	C329—C328—H328	119.6
C127—C128—H128	119.7	C327—C328—H328	119.6

C130—C129—C128	120.2 (2)	C330—C329—C328	120.2 (3)
C130—C129—H129	119.9	C330—C329—H329	119.9
C128—C129—H129	119.9	C328—C329—H329	119.9
C131—C130—C129	120.0 (2)	C331—C330—C329	120.1 (3)
C131—C130—H130	120.0	C331—C330—H330	119.9
C129—C130—H130	120.0	C329—C330—H330	119.9
C130—C131—C132	119.9 (2)	C330—C331—C332	119.9 (3)
C130—C131—H131	120.0	C330—C331—H331	120.1
C132—C131—H131	120.0	C332—C331—H331	120.1
C127—C132—C131	120.4 (2)	C327—C332—C331	120.3 (3)
C127—C132—H132	119.8	C327—C332—H332	119.9
C131—C132—H132	119.8	C331—C332—H332	119.9
C213—O201—B202	117.56 (17)	C413—O401—B402	118.31 (18)
O201—B202—C214	106.25 (18)	O401—B402—C414	106.30 (19)
O201—B202—C220	109.37 (18)	O401—B402—C420	110.09 (19)
C214—B202—C220	112.20 (18)	C414—B402—C420	113.20 (19)
O201—B202—C203	102.93 (17)	O401—B402—C403	103.22 (18)
C214—B202—C203	114.29 (18)	C414—B402—C403	112.65 (18)
C220—B202—C203	111.16 (18)	C420—B402—C403	110.79 (19)
N204—C203—N207	105.50 (19)	N404—C403—N407	106.01 (19)
N204—C203—B202	135.5 (2)	N404—C403—B402	134.2 (2)
N207—C203—B202	118.96 (19)	N407—C403—B402	119.65 (19)
C203—N204—C205	110.0 (2)	C403—N404—C405	109.59 (19)
C203—N204—C226	126.7 (2)	C403—N404—C426	124.75 (19)
C205—N204—C226	123.0 (2)	C405—N404—C426	125.62 (19)
C206—C205—N204	107.7 (2)	C406—C405—N404	107.4 (2)
C206—C205—H205	126.2	C406—C405—H405	126.3
N204—C205—H205	126.2	N404—C405—H405	126.3
C205—C206—N207	106.1 (2)	C405—C406—N407	106.6 (2)

C205—C206—H206	127.0	C405—C406—H406	126.7
N207—C206—H206	127.0	N407—C406—H406	126.7
C203—N207—C206	110.80 (19)	C403—N407—C406	110.42 (19)
C203—N207—C208	121.89 (19)	C403—N407—C408	121.86 (19)
C206—N207—C208	127.3 (2)	C406—N407—C408	127.7 (2)
C209—C208—C213	121.7 (2)	C409—C408—C413	121.5 (2)
C209—C208—N207	121.7 (2)	C409—C408—N407	122.1 (2)
C213—C208—N207	116.6 (2)	C413—C408—N407	116.4 (2)
C208—C209—C210	119.4 (2)	C408—C409—C410	119.6 (2)
C208—C209—H209	120.3	C408—C409—H409	120.2
C210—C209—H209	120.3	C410—C409—H409	120.2
C211—C210—C209	119.7 (2)	C411—C410—C409	119.4 (2)
C211—C210—H210	120.2	C411—C410—H410	120.3
C209—C210—H210	120.2	C409—C410—H410	120.3
C210—C211—C212	120.7 (2)	C410—C411—C412	121.2 (2)
C210—C211—H211	119.7	C410—C411—H411	119.4
C212—C211—H211	119.7	C412—C411—H411	119.4
C211—C212—C213	120.8 (2)	C411—C412—C413	120.4 (2)
C211—C212—H212	119.6	C411—C412—H412	119.8
C213—C212—H212	119.6	C413—C412—H412	119.8
O201—C213—C212	120.7 (2)	O401—C413—C412	120.4 (2)
O201—C213—C208	121.5 (2)	O401—C413—C408	121.7 (2)
C212—C213—C208	117.8 (2)	C412—C413—C408	117.8 (2)
C219—C214—C215	116.7 (2)	C419—C414—C415	116.4 (2)
C219—C214—B202	120.1 (2)	C419—C414—B402	120.4 (2)
C215—C214—B202	123.1 (2)	C415—C414—B402	123.1 (2)
C216—C215—C214	122.2 (2)	C416—C415—C414	122.1 (2)
C216—C215—H215	118.9	C416—C415—H415	118.9
C214—C215—H215	118.9	C414—C415—H415	118.9

C217—C216—C215	120.0 (2)	C417—C416—C415	119.7 (2)
C217—C216—H216	120.0	C417—C416—H416	120.2
C215—C216—H216	120.0	C415—C416—H416	120.2
C216—C217—C218	119.1 (2)	C418—C417—C416	119.4 (2)
C216—C217—H217	120.5	C418—C417—H417	120.3
C218—C217—H217	120.5	C416—C417—H417	120.3
C219—C218—C217	120.4 (2)	C417—C418—C419	120.6 (2)
C219—C218—H218	119.8	C417—C418—H418	119.7
C217—C218—H218	119.8	C419—C418—H418	119.7
C218—C219—C214	121.7 (2)	C418—C419—C414	121.9 (2)
C218—C219—H219	119.2	C418—C419—H419	119.1
C214—C219—H219	119.2	C414—C419—H419	119.1
C221—C220—C225	116.5 (2)	C421—C420—C425	116.5 (2)
C221—C220—B202	124.6 (2)	C421—C420—B402	124.4 (2)
C225—C220—B202	118.8 (2)	C425—C420—B402	119.2 (2)
C220—C221—C222	122.3 (2)	C420—C421—C422	122.3 (2)
C220—C221—H221	118.9	C420—C421—H421	118.8
C222—C221—H221	118.9	C422—C421—H421	118.8
C223—C222—C221	119.9 (2)	C423—C422—C421	119.8 (3)
C223—C222—H222	120.1	C423—C422—H422	120.1
C221—C222—H222	120.1	C421—C422—H422	120.1
C224—C223—C222	119.3 (2)	C424—C423—C422	119.2 (2)
C224—C223—H223	120.4	C424—C423—H423	120.4
C222—C223—H223	120.4	C422—C423—H423	120.4
C223—C224—C225	120.3 (2)	C423—C424—C425	120.7 (3)
C223—C224—H224	119.8	C423—C424—H424	119.7
C225—C224—H224	119.8	C425—C424—H424	119.7
C224—C225—C220	121.7 (2)	C424—C425—C420	121.6 (3)
C224—C225—H225	119.1	C424—C425—H425	119.2

C220—C225—H225	119.1	C420—C425—H425	119.2
N204—C226—C227	112.47 (19)	N404—C426—C427	111.88 (19)
N204—C226—H22A	109.1	N404—C426—H42A	109.2
C227—C226—H22A	109.1	C427—C426—H42A	109.2
N204—C226—H22B	109.1	N404—C426—H42B	109.2
C227—C226—H22B	109.1	C427—C426—H42B	109.2
H22A—C226—H22B	107.8	H42A—C426—H42B	107.9
C232—C227—C228	118.8 (2)	C432—C427—C428	119.1 (2)
C232—C227—C226	121.3 (2)	C432—C427—C426	121.1 (2)
C228—C227—C226	120.0 (2)	C428—C427—C426	119.8 (2)
C229—C228—C227	121.0 (2)	C429—C428—C427	120.7 (2)
C229—C228—H228	119.5	C429—C428—H428	119.7
C227—C228—H228	119.5	C427—C428—H428	119.7
C228—C229—C230	120.1 (2)	C430—C429—C428	119.8 (2)
C228—C229—H229	120.0	C430—C429—H429	120.1
C230—C229—H229	120.0	C428—C429—H429	120.1
C229—C230—C231	119.6 (2)	C429—C430—C431	120.2 (2)
C229—C230—H230	120.2	C429—C430—H430	119.9
C231—C230—H230	120.2	C431—C430—H430	119.9
C230—C231—C232	120.2 (2)	C432—C431—C430	119.7 (2)
C230—C231—H231	119.9	C432—C431—H431	120.2
C232—C231—H231	119.9	C430—C431—H431	120.2
C227—C232—C231	120.4 (2)	C431—C432—C427	120.5 (2)
C227—C232—H232	119.8	C431—C432—H432	119.7
C231—C232—H232	119.8	C427—C432—H432	119.7
C113—O101—B102—C114	-171.56 (18)	C313—O301—B302—C320	-173.12 (18)
C113—O101—B102—C120	66.9 (2)	C313—O301—B302—C314	64.8 (2)
C113—O101—B102—C103	-51.4 (2)	C313—O301—B302—C303	-53.2 (2)
O101—B102—C103—N107	33.0 (2)	O301—B302—C303—N304	-142.2 (2)

C114—B102—C103—N107	147.9 (2)	C320—B302—C303—N304	-26.8 (4)
C120—B102—C103—N107	-84.1 (2)	C314—B302—C303—N304	101.0 (3)
O101—B102—C103—N104	-144.9 (2)	O301—B302—C303—N307	33.5 (2)
C114—B102—C103—N104	-30.1 (3)	C320—B302—C303—N307	148.8 (2)
C120—B102—C103—N104	97.9 (3)	C314—B302—C303—N307	-83.3 (2)
N107—C103—N104—C105	0.3 (2)	N307—C303—N304—C305	-0.5 (2)
B102—C103—N104—C105	178.4 (2)	B302—C303—N304—C305	175.6 (2)
N107—C103—N104—C126	-170.8 (2)	N307—C303—N304—C326	-174.6 (2)
B102—C103—N104—C126	7.4 (4)	B302—C303—N304—C326	1.4 (4)
C103—N104—C105—C106	-0.5 (3)	C303—N304—C305—C306	-0.1 (3)
C126—N104—C105—C106	170.9 (2)	C326—N304—C305—C306	174.3 (2)
N104—C105—C106—N107	0.5 (2)	N304—C305—C306—N307	0.7 (2)
N104—C103—N107—C106	0.1 (2)	N304—C303—N307—C306	0.9 (2)
B102—C103—N107—C106	-178.45 (18)	B302—C303—N307—C306	-176.02 (19)
N104—C103—N107—C108	176.73 (18)	N304—C303—N307—C308	177.36 (18)
B102—C103—N107—C108	-1.8 (3)	B302—C303—N307—C308	0.5 (3)
C105—C106—N107—C103	-0.4 (2)	C305—C306—N307—C303	-1.0 (3)
C105—C106—N107—C108	-176.8 (2)	C305—C306—N307—C308	-177.2 (2)
C103—N107—C108—C109	163.9 (2)	C303—N307—C308—C309	160.3 (2)
C106—N107—C108—C109	-20.1 (3)	C306—N307—C308—C309	-23.8 (3)
C103—N107—C108—C113	-16.4 (3)	C303—N307—C308—C313	-20.0 (3)
C106—N107—C108—C113	159.6 (2)	C306—N307—C308—C313	155.8 (2)
C113—C108—C109—C110	0.9 (3)	C313—C308—C309—C310	0.6 (3)
N107—C108—C109—C110	-179.4 (2)	N307—C308—C309—C310	-179.7 (2)
C108—C109—C110—C111	0.3 (3)	C308—C309—C310—C311	-0.1 (3)
C109—C110—C111—C112	-1.3 (4)	C309—C310—C311—C312	-0.9 (4)
C110—C111—C112—C113	1.2 (4)	C310—C311—C312—C313	1.4 (4)
B102—O101—C113—C112	-141.2 (2)	B302—O301—C313—C312	-139.8 (2)
B102—O101—C113—C108	40.5 (3)	B302—O301—C313—C308	40.8 (3)

C111—C112—C113—O101	-178.4 (2)	C311—C312—C313—O301	179.7 (2)
C111—C112—C113—C108	0.0 (3)	C311—C312—C313—C308	-0.9 (3)
C109—C108—C113—O101	177.3 (2)	C309—C308—C313—O301	179.3 (2)
N107—C108—C113—O101	-2.4 (3)	N307—C308—C313—O301	-0.3 (3)
C109—C108—C113—C112	-1.0 (3)	C309—C308—C313—C312	-0.1 (3)
N107—C108—C113—C112	179.31 (19)	N307—C308—C313—C312	-179.76 (19)
O101—B102—C114—C115	-152.8 (2)	O301—B302—C314—C315	-146.7 (2)
C120—B102—C114—C115	-33.1 (3)	C320—B302—C314—C315	94.7 (3)
C103—B102—C114—C115	94.3 (3)	C303—B302—C314—C315	-33.6 (3)
O101—B102—C114—C119	25.1 (3)	O301—B302—C314—C319	35.3 (3)
C120—B102—C114—C119	144.8 (2)	C320—B302—C314—C319	-83.3 (3)
C103—B102—C114—C119	-87.8 (3)	C303—B302—C314—C319	148.4 (2)
C119—C114—C115—C116	0.2 (4)	C319—C314—C315—C316	1.0 (4)
B102—C114—C115—C116	178.2 (2)	B302—C314—C315—C316	-177.0 (2)
C114—C115—C116—C117	-0.3 (4)	C314—C315—C316—C317	-1.0 (4)
C115—C116—C117—C118	0.3 (4)	C315—C316—C317—C318	0.2 (4)
C116—C117—C118—C119	-0.1 (4)	C316—C317—C318—C319	0.6 (4)
C117—C118—C119—C114	-0.1 (4)	C317—C318—C319—C314	-0.6 (4)
C115—C114—C119—C118	0.0 (4)	C315—C314—C319—C318	-0.2 (4)
B102—C114—C119—C118	-178.0 (2)	B302—C314—C319—C318	177.9 (2)
O101—B102—C120—C121	-152.0 (2)	O301—B302—C320—C325	-154.8 (2)
C114—B102—C120—C121	90.1 (3)	C314—B302—C320—C325	-34.9 (3)
C103—B102—C120—C121	-38.8 (3)	C303—B302—C320—C325	92.1 (3)
O101—B102—C120—C125	31.6 (3)	O301—B302—C320—C321	24.4 (3)
C114—B102—C120—C125	-86.3 (3)	C314—B302—C320—C321	144.3 (2)
C103—B102—C120—C125	144.8 (2)	C303—B302—C320—C321	-88.7 (3)
C125—C120—C121—C122	0.0 (4)	C325—C320—C321—C322	-0.4 (4)
B102—C120—C121—C122	-176.4 (2)	B302—C320—C321—C322	-179.7 (2)
C120—C121—C122—C123	-0.5 (4)	C320—C321—C322—C323	0.1 (4)

C121—C122—C123—C124	0.3 (4)	C321—C322—C323—C324	0.2 (4)
C122—C123—C124—C125	0.3 (4)	C322—C323—C324—C325	-0.1 (4)
C123—C124—C125—C120	-0.8 (4)	C323—C324—C325—C320	-0.3 (4)
C121—C120—C125—C124	0.6 (4)	C321—C320—C325—C324	0.5 (4)
B102—C120—C125—C124	177.3 (2)	B302—C320—C325—C324	179.8 (2)
C103—N104—C126—C127	-137.4 (2)	C303—N304—C326—C327	-129.7 (2)
C105—N104—C126—C127	52.6 (3)	C305—N304—C326—C327	56.8 (3)
N104—C126—C127—C132	-108.6 (3)	N304—C326—C327—C328	83.6 (3)
N104—C126—C127—C128	74.5 (3)	N304—C326—C327—C332	-97.3 (3)
C132—C127—C128—C129	0.2 (4)	C332—C327—C328—C329	0.5 (4)
C126—C127—C128—C129	177.2 (2)	C326—C327—C328—C329	179.6 (2)
C127—C128—C129—C130	-0.2 (4)	C327—C328—C329—C330	0.4 (4)
C128—C129—C130—C131	0.3 (4)	C328—C329—C330—C331	-0.7 (4)
C129—C130—C131—C132	-0.5 (4)	C329—C330—C331—C332	0.2 (5)
C128—C127—C132—C131	-0.4 (4)	C328—C327—C332—C331	-1.1 (4)
C126—C127—C132—C131	-177.4 (2)	C326—C327—C332—C331	179.9 (3)
C130—C131—C132—C127	0.5 (4)	C330—C331—C332—C327	0.7 (5)
C213—O201—B202—C214	171.38 (17)	C413—O401—B402—C414	167.27 (17)
C213—O201—B202—C220	-67.3 (2)	C413—O401—B402—C420	-69.8 (2)
C213—O201—B202—C203	50.9 (2)	C413—O401—B402—C403	48.5 (2)
O201—B202—C203—N204	146.9 (2)	O401—B402—C403—N404	147.0 (2)
C214—B202—C203—N204	32.1 (3)	C414—B402—C403—N404	32.8 (3)
C220—B202—C203—N204	-96.1 (3)	C420—B402—C403—N404	-95.2 (3)
O201—B202—C203—N207	-30.9 (2)	O401—B402—C403—N407	-28.9 (3)
C214—B202—C203—N207	-145.6 (2)	C414—B402—C403—N407	-143.1 (2)
C220—B202—C203—N207	86.1 (2)	C420—B402—C403—N407	88.9 (2)
N207—C203—N204—C205	0.2 (2)	N407—C403—N404—C405	0.7 (2)
B202—C203—N204—C205	-177.7 (2)	B402—C403—N404—C405	-175.5 (2)
N207—C203—N204—C226	174.0 (2)	N407—C403—N404—C426	178.8 (2)

B202—C203—N204—C226	-4.0 (4)	B402—C403—N404—C426	2.5 (4)
C203—N204—C205—C206	0.1 (3)	C403—N404—C405—C406	-0.2 (3)
C226—N204—C205—C206	-173.9 (2)	C426—N404—C405—C406	-178.3 (2)
N204—C205—C206—N207	-0.4 (3)	N404—C405—C406—N407	-0.4 (3)
N204—C203—N207—C206	-0.5 (2)	N404—C403—N407—C406	-1.0 (2)
B202—C203—N207—C206	177.90 (19)	B402—C403—N407—C406	175.95 (19)
N204—C203—N207—C208	-179.07 (18)	N404—C403—N407—C408	-179.16 (18)
B202—C203—N207—C208	-0.7 (3)	B402—C403—N407—C408	-2.2 (3)
C205—C206—N207—C203	0.5 (3)	C405—C406—N407—C403	0.9 (3)
C205—C206—N207—C208	179.0 (2)	C405—C406—N407—C408	178.9 (2)
C203—N207—C208—C209	-161.2 (2)	C403—N407—C408—C409	-160.9 (2)
C206—N207—C208—C209	20.4 (3)	C406—N407—C408—C409	21.3 (3)
C203—N207—C208—C213	18.1 (3)	C403—N407—C408—C413	19.1 (3)
C206—N207—C208—C213	-160.2 (2)	C406—N407—C408—C413	-158.7 (2)
C213—C208—C209—C210	-0.9 (3)	C413—C408—C409—C410	-0.4 (3)
N207—C208—C209—C210	178.4 (2)	N407—C408—C409—C410	179.6 (2)
C208—C209—C210—C211	0.1 (3)	C408—C409—C410—C411	1.2 (3)
C209—C210—C211—C212	0.9 (4)	C409—C410—C411—C412	-0.5 (4)
C210—C211—C212—C213	-1.0 (4)	C410—C411—C412—C413	-1.1 (4)
B202—O201—C213—C212	140.1 (2)	B402—O401—C413—C412	143.5 (2)
B202—O201—C213—C208	-40.7 (3)	B402—O401—C413—C408	-38.5 (3)
C211—C212—C213—O201	179.4 (2)	C411—C412—C413—O401	179.9 (2)
C211—C212—C213—C208	0.3 (3)	C411—C412—C413—C408	1.8 (3)
C209—C208—C213—O201	-178.46 (19)	C409—C408—C413—O401	-179.2 (2)
N207—C208—C213—O201	2.2 (3)	N407—C408—C413—O401	0.8 (3)
C209—C208—C213—C212	0.7 (3)	C409—C408—C413—C412	-1.1 (3)
N207—C208—C213—C212	-178.62 (19)	N407—C408—C413—C412	178.86 (19)
O201—B202—C214—C219	-23.7 (3)	O401—B402—C414—C419	-27.4 (3)
C220—B202—C214—C219	-143.2 (2)	C420—B402—C414—C419	-148.4 (2)

C203—B202—C214—C219	89.1 (3)	C403—B402—C414—C419	84.9 (3)
O201—B202—C214—C215	153.0 (2)	O401—B402—C414—C415	150.3 (2)
C220—B202—C214—C215	33.5 (3)	C420—B402—C414—C415	29.3 (3)
C203—B202—C214—C215	-94.2 (3)	C403—B402—C414—C415	-97.4 (3)
C219—C214—C215—C216	-0.2 (3)	C419—C414—C415—C416	-0.3 (4)
B202—C214—C215—C216	-177.0 (2)	B402—C414—C415—C416	-178.1 (2)
C214—C215—C216—C217	0.9 (4)	C414—C415—C416—C417	0.4 (4)
C215—C216—C217—C218	-0.6 (4)	C415—C416—C417—C418	0.0 (4)
C216—C217—C218—C219	-0.4 (4)	C416—C417—C418—C419	-0.6 (4)
C217—C218—C219—C214	1.2 (4)	C417—C418—C419—C414	0.7 (4)
C215—C214—C219—C218	-0.8 (3)	C415—C414—C419—C418	-0.2 (4)
B202—C214—C219—C218	176.1 (2)	B402—C414—C419—C418	177.6 (2)
O201—B202—C220—C221	149.5 (2)	O401—B402—C420—C421	150.4 (2)
C214—B202—C220—C221	-92.9 (3)	C414—B402—C420—C421	-90.8 (3)
C203—B202—C220—C221	36.5 (3)	C403—B402—C420—C421	36.9 (3)
O201—B202—C220—C225	-32.4 (3)	O401—B402—C420—C425	-30.7 (3)
C214—B202—C220—C225	85.3 (3)	C414—B402—C420—C425	88.1 (3)
C203—B202—C220—C225	-145.4 (2)	C403—B402—C420—C425	-144.3 (2)
C225—C220—C221—C222	-0.5 (4)	C425—C420—C421—C422	-0.8 (4)
B202—C220—C221—C222	177.7 (2)	B402—C420—C421—C422	178.1 (2)
C220—C221—C222—C223	0.8 (4)	C420—C421—C422—C423	0.8 (4)
C221—C222—C223—C224	-0.5 (4)	C421—C422—C423—C424	-0.3 (4)
C222—C223—C224—C225	0.0 (4)	C422—C423—C424—C425	-0.1 (4)
C223—C224—C225—C220	0.3 (4)	C423—C424—C425—C420	0.1 (4)
C221—C220—C225—C224	0.0 (4)	C421—C420—C425—C424	0.4 (4)
B202—C220—C225—C224	-178.3 (2)	B402—C420—C425—C424	-178.6 (2)
C203—N204—C226—C227	135.9 (2)	C403—N404—C426—C427	170.6 (2)
C205—N204—C226—C227	-51.1 (3)	C405—N404—C426—C427	-11.7 (3)
N204—C226—C227—C232	100.5 (3)	N404—C426—C427—C432	-92.1 (3)

N204—C226—C227—C228	-80.5 (3)	N404—C426—C427—C428	88.0 (3)
C232—C227—C228—C229	-0.2 (4)	C432—C427—C428—C429	1.5 (4)
C226—C227—C228—C229	-179.2 (2)	C426—C427—C428—C429	-178.5 (2)
C227—C228—C229—C230	0.1 (4)	C427—C428—C429—C430	-1.0 (4)
C228—C229—C230—C231	-0.1 (4)	C428—C429—C430—C431	-0.5 (4)
C229—C230—C231—C232	0.3 (4)	C429—C430—C431—C432	1.4 (4)
C228—C227—C232—C231	0.3 (4)	C430—C431—C432—C427	-0.8 (4)
C226—C227—C232—C231	179.4 (2)	C428—C427—C432—C431	-0.6 (4)
C230—C231—C232—C227	-0.4 (4)	C426—C427—C432—C431	179.5 (2)

6.8 Crystal structure determination of (2-(3-butyl-1*H*-imidazolium-1-yl)benzyl)-tris-(perfluorophenyl)borate 74b

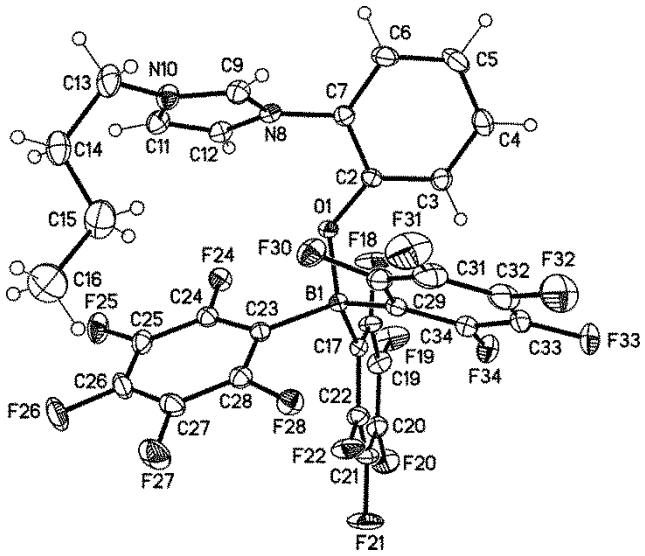


Figure 31: X-ray structure of molecule **74b**.

Table 25: Crystallography data and refinement details for **74b**.

$C_{31}H_{16}BF_{15}N_2O$	$F(000)$ = 2912
M_r = 728.27	D_x = 1.712 Mg m^{-3}
Monoclinic, $P2_1/n$ *(no.14)*	Cu $K\alpha$ radiation, λ = 1.54178 Å
a = 21.9006 (7) Å	Cell parameters from 9711 reflections

b = 13.1620 (4) Å	θ = 2.3–72.0°
c = 22.0149 (7) Å	μ = 1.55 mm^{-1}
β = 117.082 (1)°	*T* = 123 K
V = 5650.1 (3) $Å^3$	Blocks, colourless
Z = 8	0.35 × 0.25 × 0.15 mm
Refinement on F2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
R[F2 > 2σ(F2)] = 0.030	H-atom parameters constrained
wR(F2) = 0.074	w = 1/[σ2(Fo2) + (0.0309P)2 + 2.9728P] where P = (Fo2 + 2Fc2)/3
S = 1.04	(Δ/σ)max = 0.001
11099 reflections	Δ⟩max = 0.36 e Å-3
902 parameters	Δ⟩min = -0.19 e Å-3
0 restraints	Extinction correction: SHELXL2014/7 (Sheldrick 2014), Fc*=kFc[1+0.001xFc2λ3/sin(2θ)]-1/4
Primary atom site location: dual	Extinction coefficient: 0.00080 (3)

Table 26: Bond length (pm) data for **74b**.

O1—C2	1.3409 (14)	O101—C102	1.3370 (15)
O1—B1	1.4960 (15)	O101—B101	1.4868 (16)
C2—C3	1.3986 (17)	C102—C103	1.4002 (18)
C2—C7	1.3997 (17)	C102—C107	1.4053 (18)
C3—C4	1.3876 (18)	C103—C104	1.3900 (19)
C3—H3	0.9500	C103—H103	0.9500
C4—C5	1.389 (2)	C104—C105	1.388 (2)
C4—H4	0.9500	C104—H104	0.9500
C5—C6	1.384 (2)	C105—C106	1.387 (2)
C5—H5	0.9500	C105—H105	0.9500
C6—C7	1.3868 (17)	C106—C107	1.3865 (18)
C6—H6	0.9500	C106—H106	0.9500
C7—N8	1.4377 (15)	C107—N108	1.4406 (17)
N8—C9	1.3313 (16)	N108—C109	1.3320 (17)
N8—C12	1.3801 (16)	N108—C112	1.3826 (17)
C9—N10	1.3273 (17)	C109—N110	1.3280 (17)
C9—H9	0.9500	C109—H109	0.9500
N10—C11	1.3793 (17)	N110—C111	1.3791 (18)

N10—C13	1.4731 (16)	N110—C113	1.4793 (18)
C11—C12	1.3456 (18)	C111—C112	1.345 (2)
C11—H11	0.9500	C111—H111	0.9500
C12—H12	0.9500	C112—H112	0.9500
C13—C14	1.522 (2)	C113—C114	1.5062 (19)
C13—H13A	0.9900	C113—H11A	0.9900
C13—H13B	0.9900	C113—H11B	0.9900
C14—C15	1.519 (2)	C114—C115	1.5230 (18)
C14—H14A	0.9900	C114—H11C	0.9900
C14—H14B	0.9900	C114—H11D	0.9900
C15—C16	1.518 (2)	C115—C116	1.515 (2)
C15—H15A	0.9900	C115—H11E	0.9900
C15—H15B	0.9900	C115—H11F	0.9900
C16—H16A	0.9800	C116—H11G	0.9800
C16—H16B	0.9800	C116—H11H	0.9800
C16—H16C	0.9800	C116—H11I	0.9800
B1—C29	1.6459 (18)	B101—C123	1.6552 (17)
B1—C17	1.6499 (17)	B101—C129	1.6555 (18)
B1—C23	1.6630 (17)	B101—C117	1.6582 (17)
C17—C18	1.3822 (18)	C117—C118	1.3889 (17)
C17—C22	1.3898 (17)	C117—C122	1.3955 (17)
C18—F18	1.3529 (15)	C118—F118	1.3553 (14)
C18—C19	1.3861 (18)	C118—C119	1.3846 (18)
C19—F19	1.3427 (15)	C119—F119	1.3438 (15)
C19—C20	1.3747 (19)	C119—C120	1.378 (2)
C20—F20	1.3434 (15)	C120—F120	1.3434 (14)
C20—C21	1.375 (2)	C120—C121	1.375 (2)
C21—F21	1.3422 (15)	C121—F121	1.3441 (15)
C21—C22	1.3781 (19)	C121—C122	1.3822 (18)
C22—F22	1.3499 (15)	C122—F122	1.3461 (14)
C23—C28	1.3873 (17)	C123—C124	1.3878 (17)
C23—C24	1.3944 (17)	C123—C128	1.3917 (18)
C24—F24	1.3502 (14)	C124—F124	1.3513 (14)
C24—C25	1.3835 (18)	C124—C125	1.3884 (18)
C25—F25	1.3433 (15)	C125—F125	1.3517 (14)
C25—C26	1.380 (2)	C125—C126	1.3745 (19)
C26—F26	1.3462 (15)	C126—F126	1.3437 (14)
C26—C27	1.376 (2)	C126—C127	1.3791 (19)

C27—F27	1.3448 (15)	C127—F127	1.3389 (15)
C27—C28	1.3850 (18)	C127—C128	1.3803 (18)
C28—F28	1.3555 (14)	C128—F128	1.3546 (14)
C29—C34	1.3884 (18)	C129—C130	1.3894 (17)
C29—C30	1.3898 (19)	C129—C134	1.3933 (18)
C30—F30	1.3485 (15)	C130—F130	1.3495 (14)
C30—C31	1.3821 (19)	C130—C131	1.3843 (18)
C31—F31	1.3430 (19)	C131—F131	1.3490 (15)
C31—C32	1.379 (2)	C131—C132	1.378 (2)
C32—F32	1.3470 (16)	C132—F132	1.3382 (15)
C32—C33	1.371 (3)	C132—C133	1.379 (2)
C33—F33	1.3485 (17)	C133—F133	1.3457 (16)
C33—C34	1.389 (2)	C133—C134	1.3784 (19)
C34—F34	1.3492 (17)	C134—F134	1.3537 (15)
C2—O1—B1	125.18 (9)	C102—O101—B101	127.26 (10)
O1—C2—C3	124.97 (11)	O101—C102—C103	125.86 (12)
O1—C2—C7	117.56 (10)	O101—C102—C107	116.68 (11)
C3—C2—C7	117.42 (11)	C103—C102—C107	117.43 (11)
C4—C3—C2	120.35 (12)	C104—C103—C102	120.11 (13)
C4—C3—H3	119.8	C104—C103—H103	119.9
C2—C3—H3	119.8	C102—C103—H103	119.9
C3—C4—C5	121.04 (12)	C105—C104—C103	121.38 (13)
C3—C4—H4	119.5	C105—C104—H104	119.3
C5—C4—H4	119.5	C103—C104—H104	119.3
C6—C5—C4	119.65 (12)	C106—C105—C104	119.50 (12)
C6—C5—H5	120.2	C106—C105—H105	120.2
C4—C5—H5	120.2	C104—C105—H105	120.2
C5—C6—C7	119.08 (12)	C107—C106—C105	119.10 (13)
C5—C6—H6	120.5	C107—C106—H106	120.5
C7—C6—H6	120.5	C105—C106—H106	120.5
C6—C7—C2	122.44 (11)	C106—C107—C102	122.46 (12)
C6—C7—N8	119.79 (11)	C106—C107—N108	119.75 (12)
C2—C7—N8	117.76 (10)	C102—C107—N108	117.77 (11)
C9—N8—C12	108.48 (10)	C109—N108—C112	108.22 (11)
C9—N8—C7	125.22 (10)	C109—N108—C107	125.05 (11)
C12—N8—C7	126.29 (10)	C112—N108—C107	126.38 (11)
N10—C9—N8	108.52 (11)	N110—C109—N108	108.96 (11)
N10—C9—H9	125.7	N110—C109—H109	125.5

N8—C9—H9	125.7	N108—C109—H109	125.5
C9—N10—C11	108.76 (10)	C109—N110—C111	108.28 (11)
C9—N10—C13	125.23 (11)	C109—N110—C113	125.98 (11)
C11—N10—C13	125.92 (11)	C111—N110—C113	125.73 (11)
C12—C11—N10	107.03 (11)	C112—C111—N110	107.46 (12)
C12—C11—H11	126.5	C112—C111—H111	126.3
N10—C11—H11	126.5	N110—C111—H111	126.3
C11—C12—N8	107.21 (11)	C111—C112—N108	107.08 (12)
C11—C12—H12	126.4	C111—C112—H112	126.5
N8—C12—H12	126.4	N108—C112—H112	126.5
N10—C13—C14	111.14 (11)	N110—C113—C114	112.72 (11)
N10—C13—H13A	109.4	N110—C113—H11A	109.0
C14—C13—H13A	109.4	C114—C113—H11A	109.0
N10—C13—H13B	109.4	N110—C113—H11B	109.0
C14—C13—H13B	109.4	C114—C113—H11B	109.0
H13A—C13—H13B	108.0	H11A—C113—H11B	107.8
C15—C14—C13	113.35 (12)	C113—C114—C115	111.47 (11)
C15—C14—H14A	108.9	C113—C114—H11C	109.3
C13—C14—H14A	108.9	C115—C114—H11C	109.3
C15—C14—H14B	108.9	C113—C114—H11D	109.3
C13—C14—H14B	108.9	C115—C114—H11D	109.3
H14A—C14—H14B	107.7	H11C—C114—H11D	108.0
C16—C15—C14	113.24 (14)	C116—C115—C114	111.30 (12)
C16—C15—H15A	108.9	C116—C115—H11E	109.4
C14—C15—H15A	108.9	C114—C115—H11E	109.4
C16—C15—H15B	108.9	C116—C115—H11F	109.4
C14—C15—H15B	108.9	C114—C115—H11F	109.4
H15A—C15—H15B	107.7	H11E—C115—H11F	108.0
C15—C16—H16A	109.5	C115—C116—H11G	109.5
C15—C16—H16B	109.5	C115—C116—H11H	109.5
H16A—C16—H16B	109.5	H11G—C116—H11H	109.5
C15—C16—H16C	109.5	C115—C116—H11I	109.5
H16A—C16—H16C	109.5	H11G—C116—H11I	109.5
H16B—C16—H16C	109.5	H11H—C116—H11I	109.5
O1—B1—C29	107.62 (9)	O101—B101—C123	105.91 (10)
O1—B1—C17	112.56 (10)	O101—B101—C129	114.77 (10)
C29—B1—C17	113.91 (10)	C123—B101—C129	116.26 (10)
O1—B1—C23	105.02 (9)	O101—B101—C117	104.49 (9)

C29—B1—C23	113.82 (10)	C123—B101—C117	113.14 (10)
C17—B1—C23	103.62 (9)	C129—B101—C117	101.82 (9)
C18—C17—C22	113.82 (11)	C118—C117—C122	113.54 (11)
C18—C17—B1	127.12 (11)	C118—C117—B101	126.42 (11)
C22—C17—B1	118.82 (10)	C122—C117—B101	119.70 (10)
F18—C18—C17	120.92 (11)	F118—C118—C119	114.97 (11)
F18—C18—C19	115.46 (11)	F118—C118—C117	120.66 (11)
C17—C18—C19	123.62 (12)	C119—C118—C117	124.38 (12)
F19—C19—C20	119.06 (12)	F119—C119—C120	119.84 (11)
F19—C19—C18	121.27 (12)	F119—C119—C118	120.80 (12)
C20—C19—C18	119.66 (12)	C120—C119—C118	119.36 (12)
F20—C20—C21	120.42 (12)	F120—C120—C121	120.67 (12)
F20—C20—C19	120.17 (12)	F120—C120—C119	120.34 (12)
C21—C20—C19	119.40 (12)	C121—C120—C119	118.99 (11)
F21—C21—C20	119.85 (12)	F121—C121—C120	119.67 (11)
F21—C21—C22	121.34 (12)	F121—C121—C122	120.45 (12)
C20—C21—C22	118.80 (12)	C120—C121—C122	119.87 (12)
F22—C22—C21	116.51 (11)	F122—C122—C121	115.62 (11)
F22—C22—C17	118.81 (11)	F122—C122—C117	120.49 (11)
C21—C22—C17	124.68 (12)	C121—C122—C117	123.86 (11)
C28—C23—C24	113.76 (11)	C124—C123—C128	113.40 (11)
C28—C23—B1	127.04 (11)	C124—C123—B101	127.71 (11)
C24—C23—B1	118.96 (10)	C128—C123—B101	118.63 (10)
F24—C24—C25	115.83 (11)	F124—C124—C123	121.06 (11)
F24—C24—C23	120.15 (10)	F124—C124—C125	115.52 (11)
C25—C24—C23	123.97 (12)	C123—C124—C125	123.42 (12)
F25—C25—C26	119.58 (11)	F125—C125—C126	118.97 (11)
F25—C25—C24	120.92 (12)	F125—C125—C124	120.70 (12)
C26—C25—C24	119.46 (12)	C126—C125—C124	120.33 (11)
F26—C26—C27	120.39 (12)	F126—C126—C125	120.01 (11)
F26—C26—C25	120.39 (12)	F126—C126—C127	121.09 (12)
C27—C26—C25	119.17 (12)	C125—C126—C127	118.90 (11)
F27—C27—C26	119.66 (12)	F127—C127—C126	120.52 (11)
F27—C27—C28	120.83 (12)	F127—C127—C128	120.71 (12)
C26—C27—C28	119.45 (12)	C126—C127—C128	118.77 (12)
F28—C28—C27	114.83 (11)	F128—C128—C127	115.13 (11)
F28—C28—C23	120.94 (11)	F128—C128—C123	119.69 (11)
C27—C28—C23	124.19 (12)	C127—C128—C123	125.18 (12)

C34—C29—C30	114.09 (12)	C130—C129—C134	113.47 (11)
C34—C29—B1	125.78 (12)	C130—C129—B101	125.47 (11)
C30—C29—B1	119.59 (11)	C134—C129—B101	119.98 (11)
F30—C30—C31	115.94 (12)	F130—C130—C131	115.17 (11)
F30—C30—C29	119.81 (11)	F130—C130—C129	121.11 (11)
C31—C30—C29	124.25 (13)	C131—C130—C129	123.72 (12)
F31—C31—C32	120.01 (13)	F131—C131—C132	119.54 (12)
F31—C31—C30	121.21 (14)	F131—C131—C130	120.30 (12)
C32—C31—C30	118.78 (14)	C132—C131—C130	120.15 (12)
F32—C32—C33	120.43 (15)	F132—C132—C131	120.33 (13)
F32—C32—C31	119.88 (16)	F132—C132—C133	121.05 (13)
C33—C32—C31	119.69 (13)	C131—C132—C133	118.61 (12)
F33—C33—C32	119.83 (13)	F133—C133—C134	120.72 (13)
F33—C33—C34	120.66 (15)	F133—C133—C132	119.87 (12)
C32—C33—C34	119.51 (13)	C134—C133—C132	119.40 (12)
F34—C34—C29	120.92 (12)	F134—C134—C133	116.44 (11)
F34—C34—C33	115.58 (12)	F134—C134—C129	118.91 (11)
C29—C34—C33	123.47 (14)	C133—C134—C129	124.64 (12)
B1—O1—C2—C3	49.43 (17)	B101—O101—C102—C103	-15.29 (18)
B1—O1—C2—C7	-133.19 (12)	B101—O101—C102—C107	166.62 (11)
O1—C2—C3—C4	179.07 (11)	O101—C102—C103—C104	-177.50 (11)
C7—C2—C3—C4	1.68 (18)	C107—C102—C103—C104	0.57 (18)
C2—C3—C4—C5	-1.5 (2)	C102—C103—C104—C105	0.1 (2)
C3—C4—C5—C6	0.1 (2)	C103—C104—C105—C106	-1.0 (2)
C4—C5—C6—C7	1.1 (2)	C104—C105—C106—C107	1.3 (2)
C5—C6—C7—C2	-0.9 (2)	C105—C106—C107—C102	-0.69 (19)
C5—C6—C7—N8	178.02 (12)	C105—C106—C107—N108	177.60 (11)
O1—C2—C7—C6	-178.07 (11)	O101—C102—C107—C106	177.99 (11)
C3—C2—C7—C6	-0.48 (18)	C103—C102—C107—C106	-0.26 (18)
O1—C2—C7—N8	2.99 (16)	O101—C102—C107—N108	-0.33 (16)
C3—C2—C7—N8	-179.42 (10)	C103—C102—C107—N108	-178.58 (10)
C6—C7—N8—C9	-53.26 (17)	C106—C107—N108—C109	133.25 (13)
C2—C7—N8—C9	125.71 (13)	C102—C107—N108—C109	-48.39 (17)
C6—C7—N8—C12	127.51 (13)	C106—C107—N108—C112	-54.25 (17)
C2—C7—N8—C12	-53.52 (16)	C102—C107—N108—C112	124.12 (13)
C12—N8—C9—N10	-0.49 (14)	C112—N108—C109—N110	0.24 (14)
C7—N8—C9—N10	-179.83 (11)	C107—N108—C109—N110	173.89 (11)
N8—C9—N10—C11	0.24 (14)	N108—C109—N110—C111	-0.22 (15)

N8—C9—N10—C13	176.95 (12)	N108—C109—N110—C113	178.74 (12)
C9—N10—C11—C12	0.10 (15)	C109—N110—C111—C112	0.12 (16)
C13—N10—C11—C12	-176.58 (12)	C113—N110—C111—C112	-178.85 (12)
N10—C11—C12—N8	-0.39 (14)	N110—C111—C112—N108	0.03 (16)
C9—N8—C12—C11	0.54 (14)	C109—N108—C112—C111	-0.16 (15)
C7—N8—C12—C11	179.88 (11)	C107—N108—C112—C111	-173.71 (12)
C9—N10—C13—C14	-122.66 (14)	C109—N110—C113—C114	27.13 (19)
C11—N10—C13—C14	53.49 (18)	C111—N110—C113—C114	-154.08 (13)
N10—C13—C14—C15	55.99 (17)	N110—C113—C114—C115	178.52 (11)
C13—C14—C15—C16	164.56 (14)	C113—C114—C115—C116	-176.93 (12)
C2—O1—B1—C29	20.11 (15)	C102—O101—B101—C123	-59.09 (14)
C2—O1—B1—C17	-106.23 (12)	C102—O101—B101—C129	70.57 (14)
C2—O1—B1—C23	141.72 (10)	C102—O101—B101—C117	-178.80 (10)
O1—B1—C17—C18	5.19 (17)	O101—B101—C117—C118	141.25 (12)
C29—B1—C17—C18	-117.69 (13)	C123—B101—C117—C118	26.52 (17)
C23—B1—C17—C18	118.11 (13)	C129—B101—C117—C118	-99.00 (13)
O1—B1—C17—C22	-168.76 (10)	O101—B101—C117—C122	-45.89 (14)
C29—B1—C17—C22	68.36 (14)	C123—B101—C117—C122	-160.62 (11)
C23—B1—C17—C22	-55.84 (13)	C129—B101—C117—C122	73.86 (13)
C22—C17—C18—F18	-178.31 (11)	C122—C117—C118—F118	179.97 (11)
B1—C17—C18—F18	7.47 (19)	B101—C117—C118—F118	-6.79 (19)
C22—C17—C18—C19	0.90 (19)	C122—C117—C118—C119	-0.09 (18)
B1—C17—C18—C19	-173.32 (12)	B101—C117—C118—C119	173.15 (12)
F18—C18—C19—F19	0.81 (19)	F118—C118—C119—F119	-0.76 (17)
C17—C18—C19—F19	-178.44 (12)	C117—C118—C119—F119	179.29 (11)
F18—C18—C19—C20	179.62 (12)	F118—C118—C119—C120	179.17 (11)
C17—C18—C19—C20	0.4 (2)	C117—C118—C119—C120	-0.8 (2)
F19—C19—C20—F20	-1.21 (19)	F119—C119—C120—F120	1.72 (19)
C18—C19—C20—F20	179.96 (12)	C118—C119—C120—F120	-178.21 (11)
F19—C19—C20—C21	177.65 (12)	F119—C119—C120—C121	-178.99 (11)
C18—C19—C20—C21	-1.2 (2)	C118—C119—C120—C121	1.08 (19)
F20—C20—C21—F21	-0.3 (2)	F120—C120—C121—F121	0.33 (19)
C19—C20—C21—F21	-179.14 (12)	C119—C120—C121—F121	-178.95 (11)
F20—C20—C21—C22	179.52 (12)	F120—C120—C121—C122	178.74 (11)
C19—C20—C21—C22	0.7 (2)	C119—C120—C121—C122	-0.54 (19)
F21—C21—C22—F22	0.46 (19)	F121—C121—C122—F122	-0.09 (17)
C20—C21—C22—F22	-179.35 (11)	C120—C121—C122—F122	-178.49 (11)
F21—C21—C22—C17	-179.47 (12)	F121—C121—C122—C117	178.03 (11)

C20—C21—C22—C17	0.7 (2)	C120—C121—C122—C117	-0.36 (19)
C18—C17—C22—F22	178.61 (11)	C118—C117—C122—F122	178.69 (11)
B1—C17—C22—F22	-6.66 (17)	B101—C117—C122—F122	4.96 (17)
C18—C17—C22—C21	-1.46 (19)	C118—C117—C122—C121	0.66 (18)
B1—C17—C22—C21	173.27 (12)	B101—C117—C122—C121	-173.08 (11)
O1—B1—C23—C28	-137.47 (12)	O101—B101—C123—C124	110.26 (13)
C29—B1—C23—C28	-20.01 (17)	C129—B101—C123—C124	-18.53 (18)
C17—B1—C23—C28	104.25 (13)	C117—B101—C123—C124	-135.87 (13)
O1—B1—C23—C24	48.58 (14)	O101—B101—C123—C128	-63.49 (14)
C29—B1—C23—C24	166.04 (10)	C129—B101—C123—C128	167.72 (11)
C17—B1—C23—C24	-69.70 (13)	C117—B101—C123—C128	50.38 (15)
C28—C23—C24—F24	-176.93 (10)	C128—C123—C124—F124	178.50 (11)
B1—C23—C24—F24	-2.21 (16)	B101—C123—C124—F124	4.47 (19)
C28—C23—C24—C25	0.40 (18)	C128—C123—C124—C125	-0.69 (18)
B1—C23—C24—C25	175.12 (11)	B101—C123—C124—C125	-174.71 (12)
F24—C24—C25—F25	0.10 (17)	F124—C124—C125—F125	1.41 (17)
C23—C24—C25—F25	-177.33 (11)	C123—C124—C125—F125	-179.37 (11)
F24—C24—C25—C26	177.87 (11)	F124—C124—C125—C126	-178.97 (11)
C23—C24—C25—C26	0.4 (2)	C123—C124—C125—C126	0.3 (2)
F25—C25—C26—F26	-0.11 (19)	F125—C125—C126—F126	-0.99 (18)
C24—C25—C26—F26	-177.91 (12)	C124—C125—C126—F126	179.37 (11)
F25—C25—C26—C27	177.18 (12)	F125—C125—C126—C127	179.31 (11)
C24—C25—C26—C27	-0.6 (2)	C124—C125—C126—C127	-0.32 (19)
F26—C26—C27—F27	0.1 (2)	F126—C126—C127—F127	1.3 (2)
C25—C26—C27—F27	-177.18 (12)	C125—C126—C127—F127	-179.01 (12)
F26—C26—C27—C28	177.26 (12)	F126—C126—C127—C128	-178.83 (12)
C25—C26—C27—C28	0.0 (2)	C125—C126—C127—C128	0.87 (19)
F27—C27—C28—F28	0.36 (18)	F127—C127—C128—F128	-0.98 (18)
C26—C27—C28—F28	-176.76 (11)	C126—C127—C128—F128	179.15 (11)
F27—C27—C28—C23	178.08 (11)	F127—C127—C128—C123	178.43 (12)
C26—C27—C28—C23	1.0 (2)	C126—C127—C128—C123	-1.4 (2)
C24—C23—C28—F28	176.48 (10)	C124—C123—C128—F128	-179.31 (11)
B1—C23—C28—F28	2.26 (18)	B101—C123—C128—F128	-4.70 (17)
C24—C23—C28—C27	-1.10 (18)	C124—C123—C128—C127	1.30 (19)
B1—C23—C28—C27	-175.31 (12)	B101—C123—C128—C127	175.92 (12)
O1—B1—C29—C34	-104.29 (13)	O101—B101—C129—C130	12.69 (17)
C17—B1—C29—C34	21.26 (17)	C123—B101—C129—C130	137.04 (12)
C23—B1—C29—C34	139.77 (12)	C117—B101—C129—C130	-99.52 (13)

O1—B1—C29—C30	66.82 (14)	O101—B101—C129—C134	179.97 (10)
C17—B1—C29—C30	-167.64 (11)	C123—B101—C129—C134	-55.68 (15)
C23—B1—C29—C30	-49.13 (15)	C117—B101—C129—C134	67.75 (13)
C34—C29—C30—F30	175.40 (11)	C134—C129—C130—F130	-178.85 (10)
B1—C29—C30—F30	3.30 (17)	B101—C129—C130—F130	-10.86 (18)
C34—C29—C30—C31	-4.23 (19)	C134—C129—C130—C131	0.64 (17)
B1—C29—C30—C31	-176.33 (12)	B101—C129—C130—C131	168.63 (11)
F30—C30—C31—F31	5.0 (2)	F130—C130—C131—F131	-0.89 (17)
C29—C30—C31—F31	-175.37 (12)	C129—C130—C131—F131	179.59 (11)
F30—C30—C31—C32	-174.60 (12)	F130—C130—C131—C132	178.47 (11)
C29—C30—C31—C32	5.0 (2)	C129—C130—C131—C132	-1.05 (19)
F31—C31—C32—F32	-0.6 (2)	F131—C131—C132—F132	0.08 (19)
C30—C31—C32—F32	179.03 (13)	C130—C131—C132—F132	-179.29 (11)
F31—C31—C32—C33	178.77 (13)	F131—C131—C132—C133	-179.96 (12)
C30—C31—C32—C33	-1.6 (2)	C130—C131—C132—C133	0.67 (19)
F32—C32—C33—F33	-2.5 (2)	F132—C132—C133—F133	0.82 (19)
C31—C32—C33—F33	178.22 (13)	C131—C132—C133—F133	-179.14 (12)
F32—C32—C33—C34	177.27 (13)	F132—C132—C133—C134	179.98 (12)
C31—C32—C33—C34	-2.1 (2)	C131—C132—C133—C134	0.02 (19)
C30—C29—C34—F34	-177.42 (11)	F133—C133—C134—F134	0.37 (18)
B1—C29—C34—F34	-5.89 (19)	C132—C133—C134—F134	-178.78 (11)
C30—C29—C34—C33	0.24 (19)	F133—C133—C134—C129	178.73 (12)
B1—C29—C34—C33	171.77 (12)	C132—C133—C134—C129	-0.4 (2)
F33—C33—C34—F34	0.31 (18)	C130—C129—C134—F134	178.43 (10)
C32—C33—C34—F34	-179.41 (12)	B101—C129—C134—F134	9.70 (17)
F33—C33—C34—C29	-177.46 (12)	C130—C129—C134—C133	0.09 (18)
C32—C33—C34—C29	2.8 (2)	B101—C129—C134—C133	-168.63 (12)

Table 27: Selected hydrogen-bond lengths (pm) and bond angles (°) for **74b**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···F20^{i}	0.95	2.57	3.4604 (15)	155
C9—H9···F28^{ii}	0.95	2.36	3.2768 (14)	162
C11—H11···F26^{iii}	0.95	2.54	3.4188 (15)	154
C11—H11···F32^{iv}	0.95	2.57	3.1986 (15)	124
C13—H13*A*···F32^{iv}	0.99	2.62	3.2586 (18)	122
C14—H14*A*···F33^{ii}	0.99	2.49	3.4032 (17)	153
C103—H103···F124	0.95	2.57	3.4192 (16)	148

C109—H109···F128	0.95	2.33	3.2231 (15)	157
C111—H111···F125^{v}	0.95	2.48	3.3605 (15)	153
C112—H112···F18^{vi}	0.95	2.41	3.2010 (16)	141
C113—H11*A*···F125^{vii}	0.99	2.50	3.2834 (16)	135
C114—H11*D*···F128	0.99	2.55	3.2490 (14)	128
C114—H11*D*···F134^{vii}	099	2.63	3.5152 (15)	148

6.9 Crystal structure determination of 1-benzyl-3-(2hydroxyphenyl)-1,3-dihydro-2*H*-imidazole-2-thione 76d

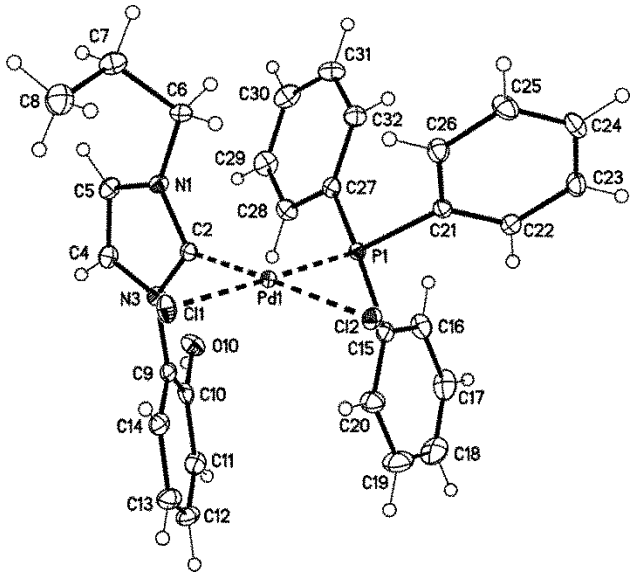


Figure 28. X-ray structure of molecule **76d**.

Table 18: Crystallography data and refinement details for **76d**.

$C_{30}H_{29}Br_{0.12}Cl_{1.88}N_2OPPd$	$F(000)$ = 1313
M_r = 647.38	D_x = 1.570 Mg m^{-3}
Monoclinic, $P2_1/n$ *(no.14)*	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 11.4229 (7) Å	Cell parameters from 9916 reflections
b = 17.2889 (10) Å	θ = 2.4–27.5°
c = 14.0836 (9) Å	μ = 1.13 mm^{-1}

β = 99.959 (2)°	*T* = 123 K
V = 2739.5 (3) Å^3	Plates, yellow
Z = 4	0.22 × 0.12 × 0.08 mm
Refinement on F2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
R[F2 > 2□(F2)] = 0.022	Hydrogen site location: difference Fourier map
wR(F2) = 0.058	H atoms treated by a mixture of independent and constrained refinement
S = 1.06	w = 1/[σ2(Fo2) + (0.0259P)2 + 2.7323P] where P = (Fo2 + 2Fc2)/3
6315 reflections	(Δ/σ)max = 0.002
341 parameters	Δ⟩max = 0.61 e Å-3
1 restraint	Δ⟩min = -0.77 e Å-3

Table 19: Bond length (pm) data for **76d**.

Pd1—C2	1.9989 (16)	P1—C21	1.8179 (17)
Pd1—P1	2.2455 (4)	P1—C27	1.8249 (17)
Pd1—Cl2	2.3599 (4)	C15—C20	1.394 (2)
Pd1—Cl1	2.380 (5)	C15—C16	1.399 (2)
Pd1—Br1	2.509 (15)	C16—C17	1.388 (3)
N1—C2	1.347 (2)	C16—H16	0.9500
N1—C5	1.387 (2)	C17—C18	1.384 (3)
N1—C6	1.466 (2)	C17—H17	0.9500
C2—N3	1.361 (2)	C18—C19	1.384 (3)
N3—C4	1.393 (2)	C18—H18	0.9500
N3—C9	1.435 (2)	C19—C20	1.389 (3)
C4—C5	1.340 (2)	C19—H19	0.9500
C4—H4	0.9500	C20—H20	0.9500
C5—H5	0.9500	C21—C22	1.393 (2)

C6—C7	1.518 (2)	C21—C26	1.397 (2)
C6—H6A	0.9900	C22—C23	1.391 (2)
C6—H6B	0.9900	C22—H22	0.9500
C7—C8	1.512 (3)	C23—C24	1.384 (3)
C7—H7A	0.9900	C23—H23	0.9500
C7—H7B	0.9900	C24—C25	1.392 (3)
C8—H8A	0.9800	C24—H24	0.9500
C8—H8B	0.9800	C25—C26	1.385 (2)
C8—H8C	0.9800	C25—H25	0.9500
C9—C14	1.385 (2)	C26—H26	0.9500
C9—C10	1.401 (2)	C27—C32	1.395 (2)
O10—C10	1.360 (2)	C27—C28	1.398 (2)
O10—H10	0.812 (16)	C28—C29	1.389 (2)
C10—C11	1.387 (2)	C28—H28	0.9500
C11—C12	1.386 (3)	C29—C30	1.390 (3)
C11—H11	0.9500	C29—H29	0.9500
C12—C13	1.386 (3)	C30—C31	1.382 (3)
C12—H12	0.9500	C30—H30	0.9500
C13—C14	1.394 (2)	C31—C32	1.392 (3)
C13—H13	0.9500	C31—H31	0.9500
C14—H14	0.9500	C32—H32	0.9500
P1—C15	1.8108 (17)		
C2—Pd1—P1	91.22 (5)	C15—P1—C21	106.74 (8)
C2—Pd1—Cl2	177.48 (5)	C15—P1—C27	106.06 (8)
P1—Pd1—Cl2	87.695 (15)	C21—P1—C27	102.18 (8)
C2—Pd1—Cl1	90.10 (17)	C15—P1—Pd1	110.86 (6)
P1—Pd1—Cl1	178.06 (16)	C21—P1—Pd1	113.21 (6)
Cl2—Pd1—Cl1	91.05 (16)	C27—P1—Pd1	116.92 (5)
C2—Pd1—Br1	90.6 (5)	C20—C15—C16	119.10 (16)

P1—Pd1—Br1	178.0 (5)	C20—C15—P1	119.26 (13)
Cl2—Pd1—Br1	90.6 (5)	C16—C15—P1	121.54 (14)
C2—N1—C5	110.75 (14)	C17—C16—C15	120.23 (18)
C2—N1—C6	124.96 (14)	C17—C16—H16	119.9
C5—N1—C6	124.12 (14)	C15—C16—H16	119.9
N1—C2—N3	105.09 (14)	C18—C17—C16	120.20 (18)
N1—C2—Pd1	126.50 (12)	C18—C17—H17	119.9
N3—C2—Pd1	128.41 (12)	C16—C17—H17	119.9
C2—N3—C4	110.29 (14)	C19—C18—C17	119.91 (18)
C2—N3—C9	126.51 (14)	C19—C18—H18	120.0
C4—N3—C9	123.21 (14)	C17—C18—H18	120.0
C5—C4—N3	106.70 (15)	C18—C19—C20	120.39 (19)
C5—C4—H4	126.7	C18—C19—H19	119.8
N3—C4—H4	126.7	C20—C19—H19	119.8
C4—C5—N1	107.17 (15)	C19—C20—C15	120.16 (18)
C4—C5—H5	126.4	C19—C20—H20	119.9
N1—C5—H5	126.4	C15—C20—H20	119.9
N1—C6—C7	113.41 (15)	C22—C21—C26	119.57 (16)
N1—C6—H6A	108.9	C22—C21—P1	121.01 (13)
C7—C6—H6A	108.9	C26—C21—P1	119.13 (13)
N1—C6—H6B	108.9	C23—C22—C21	119.99 (16)
C7—C6—H6B	108.9	C23—C22—H22	120.0
H6A—C6—H6B	107.7	C21—C22—H22	120.0
C8—C7—C6	114.60 (16)	C24—C23—C22	120.28 (16)
C8—C7—H7A	108.6	C24—C23—H23	119.9
C6—C7—H7A	108.6	C22—C23—H23	119.9
C8—C7—H7B	108.6	C23—C24—C25	119.90 (16)
C6—C7—H7B	108.6	C23—C24—H24	120.0
H7A—C7—H7B	107.6	C25—C24—H24	120.0

C7—C8—H8A	109.5	C26—C25—C24	120.16 (17)
C7—C8—H8B	109.5	C26—C25—H25	119.9
H8A—C8—H8B	109.5	C24—C25—H25	119.9
C7—C8—H8C	109.5	C25—C26—C21	120.07 (16)
H8A—C8—H8C	109.5	C25—C26—H26	120.0
H8B—C8—H8C	109.5	C21—C26—H26	120.0
C14—C9—C10	120.69 (16)	C32—C27—C28	119.38 (16)
C14—C9—N3	120.46 (15)	C32—C27—P1	120.99 (13)
C10—C9—N3	118.78 (15)	C28—C27—P1	119.54 (13)
C10—O10—H10	109.0 (17)	C29—C28—C27	119.85 (17)
O10—C10—C11	122.00 (16)	C29—C28—H28	120.1
O10—C10—C9	119.06 (15)	C27—C28—H28	120.1
C11—C10—C9	118.93 (17)	C28—C29—C30	120.40 (17)
C12—C11—C10	120.42 (17)	C28—C29—H29	119.8
C12—C11—H11	119.8	C30—C29—H29	119.8
C10—C11—H11	119.8	C31—C30—C29	119.97 (17)
C13—C12—C11	120.55 (17)	C31—C30—H30	120.0
C13—C12—H12	119.7	C29—C30—H30	120.0
C11—C12—H12	119.7	C30—C31—C32	120.09 (17)
C12—C13—C14	119.59 (17)	C30—C31—H31	120.0
C12—C13—H13	120.2	C32—C31—H31	120.0
C14—C13—H13	120.2	C31—C32—C27	120.29 (17)
C9—C14—C13	119.81 (16)	C31—C32—H32	119.9
C9—C14—H14	120.1	C27—C32—H32	119.9
C13—C14—H14	120.1		
C5—N1—C2—N3	-0.20 (18)	C21—P1—C15—C20	105.04 (15)
C6—N1—C2—N3	-175.77 (15)	C27—P1—C15—C20	-146.55 (14)
C5—N1—C2—Pd1	-179.77 (12)	Pd1—P1—C15—C20	-18.67 (16)
C6—N1—C2—Pd1	4.7 (2)	C21—P1—C15—C16	-71.17 (16)

P1—Pd1—C2—N1	-89.24 (14)	C27—P1—C15—C16	37.24 (16)
Cl1—Pd1—C2—N1	89.3 (2)	Pd1—P1—C15—C16	165.12 (13)
Br1—Pd1—C2—N1	89.8 (5)	C20—C15—C16—C17	-1.6 (3)
P1—Pd1—C2—N3	91.29 (14)	P1—C15—C16—C17	174.62 (14)
Cl1—Pd1—C2—N3	-90.1 (2)	C15—C16—C17—C18	0.8 (3)
Br1—Pd1—C2—N3	-89.6 (5)	C16—C17—C18—C19	0.5 (3)
N1—C2—N3—C4	0.08 (18)	C17—C18—C19—C20	-1.0 (3)
Pd1—C2—N3—C4	179.64 (12)	C18—C19—C20—C15	0.1 (3)
N1—C2—N3—C9	-179.21 (15)	C16—C15—C20—C19	1.2 (3)
Pd1—C2—N3—C9	0.3 (2)	P1—C15—C20—C19	-175.14 (15)
C2—N3—C4—C5	0.07 (19)	C15—P1—C21—C22	22.54 (16)
C9—N3—C4—C5	179.39 (15)	C27—P1—C21—C22	-88.59 (15)
N3—C4—C5—N1	-0.18 (19)	Pd1—P1—C21—C22	144.78 (12)
C2—N1—C5—C4	0.2 (2)	C15—P1—C21—C26	-163.77 (14)
C6—N1—C5—C4	175.86 (15)	C27—P1—C21—C26	85.10 (15)
C2—N1—C6—C7	-132.34 (17)	Pd1—P1—C21—C26	-41.53 (15)
C5—N1—C6—C7	52.7 (2)	C26—C21—C22—C23	-1.0 (3)
N1—C6—C7—C8	61.4 (2)	P1—C21—C22—C23	172.70 (13)
C2—N3—C9—C14	55.3 (2)	C21—C22—C23—C24	-0.5 (3)
C4—N3—C9—C14	-123.92 (18)	C22—C23—C24—C25	1.3 (3)
C2—N3—C9—C10	-127.75 (17)	C23—C24—C25—C26	-0.6 (3)
C4—N3—C9—C10	53.0 (2)	C24—C25—C26—C21	-0.8 (3)
C14—C9—C10—O10	179.63 (16)	C22—C21—C26—C25	1.6 (3)
N3—C9—C10—O10	2.7 (2)	P1—C21—C26—C25	-172.16 (14)
C14—C9—C10—C11	-1.3 (2)	C15—P1—C27—C32	-133.87 (14)
N3—C9—C10—C11	-178.30 (15)	C21—P1—C27—C32	-22.23 (16)
O10—C10—C11—C12	-179.97 (16)	Pd1—P1—C27—C32	101.94 (14)
C9—C10—C11—C12	1.0 (3)	C15—P1—C27—C28	49.67 (16)
C10—C11—C12—C13	-0.1 (3)	C21—P1—C27—C28	161.31 (14)

C11—C12—C13—C14	-0.5 (3)	Pd1—P1—C27—C28	-74.52 (15)
C10—C9—C14—C13	0.7 (3)	C32—C27—C28—C29	-1.4 (3)
N3—C9—C14—C13	177.63 (15)	P1—C27—C28—C29	175.08 (14)
C12—C13—C14—C9	0.2 (3)	C27—C28—C29—C30	0.7 (3)
C2—Pd1—P1—C15	-96.03 (8)	C28—C29—C30—C31	0.7 (3)
Cl2—Pd1—P1—C15	81.69 (6)	C29—C30—C31—C32	-1.2 (3)
C2—Pd1—P1—C21	144.05 (7)	C30—C31—C32—C27	0.4 (3)
Cl2—Pd1—P1—C21	-38.23 (6)	C28—C27—C32—C31	0.9 (3)
C2—Pd1—P1—C27	25.68 (8)	P1—C27—C32—C31	-175.57 (14)
Cl2—Pd1—P1—C27	-156.60 (6)		

Table 20: Selected hydrogen-bond lengths (pm) and bond angles (°) for **72d**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···Cl2^{i}	0.95	2.98	3.8636 (18)	155
C5—H5···Cl2^{ii}	0.95	2.96	3.6582 (18)	131
C7—H7*B*···Br1^{ii}	0.99	3.09	3.89 (2)	138
C7—H7*B*···Cl2^{ii}	0.99	2.83	3.549 (2)	130
O10—H10···Cl1^{i}	0.81 (2)	2.43 (2)	3.238 (7)	174 (2)
O10—H10···Br1^{i}	0.81 (2)	2.42 (3)	3.23 (2)	174 (2)
C11—H11···Cl1^{i}	0.95	2.88	3.589 (7)	133
C11—H11···Br1^{i}	0.95	2.92	3.64 (2)	133
C14—H14···Cl1	0.95	2.79	3.653 (7)	151
C14—H14···Br1	0.95	2.82	3.70 (2)	154
C22—H22···Cl1^{iii}	0.95	2.94	3.649 (6)	133
C22—H22···Br1^{iii}	0.95	2.86	3.590 (19)	134
C28—H28···O10	0.95	2.46	3.330 (2)	152

6.10 Crystal structure determination of mono(bis(3-butyl-1-(2-hydroxyphenyl)-1*H*-imidazolium-2-yl)gold) monochloride 77

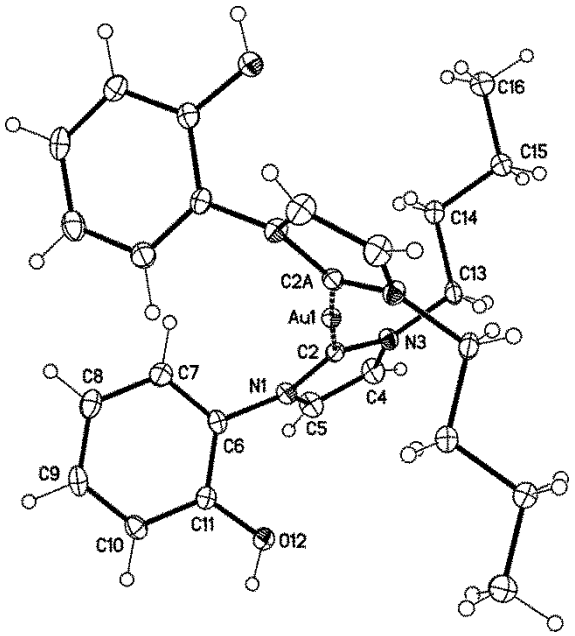


Figure 32. X-ray structure of molecule **77**.

Table 28: Crystallography data and refinement details for **77**.

$C_{26}H_{32}AuN_4O_2 \cdot 0.19(Br) \cdot 0.81(Cl)$	$F(000) = 1326$
$M_r = 673.42$	$D_x = 1.794$ Mg m^{-3}
Monoclinic, *C2/c (no.15)*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 15.0275$ (9) Å	Cell parameters from 9839 reflections
$b = 13.1392$ (7) Å	$\theta = 2.5–27.4°$
$c = 13.0205$ (7) Å	$\mu = 6.32$ mm^{-1}
$\beta = 104.161$ (2)°	$T = 123$ K
$V = 2492.8$ (2) Å^3	Blocks, colourless
$Z = 4$	0.24 × 0.12 × 0.06 mm
Refinement on F2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
R[F2 > 2σ(F2)] = 0.011	H atoms treated by a mixture of independent and constrained refinement
wR(F2) = 0.026	w = 1/[σ2(Fo2) + (0.0138P)2 + 2.5143P] where P = (Fo2 + 2Fc2)/3
S = 1.10	(Δ/σ)max = 0.002

2867 reflections	Δ⟩max = 0.40 e Å-3
162 parameters	Δ⟩min = -0.49 e Å-3
0 restraints	Extinction correction: SHELXL2014/7 (Sheldrick 2014), Fc*=kFc[1+0.001xFc2λ3/sin(2θ)]-1/4
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.00089 (5)

Table 29: Bond length (pm) data for **77.**

Au1—C2	2.0211 (15)	C9—H9	0.9500
Au1—C2^{i}	2.0211 (15)	C10—C11	1.395 (2)
N1—C2	1.3574 (18)	C10—H10	0.9500
N1—C5	1.3881 (19)	C11—O12	1.3572 (18)
N1—C6	1.4356 (18)	O12—H12	0.85 (3)
C2—N3	1.3476 (19)	C13—C14	1.519 (2)
N3—C4	1.3821 (19)	C13—H13A	0.9900
N3—C13	1.4735 (19)	C13—H13B	0.9900
C4—C5	1.345 (2)	C14—C15	1.522 (2)
C4—H4	0.9500	C14—H14A	0.9900
C5—H5	0.9500	C14—H14B	0.9900
C6—C7	1.385 (2)	C15—C16	1.524 (2)
C6—C11	1.397 (2)	C15—H15A	0.9900
C7—C8	1.391 (2)	C15—H15B	0.9900
C7—H7	0.9500	C16—H16A	0.9800
C8—C9	1.389 (2)	C16—H16B	0.9800
C8—H8	0.9500	C16—H16C	0.9800
C9—C10	1.388 (2)		
C2—Au1—C2^{i}	177.35 (8)	C11—C10—H10	120.1
C2—N1—C5	110.72 (12)	O12—C11—C10	123.59 (14)
C2—N1—C6	126.21 (12)	O12—C11—C6	117.36 (13)
C5—N1—C6	123.07 (12)	C10—C11—C6	119.06 (14)
N3—C2—N1	104.61 (12)	C11—O12—H12	110.7 (17)
N3—C2—Au1	126.89 (10)	N3—C13—C14	112.21 (12)
N1—C2—Au1	128.46 (10)	N3—C13—H13A	109.2
C2—N3—C4	111.30 (13)	C14—C13—H13A	109.2
C2—N3—C13	125.69 (12)	N3—C13—H13B	109.2
C4—N3—C13	122.95 (12)	C14—C13—H13B	109.2
C5—C4—N3	106.72 (13)	H13A—C13—H13B	107.9

C5—C4—H4	126.6	C13—C14—C15	112.03 (13)
N3—C4—H4	126.6	C13—C14—H14A	109.2
C4—C5—N1	106.64 (13)	C15—C14—H14A	109.2
C4—C5—H5	126.7	C13—C14—H14B	109.2
N1—C5—H5	126.7	C15—C14—H14B	109.2
C7—C6—C11	120.88 (14)	H14A—C14—H14B	107.9
C7—C6—N1	120.98 (13)	C14—C15—C16	111.81 (13)
C11—C6—N1	118.10 (13)	C14—C15—H15A	109.3
C6—C7—C8	119.74 (15)	C16—C15—H15A	109.3
C6—C7—H7	120.1	C14—C15—H15B	109.3
C8—C7—H7	120.1	C16—C15—H15B	109.3
C9—C8—C7	119.66 (15)	H15A—C15—H15B	107.9
C9—C8—H8	120.2	C15—C16—H16A	109.5
C7—C8—H8	120.2	C15—C16—H16B	109.5
C10—C9—C8	120.71 (15)	H16A—C16—H16B	109.5
C10—C9—H9	119.6	C15—C16—H16C	109.5
C8—C9—H9	119.6	H16A—C16—H16C	109.5
C9—C10—C11	119.88 (14)	H16B—C16—H16C	109.5
C9—C10—H10	120.1		
C5—N1—C2—N3	0.71 (17)	C5—N1—C6—C11	57.98 (19)
C6—N1—C2—N3	-179.08 (13)	C11—C6—C7—C8	-0.2 (2)
C5—N1—C2—Au1	-176.96 (11)	N1—C6—C7—C8	177.58 (13)
C6—N1—C2—Au1	3.3 (2)	C6—C7—C8—C9	-1.7 (2)
N1—C2—N3—C4	-0.30 (17)	C7—C8—C9—C10	1.6 (2)
Au1—C2—N3—C4	177.42 (11)	C8—C9—C10—C11	0.5 (2)
N1—C2—N3—C13	176.94 (13)	C9—C10—C11—O12	177.13 (14)
Au1—C2—N3—C13	-5.3 (2)	C9—C10—C11—C6	-2.4 (2)
C2—N3—C4—C5	-0.22 (19)	C7—C6—C11—O12	-177.31 (13)
C13—N3—C4—C5	-177.55 (14)	N1—C6—C11—O12	4.9 (2)
N3—C4—C5—N1	0.64 (18)	C7—C6—C11—C10	2.3 (2)
C2—N1—C5—C4	-0.86 (19)	N1—C6—C11—C10	-175.56 (13)
C6—N1—C5—C4	178.93 (14)	C2—N3—C13—C14	-71.92 (18)
C2—N1—C6—C7	59.9 (2)	C4—N3—C13—C14	105.02 (17)
C5—N1—C6—C7	-119.84 (16)	N3—C13—C14—C15	-165.46 (12)
C2—N1—C6—C11	-122.26 (16)	C13—C14—C15—C16	-179.12 (13)

Table 30: Selected hydrogen-bond lengths (pm) and bond angles (°) for **77**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···Cl1^{ii}	0.95	2.98	3.789 (8)	144
C4—H4···Br1^{ii}	0.95	3.03	3.846 (14)	144
O12—H12···Cl1	0.85 (3)	2.18 (3)	3.0022 (19)	165 (2)
O12—H12···Br1	0.85 (3)	2.18 (3)	3.013 (3)	166 (2)
C13—H13*B*···Cl1^{iii}	0.99	2.93	3.832 (9)	152
C13—H13*B*···Br1^{iii}	0.99	2.86	3.767 (16)	153

6.11 Crystal structure determination of tris(3-butyl-1-(2-oxidophenyl)-1*H*-imidazolium-2-yl)rhodium 79

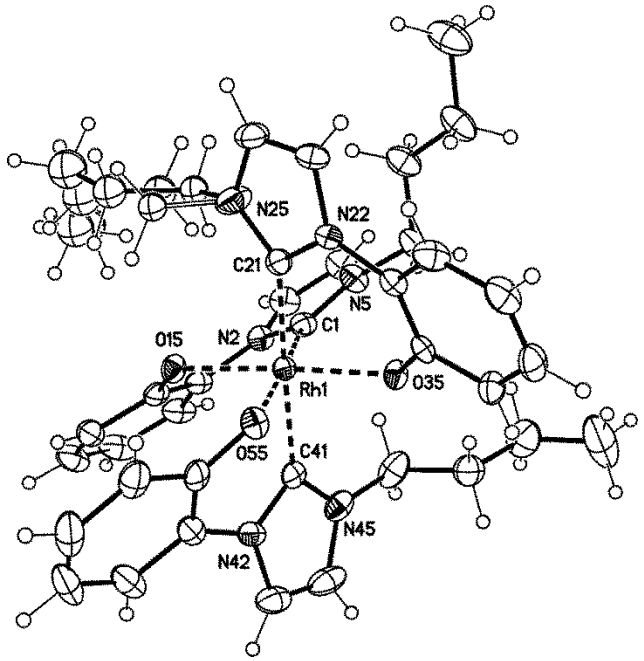


Figure 33. X-ray structure of molecule **79**.

Table 31: Crystallography data and refinement details for **79**.

$C_{39}H_{45}N_6O_3Rh$	$F(000) = 1560$
$M_r = 748.72$	$D_x = 1.429$ Mg m^{-3}
Monoclinic, $P2_1/n$ *(no.14)*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

a = 11.7692 (5) Å	Cell parameters from 9860 reflections
b = 18.8111 (7) Å	θ = 4.9–27.5°
c = 16.2459 (7) Å	μ = 0.54 mm^{-1}
β = 104.615 (2)°	*T* = 123 K
V = 3480.3 (2) $Å^3$	Plates, yellow
Z = 4	0.38 × 0.32 × 0.16 mm
Refinement on F2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
R[F2 > 2σ(F2)] = 0.032	H-atom parameters constrained
wR(F2) = 0.071	w = 1/[σ2(Fo2) + (0.0198P)2 + 4.8925P] where P = (Fo2 + 2Fc2)/3
S = 1.05	(Δ/σ)max = 0.002
8005 reflections	Δ⟩max = 0.65 e Å-3
436 parameters	Δ⟩min = -1.00 e Å-3
146 restraints	Extinction correction: SHELXL2014/7 (Sheldrick 2014, Fc*=kFc[1+0.001xFc2λ3/sin(2θ)]-1/4
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.00089 (11)

Table 32: Bond length (pm) data for **79.**

Rh1—C1	1.966 (2)	C29—H29B	0.9800
Rh1—O35	2.0244 (14)	C29—H29C	0.9800
Rh1—O15	2.0249 (14)	C26A—C27A	1.516 (5)
Rh1—C41	2.044 (2)	C26A—H26C	0.9900
Rh1—C21	2.047 (2)	C26A—H26D	0.9900
Rh1—O55	2.0998 (15)	C27A—C28A	1.548 (6)
C1—N5	1.352 (3)	C27A—H27C	0.9900
C1—N2	1.362 (3)	C27A—H27D	0.9900
N2—C3	1.394 (3)	C28A—C29A	1.481 (6)

N2—C10	1.435 (3)	C28A—H28C	0.9900
C3—C4	1.340 (3)	C28A—H28D	0.9900
C3—H3	0.9500	C29A—H29D	0.9800
C4—N5	1.388 (3)	C29A—H29E	0.9800
C4—H4	0.9500	C29A—H29F	0.9800
N5—C6	1.472 (3)	C30—C31	1.399 (3)
C6—C7	1.517 (3)	C30—C35	1.410 (3)
C6—H6A	0.9900	C31—C32	1.384 (3)
C6—H6B	0.9900	C31—H31	0.9500
C7—C8	1.519 (3)	C32—C33	1.381 (3)
C7—H7A	0.9900	C32—H32	0.9500
C7—H7B	0.9900	C33—C34	1.378 (3)
C8—C9	1.514 (3)	C33—H33	0.9500
C8—H8A	0.9900	C34—C35	1.410 (3)
C8—H8B	0.9900	C34—H34	0.9500
C9—H9A	0.9800	C35—O35	1.318 (2)
C9—H9B	0.9800	C41—N45	1.355 (3)
C9—H9C	0.9800	C41—N42	1.363 (3)
C10—C11	1.392 (3)	N42—C43	1.392 (3)
C10—C15	1.407 (3)	N42—C50	1.425 (3)
C11—C12	1.383 (3)	C43—C44	1.321 (4)
C11—H11	0.9500	C43—H43	0.9500
C12—C13	1.384 (4)	C44—N45	1.389 (3)
C12—H12	0.9500	C44—H44	0.9500
C13—C14	1.383 (3)	N45—C46	1.457 (3)
C13—H13	0.9500	C46—C47	1.501 (3)
C14—C15	1.414 (3)	C46—H46A	0.9900
C14—H14	0.9500	C46—H46B	0.9900
C15—O15	1.320 (2)	C47—C48	1.502 (3)

C21—N25	1.350 (3)	C47—H47A	0.9900
C21—N22	1.362 (3)	C47—H47B	0.9900
N22—C23	1.398 (3)	C48—C49	1.498 (4)
N22—C30	1.433 (3)	C48—H48A	0.9900
C23—C24	1.331 (3)	C48—H48B	0.9900
C23—H23	0.9500	C49—H49A	0.9800
C24—N25	1.386 (3)	C49—H49B	0.9800
C24—H24	0.9500	C49—H49C	0.9800
N25—C26A	1.514 (4)	C50—C51	1.394 (3)
N25—C26	1.538 (4)	C50—C55	1.417 (3)
C26—C27	1.515 (4)	C51—C52	1.383 (4)
C26—H26A	0.9900	C51—H51	0.9500
C26—H26B	0.9900	C52—C53	1.373 (4)
C27—C28	1.544 (5)	C52—H52	0.9500
C27—H27A	0.9900	C53—C54	1.383 (4)
C27—H27B	0.9900	C53—H53	0.9500
C28—C29	1.510 (5)	C54—C55	1.410 (3)
C28—H28A	0.9900	C54—H54	0.9500
C28—H28B	0.9900	C55—O55	1.313 (3)
C29—H29A	0.9800		
C1—Rh1—O35	96.11 (7)	C28—C29—H29A	109.5
C1—Rh1—O15	87.77 (7)	C28—C29—H29B	109.5
O35—Rh1—O15	175.74 (6)	H29A—C29—H29B	109.5
C1—Rh1—C41	92.96 (8)	C28—C29—H29C	109.5
O35—Rh1—C41	88.41 (7)	H29A—C29—H29C	109.5
O15—Rh1—C41	89.66 (7)	H29B—C29—H29C	109.5
C1—Rh1—C21	92.03 (8)	N25—C26A—C27A	106.0 (3)
O35—Rh1—C21	88.11 (7)	N25—C26A—H26C	110.5
O15—Rh1—C21	93.50 (7)	C27A—C26A—H26C	110.5

C41—Rh1—C21	174.20 (8)	N25—C26A—H26D	110.5
C1—Rh1—O55	175.97 (7)	C27A—C26A—H26D	110.5
O35—Rh1—O55	87.48 (6)	H26C—C26A—H26D	108.7
O15—Rh1—O55	88.59 (6)	C26A—C27A—C28A	106.9 (4)
C41—Rh1—O55	85.30 (7)	C26A—C27A—H27C	110.3
C21—Rh1—O55	89.91 (7)	C28A—C27A—H27C	110.3
N5—C1—N2	104.96 (18)	C26A—C27A—H27D	110.3
N5—C1—Rh1	132.71 (15)	C28A—C27A—H27D	110.3
N2—C1—Rh1	122.31 (15)	H27C—C27A—H27D	108.6
C1—N2—C3	110.15 (18)	C29A—C28A—C27A	109.9 (5)
C1—N2—C10	125.53 (18)	C29A—C28A—H28C	109.7
C3—N2—C10	124.29 (18)	C27A—C28A—H28C	109.7
C4—C3—N2	107.10 (19)	C29A—C28A—H28D	109.7
C4—C3—H3	126.4	C27A—C28A—H28D	109.7
N2—C3—H3	126.4	H28C—C28A—H28D	108.2
C3—C4—N5	106.9 (2)	C28A—C29A—H29D	109.5
C3—C4—H4	126.6	C28A—C29A—H29E	109.5
N5—C4—H4	126.6	H29D—C29A—H29E	109.5
C1—N5—C4	110.92 (18)	C28A—C29A—H29F	109.5
C1—N5—C6	125.30 (18)	H29D—C29A—H29F	109.5
C4—N5—C6	123.72 (19)	H29E—C29A—H29F	109.5
N5—C6—C7	111.83 (19)	C31—C30—C35	120.09 (19)
N5—C6—H6A	109.3	C31—C30—N22	118.78 (19)
C7—C6—H6A	109.3	C35—C30—N22	121.06 (17)
N5—C6—H6B	109.3	C32—C31—C30	121.5 (2)
C7—C6—H6B	109.3	C32—C31—H31	119.2
H6A—C6—H6B	107.9	C30—C31—H31	119.2
C6—C7—C8	112.6 (2)	C33—C32—C31	118.9 (2)
C6—C7—H7A	109.1	C33—C32—H32	120.6

C8—C7—H7A	109.1	C31—C32—H32	120.6
C6—C7—H7B	109.1	C34—C33—C32	120.4 (2)
C8—C7—H7B	109.1	C34—C33—H33	119.8
H7A—C7—H7B	107.8	C32—C33—H33	119.8
C9—C8—C7	111.2 (2)	C33—C34—C35	122.2 (2)
C9—C8—H8A	109.4	C33—C34—H34	118.9
C7—C8—H8A	109.4	C35—C34—H34	118.9
C9—C8—H8B	109.4	O35—C35—C30	125.99 (18)
C7—C8—H8B	109.4	O35—C35—C34	117.16 (19)
H8A—C8—H8B	108.0	C30—C35—C34	116.78 (18)
C8—C9—H9A	109.5	C35—O35—Rh1	122.01 (12)
C8—C9—H9B	109.5	N45—C41—N42	104.10 (18)
H9A—C9—H9B	109.5	N45—C41—Rh1	134.21 (16)
C8—C9—H9C	109.5	N42—C41—Rh1	121.40 (15)
H9A—C9—H9C	109.5	C41—N42—C43	110.9 (2)
H9B—C9—H9C	109.5	C41—N42—C50	125.43 (18)
C11—C10—C15	121.3 (2)	C43—N42—C50	123.7 (2)
C11—C10—N2	118.9 (2)	C44—C43—N42	106.7 (2)
C15—C10—N2	119.73 (18)	C44—C43—H43	126.7
C12—C11—C10	120.2 (2)	N42—C43—H43	126.7
C12—C11—H11	119.9	C43—C44—N45	107.7 (2)
C10—C11—H11	119.9	C43—C44—H44	126.2
C11—C12—C13	119.7 (2)	N45—C44—H44	126.2
C11—C12—H12	120.2	C41—N45—C44	110.6 (2)
C13—C12—H12	120.2	C41—N45—C46	127.4 (2)
C14—C13—C12	120.6 (2)	C44—N45—C46	121.9 (2)
C14—C13—H13	119.7	N45—C46—C47	113.8 (2)
C12—C13—H13	119.7	N45—C46—H46A	108.8
C13—C14—C15	121.2 (2)	C47—C46—H46A	108.8

C13—C14—H14	119.4	N45—C46—H46B	108.8
C15—C14—H14	119.4	C47—C46—H46B	108.8
O15—C15—C10	124.07 (19)	H46A—C46—H46B	107.7
O15—C15—C14	119.0 (2)	C46—C47—C48	114.2 (2)
C10—C15—C14	116.9 (2)	C46—C47—H47A	108.7
C15—O15—Rh1	118.98 (13)	C48—C47—H47A	108.7
N25—C21—N22	104.58 (18)	C46—C47—H47B	108.7
N25—C21—Rh1	132.42 (16)	C48—C47—H47B	108.7
N22—C21—Rh1	122.99 (14)	H47A—C47—H47B	107.6
C21—N22—C23	110.29 (17)	C49—C48—C47	115.1 (2)
C21—N22—C30	126.11 (17)	C49—C48—H48A	108.5
C23—N22—C30	123.56 (17)	C47—C48—H48A	108.5
C24—C23—N22	106.88 (19)	C49—C48—H48B	108.5
C24—C23—H23	126.6	C47—C48—H48B	108.5
N22—C23—H23	126.6	H48A—C48—H48B	107.5
C23—C24—N25	107.1 (2)	C48—C49—H49A	109.5
C23—C24—H24	126.4	C48—C49—H49B	109.5
N25—C24—H24	126.4	H49A—C49—H49B	109.5
C21—N25—C24	111.12 (19)	C48—C49—H49C	109.5
C21—N25—C26A	123.7 (3)	H49A—C49—H49C	109.5
C24—N25—C26A	118.1 (3)	H49B—C49—H49C	109.5
C21—N25—C26	123.7 (2)	C51—C50—C55	121.1 (2)
C24—N25—C26	120.9 (2)	C51—C50—N42	119.3 (2)
C27—C26—N25	107.2 (3)	C55—C50—N42	119.53 (19)
C27—C26—H26A	110.3	C52—C51—C50	120.8 (3)
N25—C26—H26A	110.3	C52—C51—H51	119.6
C27—C26—H26B	110.3	C50—C51—H51	119.6
N25—C26—H26B	110.3	C53—C52—C51	119.3 (2)
H26A—C26—H26B	108.5	C53—C52—H52	120.4

C26—C27—C28	112.6 (4)	C51—C52—H52	120.4
C26—C27—H27A	109.1	C52—C53—C54	120.7 (3)
C28—C27—H27A	109.1	C52—C53—H53	119.6
C26—C27—H27B	109.1	C54—C53—H53	119.6
C28—C27—H27B	109.1	C53—C54—C55	122.1 (3)
H27A—C27—H27B	107.8	C53—C54—H54	118.9
C29—C28—C27	109.9 (4)	C55—C54—H54	118.9
C29—C28—H28A	109.7	O55—C55—C54	120.1 (2)
C27—C28—H28A	109.7	O55—C55—C50	124.0 (2)
C29—C28—H28B	109.7	C54—C55—C50	115.9 (2)
C27—C28—H28B	109.7	C55—O55—Rh1	116.10 (13)
H28A—C28—H28B	108.2		
O35—Rh1—C1—N5	-33.1 (2)	C26—C27—C28—C29	71.3 (5)
O15—Rh1—C1—N5	148.6 (2)	C21—N25—C26A—C27A	-102.6 (4)
C41—Rh1—C1—N5	-121.8 (2)	C24—N25—C26A—C27A	109.6 (4)
C21—Rh1—C1—N5	55.2 (2)	N25—C26A—C27A—C28A	-178.3 (5)
O35—Rh1—C1—N2	148.71 (16)	C26A—C27A—C28A—C29A	-146.6 (6)
O15—Rh1—C1—N2	-29.55 (17)	C21—N22—C30—C31	-164.1 (2)
C41—Rh1—C1—N2	60.00 (17)	C23—N22—C30—C31	18.7 (3)
C21—Rh1—C1—N2	-122.97 (17)	C21—N22—C30—C35	18.9 (3)
N5—C1—N2—C3	-0.3 (2)	C23—N22—C30—C35	-158.26 (19)
Rh1—C1—N2—C3	178.27 (15)	C35—C30—C31—C32	2.4 (3)
N5—C1—N2—C10	-178.37 (18)	N22—C30—C31—C32	-174.6 (2)
Rh1—C1—N2—C10	0.2 (3)	C30—C31—C32—C33	-1.0 (4)
C1—N2—C3—C4	0.4 (3)	C31—C32—C33—C34	-1.2 (4)
C10—N2—C3—C4	178.5 (2)	C32—C33—C34—C35	2.1 (4)
N2—C3—C4—N5	-0.3 (3)	C31—C30—C35—O35	-178.19 (19)
N2—C1—N5—C4	0.1 (2)	N22—C30—C35—O35	-1.2 (3)
Rh1—C1—N5—C4	-178.27 (17)	C31—C30—C35—C34	-1.5 (3)

N2—C1—N5—C6	177.66 (19)	N22—C30—C35—C34	175.46 (18)
Rh1—C1—N5—C6	-0.7 (3)	C33—C34—C35—O35	176.3 (2)
C3—C4—N5—C1	0.1 (3)	C33—C34—C35—C30	-0.7 (3)
C3—C4—N5—C6	-177.5 (2)	C30—C35—O35—Rh1	-33.5 (3)
C1—N5—C6—C7	-112.0 (2)	C34—C35—O35—Rh1	149.84 (15)
C4—N5—C6—C7	65.3 (3)	C1—Rh1—O35—C35	130.91 (15)
N5—C6—C7—C8	168.67 (19)	C41—Rh1—O35—C35	-136.29 (15)
C6—C7—C8—C9	176.7 (2)	C21—Rh1—O35—C35	39.07 (15)
C1—N2—C10—C11	-156.5 (2)	O55—Rh1—O35—C35	-50.93 (15)
C3—N2—C10—C11	25.8 (3)	C1—Rh1—C41—N45	40.6 (2)
C1—N2—C10—C15	26.4 (3)	O35—Rh1—C41—N45	-55.4 (2)
C3—N2—C10—C15	-151.4 (2)	O15—Rh1—C41—N45	128.3 (2)
C15—C10—C11—C12	2.8 (3)	O55—Rh1—C41—N45	-143.0 (2)
N2—C10—C11—C12	-174.3 (2)	C1—Rh1—C41—N42	-146.61 (16)
C10—C11—C12—C13	0.1 (4)	O35—Rh1—C41—N42	117.35 (16)
C11—C12—C13—C14	-2.2 (4)	O15—Rh1—C41—N42	-58.86 (16)
C12—C13—C14—C15	1.5 (4)	O55—Rh1—C41—N42	29.75 (16)
C11—C10—C15—O15	178.2 (2)	N45—C41—N42—C43	0.7 (2)
N2—C10—C15—O15	-4.7 (3)	Rh1—C41—N42—C43	-173.94 (14)
C11—C10—C15—C14	-3.4 (3)	N45—C41—N42—C50	179.40 (18)
N2—C10—C15—C14	173.71 (18)	Rh1—C41—N42—C50	4.7 (3)
C13—C14—C15—O15	179.8 (2)	C41—N42—C43—C44	-0.5 (3)
C13—C14—C15—C10	1.3 (3)	C50—N42—C43—C44	-179.2 (2)
C10—C15—O15—Rh1	-38.0 (3)	N42—C43—C44—N45	0.0 (3)
C14—C15—O15—Rh1	143.65 (16)	N42—C41—N45—C44	-0.7 (2)
C1—Rh1—O15—C15	47.92 (15)	Rh1—C41—N45—C44	172.94 (17)
C41—Rh1—O15—C15	-45.06 (15)	N42—C41—N45—C46	-178.44 (19)
C21—Rh1—O15—C15	139.81 (15)	Rh1—C41—N45—C46	-4.8 (3)
O55—Rh1—O15—C15	-130.36 (15)	C43—C44—N45—C41	0.4 (3)

C1—Rh1—C21—N25	58.4 (2)	C43—C44—N45—C46	178.3 (2)
O35—Rh1—C21—N25	154.4 (2)	C41—N45—C46—C47	91.4 (3)
O15—Rh1—C21—N25	-29.5 (2)	C44—N45—C46—C47	-86.1 (3)
O55—Rh1—C21—N25	-118.1 (2)	N45—C46—C47—C48	176.2 (2)
C1—Rh1—C21—N22	-119.69 (18)	C46—C47—C48—C49	-177.1 (3)
O35—Rh1—C21—N22	-23.63 (17)	C41—N42—C50—C51	149.0 (2)
O15—Rh1—C21—N22	152.42 (17)	C43—N42—C50—C51	-32.5 (3)
O55—Rh1—C21—N22	63.84 (17)	C41—N42—C50—C55	-33.0 (3)
N25—C21—N22—C23	0.0 (2)	C43—N42—C50—C55	145.5 (2)
Rh1—C21—N22—C23	178.52 (15)	C55—C50—C51—C52	-2.5 (3)
N25—C21—N22—C30	-177.53 (19)	N42—C50—C51—C52	175.5 (2)
Rh1—C21—N22—C30	1.0 (3)	C50—C51—C52—C53	-0.1 (4)
C21—N22—C23—C24	0.6 (3)	C51—C52—C53—C54	1.0 (4)
C30—N22—C23—C24	178.23 (19)	C52—C53—C54—C55	0.6 (4)
N22—C23—C24—N25	-1.0 (3)	C53—C54—C55—O55	178.7 (2)
N22—C21—N25—C24	-0.6 (3)	C53—C54—C55—C50	-3.0 (3)
Rh1—C21—N25—C24	-178.94 (18)	C51—C50—C55—O55	-177.9 (2)
N22—C21—N25—C26A	-150.4 (3)	N42—C50—C55—O55	4.2 (3)
Rh1—C21—N25—C26A	31.3 (4)	C51—C50—C55—C54	3.9 (3)
N22—C21—N25—C26	156.3 (2)	N42—C50—C55—C54	-174.05 (19)
Rh1—C21—N25—C26	-22.0 (4)	C54—C55—O55—Rh1	-137.45 (17)
C23—C24—N25—C21	1.0 (3)	C50—C55—O55—Rh1	44.4 (2)
C23—C24—N25—C26A	152.7 (3)	O35—Rh1—O55—C55	-141.56 (15)
C23—C24—N25—C26	-156.7 (2)	O15—Rh1—O55—C55	36.82 (15)
C21—N25—C26—C27	116.1 (3)	C41—Rh1—O55—C55	-52.96 (15)
C24—N25—C26—C27	-89.1 (4)	C21—Rh1—O55—C55	130.32 (15)
N25—C26—C27—C28	170.5 (3)		

Table 33: Selected hydrogen-bond lengths (pm) and bond angles (°) for **79**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O55^{i}	0.95	2.58	3.524 (3)	172
C6—H6*B*···O35	0.99	2.24	3.099 (3)	144
C26—H26*B*···N2	0.99	2.64	3.623 (4)	171
C27—H27*A*···O55^{ii}	0.99	2.64	3.521 (5)	148
C27—H27*B*···O15	0.99	2.64	3.346 (5)	129
C26*A*—H26*D*···O15	0.99	2.19	2.933 (5)	131
C27*A*—H27*C*···N2	0.99	2.58	3.559 (6)	170
C46—H46*A*···N2	0.99	2.70	3.519 (3)	140
C47—H47*B*···O35	0.99	2.39	3.266 (3)	147

6.12 Crystal structure determination of bis(3-butyl-1-(2-oxidophenyl)-1*H*-imidazolium-2-yl)nickel 80

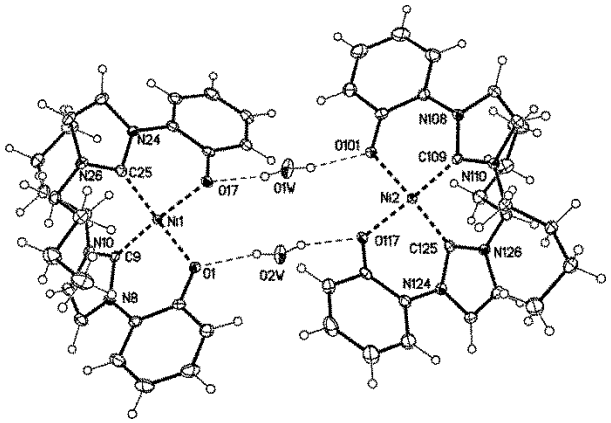


Figure 34: X-ray structure of molecule **80**.

Table 34: Crystallography data and refinement details for **80**.

$C_{26}H_{30}N_4NiO_2 \cdot H_2O$	$F(000)$ = 2144
M_r = 507.26	D_x = 1.396 Mg m^{-3}
Monoclinic, $P2_1/n$ *(no.14)*	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 11.2267 (5) Å	Cell parameters from 9286 reflections
b = 22.8310 (9) Å	θ = 2.3–27.5°

c = 19.1274 (8) Å	μ = 0.84 mm^{-1}
β = 100.099 (2)°	*T* = 123 K
V = 4826.7 (4) $Å^3$	Plates, yellow
Z = 8	0.22 × 0.12 × 0.04 mm
Refinement on F2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
R[F2 > 2σ(F2)] = 0.038	Hydrogen site location: difference Fourier map
wR(F2) = 0.095	H atoms treated by a mixture of independent and constrained refinement
S = 1.06	w = 1/[σ2(Fo2) + (0.0394P)2 + 3.7731P] where P = (Fo2 + 2Fc2)/3
11117 reflections	(Δ/σ)max = 0.001
625 parameters	Δ⟩max = 1.06 e Å-3
6 restraints	Δ⟩min = -0.37 e Å-3

Table 35: Bond length (pm) data for **80.**

Ni1—C25	1.8406 (19)	O2W—H2W1	0.848 (16)
Ni1—C9	1.8482 (19)	O2W—H2W2	0.848 (16)
Ni1—O1	1.8812 (13)	Ni2—C109	1.8458 (19)
Ni1—O17	1.8980 (13)	Ni2—C125	1.8542 (19)
O1—C2	1.328 (2)	Ni2—O101	1.8760 (13)
C2—C3	1.405 (3)	Ni2—O117	1.9011 (13)
C2—C7	1.411 (3)	O101—C102	1.330 (2)
C3—C4	1.383 (3)	C102—C103	1.408 (3)
C3—H3	0.9500	C102—C107	1.411 (3)
C4—C5	1.388 (3)	C103—C104	1.383 (3)
C4—H4	0.9500	C103—H103	0.9500
C5—C6	1.380 (3)	C104—C105	1.386 (3)
C5—H5	0.9500	C104—H104	0.9500
C6—C7	1.392 (3)	C105—C106	1.381 (3)
C6—H6	0.9500	C105—H105	0.9500
C7—N8	1.427 (2)	C106—C107	1.397 (3)
N8—C9	1.363 (2)	C106—H106	0.9500
N8—C12	1.388 (3)	C107—N108	1.427 (2)
C9—N10	1.356 (2)	N108—C109	1.365 (2)
N10—C11	1.386 (3)	N108—C112	1.391 (3)

N10—C13	1.470 (2)	C109—N110	1.357 (2)
C11—C12	1.344 (3)	N110—C111	1.383 (2)
C11—H11	0.9500	N110—C113	1.470 (2)
C12—H12	0.9500	C111—C112	1.343 (3)
C13—C14	1.521 (3)	C111—H111	0.9500
C13—H13A	0.9900	C112—H112	0.9500
C13—H13B	0.9900	C113—C114	1.524 (3)
C14—C15	1.529 (3)	C113—H11A	0.9900
C14—H14A	0.9900	C113—H11B	0.9900
C14—H14B	0.9900	C114—C115	1.527 (3)
C15—C16	1.526 (3)	C114—H11C	0.9900
C15—H15A	0.9900	C114—H11D	0.9900
C15—H15B	0.9900	C115—C116	1.522 (3)
C16—H16A	0.9800	C115—H11E	0.9900
C16—H16B	0.9800	C115—H11F	0.9900
C16—H16C	0.9800	C116—H11G	0.9800
O17—C18	1.330 (2)	C116—H11H	0.9800
C18—C19	1.406 (3)	C116—H11I	0.9800
C18—C23	1.415 (3)	O117—C118	1.328 (2)
C19—C20	1.385 (3)	C118—C119	1.407 (3)
C19—H19	0.9500	C118—C123	1.412 (3)
C20—C21	1.392 (3)	C119—C120	1.388 (3)
C20—H20	0.9500	C119—H119	0.9500
C21—C22	1.387 (3)	C120—C121	1.385 (3)
C21—H21	0.9500	C120—H120	0.9500
C22—C23	1.389 (3)	C121—C122	1.384 (3)
C22—H22	0.9500	C121—H121	0.9500
C23—N24	1.424 (2)	C122—C123	1.387 (3)
N24—C25	1.361 (2)	C122—H122	0.9500
N24—C28	1.394 (2)	C123—N124	1.425 (2)
C25—N26	1.353 (2)	N124—C125	1.361 (2)
N26—C27	1.386 (2)	N124—C128	1.385 (2)
N26—C29	1.473 (2)	C125—N126	1.359 (2)
C27—C28	1.346 (3)	N126—C127	1.383 (2)
C27—H27	0.9500	N126—C129	1.470 (2)
C28—H28	0.9500	C127—C128	1.343 (3)
C29—C30	1.521 (3)	C127—H127	0.9500
C29—H29A	0.9900	C128—H128	0.9500

C29—H29B	0.9900	C129—C130	1.513 (3)
C30—C31	1.519 (3)	C129—H12A	0.9900
C30—H30A	0.9900	C129—H12B	0.9900
C30—H30B	0.9900	C130—C131	1.534 (3)
C31—C32	1.528 (3)	C130—H13C	0.9900
C31—H31A	0.9900	C130—H13D	0.9900
C31—H31B	0.9900	C131—C132	1.517 (3)
C32—H32A	0.9800	C131—H13E	0.9900
C32—H32B	0.9800	C131—H13F	0.9900
C32—H32C	0.9800	C132—H13G	0.9800
O1W—H1W1	0.841 (16)	C132—H13H	0.9800
O1W—H1W2	0.830 (16)	C132—H13I	0.9800
C25—Ni1—C9	95.18 (8)	H2W1—O2W—H2W2	110 (2)
C25—Ni1—O1	165.12 (7)	C109—Ni2—C125	95.63 (8)
C9—Ni1—O1	91.19 (7)	C109—Ni2—O101	91.46 (7)
C25—Ni1—O17	89.10 (7)	C125—Ni2—O101	164.09 (7)
C9—Ni1—O17	164.34 (7)	C109—Ni2—O117	161.59 (7)
O1—Ni1—O17	88.34 (6)	C125—Ni2—O117	90.20 (7)
C2—O1—Ni1	120.43 (12)	O101—Ni2—O117	87.47 (6)
O1—C2—C3	120.02 (18)	C102—O101—Ni2	123.69 (12)
O1—C2—C7	123.80 (17)	O101—C102—C103	119.71 (18)
C3—C2—C7	116.18 (17)	O101—C102—C107	123.81 (17)
C4—C3—C2	121.56 (19)	C103—C102—C107	116.43 (17)
C4—C3—H3	119.2	C104—C103—C102	121.5 (2)
C2—C3—H3	119.2	C104—C103—H103	119.2
C3—C4—C5	121.1 (2)	C102—C103—H103	119.2
C3—C4—H4	119.5	C103—C104—C105	121.0 (2)
C5—C4—H4	119.5	C103—C104—H104	119.5
C6—C5—C4	118.8 (2)	C105—C104—H104	119.5
C6—C5—H5	120.6	C106—C105—C104	119.1 (2)
C4—C5—H5	120.6	C106—C105—H105	120.5
C5—C6—C7	120.4 (2)	C104—C105—H105	120.5
C5—C6—H6	119.8	C105—C106—C107	120.4 (2)
C7—C6—H6	119.8	C105—C106—H106	119.8
C6—C7—C2	121.81 (18)	C107—C106—H106	119.8
C6—C7—N8	119.81 (18)	C106—C107—C102	121.51 (18)
C2—C7—N8	118.36 (17)	C106—C107—N108	119.28 (18)
C9—N8—C12	110.83 (16)	C102—C107—N108	119.03 (16)

C9—N8—C7	123.38 (17)	C109—N108—C112	110.46 (16)
C12—N8—C7	125.46 (16)	C109—N108—C107	124.15 (16)
N10—C9—N8	104.48 (16)	C112—N108—C107	124.72 (16)
N10—C9—Ni1	130.43 (14)	N110—C109—N108	104.61 (16)
N8—C9—Ni1	124.22 (14)	N110—C109—Ni2	129.57 (14)
C9—N10—C11	110.92 (16)	N108—C109—Ni2	125.18 (14)
C9—N10—C13	126.65 (16)	C109—N110—C111	110.94 (16)
C11—N10—C13	122.18 (16)	C109—N110—C113	126.74 (16)
C12—C11—N10	107.06 (18)	C111—N110—C113	121.61 (16)
C12—C11—H11	126.5	C112—C111—N110	107.10 (18)
N10—C11—H11	126.5	C112—C111—H111	126.4
C11—C12—N8	106.71 (17)	N110—C111—H111	126.4
C11—C12—H12	126.6	C111—C112—N108	106.88 (17)
N8—C12—H12	126.6	C111—C112—H112	126.6
N10—C13—C14	112.76 (15)	N108—C112—H112	126.6
N10—C13—H13A	109.0	N110—C113—C114	112.56 (15)
C14—C13—H13A	109.0	N110—C113—H11A	109.1
N10—C13—H13B	109.0	C114—C113—H11A	109.1
C14—C13—H13B	109.0	N110—C113—H11B	109.1
H13A—C13—H13B	107.8	C114—C113—H11B	109.1
C13—C14—C15	112.37 (16)	H11A—C113—H11B	107.8
C13—C14—H14A	109.1	C113—C114—C115	111.62 (16)
C15—C14—H14A	109.1	C113—C114—H11C	109.3
C13—C14—H14B	109.1	C115—C114—H11C	109.3
C15—C14—H14B	109.1	C113—C114—H11D	109.3
H14A—C14—H14B	107.9	C115—C114—H11D	109.3
C16—C15—C14	113.71 (17)	H11C—C114—H11D	108.0
C16—C15—H15A	108.8	C116—C115—C114	113.49 (17)
C14—C15—H15A	108.8	C116—C115—H11E	108.9
C16—C15—H15B	108.8	C114—C115—H11E	108.9
C14—C15—H15B	108.8	C116—C115—H11F	108.9
H15A—C15—H15B	107.7	C114—C115—H11F	108.9
C15—C16—H16A	109.5	H11E—C115—H11F	107.7
C15—C16—H16B	109.5	C115—C116—H11G	109.5
H16A—C16—H16B	109.5	C115—C116—H11H	109.5
C15—C16—H16C	109.5	H11G—C116—H11H	109.5
H16A—C16—H16C	109.5	C115—C116—H11I	109.5
H16B—C16—H16C	109.5	H11G—C116—H11I	109.5

C18—O17—Ni1	114.67 (12)	H11H—C116—H11I	109.5
O17—C18—C19	120.32 (17)	C118—O117—Ni2	116.06 (12)
O17—C18—C23	123.07 (17)	O117—C118—C119	120.45 (18)
C19—C18—C23	116.60 (17)	O117—C118—C123	123.01 (17)
C20—C19—C18	121.56 (19)	C119—C118—C123	116.52 (17)
C20—C19—H19	119.2	C120—C119—C118	121.08 (19)
C18—C19—H19	119.2	C120—C119—H119	119.5
C19—C20—C21	120.63 (19)	C118—C119—H119	119.5
C19—C20—H20	119.7	C121—C120—C119	121.1 (2)
C21—C20—H20	119.7	C121—C120—H120	119.5
C22—C21—C20	119.22 (19)	C119—C120—H120	119.5
C22—C21—H21	120.4	C122—C121—C120	119.2 (2)
C20—C21—H21	120.4	C122—C121—H121	120.4
C21—C22—C23	120.26 (19)	C120—C121—H121	120.4
C21—C22—H22	119.9	C121—C122—C123	120.0 (2)
C23—C22—H22	119.9	C121—C122—H122	120.0
C22—C23—C18	121.65 (18)	C123—C122—H122	120.0
C22—C23—N24	120.90 (18)	C122—C123—C118	122.06 (18)
C18—C23—N24	117.43 (17)	C122—C123—N124	120.24 (18)
C25—N24—C28	110.26 (16)	C118—C123—N124	117.70 (17)
C25—N24—C23	121.60 (16)	C125—N124—C128	110.86 (16)
C28—N24—C23	127.94 (16)	C125—N124—C123	122.95 (16)
N26—C25—N24	105.04 (16)	C128—N124—C123	126.19 (16)
N26—C25—Ni1	130.23 (14)	N126—C125—N124	104.43 (16)
N24—C25—Ni1	123.95 (14)	N126—C125—Ni2	131.26 (14)
C25—N26—C27	110.88 (16)	N124—C125—Ni2	123.53 (14)
C25—N26—C29	124.72 (16)	C125—N126—C127	110.84 (16)
C27—N26—C29	124.35 (16)	C125—N126—C129	126.51 (16)
C28—C27—N26	106.95 (17)	C127—N126—C129	122.64 (16)
C28—C27—H27	126.5	C128—C127—N126	107.08 (17)
N26—C27—H27	126.5	C128—C127—H127	126.5
C27—C28—N24	106.86 (17)	N126—C127—H127	126.5
C27—C28—H28	126.6	C127—C128—N124	106.79 (17)
N24—C28—H28	126.6	C127—C128—H128	126.6
N26—C29—C30	111.63 (16)	N124—C128—H128	126.6
N26—C29—H29A	109.3	N126—C129—C130	113.25 (16)
C30—C29—H29A	109.3	N126—C129—H12A	108.9
N26—C29—H29B	109.3	C130—C129—H12A	108.9

C30—C29—H29B	109.3	N126—C129—H12B	108.9
H29A—C29—H29B	108.0	C130—C129—H12B	108.9
C31—C30—C29	112.43 (18)	H12A—C129—H12B	107.7
C31—C30—H30A	109.1	C129—C130—C131	111.55 (18)
C29—C30—H30A	109.1	C129—C130—H13C	109.3
C31—C30—H30B	109.1	C131—C130—H13C	109.3
C29—C30—H30B	109.1	C129—C130—H13D	109.3
H30A—C30—H30B	107.8	C131—C130—H13D	109.3
C30—C31—C32	111.40 (19)	H13C—C130—H13D	108.0
C30—C31—H31A	109.3	C132—C131—C130	114.69 (19)
C32—C31—H31A	109.3	C132—C131—H13E	108.6
C30—C31—H31B	109.3	C130—C131—H13E	108.6
C32—C31—H31B	109.3	C132—C131—H13F	108.6
H31A—C31—H31B	108.0	C130—C131—H13F	108.6
C31—C32—H32A	109.5	H13E—C131—H13F	107.6
C31—C32—H32B	109.5	C131—C132—H13G	109.5
H32A—C32—H32B	109.5	C131—C132—H13H	109.5
C31—C32—H32C	109.5	H13G—C132—H13H	109.5
H32A—C32—H32C	109.5	C131—C132—H13I	109.5
H32B—C32—H32C	109.5	H13G—C132—H13I	109.5
H1W1—O1W—H1W2	112 (2)	H13H—C132—H13I	109.5
C25—Ni1—O1—C2	71.0 (3)	C109—Ni2—O101—C102	37.58 (16)
C9—Ni1—O1—C2	-44.48 (15)	C125—Ni2—O101—C102	-79.0 (3)
O17—Ni1—O1—C2	151.18 (15)	O117—Ni2—O101—C102	-160.80 (15)
Ni1—O1—C2—C3	-145.65 (15)	Ni2—O101—C102—C103	154.73 (15)
Ni1—O1—C2—C7	35.0 (3)	Ni2—O101—C102—C107	-27.9 (3)
O1—C2—C3—C4	176.95 (19)	O101—C102—C103—C104	-179.9 (2)
C7—C2—C3—C4	-3.6 (3)	C107—C102—C103—C104	2.5 (3)
C2—C3—C4—C5	0.5 (4)	C102—C103—C104—C105	0.6 (4)
C3—C4—C5—C6	1.9 (4)	C103—C104—C105—C106	-2.5 (4)
C4—C5—C6—C7	-1.0 (4)	C104—C105—C106—C107	1.2 (3)
C5—C6—C7—C2	-2.4 (3)	C105—C106—C107—C102	2.1 (3)
C5—C6—C7—N8	175.8 (2)	C105—C106—C107—N108	-173.03 (19)
O1—C2—C7—C6	-176.04 (19)	O101—C102—C107—C106	178.69 (19)
C3—C2—C7—C6	4.6 (3)	C103—C102—C107—C106	-3.9 (3)
O1—C2—C7—N8	5.7 (3)	O101—C102—C107—N108	-6.2 (3)
C3—C2—C7—N8	-173.65 (18)	C103—C102—C107—N108	171.26 (18)
C6—C7—N8—C9	154.9 (2)	C106—C107—N108—C109	-164.12 (19)

C2—C7—N8—C9	-26.8 (3)	C102—C107—N108—C109	20.6 (3)
C6—C7—N8—C12	-32.1 (3)	C106—C107—N108—C112	26.1 (3)
C2—C7—N8—C12	146.1 (2)	C102—C107—N108—C112	-149.11 (19)
C12—N8—C9—N10	0.4 (2)	C112—N108—C109—N110	0.0 (2)
C7—N8—C9—N10	174.25 (17)	C107—N108—C109—N110	-170.99 (17)
C12—N8—C9—Ni1	-169.86 (14)	C112—N108—C109—Ni2	171.59 (14)
C7—N8—C9—Ni1	4.0 (3)	C107—N108—C109—Ni2	0.6 (3)
C25—Ni1—C9—N10	51.64 (19)	C125—Ni2—C109—N110	-48.96 (18)
O1—Ni1—C9—N10	-141.83 (18)	O101—Ni2—C109—N110	145.31 (17)
O17—Ni1—C9—N10	-53.7 (4)	O117—Ni2—C109—N110	58.9 (3)
C25—Ni1—C9—N8	-140.77 (17)	C125—Ni2—C109—N108	141.66 (16)
O1—Ni1—C9—N8	25.77 (16)	O101—Ni2—C109—N108	-24.07 (16)
O17—Ni1—C9—N8	113.9 (3)	O117—Ni2—C109—N108	-110.4 (2)
N8—C9—N10—C11	-0.5 (2)	N108—C109—N110—C111	-0.2 (2)
Ni1—C9—N10—C11	168.96 (15)	Ni2—C109—N110—C111	-171.24 (15)
N8—C9—N10—C13	-174.62 (17)	N108—C109—N110—C113	170.21 (17)
Ni1—C9—N10—C13	-5.2 (3)	Ni2—C109—N110—C113	-0.8 (3)
C9—N10—C11—C12	0.3 (2)	C109—N110—C111—C112	0.3 (2)
C13—N10—C11—C12	174.81 (18)	C113—N110—C111—C112	-170.69 (17)
N10—C11—C12—N8	-0.1 (2)	N110—C111—C112—N108	-0.3 (2)
C9—N8—C12—C11	-0.2 (2)	C109—N108—C112—C111	0.1 (2)
C7—N8—C12—C11	-173.90 (19)	C107—N108—C112—C111	171.10 (18)
C9—N10—C13—C14	-108.9 (2)	C109—N110—C113—C114	115.6 (2)
C11—N10—C13—C14	77.6 (2)	C111—N110—C113—C114	-74.9 (2)
N10—C13—C14—C15	-167.19 (17)	N110—C113—C114—C115	166.69 (16)
C13—C14—C15—C16	-62.3 (2)	C113—C114—C115—C116	60.6 (2)
C25—Ni1—O17—C18	-55.54 (14)	C109—Ni2—O117—C118	-56.6 (3)
C9—Ni1—O17—C18	50.6 (3)	C125—Ni2—O117—C118	52.15 (14)
O1—Ni1—O17—C18	139.12 (13)	O101—Ni2—O117—C118	-143.60 (14)
Ni1—O17—C18—C19	-133.05 (16)	Ni2—O117—C118—C119	134.17 (16)
Ni1—O17—C18—C23	46.6 (2)	Ni2—O117—C118—C123	-46.9 (2)
O17—C18—C19—C20	177.37 (18)	O117—C118—C119—C120	178.9 (2)
C23—C18—C19—C20	-2.3 (3)	C123—C118—C119—C120	-0.1 (3)
C18—C19—C20—C21	0.2 (3)	C118—C119—C120—C121	-0.6 (4)
C19—C20—C21—C22	0.9 (3)	C119—C120—C121—C122	0.9 (4)
C20—C21—C22—C23	0.2 (3)	C120—C121—C122—C123	-0.3 (4)
C21—C22—C23—C18	-2.4 (3)	C121—C122—C123—C118	-0.4 (3)
C21—C22—C23—N24	179.18 (19)	C121—C122—C123—N124	-179.9 (2)

O17—C18—C23—C22	-176.27 (18)	O117—C118—C123—C122	-178.30 (19)
C19—C18—C23—C22	3.4 (3)	C119—C118—C123—C122	0.6 (3)
O17—C18—C23—N24	2.2 (3)	O117—C118—C123—N124	1.2 (3)
C19—C18—C23—N24	-178.16 (17)	C119—C118—C123—N124	-179.86 (18)
C22—C23—N24—C25	147.49 (19)	C122—C123—N124—C125	-150.7 (2)
C18—C23—N24—C25	-31.0 (3)	C118—C123—N124—C125	29.8 (3)
C22—C23—N24—C28	-38.2 (3)	C122—C123—N124—C128	29.3 (3)
C18—C23—N24—C28	143.3 (2)	C118—C123—N124—C128	-150.20 (19)
C28—N24—C25—N26	0.5 (2)	C128—N124—C125—N126	0.0 (2)
C23—N24—C25—N26	175.72 (17)	C123—N124—C125—N126	-179.98 (17)
C28—N24—C25—Ni1	-170.26 (14)	C128—N124—C125—Ni2	170.93 (14)
C23—N24—C25—Ni1	5.0 (3)	C123—N124—C125—Ni2	-9.1 (3)
C9—Ni1—C25—N26	58.66 (19)	C109—Ni2—C125—N126	-55.25 (19)
O1—Ni1—C25—N26	-56.3 (4)	O101—Ni2—C125—N126	60.8 (4)
O17—Ni1—C25—N26	-136.43 (19)	O117—Ni2—C125—N126	142.24 (18)
C9—Ni1—C25—N24	-133.07 (17)	C109—Ni2—C125—N124	136.48 (16)
O1—Ni1—C25—N24	111.9 (3)	O101—Ni2—C125—N124	-107.5 (3)
O17—Ni1—C25—N24	31.85 (17)	O117—Ni2—C125—N124	-26.03 (16)
N24—C25—N26—C27	-0.6 (2)	N124—C125—N126—C127	0.2 (2)
Ni1—C25—N26—C27	169.31 (15)	Ni2—C125—N126—C127	-169.69 (15)
N24—C25—N26—C29	-178.50 (17)	N124—C125—N126—C129	-178.79 (17)
Ni1—C25—N26—C29	-8.6 (3)	Ni2—C125—N126—C129	11.3 (3)
C25—N26—C27—C28	0.6 (2)	C125—N126—C127—C128	-0.4 (2)
C29—N26—C27—C28	178.43 (17)	C129—N126—C127—C128	178.67 (17)
N26—C27—C28—N24	-0.2 (2)	N126—C127—C128—N124	0.4 (2)
C25—N24—C28—C27	-0.2 (2)	C125—N124—C128—C127	-0.3 (2)
C23—N24—C28—C27	-175.01 (19)	C123—N124—C128—C127	179.74 (18)
C25—N26—C29—C30	64.1 (2)	C125—N126—C129—C130	-75.1 (2)
C27—N26—C29—C30	-113.5 (2)	C127—N126—C129—C130	106.0 (2)
N26—C29—C30—C31	-179.59 (17)	N126—C129—C130—C131	-172.91 (17)
C29—C30—C31—C32	173.19 (19)	C129—C130—C131—C132	-62.8 (3)

Table 36: Selected hydrogen-bond lengths (pm) and bond angles (°) for **80**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···O1*W*^{i}	0.95	2.45	3.340 (3)	155
C13—H13*A*···O101^{i}	0.99	2.35	3.323 (2)	169
C14—H14*A*···N26	0.99	2.62	3.476 (3)	145

C29—H29*B*···O2*W*^{ii}	0.99	2.29	3.229 (2)	157
O1*W*—H1*W*1···O101	0.84 (2)	2.06 (2)	2.875 (2)	164 (2)
O1*W*—H1*W*2···O17	0.83 (2)	2.05 (2)	2.864 (2)	169 (3)
O2*W*—H2*W*1···O117	0.85 (2)	2.05 (2)	2.876 (2)	163 (2)
O2*W*—H2*W*2···O1	0.85 (2)	2.03 (2)	2.848 (2)	163 (2)
C111—H111···O2*W*^{iii}	0.95	2.51	3.387 (3)	153
C113—H11*B*···O1^{iii}	0.99	2.37	3.326 (2)	163
C114—H11*D*···N126	0.99	2.65	3.490 (3)	142
C127—H127···O1*W*^{iv}	0.95	2.42	3.195 (3)	139
C129—H12*A*···O1*W*^{iv}	0.99	2.52	3.301 (2)	136

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