Hydroxy-1*H*-imidazole-3-oxides – Synthesis, Kinetic Acidity, and Application in Catalysis and Supramolecular Anion Recognition

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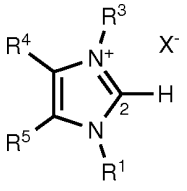
Dedicated to Professor Gerhard Maas on the occasion of his 60th birthday

Using *ab initio* calculations (B3LYP 6-31G*) the geometries of diethyl, dimethoxy and dimethylamino imidazolium salts were studied as representative models of imidazolium salts bearing heteroatoms directly attached to the ring nitrogen atoms of the imidazolium core units. In all cases the *syn* and *anti* arrangement of the substituents could be identified. In addition to the theoretical studies, eleven dialkoxy imidazolium salts were prepared by alkylation of six 1-hydroxy-imidazole-3-oxides using dimethyl or diethyl sulfate as strong alkylating reagents. The kinetic acidities of these compounds were studied by measuring the pseudo-first order reaction rates of the H/D exchange process of the C^2-H proton of compounds **3** – **9**. The observed kinetic acidities are much higher than reaction rates observed for simple imidazolium salts; half-lifes of the H/D exchange are usually in the range of minutes. Similar to dialkyl/aryl imidazolium salts, all prepared dialkoxy imidazolium salts could be used as precatalysts in standard aqueous Suzuki coupling reactions. In addition, two representative dialkoxy imidazolium salts could be used in supramolecular anion recognition, as demonstrated by binding studies towards iodide as guest.

Key words: Imidazolium Salts, Kinetic Acidity, Catalysis, Suzuki Reaction, Anion Receptors

Introduction

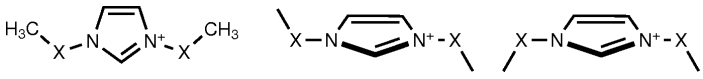
In recent years, imidazolium salts of the general structure **1** (Scheme 1) found a plethora of applications in organic chemistry. The properties of such salts can be easily adjusted and fine-tuned by modification of both the substituents $R^1 - R^5$ directly attached to the heterocyclic skeleton, and the counterion X. In cases where non-nucleophilic, sterically demanding anions such as hexafluorophosphate are used, such salts can be employed as ionic liquids as alternative reaction media [1].



1 Scheme 1.

In addition, imidazolium salts bearing a proton attached at the C^2 position are ideal precursors for *N*-heterocyclic carbenes (NHC) which have found widespread application as "phosphine ligand-analogs" in coordination chemistry [2]. The acidic C^2–H bond can also be exploited in imidazolium-based anion receptor molecules. Besides non-specific electrostatic attraction between the positively charged imidazolium cations and the anionic guests, the directed C–H$\cdots$X$^-$ interactions makes these salts ideal receptor moieties in supramolecular chemistry [3].

Owing to all these important applications, the chemistry of imidazolium salts is well established, and even "abnormal" binding modes of NHCs stemming from imidazolium salts are already well documented [4]. Surprisingly, very little is known about compounds **1** with heteroatoms (O, N, S) directly attached to the ring nitrogen atoms, *e. g.* R^1, R^3 = OR, NHR, or



1a: X = CH_2
2: X = O
3: X = NH

anti *syn*

Scheme 2.

NR_2. Only limited accounts on formal imidazolium *N*-oxide derivatives [5], *N*,*N*′-dialkoxy imidazolium salts [6], alkylamino [7], or *N*,*N*′-*bis*(alkylamino) imidazolium derivatives [8] are available. Recent work of Schottenberger and colleagues attracted our attention because of our own interest in basic properties of imidazolium salts such as kinetic acidity [9] and their use as anion receptors [10] or precatalysts in aqueous Suzuki coupling reactions [11]. They reported on the synthesis, ionic liquid behavior and use of simple *N*,*N*′-dialkoxy imidazolium salts as NHC precursors [12]. Inspecting the experimental NMR data of dimethoxy and diethoxy imidazolium salts revealed a difference in the C^2-H proton resonance of about 0.1 ppm by exchanging the counterion from *e. g.* PF_6^- to bromide [12a]. Therefore, we decided to check whether these novel imidazolium salts are useful for our application in supramolecular chemistry and catalysis.

Results and Discussion

Quantum chemical calculations

To get a first insight into the influence of *N*,*N* heterofunctionalization on the electronic properties of imidazolium salts, model quantum chemical calculations were performed on the three model compounds **1a** – **3** (Scheme 2).

Here, the conformational space of all three cations – neglecting any counterion – was explored at a pm3 semi-empirical level using the "conformer distribution" methodology as implemented in the program package SPARTAN'08 [13]. In every case two major conformers could be identified with the methyl group of the X-CH_3 substituents pointing towards the same side (*syn*) or different sides (*anti*) of the imidazolium core unit used as a reference plane. Based on these two major isomers further optimizations assuming DMSO as solvent were performed using density functional methods (DFT, B3LYP 6-31G* basis set); both the *syn* and the *anti* arrangements were characterized as minima structures using frequency calculations on the same level of theory. The results of this approach are summarized in Table 1.

Table 1. Results of quantum chemical calculations of model compounds **1** – **3** (B3LYP 6-31G*, solvent: DMSO).

Compounds	Conformation	*E*+ZPE (kJ mol^{-1})	E_{rel}/ kJ mol^{-1}	α (deg)[a]
1a (X = CH_2)	*anti*	−1007565.0	0.3	70.2, 70.4
	syn	−1007565.3	= 0.0	70.9, 70.9
2 (X = O)	*anti*	−1195827.8	0.3	81.2, 81.5
	syn	−1195828.1	= 0.0	81.1, 82.0
3 (X = NH)	*anti*	−1091611.3	3.0	61.9, 73.8
	syn	−1091614.3	= 0	40.2, 62.4

[a] α: angle formed by the H_3C–X bond against the mean plane formed by the atoms of the imidazolium ring.

For both the imidazolium salts **1a** and **2** the energy differences between the *syn* and *anti* arrangement are small (0.3 kJ mol^{-1}). This is in good agreement with the experimental observation of both isomers for the dimethoxy imidazolium hexafluorophosphate **2**-PF_6^- in the solid state – with a dominance of the *syn* conformer in the bulk material [12]. The geometries of the *syn* and *anti* isomers of **1a** and **2** are comparable: The angles formed between the Me–CH_2 bond and the mean plane formed by the atoms of the imidazolium ring of the diethyl derivate **1a** are about 70°, in the *anti* arrangement only one ethyl substituent is flipped around to the other side of the imidazolium ring used as a reference plane. For the dimethoxy imidazolium salt **2** the MeO-imidazolium ring angles are somewhat larger (81° – 82°). Interestingly, the *syn* conformer identified by the DFT optimization is very similar to the corresponding isomer found in the solid state [12]. Here, the angles between the Me–O bond and the imidazolium ring are 79.9° and 82.6° *versus* 81.1° and 82.0° calculated. A distinctive difference could be found for *anti*-**2**. In the experimental geometry, the angles of the substituents against the heterocyclic plane are quite imbalanced. One methoxy group is nearly perpendicular (88.8°) whereas the second one is at an angle of 63.2°. In the calculated structure such a mismatch could not be observed, both angles are about 81°.

For the *bis*(methylamino) derivate **3** the energy difference between the *syn* and *anti* isomer is about 10 times bigger than in **1a** and **2**. This is also reflected in the geometries: in the *syn* isomer the MeN-

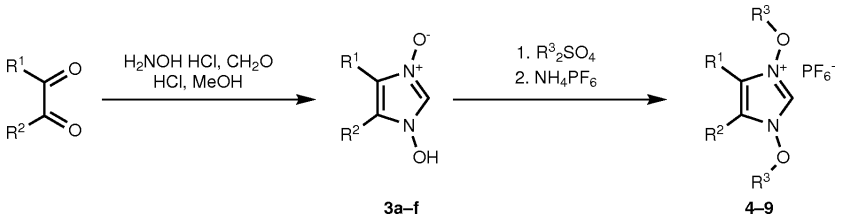


Table 2. Yields of 1-hydroxy-imidazole-3-oxides **3** and alkylation products **4**–**9** thereof.

Compound	R^1	R^2	R^3	Yield (%)	Compound	R^1	R^2	R^3	Yield (%)
3a	H	H	–	41	**3b**	Me	Me	–	26
3c	Et	Et	–	16	**3d**	Me	Et	–	24
3e	Me	*n*-Pr	–	25	**3f**	Ph	Ph	–	20
4a	H	H	Me	31	**4b**	H	H	Et	10
5a	Me	Me	Me	31	**5b**	Me	Me	Et	90
6a	Et	Et	Me	31	**6b**	Et	Et	Et	68
7a	Me	Et	Me	83	**7b**	Me	Et	Et	38
8a	Me	*n*-Pr	Me	26	**8b**	Me	*n*-Pr	Et	8
9	Ph	Ph	Me	50					

imidazolium ring plane angles are 62.4° and 40.2°, in the *anti* isomer 73.8° and 61.9°, respectively. Inspecting the *syn* conformer it became apparent that the lone pair of electrons located at the methylamino group is nearly perfectly parallel to the C^2–H bond probably balancing the positive partial charge of that part of the molecule. One can assume that this small favorable interaction gives the *syn*-**3** isomer an extra stabilization increasing the energy difference between *syn* and *anti*, and thus makes the *bis*(methylamino) derivate **3** an interesting candidate for further applications known from simple alkyl imidazolium salts.

Synthesis

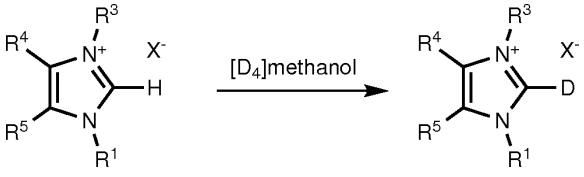
For the syntheses of various alkoxy imidazolium salts of general structure **2** the established protocol [12] could be adapted. Starting from symmetrically or unsymmetrically substituted 1,2-dicarbonyl compounds, condensation with hydroxylamine hydrochloride and formaldehyde under acidic conditions gave rise to six 1-hydroxyimidazole-3-oxides **3a**–**f** in modest yields (Table 2). However, owing to the simplicity of the synthetic approach reasonable quantities of the desired compounds could easily be prepared. Alkylation was possible using methyl or ethyl sulfate and yielded the dialkoxy derivatives **4**–**9**. By the alkylation process, the C^2-H proton resonance of the 1-hydroxy-imidazolium-3-oxides **3**, which usually appears at 8.2–8.4 ppm, is shifted by roughly 2 ppm towards 10.2–10.7 ppm for the alkylated products **4**–**9**. In our hands, this alkylation step is somewhat limited in scope: only strong alkylating agents could be used successfully.

In case 4-nitro benzyl chloride or benzyl chloride was used, no alkylation could be observed with any of the 1-hydroxy-imidazole-3-oxides **3**–**7**; only starting material could be recovered.

Kinetic acidity of oxy-imidazolium salts

A key reaction of imidazolium salts is often the deprotonation of C^2-H to give *N*-heterocyclic carbenes (NHC) used as ligands in metal-organic chemistry or catalysis. Despite these manifold applications considerably less information is available about fundamental acid-base properties of such salts. Both experimental and theoretical investigations have characterized nucleophilic carbenes as strong bases ($pK_a \sim 20-30$) [14] with a high proton affinity [14d]. However, for the application of azolium salts as precursor of nucleophilic carbenes not only the thermodynamics of the deprotonation are important but also its kinetics. Because protonation of the NHC can be assumed to be fast compared to the formation of the NHC [15b], the H/D exchange rates of the C^2-H group gives an indirect estimate for the reaction rate of its formation. Here, only very limited data are available [9, 15]. Therefore, we measured the overall H/D exchange rates k_{obs} by monitoring the decrease of the integral of the C^2-H proton resonance. As solvent pure deuterated methanol was used, and the concentrations of compounds **1**, **3**–**9** were fixed at 10 millimolar to facilitate the comparison of the kinetic data. In all cases, a clear pseudo-first order decrease of the C^2 proton resonance could be observed, and from these data pseudo-first order rate

Table 3. Observed, pseudo-first order rate constants of the H/D exchange in [D_4]MeOD at r. t. (c_{salt} = 10.0 mmol L^{-1})[a].



No.	X	R^1	R^3	R^4	R^5	k_{obs} (d^{-1})
1b	Cl	Mes	Mes	H	H	too fast
1c	Cl	Dip	Dip	H	H	0.0580
3a	–	OH	O^-	H	H	46.3
3b	–	OH	O^-	Me	Me	14.3
3c	–	OH	O^-	Et	Et	15.5
3d	–	OH	O^-	Et	Me	14.2
3e	–	OH	O^-	Pr	Me	11.6
3f	–	OH	O^-	Ph	Ph	8.37
4a	PF_6	OMe	OMe	H	H	too fast
4b	PF_6	OEt	OEt	H	H	too fast
5a	PF_6	OMe	OMe	Me	Me	too fast
5b	PF_6	OEt	OEt	Me	Me	too fast
6a	PF_6	OMe	OMe	Et	Et	too fast
6b	PF_6	OEt	OEt	Et	Et	11.4
7a	PF_6	OMe	OMe	Me	Et	too fast
7b	PF_6	OEt	OEt	Me	Et	14.7
8a	PF_6	OMe	OMe	Me	Pr	13.9
8b	PF_6	OEt	OEt	Me	Pr	too fast
9	PF_6	OMe	OMe	Ph	Ph	3.05

[a] Mes = mesityl, Dip = 2,6-diisopropylphenyl.

constants k_{obs} were obtained by non-linear curve fits (Table 3) [9].

The imidazolium salts **1b** and **1c** were included as representatives for well established NHC precursors used in metal-organic chemistry. Here – as already reported before [9] – it is obvious that small changes in the salt structure have a significant influence on the H/D exchange rates. In case of the mesityl (mes)-substituted imidazolium salt **1b** the exchange is too fast to be measured reliably using the aforementioned NMR technique. In contrast, the 2,6-diisopropylphenyl (dip) substituents in **1c** seem to be large enough to shield the C^2-H group very effectively; the exchange is highly retarded, and the half-life is increased from minutes to about 12 d switching from **1b** to **1c**.

Simple imidazolium salts usually exhibit slow to mediocre H/D exchange rates [9] with pseudo-first order rate constants ranging from 0 – 12 d^{-1} corresponding to half-lifes in the range of several hours or days. Introducing two oxygen atoms at the heterocyclic skeleton speeds up the exchange process, typical half-lifes values for compounds **3** are in the range of 30 – 60 min.

In case of the dialkoxy salts **4** – **9** the additional cationic charge in the heterocycle usually leads to an acceleration of the H/D exchange process by a factor of > 50. In most cases the NMR method used was too slow to get reliable reaction rates. Here, only the residual proton content could be detected after a few minutes necessary to obtain the first NMR spectra, indicating an estimate for $k_{obs} > 800\ d^{-1}$. However, this trend is not clear-cut. Salts **6b**, **7b**, and **8a** exhibit reaction rates in the same order of magnitude as the corresponding basic skeletons **3**; for the *bis*(phenyl)-substituted derivative **9** only half of the rate compared to **3f** was found. Currently, there is no easy explanation for this observation, but the previous study with simple imidazolium salts already proved that subtle structural changes can have significant influence on these acid-base properties [9]. However, it can be assumed that the comparatively slow exchange of salts **6b**, **7b**, **8a**, and **9** could be based on sterical reasons. Substituents R^4 and R^5 in the "back" of the heterocyclic ring could force the methoxy or ethoxy groups to the front. This kind of buttressing effect would lead to a sterical shielding of the C^2-H position hampering the attack of deuterium cations.

Oxyimidazolium salts in Suzuki cross coupling reactions

For the synthetic organic chemist the formation of C–C bonds is presumably the most important and challenging task. Many transition metal-catalyzed coupling protocols have been introduced during the last decades. Amongst them, the palladium-catalyzed Suzuki-Miyaura reaction [16] has attracted much attention because this reaction allows aryl-aryl couplings using basically non-toxic staring materials, mild conditions and tolerates many functional groups. In recent years, much effort has been made to investigate NHCs as ligands for palladium-catalyzed cross-coupling reactions of aryl halides, and here especially aryl chlorides [17].

Owing to our ongoing interest in organic transformations in aqueous solution we recently reported that water-soluble calixarenes bearing imidazolium moieties are beneficial for the Suzuki cross-coupling in aqueous media [11]. Therefore, it was obvious to test the novel dialkoxy imidazolium salts in standard Suzuki coupling reactions. This idea was supported by a very recent finding that salt **5a** can enhance the ruthenium-catalyzed metatheses in pure water using the Grubbs-II catalyst [18].

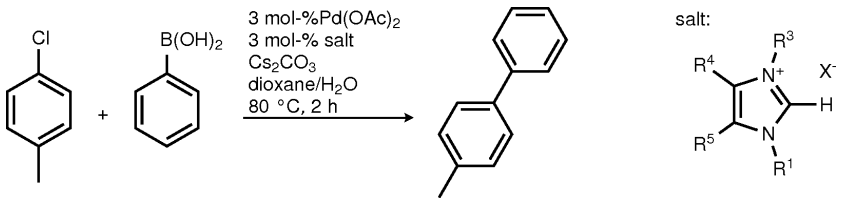


Table 4. Suzuki coupling reaction of 4-chloro-toluene with benzene boronic acid catalyzed by an *in situ* catalytic system (Mes = mesityl).

Salt	X	R^{1a}	R^{3a}	R^4	R^5	Rel. yields	Salt	X	R^{1a}	R^{3a}	R^4	R^5	Rel. yields
1b	Cl	Mes	Mes	H	H	=1							
3a		OH	O^-	H	H	0.35	**3b**		OH	O^-	Me	Me	0.10
3c		OH	O^-	Et	Et	0.10	**3d**		OH	O^-	Et	Me	0.10
3e		OH	O^-	Pr	Me	0.10	**3f**		OH	O^-	Ph	Ph	0.20
4a	PF_6	OMe	OMe	H	H	0.15	**4b**	PF_6	OEt	OEt	H	H	0.25
5a	PF_6	OMe	OMe	Me	Me	0.15	**5b**	PF_6	OEt	OEt	Me	Me	0.30
6a	PF_6	OMe	OMe	Et	Et	0.30	**6b**	PF_6	OEt	OEt	Et	Et	0.10
7a	PF_6	OMe	OMe	Me	Et	0.20	**7b**	PF_6	OEt	OEt	Me	Et	0.10
8a	PF_6	OMe	OMe	Me	Pr	0.25	**8b**	PF_6	OEt	OEt	Me	Pr	0.15
9	PF_6	OMe	OMe	Ph	Ph	0.10	–	without ligand precursor					0

To test the performance of simple dialkoxy imidazolium salts **4**–**9** and the parent heterocyclic systems **3a**–**f** in the Suzuki coupling a catalytic system was used, in which the catalytic species was prepared, as reported before [11], *in situ* from ligand precursors, palladium acetate as a source of palladium and cesium carbonate as a standard base. As reaction medium a mixture of dioxane/water approximately 5 : 1 (*cf.* Experimental Section) was used. Under these non-optimized standard conditions all ligand precursors were tested in the Suzuki coupling of 4-chlorotoluene with benzene boronic acid yielding 4-methylbiphenyl. As by-products 4,4-dimethyl-biphenyl and toluene stemming from homo-coupling and dehalogenation could be expected and were observed in traces in all reaction runs.

The relative yields of coupled product are summarized in Table 4; the yield of IMes **1b** as ligand precursor was used as a "benchmark", and all yields obtained for salts **3**–**9** were related to this yield. Here, we were not interested in optimizing the catalytic system or get high conversions. Main target of this study was to get a quick qualitative insight into the catalytic abilities of the novel oxy imidazolium salts **3**–**9**.

As expected, the catalytic abilities of all ligand precursors were inferior to the standard and often used IMes system **1b**. This is mainly due to the lack of steric bulk near the carbenoid center which is necessary to speed up the catalytic cycle. However, even with these simple systems about 10–30 % of the performance of IMes could be observed; even the neutral 1-hydroxy-imidazolium-3-oxides **3a**–**f** could be used in the Suzuki coupling reaction with mainly the same activity as compared to cationic species **4**–**9**.

Currently, we are exploring new synthetic pathways to dialkoxy imidazolium salts with considerably higher steric bulk at C^1 and C^3 because simple alkylation methods proved not useful for that purpose in our hands. Here, recent, preliminary findings showed that dialkoxy imidazolium salts bearing such sterically demanding groups can compete with or even excel the IMes system in Suzuki reactions.

Oxy imidazolium salts as novel anion recognition elements in supramolecular chemistry

We were also interested in the basic supramolecular properties of the synthesized imidazolium derivatives. The observed high kinetic acidity of the imidazolium derivatives of interest is, however, a major drawback for the application in anion recognizing moieties; by this exchange process the testing probe for the interaction with anions is lost in protic solvents. Nevertheless, the exchange process is slow in solvents such as DMSO or acetonitrile often used to study anion binding processes. In these media standard NMR titration experiments were possible yielding association constants K_{ass} ($L\,mol^{-1}$) and complexation-induced chemical shifts $\Delta\delta$ (ppm) by non-linear curve fits of the experimental data as reported before [10a]. The obtained data are summarized in Table 5.

In acetonitrile as solvent, a high response as expressed in the complexation-induced shift (CIS) $\Delta\delta$ (*i. e.* the difference of the C^2-proton resonance of the

Table 5. Association constants of imidazolium salts with iodide (NaI) determined by standard NMR titration experiments (errors ~ 10 %).

Entry	Salt	Solvent	K_{ass} (M^{-1})	$\Delta\delta$ (ppm)
1	**4a**	CD_3CN	32	−0.69
2	**4a**	CD_3CN / D_2O 80 : 20	n. c.[a]	−0.02
3	**4a**	CD_3CN / D_2O 50 : 50	–	–
4	**8a**	CD_3CN	29	−0.85
5	**8a**	CD_3CN / D_2O 80 : 20	20	−0.08
6	**4a**	DMSO	10	−0.04
7	**4b**	DMSO	10	−0.03
8	**5a**	DMSO	5	−0.06
9	**5b**	DMSO	5	−0.08

[a] Not calculated owing to the small change in chemical shift leading to non-reliable values.

pure host with the chemical shift extrapolated towards quantitative complex formation) of the salts **4a** and **8a** using iodide as a guest molecule could be observed (Table 5, entries 1 and 4). By the complexation process, the C^2-H resonance is shifted high-field by 0.7 – 0.8 ppm. No other protons in the imidazolium salts are affected indicating that the binding process takes place directly at this C–H acidic bond. The observed association constants are low compared to designed imidazolium-based anion receptors. However, taking into account that these data were obtained with very simple salts without any rational design and optimization towards binding, the anion receptor properties can be regarded as very promising.

As expected, adding small amounts of D_2O (Table 5, entries 2, 3, and 5) basically interrupts the binding process, and only a small response could be observed towards the added anion. The association constants dropped owing to competition of water in the solvation process of the anion. Furthermore, the fast H/D exchange process in the protic environment strongly interfered with the measurements. In DMSO as an alternative medium the salts **4** and **5** exhibited only slight affinity towards iodide as an anion (Table 5, entries 6 – 9).

In summary, dialkoxy imidazolium salts proved to be a valuable extension of the well known and established family of imidazolium salts. The heterofunctionalization on the core imidazolium skeleton modifies the electronic properties, and the kinetic acidity of the C^2-proton is highly increased. This feature could be exploited in first Suzuki coupling reactions using these salts as ligand precursors. Here, further optimization of the catalytic performance of ligand precursors by the introduction of bulky substituents can be envisaged.

Experimental Section

Melting points were determined on an Electrothermal IA9100 apparatus and are uncorrected. Infrared (IR) spectra were obtained on an ASI React IR-1000 instrument using ATR. Absorption maxima are given in wave numbers (cm^{-1}). NMR spectra were recorded on Varian 200 (200.10 MHz for ^1H and 50.32 MHz for ^{13}C), Bruker Avance 300 (300.13 MHz for ^1H and 75.47 MHz for ^{13}C), Bruker Avance 400 (400.13 MHz for ^1H and 100.62 MHz for ^{13}C), Joel JNM EX400 (400.05 MHz for ^1H and 100.50 MHz for ^{13}C), or Joel JNM EX400 (400.13 MHz for ^1H and 100.62 MHz for ^{13}C) instruments. Tetramethylsilane was used as internal standard (δ = 0.00 ppm) for the ^1H NMR spectra and the solvent signals for the ^{13}C NMR spectra [$\delta_C(CDCl_3)$ = 77.0, $\delta_C([D_6]DMSO)$ = 39.5, $\delta_C([D_4]methanol)$ = 49.3 ppm]. For measurements in D_2O, the solvent signal was used as reference ($\delta_H(D_2O)$ = 4.80 ppm) and a trace amount of $[D_4]$methanol for ^{13}C spectra. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. Mass spectra were obtained with spectrometers Finnigan MAT 95 XP (EI), Micromass Zabspec (FAB), Shimadzu Biotech AXIMA Confidence (MALDI-TOF spectra), or Thermo Finnigan LTQ FT (ESI). Matrices for FAB and MALDI ionization are given individually. Microanalyses were performed on a Ce Instruments EA 1119 CHNS.

Solvent mixtures used for chromatography or recrystallization are volume/volume (v/v) mixtures. Solvents were dried by standard procedures. All reaction mixtures were stirred magnetically, unless otherwise noted.

General procedure for the preparation of 1-hydroxy-1H-imidazole-3-oxide derivatives

In methanol, the appropriate diketone (1 equivalent) and paraformaldehyde (1.2 equivalent) were dissolved. After cooling, the reaction mixture was stirred for 20 min, and then an aqueous solution of hydroxylamine hydrochloride and 10 N HCl was added and the mixture stirred for further 20 h at r. t. Subsequently the pH value of the solution was adjusted to 5 by using 12 N NaOH. The formed precipitate was filtered, washed with cold water, cold MeOH and cold Et_2O, and finally dried *in vacuo*.

*1-Hydroxy-4,5-dimethyl-1H-imidazole-3-oxide (**3b**)*

A mixture of diacetyl (8.70 mL, 100 mmol), paraformaldehyde (3.60 g, 120 mmol), hydroxylamine hydrochloride (14.0 g, 200 mmol) and 10 N HCl (2 mL) was stirred for 20 h at r. t. A colorless product was obtained (3.37 g, 26.0 mmol, 26 %). M. p. 204 – 205 °C. – IR: ν = 3100, 2360, 2340, 1440, 1391, 1233, 1191, 993, 854, 765, 726, 635 cm^{-1}. – ^1H NMR (200 MHz, $[D_6]$DMSO): δ = 2.12 (s, 6 H), 8.22 (s, 1 H). – ^{13}C NMR (100 MHz, $[D_6]$DMSO): δ = 6.72,

120.32, 121.34. – MS ((+)-ESI): *m/z* = 129 (calcd. 129.1 for $C_5H_9N_2O_2$, $[M+H]^+$).

*1-Hydroxy-4,5-diethyl-1H-imidazole-3-oxide (**3c**)*

3,4-Hexadion (5.32 mL, 43.8 mmol), paraformaldehyde (1.58 g, 52.6 mmol), hydroxylamine hydrochloride (6.09 g, 87.6 mmol) and 10 N HCl (1 mL) were stirred together for 20 h at r. t. A colorless product was obtained (1.07 g, 7.00 mmol, 16 %). M. p. 132 – 133 °C. – IR: ν = 3113, 2976, 2939, 2877, 1457, 1328, 1228, 1116, 982 cm^{-1}. – ^1H NMR (200 MHz, D_2O): δ = 1.13 (t, *J* = 7.5 Hz, 6H), 2.59 (q, *J* = 7.5 Hz, 4H), 8.18 (s, 1 H). – ^{13}C NMR (100 MHz, D_2O): δ = 12.60, 14.73, 121.70, 126.80. – MS ((+)-ESI): *m/z* = 157 (calcd. 157.1 for $C_7H_{13}N_2O_2$, $[M+H]^+$).

*5-Ethyl-1-hydroxy-4-methyl-1H-imidazole-3-oxide (**3d**)*

2,3-Pentadion (5.22 mL, 50.0 mmol), paraformaldehyde (1.80 g, 60.0 mmol), hydroxylamine hydrochloride (6.94 g, 100 mmol) and 10 N HCl (1 mL) were stirred together for 20 h at r. t. A colorless product was obtained (1.72 g, 12.0 mmol, 24 %). M. p. 154 – 155 °C. – IR: ν = 3106, 2980, 2940, 2890, 1461, 1339, 1226, 1106, 997, 772, 612 cm^{-1}. – ^1H NMR (200 MHz, D_2O): δ = 1.14 (t, *J* = 7.6 Hz, 3 H), 2.15 (s, 3 H), 2.61 (q, *J* = 7.6 Hz, 2 H), 8.23 (s, 1 H). – ^{13}C NMR (100 MHz, D_2O): δ = 5.98, 12.10, 14.75, 121.51, 121.93, 126.99. – MS ((+)-ESI): *m/z* = 143 (calcd. 143.1 for $C_6H_{11}N_2O_2$, $[M+H]^+$).

*1-Hydroxy-4-methyl-5-propyl-1H-imidazole-3-oxide (**3e**)*

2,3-Hexadion (3.21 mL, 26.3 mmol), paraformaldehyde (950 mg, 31.5 mmol), hydroxylamine hydrochloride (3.65 g, 52.5 mmol) and 10 N HCl (1 mL) were stirred together for 20 h at r. t. A beige product was obtained (1.04 g, 6.70 mmol, 25 %). M. p. 65 – 66 °C. – IR: ν = 3112, 3021, 2956, 2918, 2868, 1615, 1462, 1228, 1112, 899, 772, 684 cm^{-1}. – ^1H NMR (200 MHz, D_2O): δ = 0.77 (t, *J* = 7.4 Hz, 3 H), 1.48 (m, 2 H), 2.07 (s, 3 H), 2.49 (t, *J* = 7.3 Hz, 2 H), 8.40 (s, 1 H). – ^{13}C NMR (100 MHz, D_2O): δ = 6.18, 12.46, 20.97, 22.89, 122.23, 122.28, 125.60. – MS ((+)-ESI): *m/z* = 157.1 (calcd. 157.1 for $C_7H_{12}N_2O_2$, $[M+H]^+$).

*1-Hydroxy-4,5-diphenyl-1H-imidazole-3-oxide (**3f**)*

To a solution of benzil (42.1 g, 200 mmol) in glacial acetic acid (160 mL), paraformaldehyde (9.00 g, 300 mmol) and hydroxylamine hydrochloride (27.8 g, 400 mmol) were added. After stirring for 8 h at 50 °C a colorless precipitate was formed, isolated by filtration, washed with water, and recrystallized from chloroform yielding the colorless product (9.10 g, 40.0 mmol, 20 %). M. p. 227 – 229 °C. – IR: ν = 3391, 3151, 2983, 1443, 1212, 1074, 1028, 914, 839, 749, 686 cm^{-1}. – ^1H NMR (200 MHz, $CDCl_3$): δ = 7.34 (10 H, m, Ar*H*), 8.42 (1 H, s, NC*H*N). – MS ((+)-ESI): *m/z* = 253 (calcd. 252.3 for $C_{15}H_{12}N_2O_2$, $[M+H]^+$).

General procedure for the alkylation of 1-hydroxy-1H-imidazole-3-oxide derivatives

The corresponding 1-hydroxy-1*H*-imidazole-3-oxide derivative **3** (1 equivalent) was added to dimethylsulfate or diethylsulfate (2 equivalents) and the mixture stirred for 2 h. After addition of $NaHCO_3$ (1 equivalent) stirring was continued for further 20 h. First H_2O_{dest}, then NH_4PF_6 (1 equivalent) were added, and the reaction mixture was placed in an ultrasonic bath. The white precipitate was filtered, washed with H_2O_{dest}, recrystallized several times from methanol, and finally dried *in vacuo*.

*1,3-Dimethoxy-1H-imidazol-3-ium hexafluorophosphate (**4a**)*

1-Hydroxy-1*H*-imidazole-3-oxide (**3a**, 8.01 g, 80.0 mmol), dimethylsulfate (15.2 mL, 160 mmol) and $NaHCO_3$ (6.71 g, 80.0 mmol) were stirred together for 20 h, and H_2O_{dest} (20 mL) and NH_4PF_6 (13.1 g, 80.0 mmol) were added. A colorless product was obtained (6.86 g, 25.0 mmol, 31 %). M. p. 84 – 85 °C (lit. [12] 83 – 84 °C). – IR: ν = 3163, 2958, 1556, 1456, 1445, 1376, 1015, 944, 760, 719, 707 cm^{-1}. – ^1H NMR (200 MHz, [D$_6$]DMSO): δ = 4.25 (d, *J* = 0.7 Hz, 6H), 8.29 (dd, *J* = 2.0 Hz, 0.7 Hz, 2 H), 10.31 (td, *J* = 2.0 Hz, 0.7 Hz, 1 H). – ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 69.38, 116.90, 124.61. – MS ((+)-ESI): *m/z* = 129 (calcd. 129.07 for $C_5H_9N_2O_2$, $[M]^+$). – MS ((–)-ESI): *m/z* = 145 (calcd. 144.9 for PF_6, $[PF_6]^-$).

*1,3-Diethoxy-1H-imidazol-3-ium hexafluorophosphate (**4b**)*

1-Hydroxy-1*H*-imidazole-3-oxide (**3a**, 1.01 g, 10.0 mmol), diethylsulfate (2.60 mL, 20.0 mmol) and $NaHCO_3$ (0.840 g, 10.0 mmol) were stirred together for 20 h, and H_2O_{dest} (2.5 mL) and NH_4PF_6 (1.63 g, 10.0 mmol) were added. A colorless product was obtained (400 mg, 1.00 mmol, 10 %). M. p. 101 – 102 °C (lit. [12] 99 – 102 °C). – IR: ν = 3157, 3002, 1559, 1479, 1446, 1395, 1120, 1006, 802, 726, 599 cm^{-1}. – ^1H NMR (200 MHz, [D$_6$]DMSO): δ = 1.33 (t, *J* = 7.0 Hz, 6 H), 4.50 (q, *J* = 7.0 Hz, 4H), 8.27 (d, *J* = 2.0 Hz, 2 H), 10.27 (t, *J* = 2.0 Hz, 1 H). – ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 12.73, 78.14, 117.68, 130.15. – MS ((+)-ESI): *m/z* = 157 (calcd. 157.1 for $C_7H_{13}N_2O_2$, $[M]^+$). – MS ((–)-ESI): *m/z* = 145 (calcd. 144.9 for PF_6, $[PF_6]^-$).

*1,3-Dimethoxy-4,5-dimethyl-1H-imidazol-3-ium hexafluorophosphate (**5a**)*

Compound **3b** (1.71 g, 13.0 mmol), dimethylsulfate (2.53 mL, 27.0 mmol) and $NaHCO_3$ (1.09 g, 13.0 mmol)

were stirred together for 20 h, and H_2O_{dest} (3.4 mL) and NH_4PF_6 (2.12 g, 13.0 mmol) were added. A colorless product was obtained (1.23 g, 4.00 mmol, 31 %). M. p. 130 – 131 °C. – IR: ν = 3161, 3011, 2960, 1640, 1554, 1461, 1450, 1394, 1119, 1084, 948, 812, 779, 572 cm^{-1}. – ^1H NMR (200 MHz, [D_6]DMSO): δ = 2.29 (s, 6H), 4.21 (s, 6 H), 10.21 (s, 1 H). – ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 6.13, 69.41, 121.98, 127.26. – MS ((+)-ESI): *m/z* = 157 (calcd. 157.1 for $C_7H_{13}N_2O_2$, $[M]^+$). – MS ((–)-ESI): *m/z* = 145 (calcd. 144.9 for PF_6, $[PF_6]^-$).

*1,3-Diethoxy-4,5-dimethyl-1H-imidazol-3-ium hexafluorophosphate (**5b**)*

Compound **3b** (1.28 g, 10.0 mmol), diethylsulfate (2.60 mL, 20.0 mmol) and $NaHCO_3$ (0.840 g, 10.0 mmol) were stirred together for 20 h, and H_2O_{dest} (5 mL) and NH_4PF_6 (1.63 g, 10.0 mmol) were added. A colorless product was obtained (3.11 g, 9.00 mmol, 90 %). M. p. 124 – 125 °C. – IR: ν = 3159, 2991, 2945, 1632, 1540, 1479, 1447, 1396, 1120, 1086, 1008, 880, 813, 740, 576 cm^{-1}. – ^1H NMR (200 MHz, [D_6]DMSO): δ = 1.35 (t, *J* = 7.0 Hz, 6H), 2.28 (s, 6H), 4.44 (q, *J* = 7.0 Hz, 4H), 10.17 (s, 1 H). – ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 6.51, 12.84, 78.12, 122.42, 128.03. – MS ((+)-ESI): *m/z* =185 (calcd. 185.1 for $C_9H_{17}N_2O_2$, $[M]^+$). – MS ((–)-ESI): *m/z* = 145 (calcd. 144.9 for PF_6, $[PF_6]^-$).

*4,5-Diethyl-1,3-dimethoxy-1H-imidazol-3-ium hexafluorophosphate (**6a**)*

Compound **3c** (0.920 g, 5.92 mmol), dimethylsulfate (1.12 mL, 11.8 mmol) and $NaHCO_3$ (0.500 g, 11.8 mmol) were stirred together for 20 h, and H_2O_{dest} (2 mL) and NH_4PF_6 (0.970 g, 5.92 mmol) were added. A colorless product was obtained (0.600 g, 1.81 mmol, 31 %). M. p. 120 – 122 °C. – IR: ν = 3152, 2998, 2953, 2888, 1452, 1327, 1233, 1209, 1108, 950, 877, 820, 741, 555 cm^{-1}. – ^1H NMR (200 MHz, [D_6]DMSO): δ = 1.18 (t, *J* = 7.5 Hz, 6H), 2.74 (q, *J* = 7.5 Hz, 4H), 4.25 (s, 6H), 10.27 (s, 1 H). – ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 13.54, 15.08, 70.26, 78.15, 126.92, 127.84. – MS ((+)-ESI): *m/z* = 185 (calcd. 185.1 for $C_9H_{17}N_2O_2$, $[M]^+$). – MS ((–)-ESI): *m/z* = 145 (calcd. 144.9 for PF_6, $[PF_6]^-$).

*1,3-Diethoxy-4,5-diethyl-1H-imidazol-3-ium hexafluorophosphate (**6b**)*

Compound **3c** (2.00 g, 12.8 mmol), diethylsulfate (3.35 mL, 25.6 mmol) and $NaHCO_3$ (1.08 g, 12.8 mmol) were stirred together for 20 h, and H_2O_{dest} (4 mL) and NH_4PF_6 (2.09 g, 12.8 mmol) were added. A colorless product was obtained (3.12 g, 8.72 mmol, 68 %). M. p. 86 – 87 °C. – IR: ν = 3149, 2989, 2944, 1482, 1455, 1333, 1206, 1109, 1006, 825, 740 cm^{-1}. – ^1H NMR (200 MHz, [D_6]DMSO): δ = 1.18 (t, *J* = 7.5 Hz, 6 H), 1.37 (t, *J* = 7.0 Hz, 6 H), 2.73 (q, *J* = 7.5 Hz, 4 H), 4.48 (q, *J* = 7.0 Hz, 4 H), 10.20 (s, 1 H). – ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 12.91, 12.94, 14.67, 78.57, 126.81, 128.03. – MS ((+)-ESI): *m/z* = 213 (calcd. 213.2 for $C_{11}H_{21}N_2O_2$, $[M]^+$). – MS ((–)-ESI): *m/z* = 145 (calcd. 144.9 for PF_6, $[PF_6]^-$).

*1,3-Dimethoxy-5-ethyl-4-methyl-1H-imidazol-3-ium hexafluorophosphate (**7a**)*

Compound **3d** (1.60 g, 11.3 mmol), dimethylsulfate (2.14 mL, 22.6 mmol) and $NaHCO_3$ (0.950 g, 11.3 mmol) were stirred together for 20 h, and H_2O_{dest} (3 mL) and NH_4PF_6 (1.84 g, 11.3 mmol) were added. A colorless product was obtained (2.96 g, 9.40 mmol, 83 %). M. p. 116 – 118 °C. – IR: ν = 3155, 2992, 2964, 1628, 1552, 1456, 1444, 1213, 1101, 1008, 998, 948, 877, 810, 740, 576, 555 cm^{-1}. – ^1H NMR (200 MHz, [D_6]DMSO): δ = 1.17 (t, *J* = 7.5 Hz, 3 H), 2.31 (s, 3 H), 2.73 (q, *J* = 7.5 Hz, 2 H), 4.23 (d, *J* = 4.2 Hz, 6 H), 10.23 (s, 1 H). – ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 6.21, 12.51, 14.58, 69.40, 69.76, 121.73, 126.58, 127.27. – MS ((+)-ESI): *m/z* = 171 (calcd. 171.1 for $C_8H_{15}N_2O_2$, $[M]^+$). – MS ((–)-ESI): *m/z* = 145 (calcd. 144.9 for PF_6, $[PF_6]^-$).

*1,3-Diethoxy-5-ethyl-4-methyl-1H-imidazol-3-ium hexafluorophosphate (**7b**)*

Compound **3d** (2.00 g, 14.1 mmol), diethylsulfate (3.69 mL, 28.1 mmol) and $NaHCO_3$ (1.18 g, 14.1 mmol) were stirred together for 20 h, and H_2O_{dest} (4 mL) and NH_4PF_6 (2.29 g, 14.1 mmol) were added. A colorless product was obtained (1.81 g, 5.26 mmol, 38 %). M. p. 74 – 75 °C. – IR: ν = 3159, 2986, 2942, 1480, 1445, 1396, 1215, 1117, 1009, 885, 818, 741 cm^{-1}. – ^1H NMR (200 MHz, [D_6]DMSO): δ = 1.17 (t, *J* = 7.5 Hz, 3 H), 1.36 (td, *J* = 7.0 Hz, 1.6 Hz, 6H), 2.30 (s, 3 H), 2.72 (q, *J* = 7.5 Hz, 2 H), 4.46 (qd, *J* = 7.0 Hz, 3.0 Hz, 4H), 10.18 (s, 1 H). – ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 6.41, 12.41, 12.86, 12.91, 14.70, 78.15, 78.55, 122.18, 126.97, 127.98. – MS ((+)-ESI): *m/z* = 199 (calcd. 199.1 for $C_{10}H_{19}N_2O_2$, $[M]^+$). – MS ((–)-ESI): *m/z* = 145 (calcd. 144.9 for PF_6, $[PF_6]^-$).

*1,3-Dimethoxy-4-methyl-5-propyl-1H-imidazol-3-ium hexafluorophosphate (**8a**)*

Compound **3e** (8.00 g, 51.2 mmol), dimethylsulfate (9.71 mL, 102 mmol) and $NaHCO_3$ (4.30 g, 51.2 mmol) were stirred together for 20 h, and H_2O_{dest} (10 mL) and NH_4PF_6 (8.35 g, 51.2 mmol) were added. A beige product was obtained (4.29 g, 13.0 mmol, 26 %). M. p. 40 – 42 °C. – IR: ν = 3486, 3148, 2972, 2874, 1631, 1443, 1213, 1106, 1004, 948, 845, 820, 733 cm^{-1}. – ^1H NMR (200 MHz, [D_6]DMSO):

δ = 0.91 (t, J = 7.4 Hz, 3 H), 1.58 (m, 2 H), 2.30 (s, 3 H), 2.67 (t, J = 7.4 Hz, 2 H), 4.23 (d, J = 1.8 Hz, 6H), 10.25 (s, 1 H). – ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 6.38, 13.07, 21.04, 22.62, 69.38, 69.72, 122.23, 125.17, 127.36. – MS ((+)-ESI): *m/z* = 185 (calcd. 185.1 for $C_9H_{17}N_2O_2$, $[M]^+$). – MS ((–)-ESI): *m/z* = 145 (calcd. 144.9 for PF_6, $[PF_6]^-$).

*1,3-Diethoxy-4-methyl-5-propyl-1H-imidazol-3-ium hexafluorophosphate (**8b**)*

Compound **3e** (8.00 g, 51.2 mmol), diethylsulfate (13.4 mL, 102 mmol) and $NaHCO_3$ (4.30 g, 51.2 mmol) were stirred together for 20 h, and H_2O_{dest} (10 mL) and NH_4PF_6 (8.35 g, 51.2 mmol) were added. A colorless product was obtained (1.55 g, 4.53 mmol, 8 %). M. p. 70 – 71 °C. – IR: ν = 3153, 2968, 2939, 2874, 1632, 1452, 1397, 1214, 1104, 1009, 948, 822, 740 cm^{-1}. – ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 0.91 (t, J = 7.4 Hz, 3 H), 1.36 (td, J = 7.0 Hz, 0.7 Hz, 6 H), 1.58 (m, 2 H), 2.29 (s, 3 H), 2.70 (t, J = 7.4 Hz, 2 H), 4.46 (q, J = 7.0 Hz, 4H), 10.25 (s, 1 H). – ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 6.57, 12.87, 12.92, 13.08, 20.94, 22.75, 78.13, 78.50, 122.65, 125.53, 128.17. – MS ((+)-ESI): *m/z* = 213 (calcd. 213.2 for $C_{11}H_{21}N_2O_2$, $[M]^+$). – MS ((–)-ESI): *m/z* = 145 (calcd. 144.9 for PF_6, $[PF_6]^-$).

*1,3-Dimethoxyy-4,5-diphenyl-1H-imidazol-3-ium hexafluorophosphate (**9**)*

Compound **3f** (5.00 g, 20.0 mmol), dimethylsulfate (9.48 mL, 100 mmol) and $NaHCO_3$ (1.68 g, 20.0 mmol) were stirred together for 20 h, and H_2O_{dest} (5.5 mL) and NH_4PF_6 (3.26 g, 20.0 mmol) were added. A colorless product was obtained (3.80 g, 10.0 mmol, 50 %). M. p. 178 – 180 °C. – IR: ν = 3145, 2772, 1448, 1199, 1050, 954, 824, 756, 692 cm^{-1}. – ^{1}H NMR (200 MHz, [D$_6$]DMSO) δ = 4.09 (s, 6 H), 7.49 (m, 10 H), 10.67 (s, 1 H). – ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 69.56, 122.56, 125.42, 128.82, 129.10, 130.00, 130.60. – MS ((+)-ESI): *m/z* = 281 (calcd. 281.1 for $C_{15}H_{17}N_2O_2$, $[M]^+$). – MS ((–)-ESI): *m/z* = 145 (calcd. 144.9 for PF_6, $[PF_6]^-$).

General procedure for the Suzuki coupling reactions

In a small vial Cs_2CO_3 (652 mg, 2.00 mmol) was added to a solution of the ligand precursor (0.03 mmol) in 0.400 mL of water and heated to 80 °C. After that, a solution of $Pd(OAc)_2$ in dioxane [0.600 mL, concentration of the stock solution c = 0.05 mol L^{-1}, 0.03 mmol $Pd(OAc)_2$] was added. The resulting mixture was stirred at 80 °C for 30 min. Then, 4-chloro-toluene (118 μL, 1.00 mmol) and benzene boronic acid dissolved in dioxane (1.5 mL, concentration of the stock solution c = 1.5 mol L^{-1}) were added, and the resulting mixture was stirred for 2 h (80 °C). After cooling to r. t., the aqueous phase was extracted with chloroform, the organic phases filtered over Celite® and dried using molecular sieves (3 Å). A 0.3 mL aliquot of the chloroform extract was diluted with $CDCl_3$ (0.3 mL), and the relative content of 4-chloro-toluene, 4-methyl-biphenyl as well as the (potential) by-products 4,4′-dimethyl-biphenyl and toluene was determined using ^{1}H NMR spectroscopy. Using IMes **1b** as ligand precursor in this experimental setup, after 2 h reaction time 30 % conversion was observed. By blank experiments using premixed samples of starting material and all potential products it could be proven that the extraction process did not affect the composition of the samples.

General procedure for NMR titration experiments

All ^{1}H NMR titration experiments were performed in the deuterated solvent as follows: The host concentration was kept constant at 2.50×10^{-3} mol L^{-1}. The guest solutions were added from stock solutions (0.15 mol L^{-1}) in the appropriate solvent; the guest concentration was varied with the ratio host/guest ranging from about 1 to 10. Each experiment consisted of 10 – 15 points. In all cases, the C^2-H signal was followed, and association constants (K_{ass}) were calculated using a non-linear curve fit of the observed chemical shifts using the program CHEMEQUI [19].

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