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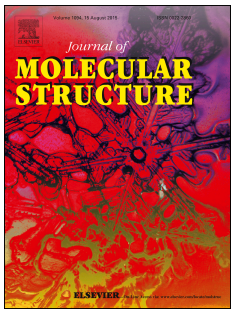

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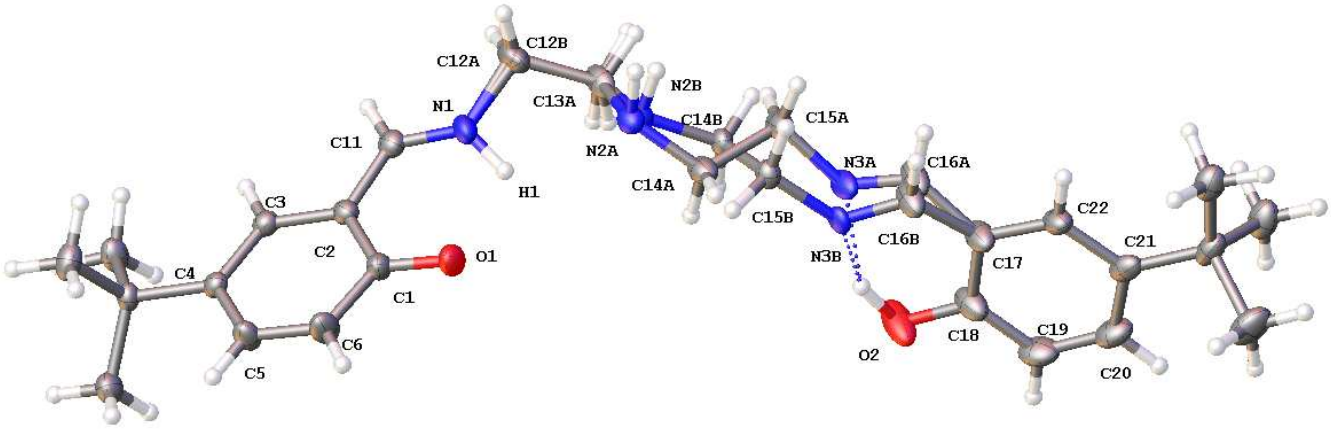

Synthesis and characterization of 5- and 7-donor Schiff base ligands and spectroscopic evidence for tautomerism: a crystal structure showing tautomeric forms within one ligand

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Abstract

An improved method for the synthesis of fifteen Schiff base ligands, of which six are novel, are reported. Optimised yields were obtained and the ligands have been fully characterized via several analytical techniques. It was found that tautomeric forms of these novel ligands exist and spectroscopic evidence for this phenomenon is provided. A crystal structure illustrating both enol and keto tautomeric forms in a new ligand, complements spectroscopic evidence obtained. To our knowledge, this is the first reported evidence of tautomeric forms within the same ligand.

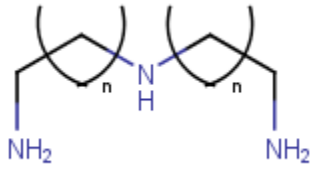
1. Introduction

The condensation reaction of substituted *salicylaldehyde's,* or substituents of 2-hydroxy naphthylaldehydes with primary amines usually results in the formation of multi-donor Schiff base ligands [1-3]. Symmetrical salen type ligands such as *saldienH2*, *salnH3* or *saltrin* (see figure 1 for structures of these ligands) have found various applications [4,5] which include making dyes or pigments and in making of polymers[6]. These ligands are malleable with the ability to have multiple donor groups. One of the properties of these ligands is their abilityto complex to a range of metal ions forming very stable metal complexes. The formed complexes have been studied for catalysis, photochromism and biological studies[7]. Because these ligands are multi-donor with various donor groups, they also have high chelation ability and therefore can be used in hydrometallurgical solvent extraction studies [4,8,9].

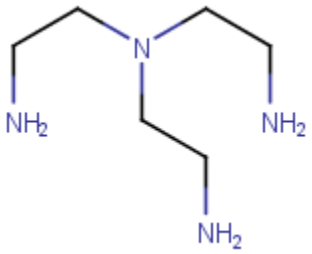
There has been considerable effort given to the different ways of synthesising salen type ligands[4,10-12]. From literature El Sheriff *et. al.* [4] reviews two of the commonly used methods; the Schiff base condensation and the template synthesis method. For *saldienH2*, *salnH3* and *sal-*

trin type ligands, the Schiff base condensation method is the preferred method [13-17]. For ligands with *stereogenic* centres the template synthesis method is the preferred method [4].

The template synthesis often involves the use of an appropriate template; for example, the use of metal ion to form the desired products[18]. The formed complex can then be reduced to the desired ligand as shown in Scheme 1. The Schiff base condensation method on the other hand is often associated with relatively moderate to low yield and difficulties in purification[4]. The difficulties in the synthesis of these ligands are often associated with the sensitivity of the imine bond and the difficulty in separation of the formed products from the reactants. The sensitivity of the formed imine bond in the presence of an acid or base is often accompanied with re-hydrolysis of the formed imine to the starting reactants [4].



SaldienH2 (class A) and *salnH3* (class B) for n =1 and 2



saltrin (class C) ligands

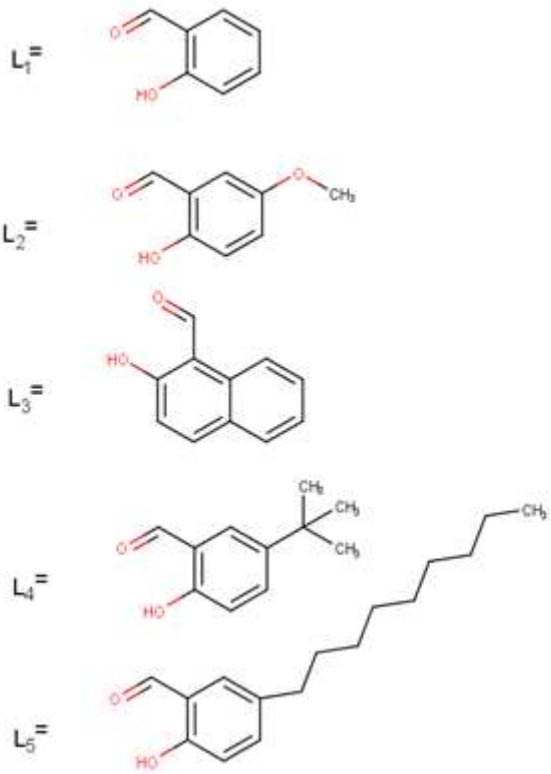
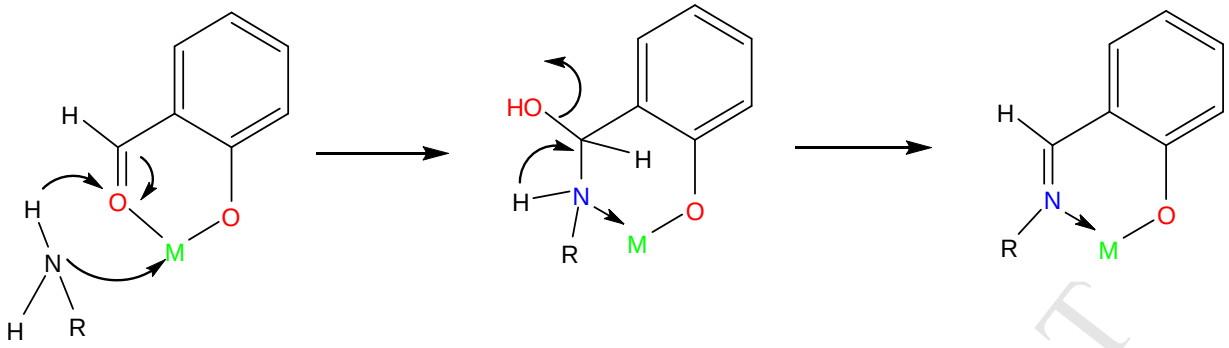
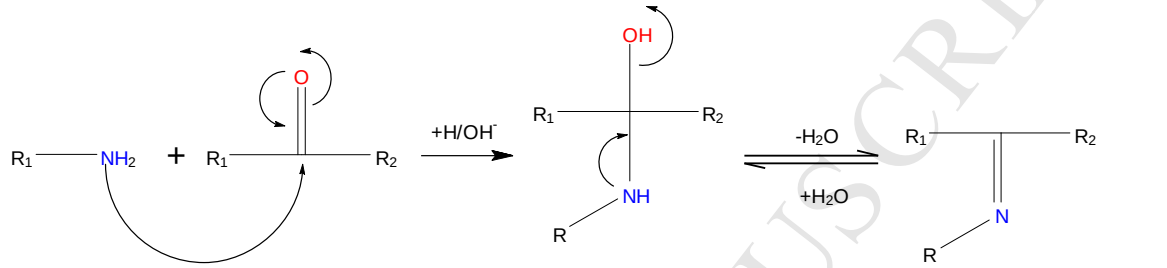


Figure 1 Representation of the N-donor starting amines and aldehydes (L_1- L_5). The typical reaction involves 1 equivalent of amine with 2 equivalents of aldehyde. For class C ligands, 3 equivalents of aldehyde are required.



Scheme 1 The template synthesis of Schiff base complexes according to El-Sheriff *et al*[4]



Scheme 2 The condensation reaction of a primary amine with a carbonyl group incorporating the mechanistic arrows according to Zoubi *et al*[10].

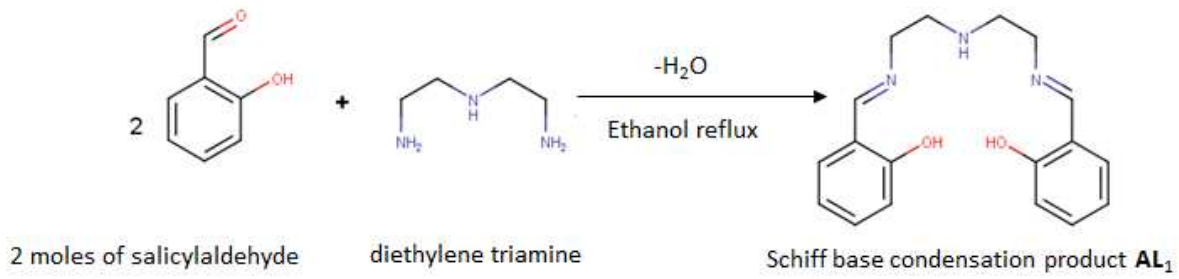
There are extensive efforts that have been developed in the synthesis of these Schiff base ligands [6]. Most of these methods deal with the various modifications that have been undertaken to increase yield and purity. In this paper we synthesize fifteen Schiff base ligands which we have divided into three classes as shown in **Figure 1**. Various optimization techniques are used to increase yield and purity. Six new ligands **AL_4**, **AL_5**, **BL_2**, **BL_4**, **BL_5** and **CL_5** are synthesised and discussed while the other nine ligands have previously been synthesised and are given in supplementary material, sections **S1** and **S2**. The electronic effect of the various substituents and different alkyl groups added between the central N-donor atoms are also studied. The tautomeric behaviour of ligand **BL_3** is explicitly elucidated through spectroscopic means. For the first time, a crystal structure of the new ligand **AL_4** is shown to display tautomeric behaviour within the same ligand which is also discussed.

2. Results and Discussion

2.1 Synthetic procedures

Method 1: Synthesis of class A ligands

For ligand **AL_1** two equivalents of *salicylaldehyde*, was weighed and dissolved in ethanol under reflux. One equivalent of *diethylenetriamine* was weighed and immediately dissolved in ethanol. This was then added slowly to the reaction solution and then allowed to reflux for 24 hours to obtain a clear yellow solution. The ethanol solution was evaporated using rotary evaporation. As the solvent was reduced, a yellow crystalline solid was obtained, filtered, dried and characterized. The reaction equation is given in **Scheme 3**. The same method was used for all other ligands under this class. All the molecular weights are given in the supplementary materials provided.



Scheme 3 Synthesis of Ligand **AL_1** through condensation reaction with *salicylaldehyde*

For ligand **AL_1**, **AL_3** and **AL_4** these were obtained as solids with yields of 84 %, 86 % and 89 % respectively. The new ligand **AL_5** was obtained as a yellow viscous liquid at 89 % yield. The ligand **AL_3** was obtained in excessively higher yield than reported by Heindel *et al*[19] who reported a 45 % yield. The ligand **AL_2** was obtained as a red black solid that slowly turned completely black. This black mass was also reported by Parida *et al*[20]. The analysis of this black mass indicated a mixture of imine and the various products of incomplete reaction and therefore this ligand was resynthesized using method 2 below.

Method 2:

The second method used chloroform in place of ethanol as used in method 1. Therefore, two equivalents of **L_2** aldehyde (4-methoxy *salicylaldehyde*) was dissolved in 40 ml of chloroform under reflux. One equivalent of diethylenetriamine was measured and dissolved in 10ml ethanol. The diamine was added slowly to the chloroform solution over a 1hr period. The volume of the resultant yellow solution was reduced using a rotary evaporator and a yellow solid was

obtained after almost all the solvent was removed. This was analysed as pure and in high yield of 83 %.

Method 3: Synthesis of class B ligands

An attempt was made to synthesise ligand **BL_1** using the same Schiff base condensation method 1 above, however the products obtained were in moderate yield (65 %) as had also been reported by Heindel *et al*[19] and upon analyses it showed the presence of some of the starting materials. The ligand was therefore synthesised using an excess of the diamine. Since the use of excess amine could potentially lead to formation of unsymmetrical ligand the diamine was added over two hours with reflux to form the yellow solution. The product was allowed to reflux for a further 22 hours, the ethanol was subsequently evaporated using the rotary evaporator and the resulting product washed 3 times to get rid of amine and unsymmetrical products. The final "wet" product was dried under vacuum for 3 days and analysed as pure.

The same method was used for the other ligands under the same class ligand **BL_1**, **BL_2**, **BL_4** and **BL_5** were obtained with high purity at 86 %, 67 %, 68 % and 89 %. For ligand **BL_3** two products were obtained **BL_{3a}** and **BL_{3b}** at 22 % and 70 % yield respectively. The melting point for the yellow compound is 215 – 217 °C and the orange compound melted at 217 – 219 °C. These two products are discussed in the tautomerism study section in 2.6.

Synthesis of class C ligands

These ligands were synthesised using both methods 1 and 2. The ligands **CL_1** and **CL_2** were synthesised using method 1 to obtain crystalline solids that could be recrystallized in ethanol to obtain highly pure products at 89 % yield each, this value is improved compared to the literature value by Mustapha *et al*[16] who recorded 55 % for **CL_1** while Kim *et al*[21] reported a comparable 90 % yield. The ligands **CL_3**, **CL_4** and **CL_5** were synthesised using method 2 and **CL_3** was obtained as a yellowish green powder while **CL_4** and **CL_5** were obtained as very viscous yellow oils. These were obtained in 87 %, 85 % and 86 % yield respectively. The ligand **CL_3** had previously been reported at 76% yield using THF solution by Kaur *et al*[17], while **CL_2** was synthesised by Bhattacharyya *et al*[22], however, no yield was given. NMR spectra for **CL_1** is shown in **figures S15** and **S16** in the supplementary material on pages 14 and 15.

Method 4: Synthesis of tautomeric product **BL_3**

Ligand **BL_3** was initially synthesised using method 2 above and the results obtained showed two products, see **Figure 2**. The results of the product is further discussed in section 2.6. To counter the above formation of the two products Method 4 was then used for the optimised synthesis of **BL_3**. An appropriate mass of 2-hydroxy naphthylaldehyde was weighed and completely dissolved in 40ml chloroform. Half an equivalent of *bis(3-aminopropyl)amine* was weighed and dissolved in 10 ml ethanol. The resultant mixture was allowed to stir at room temperature using a magnetic stirrer for 24 hours to obtain a yellow solution. The solution was evaporated using a rotary evaporator at room temperature to remove the chloroform and the resultant product washed 3 times with water so as to remove excess amine and unsymmetrical products. The obtained "wet" yellow solid was vacuum dried for 3 days to obtain dry yellow lumps, yield 86 %, mp 215-217 °C. The melting point was the same as previously, but with an improved yield.

Figure 2 The yellow solid product obtained for **BL_{3a}** (right) and orange product, **BL_{3b}** (left)

2.2 Study of the electronic effect (IR spectroscopy)

From the IR spectra, the presence of the Schiff base product was confirmed by the signal of the imine peak shown by the vibrational bands ($(C=N)_v$); at 1627 cm^{-1} for ligand **AL_1**, 1631 cm^{-1}, for **AL_2**, 1610 cm^{-1} for ligand **AL_3**, 1633 cm^{-1} for ligand **AL_4** and 1632 cm^{-1} for ligand **AL_5**. Some IR spectra are shown for starting materials and for ligand **AL_1** in **Figure S2** in the supplementary material on page 8. The appearance of this peak together with the disappearance of the aldehyde peaks confirmed the presence of the imine product. These results furthermore indicate a slight signal shift in the IR of the various ligands which is caused by the different substituents on the phenyl ring. The *naphthylaldehyde* moiety shows a shift in the IR spectrum. Upon change of the spacer group given by the increased number of methylene

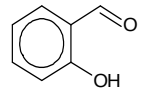
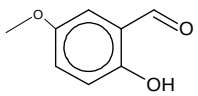
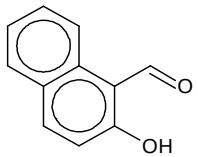
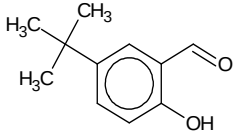
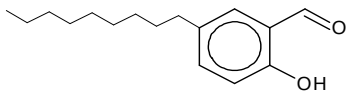
carbon groups from two to three for the class B ligands or the use of the *tripodal* ligands in the class C ligands, the same trend is observed in the IR with the imine peaks being observed at 1628 cm^{-1}, 1634 cm^{-1}, 1614 cm^{-1}, 1635 cm^{-1}, 1634 cm^{-1} for the ligands **BL_1**, **BL_2**, **BL_3**, **BL_4**, **BL_5** respectively. For **CL_1**, **CL_2**, **CL_3**, **CL_4** and **CL_5** being observed at 1630 cm^{-1}, 1633 cm^{-1}, 1620 cm^{-1}, 1631 cm^{-1} and 1631 cm^{-1} respectively. The shift of this imine peak for class A and class B ligands compared to the shift due to the various substituents on the benzene ring indicated a lower shift between class A and class B ligands than the shift due to the substituents on the phenyl ring. This low shift can be attributed to the low effect of the added -CH_2- group in the spacer mainly due to the dominating nature of the donor group[23]. The general analysis of the IR spectra indicates a higher shift due to the naphthyl group than the benzyl group and its substituents. This can be attributed to both the high stability brought about by the aromatic system of the naphthyl group which is electron rich. This shift was also observed by an analogous ligand bearing a cyclic system next to the imine by Shamsipur *et al* [24]. The imine signals from IR for all ligands are captured in **Table 1**.

2.3 Discussion of the NMR results

The ^{1}H NMR analyses were obtained for the different ligands showing in general two signals of doublets at 2.99 ppm and 3.70 ppm for ligand **AL_1**. NMR spectra are shown in **figures S2, S3 and S4** on pages 9 and 10 in the supplementary material. These were assigned to the -CH_2-CH_2- group. Each of these integrates to four equivalent protons. The proton signals indicated by the peak at 2.99 ppm were assigned to the hydrogen protons on NH-CH_2 while the downfield ones at 3.70 ppm were assigned to the CN-CH_2 protons next to the imine. The signals between 6.83 ppm and 7.30 ppm were assigned to the four aromatic protons on the phenyl group. The typical signal at around 8.34 ppm was assigned to the imine protons. The lack of the carbonyl proton peak at 9-11 ppm for the starting aldehydes indicated the formation of the Schiff base product. It is important to note that the NH proton on the linker is usually very difficult to observe due to the high shielding effect of the N-donor atom. The addition of the different substituents led to the slight shift of the imine proton and a slight shift in both the aromatic protons and the spacer protons. For ligands **AL_2**, **AL_4** and **AL_5** the added phenyl substituent resulted in an added signal in the downfield(aliphatic) region next to the spacer proton signals, while the aromatic proton signals are observed in the same region. The imine signal was therefore observed at 8.31 ppm, 8.79 ppm, 8.37 ppm and 8.35 ppm respectively for

the **AL_2**, **AL_3**, **AL_4** and **AL_5** ligands. The lack of any extraneous peaks indicates good purity of the product.

Table 1 Summary of the IR and NMR spectra of the imine in different Schiff base products synthesized by the different linkers and aldehydes

Substituted Aldehyde	Schiff base product synthesized by using diethylenetriamine linker				Schiff base product synthesized by using bis(3-aminopropyl)amine linker				Schiff base product synthesized by using 2-*N,N-bis(2-aminoethyl)ethane-1,2-diamine*			
		NCH				NCH				NCH		
		IR cm^{-1}	^{1}H NMR (in $CDCl_3$) ppm	$^{13}C\{^{1}H\}$NMR (in $CDCl_3$) ppm		IR cm^{-1}	^{1}H NMR (in $CDCl_3$) ppm	$^{13}C\{^{1}H\}$NMR (in $CDCl_3$) ppm		IR cm^{-1}	^{1}H NMR (in $CDCl_3$) ppm	$^{13}C\{^{1}H\}$NMR (in $CDCl_3$) ppm
	**AL_1**	1627	8.34	166.15	**BL_1**	1628	8.33	165.04	**CL_1**	1630	7.82	166.27
	**AL_2**	1631	8.31	165.90	**BL_2**	1634	8.27	165.15	**CL_2**	1633	8.31	165.88
	**AL_3**	1610	8.79	159.14	**BL_3**	1614	8.76	157.99	**CL_3**	1622	8.72	158.93
	**AL_4**	1633	8.37	166.58	**BL_4**	1635	8.33	165.88	**CL_4**	1631	8.35	166.34
	**AL_5**	1632	8.35	165.67	**BL_5**	1634	8.32	165.58	**CL_5**	1631	8.35	166.46

For the proton decoupled ^{13}C NMR, ligand **AL_1** is used as a representative ligand in the discussion. The formation of a strong signal at 166.15 ppm in the spectrum is assigned to the imine (HC=N) carbon as indicated. The four signals between 116 ppm to 162 ppm are assigned to the four aromatic carbons. The alkyl group (aliphatic) signals between the imine and the amine appear as two signals at 59.60 ppm and at 49.75 ppm. The lack of any signal above the 190-ppm range which is for the starting carbonyl group confirms the synthesis of the Schiff base product **AL_1**. The lack of any other signals in this case also indicates the formation of the pure Schiff base product. For the other ligands in this class the imine signal was observed at 166 ppm, 165 ppm,158 ppm, 166 ppm and 165 ppm for **AL_1**, **AL_2**, **AL_3**, **AL_4** and **AL_5** respectively. The analysis of the ^{13}C NMR spectra for the class B ligands showed that they were relatively similar to the results of the previously synthesized class A ligands. The comparative results of the shift of the imine in the IR spectra, important signals in the ^{1}H NMR and ^{13}C $\{^{1}H\}$ NMR for all 15 ligands are listed in **Table 1** giving a summary of important signals of these N-donor ligands.

There is a limited inductive effect that is observed with the increase of the number of the methylene groups between the donor groups. This is due to the higher inductive effect of the donor group. This inductive effect is subsequently referred to as the hidden inductive effect [23].

Finally, for the class C *tripodal* ligands all signals were observed to be very close to that of the class A and class B ligands. Structural formulae of **AL_2** and **BL_2** as well as their appearance is shown in figures **S5** and **S6** on page 10 in the supplementary material.

2.4 Mass spectrometry (MS)

The products obtained from the synthesis of these ligands were subsequently analysed through the MS technique. The obtained fragmentation patterns for these ligands were relatively similar for the class **A** and **B** ligands. Both classes of ligands showed that the species have two main fragmentation species [M+H and $[(M/2) + H]^{+}$ species. For the class C ligands with three *salicylaldehyde* groups these were observed to show 4 fragmented species as shown in **Figure 3**.

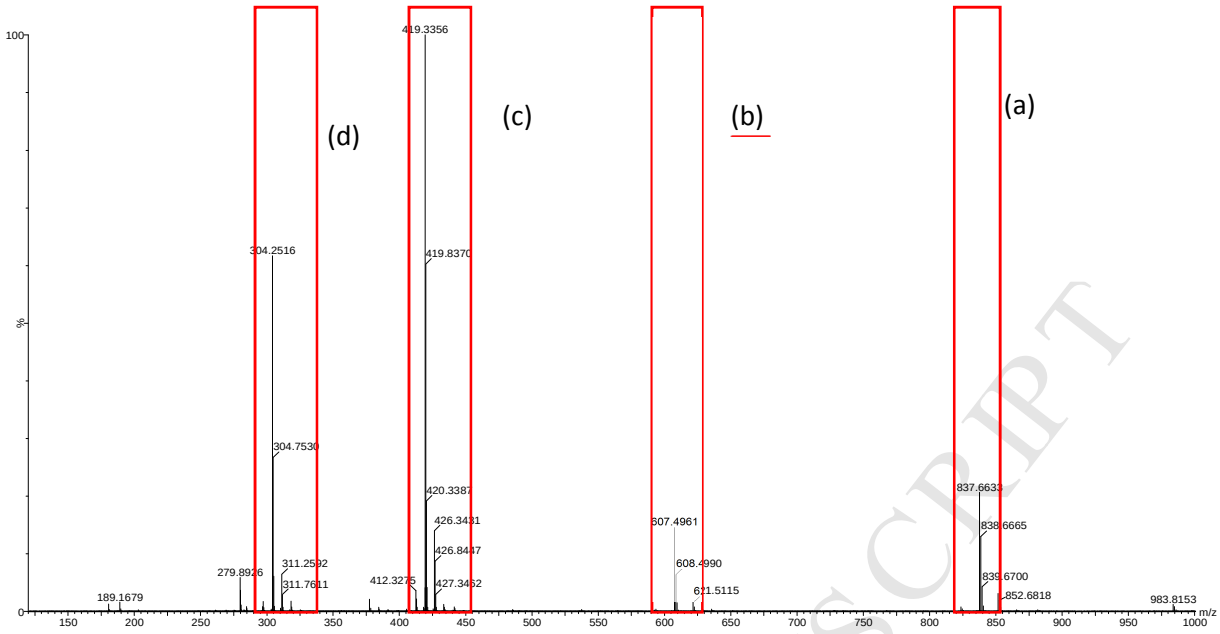


Figure 3 Mass spectrum of ligand **CL_5** with x- axis showing the m/z value and the y-axis showing the % abundance of the different fragments.

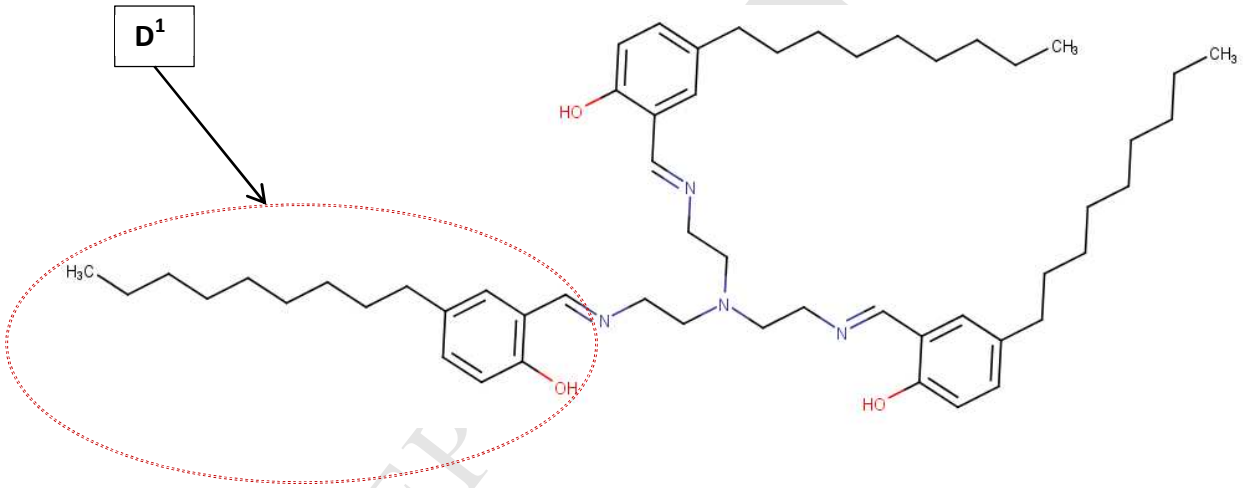


Figure 4 Ligand **CL_5** with the area circled and labelled D^1 as a fragment which is lost in the MS analysis

The representative mass spectrum obtained for the *tripodal* ligand **CL_5** as illustrated in **Figure 3** showed that the ligand has three ionisable fragments. These are proposed to contain different species. The species (c) is proposed to be the base peak at 100 % relative abundance representing $[M\text{-}C_{27}H_{42}N_2O_{1.5}]^+$ or the $[(M/2) +H]^+$ species. Species (a) would represent the ionisable mass fragment at 25 % relative abundance which confirms the mass of the Schiff base product. The fragmented species (b) represents the ionisable $[M\text{-}D^1]^+$ species, where the species D^1 is shown in **Figure 4**. The species (d) represents the species $[M\text{-}C_{36}H_{39}N_3]^+$ or

[(M-D^1)/2] at 60 % abundance. It is important to remember that all these species are only present in the ionisable environment and are not products of the synthesis.

Analyses of the spectra obtained for the Class **A** and **B** ligands showed that, the general trend observed in the addition of bulky alkyl substituents on the phenolic ring has the effect of increasing the bulkiness of the Schiff base product and this leads to stabilization of the ionisable species. Therefore, the ligands **AL_5** and **BL_5** containing the bulky nonyl-substituents showed one fragmented species with the species [(M/2) + H] representing the base peak. The [M+H] species was observed at 50 % relative abundance. For **AL_4** and **BL_4** ligands both had the species [M+H] as the base peak at 100 % relative abundance while the species [(M/2) + H] species was observed to be at 25 % relative abundance. For class A and B ligands made from aldehydes **L1** to **L3,** these only showed the [M+H] peak at 100 % relative abundance. This indicates the stability of these ligands under the MS conditions analysed. Further mass spectra for **AL_5, BL_{3a}** and **BL_{3b}** are shown in **figures S18, S19** and **S20** on pages 16 and 17 in the supplementary material.

2.5 Elemental analysis

All the ligands synthesised were subsequently analysed and confirmed to contain the Schiff base product in high purity through CHN microanalyses. It is also important to note that ligands **AL_2**, **BL_3**, **CL_2** and **CL_4** could not be dried completely so they contained some reaction solvents such as methanol and ethanol. This was also the case for the crystals obtained for the class C ligands. The results from CHN analyses are therefore summarized in **Table 2** below.

Table 2 Comprehensive CHN analysis table for all the ligands

	FORMULA	%CALCULATED			%OBTAINED		
		C	H	N	C	H	N
AL_1	$C_{18}H_{21}N_3O_2$	69.43	6.80	13.49	69.27	6.62	13.48
AL_2	$C_{20}H_{25}N_3O_4(H_2O)$	61.68	6.94	10.79	61.82	6.59	10.11
AL_3	$C_{26}H_{25}N_3O_2$	75.89	6.12	10.21	75.07	6.32	10.06
AL_4	$C_{26}H_{37}N_3O_2$	73.72	8.80	9.92	73.91	8.44	9.80
AL_5	$C_{36}H_{57}N_3O_2$	76.68	10.19	7.45	76.14	10.08	7.62

BL_1	$C_{20}H_{25}N_3O_2$	70.77	7.42	12.38	70.29	7.26	12.38
BL_2	$C_{22}H_{29}N_30_4$	66.14	7.32	10.52	66.17	7.03	10.13
BL_3	$C_{28}H_{29}N_3O_2(C_2H_5OH)$	74.20	6.65	8.65	74.07	6.14	9.07
BL_4	$C_{28}H_{41}N_3O_2$	74.46	9.15	9.30	74.23	9.11	9.42
BL_5	$C_{38}H_{61}N_3O_2$	77.11	10.39	7.10	77.89	10.34	7.95
CL_1	$C_{27}H_{30}N_4O_2$	70.72	6.59	12.22	70.86	6.61	11.70
CL_2	$C_{30}H_{36}N_4O_6(C_2H_5OH)$	64.63	7.12	9.42	64.79	6.57	9.85
CL_3	$C_{39}H_{36}N_4O_3.2H_20$	73.68	6.18	8.81	73.77	6.38	9.23
CL_4	$C_{39}H_{54}N_4O_3(C_2H_5OH)$	73.18	8.99	8.33	73.29	8.51	8.33
CL_5	$C_{54}H_{84}N_4O_3$	77.46	10.11	6.69	77.43	10.09	6.07

2.6 Tautomeric study of the BL_3 ligand

2.6.1 Spectroscopic Evidence

The results from the synthesis of **BL_3** ligand using method 2 showed the presence of two products that were isolated in high purity at 72 % yield of **BL_{3a}** product and 22 % **BL_{3b}** product (**Figure 2**). The analysis of the two products using IR spectra showed the presence of the imine . Further IR analyses shows a broad peak in the region of 3340 cm^{-1} due to the –OH group in the yellow product BL_{3a} which is absent in the case of the orange product BL_{3b}. Use of the imine and carbonyl peaks is not definitive due to the overlap of these peaks in this region (see supplementary material **figure S9, S10**). To elucidate the structures the analysis of the two products via ^{1}H NMR spectroscopy indicated the formation of the desired imine product. These ^{1}H NMR spectra showed identical signals in $CDCl_3$ (see **figures S11, S12, S13 and S14** in the supplementary data). While this ligand as indicated above is known in the literature [25], Amirnasr *et al*[25] synthesised and reported a 90% yield of the product, but did not however report the method or the formation of these two products as shown in **Figure 2**.

To try to understand the reason for the difference of the colour, this sample set was then re-analysed for ^{1}H NMR in the same NMR tube by mixture of these two samples at a mass ratio of 1:10 for the orange to yellow product respectively. This indicated a slight difference in the spectra as shown by a shift of some of the proton signals as seen in **Figure 5**. This spectrum indicated a second imine signal of integration ratio 1:10. From various studies of the *salic-*

ylaldehyde based ligands these ligands are known to undergo tautomerism between the -OH tautomer and the –C=O tautomer[16, 26-30]. This tautomeric effect occurs through the formation of a H-bond between the phenolic hydrogen and the imine N-atom first, this later results in complete transfer of the H-atom from the phenolic group to the imine nitrogen[26]. The resultant product is the –C=O tautomer [27]. It was therefore hypothesized that the two compounds are possible *tautomers* of each other. The tautomerism was attributed to a Proton transfer which causes a change in the p-electron configuration and consequently in the molecular conformation. The analysis of the two products using ^{13}C {^{1}H} NMR in $CDCl_3$ indicated the formation of the carbonyl group in the orange product as shown in **Figure 6**. The possible mechanism of tautomer formation is given by **Scheme 4** and the MS of the two tautomer's give in S20 and S21 in the supplementary data provided.

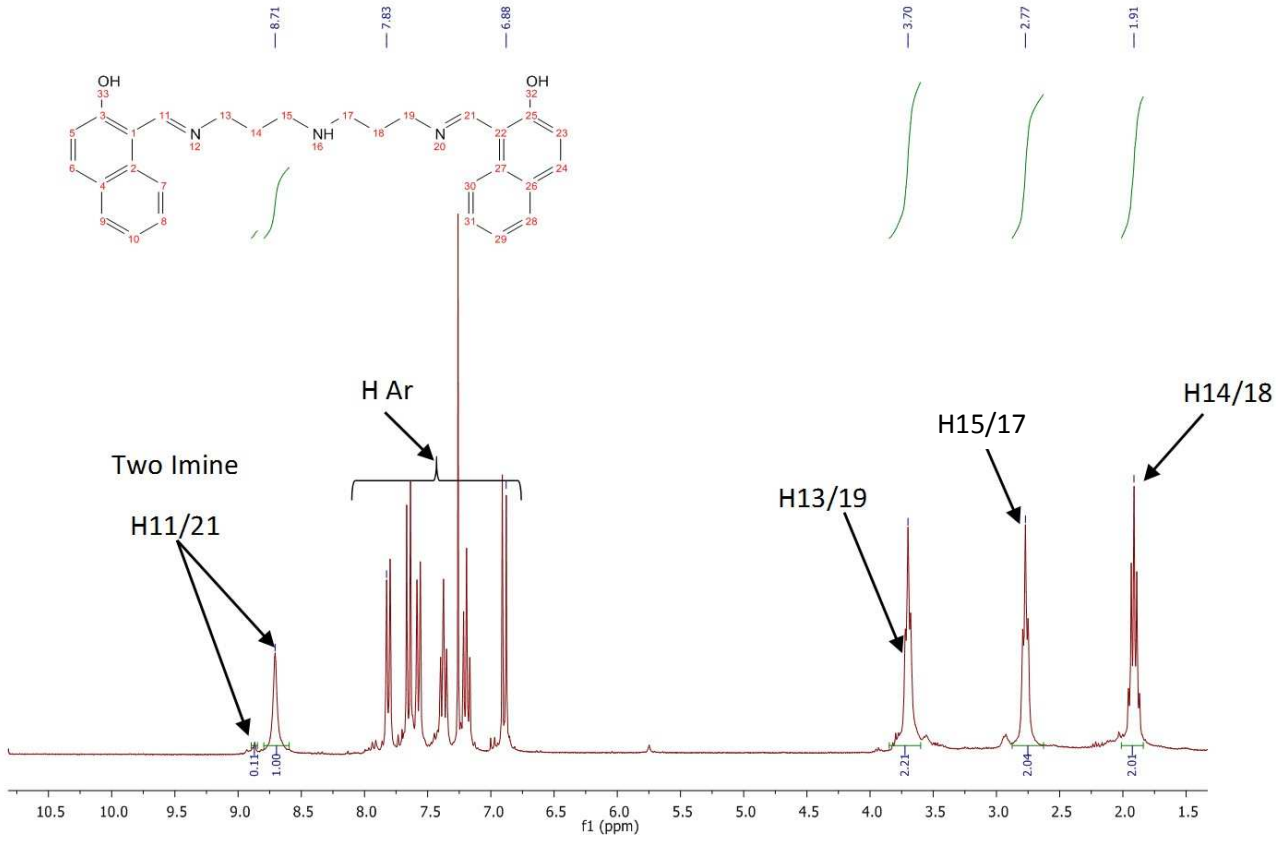


Figure 5 The ^{1}H NMR of ligand **BL_{3a}** and **BL_{3b}** mixed together in a 1:10 ratio of orange to yellow product in $CDCl_3$

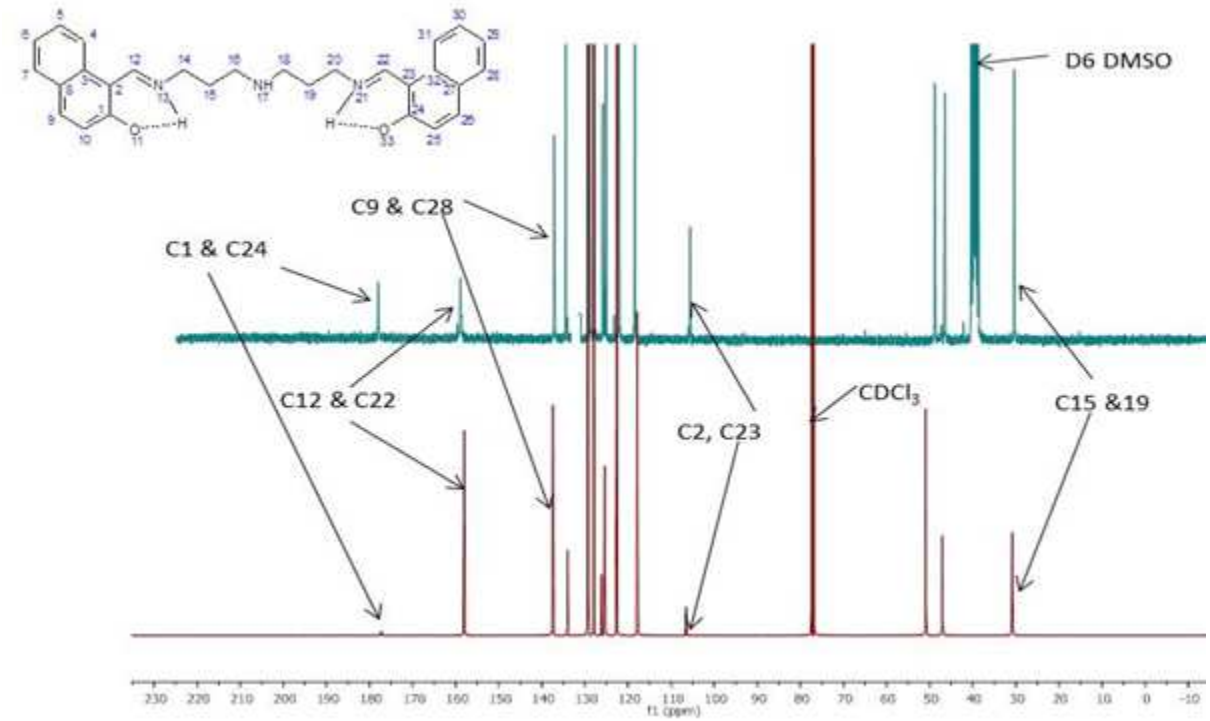
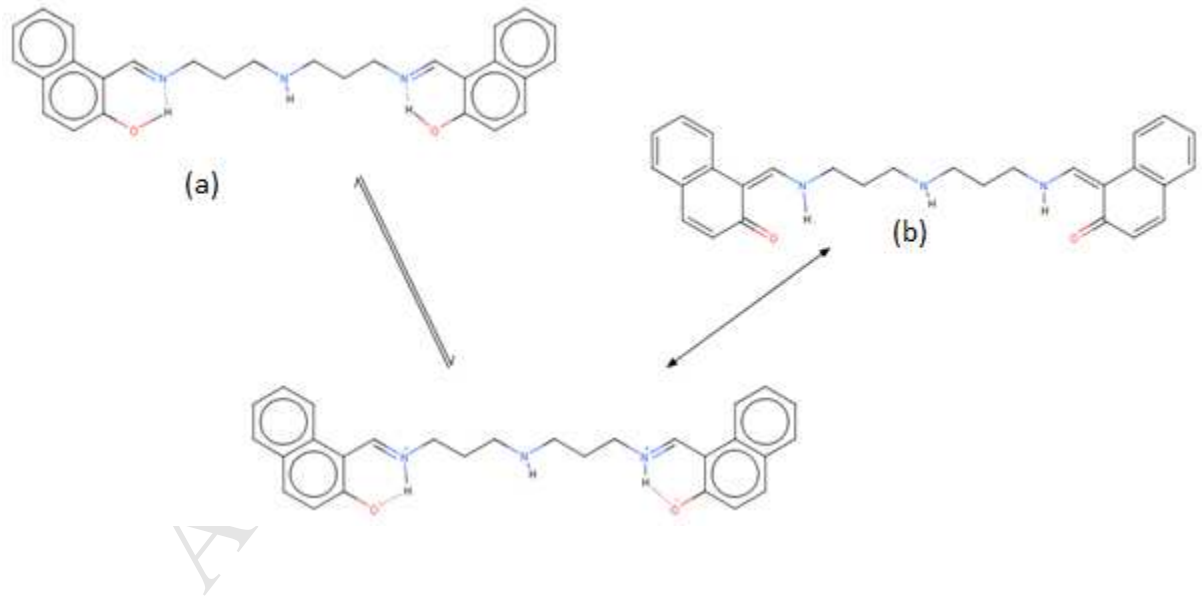


Figure 6 The stacked ^{13}C {^{1}H} NMR spectra of Ligand BL_{3b} (top) in d-DMSO and BL_{3a} (bottom) in $CDCl_3$



Scheme 4 Tautomerism of the Schiff base product BL_3, (a) represents the hydroxyl tautomer product (yellow) and (b) represents the –C=O tautomer product (orange).

The above results therefore confirmed the yellow product to be the OH tautomer and the orange product to be the –C=O tautomeric product. The different tautomer's and the odds of

getting each of the tautomers is directed by heat or light[28]. Since most of the Schiff base condensation reactions are accompanied by refluxing, the predominance of the –C=O form (orange product) is shown through the various crystal structures obtained for *salicylaldehyde* Schiff base ligands which predominantly exist in the –C=O form (90% in CCD[29] search 02-08-2018). In our investigation we therefore show a crystal structure of the novel ligand **AL_4** discussed in the next section 2.6.2 with one end forming the OH form while the other end shows the –C=O form. To try and control the formation of the orange product the ligand was resynthesized without heat and light using a simple condensation method 4 above. Further spectroscopic evidence is shown in section **S5** on pages 11-14 in the supplementary material.

2.6.2 Crystal structure discussion

Single crystals of ligand **AL_4** were obtained by crystallizing the formed yellowish red ligand in ethanol and using diethyl ether by the vapour diffusion method. The yellow crystal was obtained in a monoclinic C2/c crystal system as shown in **Table 3**.

Table 3 Crystal structure data for **AL_4**

Identification code	SW038_25_05_15_0m
Empirical formula	$C_{26}H_{36}N_2O_3$
Formula weight	424.57
Temperature (K)	100.03
Crystal system (Space group)	monoclinic **(**C2/c**)**
a/Å	14.407(2)
b/Å	13.744(2)
c/Å	24.944(4)
α/°	90.00
β/°	91.152(2)
γ/°	90.00
Volume/$Å^3$	4938.2(13)
Z	8
Volume (ρ_{calc}g/cm^3)	1.142
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.26 to 53.04
Index ranges	-18 ≤ h ≤ 17, -12 ≤ k ≤ 17, -30 ≤ l ≤ 31
Reflections collected	14330
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0606, wR_2 = 0.1679
Final R indexes [all data]	R_1 = 0.0786, wR_2 = 0.1827
Largest diff. peak/hole / e $Å^{-3}$	0.80/-0.40

The crystals show a disordered spacer group that was refined in two positions. The structure obtained shows one of the *salicylaldehyde* ends of the symmetrical molecule forming the –C=O *tautomers* while the other end forming the -OH tautomer. Both these opposite ends show internal H-bonding between the appropriate atoms as shown in **Figure 7**. The structure also confirms synthesis of the ligand, complementing all other analytical data.

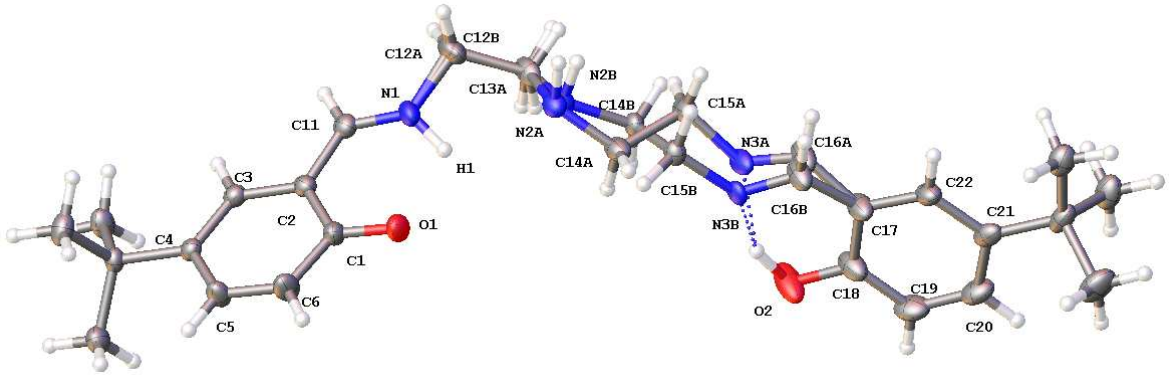


Figure 7 Ortep diagram of the ligand **AL_4** showing the hydrogen bonding of the NH and the phenyl O-atom, ellipsoids are drawn at 50% probability and picture quality generated by Olex[30]

Analysis of the bond lengths and bond angles shows slight differences of the two ends of the asymmetrical unit. The O1 C1 bond length was observed to be 1.280 Å this which is slightly shorter than 1.352 Å which is for the O2 C18 bond length. The shorter O1 C1 indicates the formation of the carbonyl group, while the longer O2 C18 indicates the single bonded phenolic group. The C11 N1 bond length (1.303 Å) and the imine N3A C16A at 1.3020 (19) Å are within experimental deviation of the same size. This shows that the electrons in the system are delocalised between the benzyl system and the imine system. The one C-O bond length is shorter than the standard single C-O bond length at 1.34 Å [31]. The measured torsion angle around the molecule however shows that the molecule is slightly strained around the OH tautomer compared to the –C=O tautomer section. The selected bond lengths, bong angles and torsion angles are provided in **Table 4**.

Table 4 Selected bond lengths, bond angles and torsion angles

selected bond lengths		selected bond angles		selected torsion angles	
bond	Length (Å)	bonds	Angle (˚)	Bond	Angle (˚)
O1 C1	1.280(2)	C11 N1 C12B	127.4(7)	C1 C2 C11 N1	2.1(3)
N1 C11	1.303(3)	O1 C1 C2	122.82(18)	N2B C14B C15B N3B	165.0(5)
N1 C12B	1.460(2)	C14A N2A C13A	115.5(3)	N1 C12A C13A N2A	57.2(8)
N1 C12A	1.461(1)	N3A C16A C17	124.1(3)	C18 C17 C16B N3B	13.2(9
N1 H1	O.9995	O2 C18 C17	120.9(2)	O1 C1 C2 C11	5.6(3)
C2 C11	1.421(3)	N1 C11 C2	122.2(2)	C16B C17 C18 O2	17.5(6)
C3 C4	1.375(3)	N3B C16B C17	117.0(4)	C16A C17 C18 O2	9.4(4)

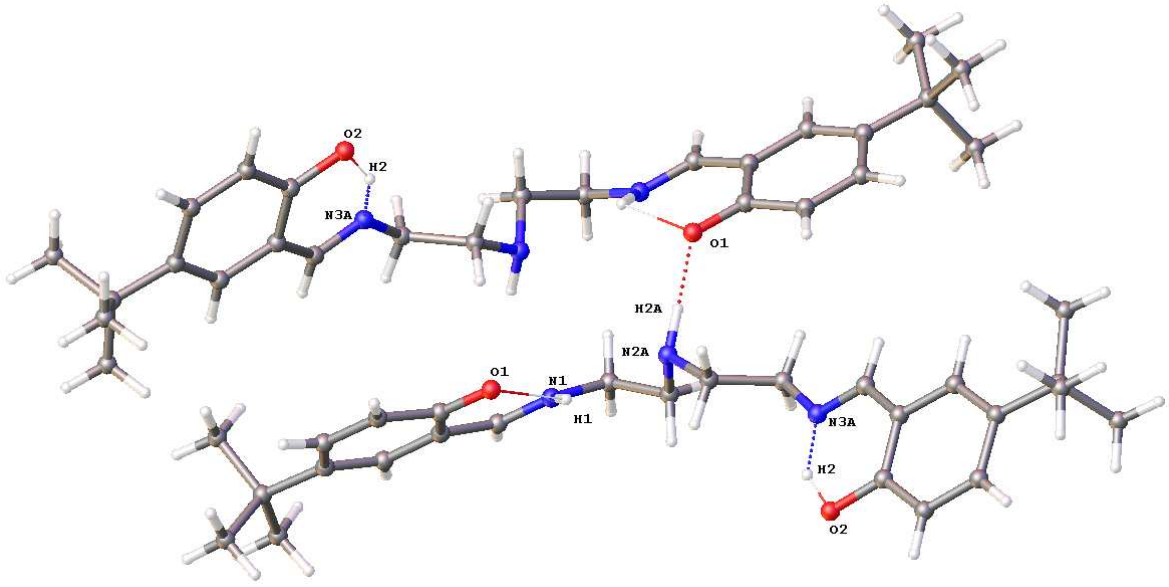


Figure 8 Ball and stick diagram showing the inter-molecular H-bonding in the packing of the AL_4 ligand (All H-bonding are indicated by broken lines)

The analysis of the packing system of the ligand shows that there are various other intermolecular H-bonding interactions between the subsequent groups as shown by **Figure 8**. Selected H-bonding and angles are given in **Table 5**.

Table 5 Selected H-bonding with donor acceptor bond length and bond angles for ligand **AL_4**

Bond	Donor -Acceptor length (Å˚)	Bond Angle (˚)
N(1) --H(1) ..O(1)	2.02	113
N(1) --H(1) ..N(2A)	2.29	115
O(2) --H(2) ..N(3A)	1.76	143
N(2A) --H(2A) ..O(1)	1.98(3)	162(2)
C(12A)--H(12C) ..N(2A)	2.51	136
C(12A)--H(12D) ..O(2)	2.56	134
C(14A)--H(14A) ..O(2)C	2.59	167

3. Conclusion

Fifteen different multidentate Schiff base ligands were synthesized containing the N_3O_2 and N_4O_3 donor groups of which six ligands are new. They were comprehensively analysed through different analytical techniques. The ligands **AL_1**, **AL_3**, **AL_4**, **AL_5**, **BL_1**, **BL_4** and **BL_5** were all synthesized with the Schiff base condensation method 2, while ligands bearing the methoxy substituent **AL_2** and **BL_2** were synthesized using a modified method 3. The ligand with *naphthylaldehyde* **BL_3** with the propyl spacer was also synthesized using method 3 and the products obtained were confirmed to undergo tautomerism. The synthesized ligands were further studied for the electronic and steric effects due to the addition of the different substituents on the phenyl ring and the effect of adding the alkyl group between the donor groups. The results indicated that the addition of the substituent on the phenyl group had a much greater effect on the shift of the imine on both the IR and NMR analysis. The effect of adding the alkyl groups between the donor atoms was on the other hand observed to have minimal shift of the imine signals. The heptadentate *tripodal* ligands showed a much greater shift of the imine due to the increased number of donor groups and the increased bulkiness of these ligands. The crystal structure of the novel **AL_4** ligand was also discussed showing the formation of an unsymmetrical molecule with one end showing the -OH tautomer and the other end showing the –C=O tautomer.

4. Experimental

4.1 Reagents

The following chemicals and reagents were used in the synthesis and characterization procedure and include; 2-hydroxyl phenylaldehyde (L_1), 5-methoxy-2-hydroxylphenylaldehyde (L_2), 2-hydroxyl naphthylaldehyde (L_3) which were all purchased from Sigma Aldrich. The 5-tert butyl-2-hydroxyl phenylaldehyde (L_4) and 5-nonyl-2-hydroxyl phenylaldehyde (L_5) were synthesized and obtained in high yield using a literature procedure by Aldred *et al*[32] (See supplementary information, section **S1B**). The two corresponding alcohols 4-tert butyl-phenol and 4-nonyl-phenol together with paraformaldehyde were all purchased from Sigma Aldrich. The magnesium turnings were purchased from Merck Schuchardt OHG. The toluene solvent, sulfuric acid (H_2SO_4) and nitric acid (HNO_3) were bought from Merck laboratory supplies. All these reagents were used without further purification. The corresponding three diamines bearing the added N-donor group; N-(2-aminoethyl)ethane-1,2-diamine, N-(3-aminopropyl)propane-1,3-diamine and N,N-bis(2-aminoethyl)ethane-1,2-diamine were also bought from Sigma Aldrich and used without further purification. The D-chloroform and D^6 DMSO used for NMR studies were bought from Sigma Aldrich. The 99% pure ethanol solution and 99% methanol were bought from B & M Scientific and were used after dry distillation. The cold ethanol was obtained by placing the dried ethanol (in a sealed 250 ml volumetric flask) in an ice bath for 24 hours. All aqueous solutions were prepared using double distilled deionized water from an econoPure16 reverse osmosis system.

4.2 Instrumentation

The IR analysis was carried out using the Nicolet Avatar 330 FT-IR instrument with ATR accessory with a ZnSe/Diamond crystal. The analysis was carried out in transmission mode with 32 scans at a range between 4000-400 cm^{-1}. The ^1H NMR and the ^{13}C NMR were carried out using the Varian Unity Inova 300 Liquid State NMR Spectrometer, Varian Unity Inova 400 Liquid State NMR Spectrometer and the higher magnitude NMR Varian Unity Inova 600 Liquid State NMR Spectrometer which was used only when necessary to obtain better resolution of the spectra. Approximately 20 mg of the synthesized samples were weighed into an NMR tube and $CDCl_3$ or D^6 DMSO depending on the sample was then added and analysed. The mass spectral analysis and CHN analyses were carried out on a Waters Synapt G2 High Resolution

Mass Spectrometer, with a cone voltage of 15V. The analysis was done on a TOF (Time of flight) positive and negative electrospray ionisation (ESI+) and (ESI-). The CHN analysis on the other hand was carried out using a Perkin-Elmer CHNS elemental analyser model 240. Crystalline samples or powder samples were analysed for melting points on a Stuart Scientific Melting Point apparatus SMP30. The crystal structure was carried out using a Bruker SMART-APEX II DUO diffractometer instrument under liquid nitrogen stream at 100 K.

The synthetic procedure of all the ligands previously made is given in the supplementary material (sections S2A, S2B and S2C), however, that of the new ligands and ligand **BL_3** is given below:

4.3 Synthesis and characterization of class A ligands

4.3.1 Characterization of 2, 2'-{iminobis[ethane-2,1-diylnitrilo(E) methylylidene]}di-(4-tert butylphenol) (Ligand AL_4, using method 1)

A 4.33 g (0.0242 moles) of 4-*tert* butyl *salicylaldehyde* and 1.30 g (0.0126 moles) of *diethylenetriamine* was used. Yellowish orange viscous oil that solidified slowly mp 64.9-66.2 °C, yield 88 %, For $C_{26}H_{37}N_3O_2$: EA calculated (%) C (73.72%) H (8.80%) N (9.92%), EA Found (%); C (73.91%), H (8.44) ,N(9.80); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H ppm; 8.37 (2 H, s, NCH), 7.39 – 6.79 (6 H, m, ArH), 3.76 – 3.66 (4 H, m, (NCH_2CH_2)), 3.01 (4 H, d, *J* 5.4 Hz, (NCH_2CH_2)), 1.30 (18 H, s, $C(CH_3)_3$). ^{13}C {^{1}H} NMR. (300 MHz, $CDCl_3$) δ_C ppm 166.58 (N*C*H), 159.97 (C_{Ar}OH), 141.15 (C_{Ar}H), 129.77 (C_{Ar}H), 127.88 (C_{Ar}H), 118.06 (C_{Ar}CN), 116.41 (C_{Ar}H), 59.73 (NCH_2CH_2), 49.97 (NCH_2CH_2), 31.87 ($C(CH_3)_3$), 31.54 (CH_3)$_3$. IR (ATR, neat, cm^{-1}); 2865 (m, C-H); 1633 (s, C=N); 1589 (m, C=C); 1491 (m, C-H); 1266 cm^{-1} (s, C_{Ar}-O); ESI-MS (ES+); Expected m/z (%) 424.3, Obtained m/z(%) 212.65 (25%), $[(M/2)+H]^+$, 424.3 (100) $[M+H]^+$.

4.3.2 Characterization of (2, 2'-{iminobis[ethane-2,1-diylnitrilo(E) methylylidene]}di-(4-nonylphenol) (Ligand AL_5, using method 1)

A 5.81 g (0.0234 moles) of 4-nonyl *salicylaldehyde* and 1.13g (0.0109 moles) of *diethylenetriamine* was used. Orange viscous oil was obtained, yield 87 %, For $C_{36}H_{57}N_3O_2$ EA calculated (%); (76.68%) H (10.19%) N (7.45%), EA Found (%): C (76.14%) H (10.08) N (7.62); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H ppm; 13.04 (2 H, s, OH), 8.35 (2 H, s, NCH), 7.39 – 7.01 (4 H, m, ArH), 6.88 (2 H, d, *J* 8.6 Hz, ArH), 3.87 – 3.50 (4 H, m, NCH_2CH_2), 3.00 (4 H, t, *J* 5.9 Hz, NCH_2CH_2), 1.61 – 0.33 (36 H, m, $(CH_2)_8CH_3$). ^{13}C {^{1}H} NMR. (300 MHz, $CDCl_3$) δ_C ppm; 166.67 (N*C*H),

158.71 (C_{Ar}OH), 138.16 ($C_{Ar}C_9H_{19}$), 130.24 (C_{Ar}H), 117.99 (C_{Ar}CN), 116.42 (C_{Ar}H), 59.90 (NCH_2CH_2), 50.10 (NCH_2CH_2), 41.56- 8.75 (C_9H_{19}). IR (ATR, neat, cm^{-1}); 2955 (m, C-H), 2870 (m, C-H); 1632 (s, C=N); 1588 (m, C=C); 1490 (m, C-H); 1280cm^{-1} (m, C_{Ar}-O); ESI-MS (ES+); Expected m/z(%) 564.5 Obtained m/z(%) 282.7 (100) $[(M/2)+H]^{2+}$, 564.5 (50) $[M+H]^+$.

4.4 Synthesis and characterization of class B ligands

4.4.1 *Characterization of 2,2'-{iminobis[propane-3,1-diylnitrilo(E)methyl idene]}di-2-hydroxy naphthalene) (ligand* ***BL_3****, using method 3)*

A 2.66 g (0.0150 moles) of 2-hydroxy *naphthylene* and 1.02 g (0.00800 moles) of *bis(3-aminopropyl)amine* was used, Yellow dry lumps were obtained mp 215-217 °C yield 86%, For Anal. Calc. For $C_{28}H_{29}N_30_2(C_2H_5OH)$ EA calculated (%) C (74.20) H (6.65%) N (8.65%), EA Found (%): C (74.07) H (6.14) N (9.07); ^{1}HNMR (400 MHz, $CDCl_3$) δ_H ppm; 8.76 (2 H, s, NCH), 7.83 (2 H, d, *J* 8.3 NCH), 7.64 (2 H, d, *J* 9.3 Hz, ArH), 7.57 (2 H, d, *J* 7.9 Hz, ArH), 7.38 (2 H, dd, *J* 6.8 Hz, 1.1 Hz, ArH), 7.20 (2 H, ddd, *J* 8.0 Hz, 7.1 Hz, 1.0 Hz, Ar*H*), 6.89 (2 H, d, *J* 9.3 Hz, ArH), 3.67 (4 H, t, *J* 5.9 Hz, NC*H*$_2CH_2CH_2$), 2.99 (4 H, t, *J* 5.8 Hz, $NCH_2CH_2CH_2$), 1.23 (4 H, t, *J* 7.0 Hz, ($NCH_2CH_2CH_2$). ^{13}C {^{1}H} NMR. (75 MHz, $CDCl_3$) δ_C ppm; 176.14(C_{Ar}OH), 158.35(N*C*H) 137.30 (C_{Ar}CN), 133.84 (C_{Ar}H, 129.29 (C_{Ar}H), 128.08 (C_{Ar}H), 122.87 (C_{Ar}H), 106.92 (C_{Ar}H), 53.83 (N*C*$H_2CH_2CH_2$), 49.50 ($NCH_2CH_2CH_2$), 29.90 ($NCH_2CH_2CH_2$), IR (ATR, neat, cm^{-1}); 2955 (m, C-H), 2738 (m, C-H); 1614 (m, C=N); 1541 (s, C=C); 1491 (m, CH); 1273cm^{-1} (m, C_{Ar}-O); ESI-MS (ES+); Expected m/z(%) 440.54, obtained m/z(%) 440.23 (100) $[M+H]^+$.

4.4.2 *Characterization of 2, 2'-{iminobis [propane-3,1-diylnitrilo(E)methylylidene]} di-(4-tert butylphenol) (ligand* ***BL_4****, using method 3)*

A 5.59g (0.0313 moles) of 4-*tert* butyl-2 hydroxyl aldehyde and 2.10g (0.0160 moles) of *bis(3-aminopropyl)amine.* Orange viscous oil was obtained, yield 84%, For Anal Calc. For $C_{28}H_{41}N_3O_2$; EA calculated (%); C (74.46%) H (9.15%) N (9.30%), EA Found (%); C (74.23%) H (9.11) N (9.42); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H ppm; 8.33 (2 H, s, NCH), 7.33 – 7.27 (2 H, m, ArH), 7.19 (2 H, d, *J* 2.2 Hz, ArH), 6.85 (2 H, d, *J* 8.6 Hz, ArH), 3.56 (4 H, t, *J* 33.5 Hz, NCH_2CH_2CH2), 2.68 (4 H, d, *J* 6.8 Hz, NCH_2CH_2CH2), 1.88 – 1.82 (4 H, m, NCH_2CH_2CH2), 1.30 – 1.21 (18 H, s, $C(CH_3)_3$). ^{13}C {^{1}H} NMR. (75 MHz, $CDCl_3$) δ_C ppm; 165.88 (N*C*H); 158.71 (C_{Ar}OH), 142.03 ($C_{Ar}C(CH_3)_3$), 126.23 (C_{Ar}H), 116.52 (C_{Ar}H), 115.03 (C_{Ar}H), 57.12 ($NCH_2CH_2CH_2$), 48.22 ($NCH_2CH_2CH_2$), 40.46 ($NCH_2CH_2CH_2$), 31.49 ($C(CH_3)_3$). IR (ATR, neat, cm^{-1}); 2960(m, C-H),

28649 (m, C-H); 1635 (s, C=N); 1590 (m, C=C); 1493 (m, CH); 1281 cm^{-1} (m, C_{Ar}-O); ESI-MS (ES+); Expected m/z(%) 452.3 Obtained m/z (%) 452.3 (100) $[M+H]^+$.

***4.4.3** Characterization of 2,2'-{iminobis[propane-3,1-diylnitrilo(E)methylylidene]} di-(4-nonylphenol) (Ligand **BL_5,** using method 3)*

A 7.52 g (0.0303 moles) of 4-nonyl *salicylaldehyde* and 1.98 g (0.0151 moles) of *bis(3-aminopropyl)amine.* Dark reddish-yellow viscous oil, yield 87%, For Anal. Calc. For $C_{38}H_{61}N_3O_2$: EA calculated (%) C (77.11%) H (10.39%) N (7.10%), EA Found (%); C (77.89%) H (10.34) N (7.95); ^{1}HNMR (400 MHz, $CDCl_3$) δ_H ppm; 8.32 (2 H, s, NCH), 7.07 (2 H, d, *J* 7.2 Hz, ArH), 6.87 (2 H, d, *J* 8.3 Hz, ArH), 6.70 (2 H, d, *J* 8.6 Hz, ArH), 3.60 (4 H, s, $NCH_2CH_2CH_2$), 2.72 (4 H, d, $NCH_2CH_2CH_2$), 1.85 (4 H, d, *J* 6.0 Hz, $NCH_2CH_2CH_2$), 1.72 – 0.45 (38H, m, C_9H_{19}). ^{13}C {^{1}H} NMR. (151 MHz, $CDCl_3$) δ_C ppm; 165.58 (N*C*H), 158.53 (C_{Ar}OH), 116.49 ($C_{Ar}CH_2$), 116.41 (C_{Ar}H), 57.66 (N*C*$H_2CH_2CH_2$), 47.78 (NCH_2CH_2*C*H_2), 43.52 (NCH_2*C*H_2CH_2), 37.41-8.77 (C_9H_{19}). IR (ATR, neat, cm^{-1}); 2956(w, C-H); 2871 (w, C-H); 1634 (s, C=N); 1589 (s, C=C); 1492 (m, C-H); 1283cm^{-1} (m, C_{Ar}-O); ESI-MS (ES+); Expected m/z(%) 592.5 Obtained :m/z (%) 592.8 (100) $[M+H]^+$.

4.5 Synthesis and characterization of class C ligands

*Characterization of 5-nonyl salicylaldehyde and 2,2'-[ethane-1,2-diylbis(oxy)] diethanamine (ligand **CL_5,** using method 2)*

A 6.37 g (0.0256 moles) of 5-nonyl *salicylaldehyde* and 1.26 g (0.00862 moles) of 2-*N,N-bis(2-aminoethyl)ethane-1,2-diamine.* Product obtained as yellow viscous oil, yield 87.3 %, FM $C_{54}H_{84}N_4O_3$, EA calculated (%) C (77.46) H (10.11) N (6.69) EA Found (%) C (77.43) H (10.09) N (6.07), ^{1}H NMR (600 MHz, $CDCl_3$) δ_H ppm; 8.28 (3 H, s, NCH), 7.15 (3 H, t, *J* 13.3, C_{Ar}H), 7.10 (3 H, d, *J* 17.0, C_{Ar}H), 6.88 (3 H, d, *J* 8.4, C_{Ar}H), 3.67 (6 H, d, *J* 14.5Hz, N*C*H_2CH_2), 2.94 (6 H, s, N*C*H_2CH_2), 1.75 – 0.52 (57 H, m, $(C_9H_{19})_3$): ^{13}C {^{1}H} NMR. (151 MHz, $CDCl_3$) δ_C ppm; 166.46 (N*C*H), 158.77 (C_{Ar}OH), 138.41 (C_{Ar}CN), 130.35 ($C_{Ar}CH_2$), 118.12 (C_{Ar}H), 116.49 (C_{Ar}H), 116.42 (C_{Ar}H), 58.64(N*C*H_2CH_2), 56.14 (N*C*H_2*C*H_2), 41.57- 14.23 (C_9H_{19}): IR (ATR, neat, cm^{-1}); 2969(m, C-H), 2864 (m, C-H), 1631 (m, C=N). 1587 (s, C=C), 1490 (m, CH), 1279 cm^{-1} (m, C_{Ar}-O): ESI-MS (ES+); Expected m/z(%) 837.6, Obtained m/z (%) 304.3(65) $(([M-C_{16}H_{26}O])/2)^+$, 419.3 (100) $[(M/2)+H]^+$, 607.5 (15) $[M-C_{16}H_{26}O]^+$, 837.7) (15) $[M+H]^+$.

5. Supplementary Information

Supplementary data are available for this publication. Crystallographic data including atomic coordinates, bond distances and angles have been deposited with the CCDC (Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336 033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) and may be obtained free of charge by quoting the deposition number CCDC 1418740.

6. Acknowledgements

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7. Conflict of Interest

There is no conflict of interest for this work.

8. References

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Highlights

This publication displays the following highlights:

(i) 6 new Schiff base ligands have been synthesized and characterized

(ii) The yields on nine previously made Schiff bases have been optimized by various methods

(iii) A ligand which was previously made came out in 2 different colours and the structure of these "2 ligands" was explored using various spectroscopic techniques – this led us to the fact that tautomerism was at display

(iv) A crystal structure of a new ligand is obtained which displays keto and enol tautomeric forms within the same ligand