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The Transfer Hydrogenation Reactions Catalyzed by Rhodium Schiff Base Complexes

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Abstract

Three new Schiff base rhodium (III) complexes, derived from three ligands, L1, L2 and L3 have been prepared and characterized by IR, ^{1}HNMR, mass spectra and the elemental analysis. These complexes have shown efficient catalytic activity in the transfer hydrogenation of wide variety ketones to the corresponding alcohols in formic acid/triethylamine solution under mild reaction conditions. Depending on the ketone, the percentage of conversion for RhL1 have been found to be (51-92%) compared to RhL2 which had a yield of (42-92%) while for RhL3 (71-94%), within time range of 0.5-12 hrs.

Keywords: Schiff base; Rhodium (III) complex; Transfer hydrogenation; Diamine.

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1. Introuction

Reactions between carbonyl compounds and primary amines have provided one of the most important and widely studied classes of chelating ligand. A wide variety of ligand may be obtained via Schiff base. The family of Schiff bases derived from aromatic or aliphatic diamine and phenolic aldehydes which proved to be the source of tetradentate ligands for many transition metals complexes show a great potential as catalysts for various reactions [1-8].

Transition metal complexes have long been used as catalysts for the dihydrogen reduction of organic substrates such as nitro compound [9],alkenes [10], alkynes [11] and carbonyl compounds [12-14]. The hydrogen transfer reduction of carbonyl functionality is widely used in organic synthesis. The reduction of ketone by transfer hydrogenation from H_2 gas or isopropanol or formic acid / triethylamine has been well documented as standard techniques [15-19]. Many kinds of rhodium (III) complexes are

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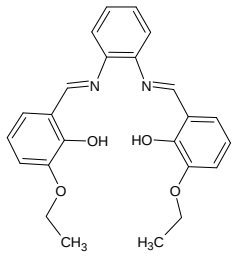
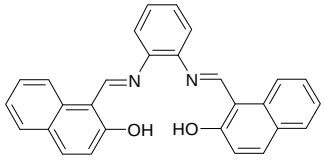
derived from ligands other than Schiff bases [20, 21]. Some of rhodium (III) complexes derived from thiosemicarbazide studied as anti microbial shown higher biotical activity [22]. Some Schiff bases and their transition metal complexes have often exhibited biological activity as antibiotics, antiviral and antitumor agents [23]. Tridentate Schiff base of the type N, N, O bund with rhodium to give five member ring rhodium (II) complexes [24].

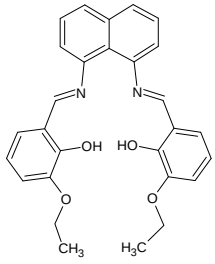
The tetradentate ligand from phenylenediamine condensate with 3,5-ditert.butyl salicylaldehyde to give a square pyramidal rhodium(III) complex [25]. Little has been known about the organometallic rhodium(III) complexes with tetradentate Schiff base and their reactivity. In the present study we describe the reaction chemistry of rhodium(III) Schiff base sequarpyramidal complexes derived from tetradentate ligands L1, L2 [26] along with a new ligand L3 fabricated specially to study the catalytic activity of RhLx (x=1, 2 and 3) complexes with regard to the transfer hydrogenation reaction shown as scheme 1. The structural formula for L1, L2 and L3:



L1

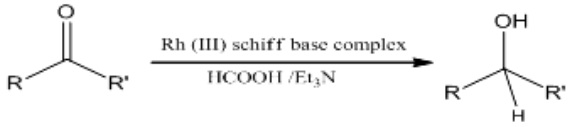


L2



L3

Scheme 1 shows the rhodium complexes catalyzed transfer hydrogenation ketones to the corresponding secondary alcohols as:



Scheme 1

2. Experimental Section

2.1. *Materials*

Chemicals like rhodium (III) chloride tri hydrate (Aldrich), *o*-phenylenediamine, naphthalene-1,8-diamine and 3-ethoxysalicylaldehyde (Merck) were all of A.R. grade and

used as received. All other chemical reagents and solvents were used after being purified according to the standard methods described in other earlier work.

2.2. *Instruments*

Infrared spectra were performed on KBr pellets on a BUCK-500 spectrometer. The ^{1}HNMR spectra were recorded on a Bruker 500(500 MHz) using d_6-DMSO or $CDCl_3$ as a solvent and TMS as internal standard. GC-Mass spectra (E1, 70ev) were recorded on Helwett Packard instruments. The elemental analysis was performed on Euro Vectro EA 3000A (Italy). All catalyzed reactions products were analyzed using Shimadzu gas chromatography (GC-14B) fitted with FID detector.

2.3. *Preparation methods*

2.3.1. *General method of the ligand preparation* [27]

Ligands were prepared from diamine (1mmol) and aldehyde (2 mmol) in absolute ethanol mixed in 50 ml reaction flask fitted with a condenser. The mixture was refluxed for 2 hrs, the solid product formed as a result of the reaction were filtered off, washed with cold ethanol then recrystalized. The synthesized ligands are.

(L1): 6,6'-(1E,1'E)-(1,2-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(2-ethoxyphenol):

o-phenylenediamine (0.108g), 3-ethoxysalicylaldehyde (0.332g), the product were orange crystals, recrystalized from ethanol, 68% yield; m. p. 122-124 ^{o}C; IR (KBr, cm^{-1}), 3343vs (υOH), 1625 υ (C=N). E1-mass(m/z), 405 (12.3) [M+1], 404(18.5)M+, 254(51), 239(100), 197(72). ^{1}HNMR δppm ($CDCl_3$): 1.56 (t,CH_3, J=7.0), 4.20(q, CH_2, J=6.9), 6.82-7.31(m,10H, Ar-H), 8.68 (s, 2H, HC=N), 13.5 (s, 2H,OH).

(L2): 1,1'-(1E,1'E)-(1,2-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol

o-Phenylenediamine (0.108g), 2-hydroxynaphthaldehyde (0.344g),the product were orange crystals, recrystalized from ethylacetate, 56% yield; m.p. 224-226 ^{o}C; IR (KBr , cm^{-1}), 3369 m (υOH), 1609s (υC=N). E1-mass(m/z), 416 (28.2) $[M]^+$, 415(3)$[M-H]^+$, 260(100), 246(14.6), 127(6.4), 115(15.5). ^{1}HNMR δppm ($CDCl_3$), 6.9-8.02(m ,16H, Ar-H), 9.33(s ,1H , HC=N), 14.9(s ,1H, OH).

(L3): 66,6'-(1E,1'E)-(naphthalene-1,8-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(2-ethoxyphenol)

Naphthalene-1,8-diamine (0.158g), 3-ethoxysalicylaldehyde (0.332g) , the product were brown crystals, recrystalized from cyclohexane 36% yield; m.p. 142-144 ^{o}C; IR (KBr,cm^{-1}), 3358 s (υOH), 1614 vs(υC=N). E1-mass(m/z), 455(66)$[M+1]^+$ 454(82.4)M^+,

436(25.3), 391(44), 304(97), 290(15.4), 245(100); ^{1}HNMR δppm (d_6-DMSO), 1.37(t ,CH_3, J=6.8), 4.08(q ,CH_2 , J=6.9), 6.5-7.2 (m,12H,Ar-H), 8.8(s,1H,HC=N), 5.71(s,1H,OH).

2.3.2. *Preparation of the rhodium complexes*

All complexes were prepared according to the following procedure: an ethanolic solution of $RhCl_3.3H_2O$ (0.263g ,1mmol), was added drop-wise to the hot ethanolic solution of the ligand (1mmol), the mixture was then heated under reflux for two hours, the obtained precipitate was filtered, washed with hot ethanol and dried under vacuum. Fig. 1 shows the structures of the different complexes.

Comp. RhL1: brown ppt., m. p. >300 ^{o}C; IR (KBr , cm^{-1}), 3069 (υC-H aromatic), 1607 υ(C=N), 1590-1500 υ(C=C ring) 1241υ(C-N),1180 υ(C-O). ^{1}HNMR δ ppm (d_6-DMSO); 1.34 (t, 3H, J=7.0 ,CH_3), 3.93 (q, 2H, J=6.8 ,CH_2), 6.8 – 7.7 (m, 10H, Ar-H) 9.12 (s, 1H, HC=N). Anal. calcd. for $C_{24}H_{22}ClN_2O_4Rh$: C 53.29 ; H 4.09 ; N 5.179, found : C 53.09, H 4.26, N 5.31.

Comp. RhL2: red -brown ppt., m. p. >300 ^{o}C, IR (KBr , cm^{-1}), 3064 υ(C-H aromatic), 1602 υ(C=N), 1590-1500 υ(C=C ring), 1250 υ(C-N), 1163 υ(C-O). ^{1}HNMR δ ppm (d_6-DMSO); 6.82-8.14 (m, 16 H, Ar-H), 9.69 (s, 1H, HC=N). Anal. Calcd. for $C_{28}H_{18}ClN_2O_2Rh$: C 60.83; H 3.28; N 5.06, found: C 61.04; H 3.30; N 5.91.

Comp. RhL3: brown ppt., m. p. >300^{o}C, IR (KBr , cm^{-1}), 3053 υ(C-H aromatic) , 1603 υ(C=N), 1600-1467 υ(C=C ring), 1241 (υC-N), 1161 υ(C-O). ^{1}HNMR δppm (d_6-DMSO): 1 .35 (t, 3H, J=6.9 , CH_3), 4.02 (q, 2H, J=6.9 , CH_2) 6.6-7.56 (m, 12H, Ar-H), 8.6 (s,1H, HC=N). Anal. calcd . for $C_{28}H_{24}ClN_2O_4Rh$: C 56.918 ; H 4.09; N 4.74, found: C 56.51; H 4.23; N, 4.59.

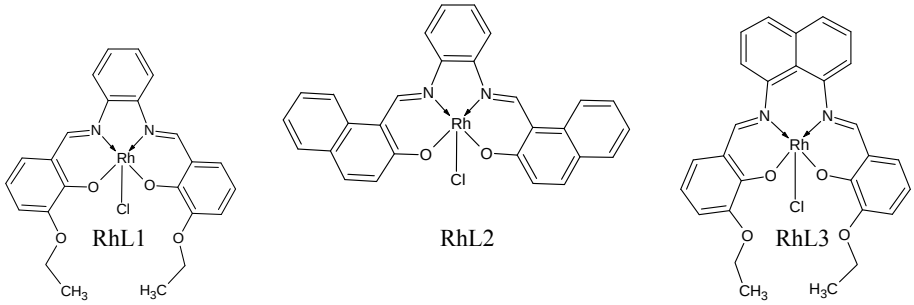


Fig. 1. The structure of RhLx complexes (x=1, 2 and 3).

2.3.3. *General method for the catalyzed reduction of the ketones*

The catalytic activity examinations were carried out in a 50 ml reaction flask fitted with a water condenser. Ketone (5 mmol) mixed with rhodium complex (0.01g) and 1 ml freshly

mixed ($HCOOH/Et_3N$) (5:2) was added along with 2 ml solvent. The mixture was stirred at room temperature. The progress of the reaction was monitored by TLC (SiO_2 gel). After completion, the mixture was evaporated under reduced pressure, the residual was dissolved in a mixture of (pet. ether/ethanol) (8:2), then passed through a short column of silica gel using (pet. ether/ethanol) (8:2) as an eluent. Finally, the solvent is removed and the residual was examined by gas chromatography using the standard method.

3. Results and Discussion

3.1. *Characterization of the ligands and the rhodium complexes*

All ligands exhibit a strong band in the 3340-3360 cm^{-1} due to intermolecular hydrogen bonding between phenolic OH and nitrogen of azomethine(-N=CH-) , a strong band in the range 1609-1625 cm^{-1} is due to the stretching vibration of azomethine groups. The absence of υOH stretching vibration in IR spectra of complexes could be taken as an evidence for the complexation of the Schiff bases with rhodium. This confirms that bonding to the ligand takes place through the displacement of the proton from the OH group followed by the coordination of phenolic oxygen with rhodium ion. The strong

Table 1. IR data for ligands and complexes.

Comp.	υ O-H	υ C-H Aromatic Aliphatic	υ C=N	υ C=C Ring	others
L1	3430 s 3343 vs	3070-3025 m 2974-2876 m	1625 vs	1600-1461	υ C-N 1250 vs υ C-O 1170 m
L2	3358 s 3265 s	2980-2800 m	1614 vs	1600-1478	υ C-N 1247 vs υ C-O 1170 m
L3	3369 m -	3047 m -	1609 vs	1569-1540	υ C-O 1180 m
RhL1	-	3069 m 2985 w	1607 vs	1590-1500	υ C-N 1241 s υ C-O 1180 s
RhL2	-	3053 w 2974 w	1631 vs	1600-1467	υ C-N 1241 s υ C-O 1061 m
RhL3	-	3064 s -	1602 vs	1590-1500	υ C-N 1250 m υ C-O 1163 s

band at 1625 cm^{-1} L1, 1609 cm^{-1} L2, 1614 cm^{-1} L3, which was attributed to υC=N shift to lower wave number 1607 RhL1, 1602 RhL2 and 1603 RhL3 in the IR spectra of complexes, indicate the involvement of azomethine nitrogen in coordination [28-30] all IR data are shown in Table 1. The results are in agreement with the data of ^{1}HNMR spectra (Table 2) where the signals of the azomethine groups are shifted to downfield compared with the corresponding ligands. The disappearance of OH signals in the spectra of complexes gives evidence of the deprotenation of the OH group and its subsequent bond between O^{-} and metal ion .The elemental analysis of the complexes is an agreement with the molecular formula. The results of GC-mass indicate that the ligands have 1:1 stiochiometry, where the molecular ions are in agreement with the suggested molecular weight of the compounds. The complexes were found to be nonvolatile and as a result, difficult to be assessed using the mass spectra by E1 methods of ionization.

Table 2. ^{1}HNMR data for ligands and complexes.

Comp.	Chemical shift δ (ppm) , *J* (H_Z)
L1	1.56 (t , 3H , CH_3 , *J* = 7) , 4.20 (q , 2H , CH_2 , *J* = 6.95), 6.8 – 7.3 (m , 10H , Ar-H) , 8.68 (s , 1H , HC=N) , 13.5 (s , 1H , OH)
L2	1.376 (t , 3H , CH_3 , *J* = 6.88) , 4.08 , (q ,2H , CH_2 *J* = 6.9) , 6.5-7.2 (m ,12H , Ar-H) , 8.8 (s , 1H , HC=N) , 5.71 (s ,1H ,OH).
L3	6.96-8.02 (m , 16H , Ar-H) , 9.33 (s , 1H , HC=N) ,14.9 (s , 1H , OH)
Rh L1	1.34 (t , 3H , CH_3) , 3.93 (q , 2H , CH_2) 6.83 – 7.71 (m , 10H , Ar-H) , 9.12 (s , 1H , HC=N).
Rh L2	1.35 (t , 3H , CH_3) , 4.02 (q , 2H ,CH_2) 6.60-7.56 (m , 12H , Ar-H) , 8.6 (s ,1H , HC=N)
Rh L3	6.82-8.14 (m , 16H , Ar-H) , 9.69 (s ,1H , HC=N)

s : singlet , t : triplet , q : quartet , m : multiplet

3.2. *Catalytic activity*

The catalytic activity for reduction of ketone usually gives a secondary alcohol as shown by scheme 1. The scope of this nucleophilic addition reaction was examined with a variety of ketones with rhodium complexes as catalysts. Such a reaction is usually catalyzed by the presence of a base, represented in this case by the hydrogen ion (H^{+}). The mixture of formic acid and triethylamine (5:2) was confirmed to be the source for hydrogen donation [18, 31]. The results showed a significant improvement in the catalytic activity depending on the type of ketone and the rhodium complex. Using RhL1 complex as catalyst has given the highest percentage of conversion, as shown by the GC analysis to be (89-92%) compared to other complexes; RhL2 (42-76%); RhL3 (71-87%). Tables 3, 4, and 5 summarize the catalytic activity for the three complexes. Depending on the ketone used, the time of conversion was within the range of 0.5-12h. The turn over frequency (TOF)

was the highest when RhL3 was used as a catalyst. Since RhL1 and RhL2 complexes are virtually identical apart from the two ethoxy ($-OC_2H_5$) substituent each attached to a phenyl ring, the existence of such substituent seem to play an important role in the catalyzed process giving rise to the percentage conversion for RhL1 and making it the highest. This initially was thought to be due to the stereochemistry associated with the catalyzed process. However, the catalytic activity for RhL3 seem to contradict such proposed mechanisms and the process seems to be much more complicated than suggested. The still high percentage yield of conversion shown by RhL3 suggests that

Table 3**.** Transfer hydrogenation of ketones catalyzed by RhL1 complex.

Entry	Ketone	Secondary Alcohol	Reaction solvent					
			MeCN			C_6H_6		
			Time (h)	TOF[a]	Yield [b](%)	Time (h)	TOF[a]	Yield[b] (%)
1	Acetophenone	1-Phenyl ethanol	12.0	35	83	8.5	41	85
2	4-Bromoacetophenone	1-(4-bromoPhenyl) ethanol	7.0	64	89	6.0	62	92
3	2-Bromoacetophenone	1-(2-bromoPhenyl) ethanol	5.5	89	68	5.0	70	73
4	2,4-Dimethylacetophenone	1-(2,4-Dimethylphenyl) ethanol	1.0	426	84	1.5	365	78
5	Benzophenone	Diphenyl ethanol	0.5	933	92	0.5	971	90
6	Cyclohexanone	Cyclohexanol	4.0	99	78	4.5	89	73
7	2-Acetylthiophene	1-(thiophene-2-yl)ethanol	2.0	102	66	1.5	142	51
8	2-Acetylpyrrol	1-(pyrrol-2-yl)ethanol	3.5	86	69	3.0	73	76

[a] TOF: turn over frequency –moles of substrate converted per mole of catalyst per hour.
[b] Determined by GC analysis.

Table 4. Transfer hydrogenation of ketones catalyzed by RhL2 complex.

Entry	Ketone	Secondary Alcohol	Reaction solvent					
			MeCN			C_6H_6		
			Time h	TOF[a]	Yield[b] (%)	Time h	TOF[a]	Yield[b] (%)
1	Acetophenone	1-Phenyl ethanol	2.0	158	61	1.5	224	70
2	4-Bromoacetophenone	1-(4-bromoPhenyl) ethanol	2.0	148	57	2.0	150	54
3	2-Bromoacetophenone	1-(2-bromoPhenyl) ethanol	3.0	87	65	1.5	85	66
4	2,4-Dimethylaceto phenone	1-(2,4-Dimethylphenyl) ethanol	4.0	55	42	3.5	63	59
5	Benzophenone	Diphenyl ethanol	2.0	197	76	2.5	160	83
6	Cyclohexanone	Cyclohexanol	6.0	46	53	6.5	58	61
7	2-Acetylthiophene	1-(thiophene-2-yl)ethanol	2.0	91	87	2.0	111	92
8	2-Acetylpyrrol	1-(pyrrol-2-yl)ethanol	4.0	88	69	2.0	94	50

[a] TOF: turn over frequency –moles of substrate converted per mole of catalyst per hour.
[b] Determined by GC analysis.

replacing the phenyl by the nephthyl has actually slightly hindered the catalyzed process although the unusually high TOF and lower time associated with it, suggests the possibility of two parallel processes competing in the overall mechanism of the reaction. Further detailed work is needed to establish such an interesting process and may be the subject of a future paper.

Table 5. Transfer hydrogenation of ketones catalyzed by RhL3 complex.

Entry	Ketone	Secondary Alcohol	Reaction solvent					
			MeCN			C_6H_6		
			Time h	TOF[a]	Yield[b] (%)	Time (h)	TOF[a]	Yield[b] (%)
1	Acetophenone	1-Phenyl ethanol	0.5	935	84	1.0	855	89
2	4-Bromoacetophenone	1-(4-bromoPhenyl) ethanol	0.5	902	81	0.5	918	91
3	2-Bromoacetophenone	1-(2-bromoPhenyl) ethanol	9.0	163	73	7.5	137	76
4	2,4-Dimethylaceto phenone	1-(2,4-Dimethylphenyl) ethanol	7.0	63	79	6.0	94	73
5	Benzophenone	Diphenyl ethanol	2.0	242	87	3.0	210	90
6	Cyclohexanone	Cyclohexanol	2.0	198	71	2.0	164	64
7	2-Acetylthiophene	1-(thiophene-2-yl)ethanol	4.0	65	86	3.5	81	94
8	2-Acetylpyrrol	1-(pyrrol-2-yl)ethanol	3.5	134	73	3.5	178	87

[a] TOF: turn over frequency –moles of substrate converted per mole of catalyst per hour.
[b] Determined by GC analysis.

4. Conclusion

Three Schiff base ligands complexes containing rhodium (III) have been synthesized from the tetradentate ligands L1, L2 and L3. These complexes demonstrated good catalytic activity for the catalytic transfer hydrogenation of ketone giving good yield of the corresponding alcohol in moderate time. The catalytic activity is partly attributed to the ethoxy group as part of the RhL1 and RhL3.

Appendix (Spectroscopic Charts) pp. 510-511

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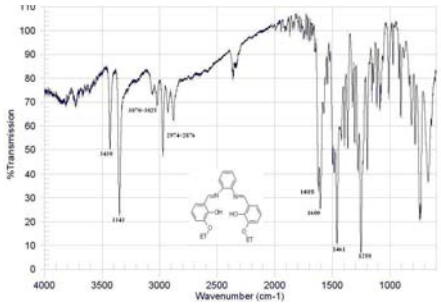
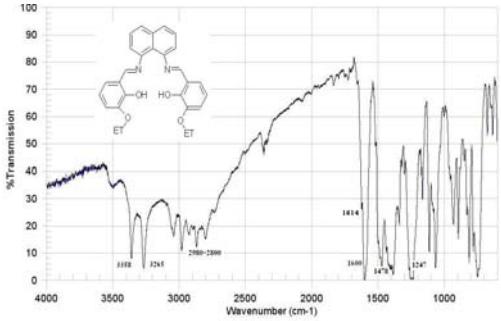
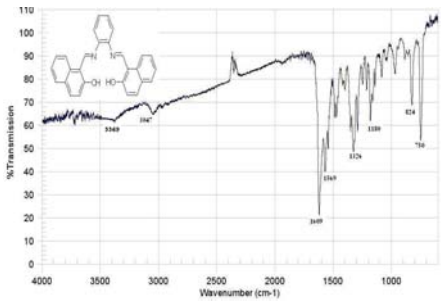
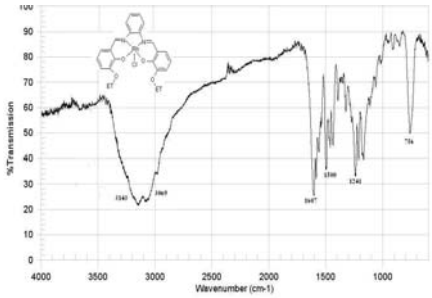
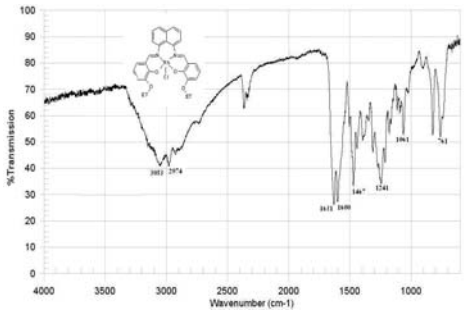
Appendix: *Spectroscopic Charts*

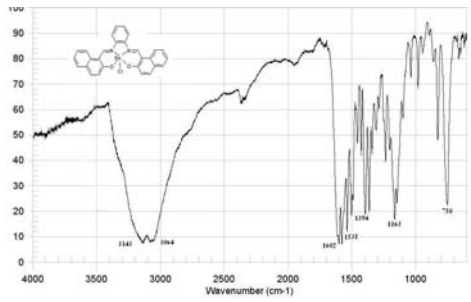


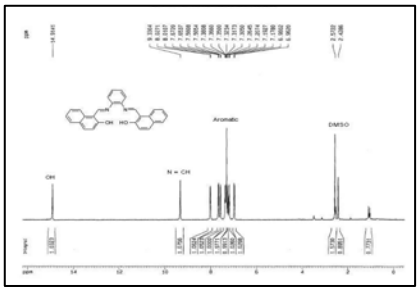








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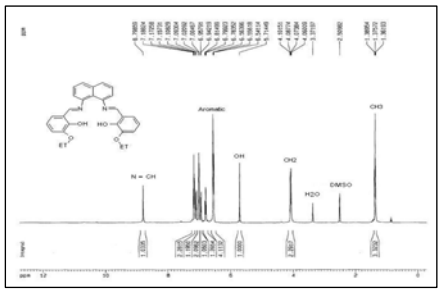
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CH3
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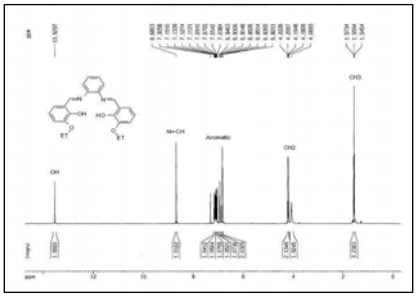
H2O
DMSO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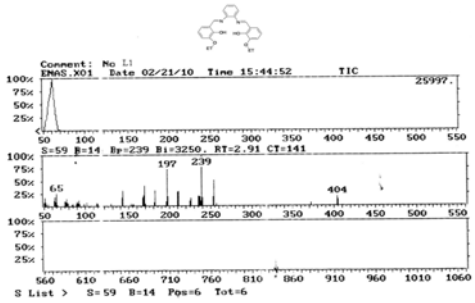
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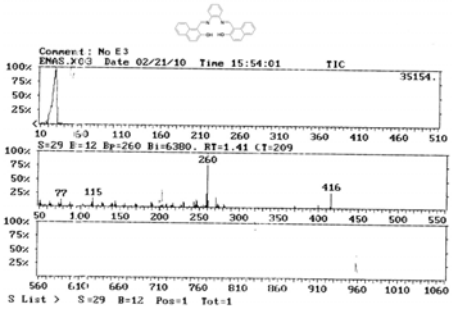
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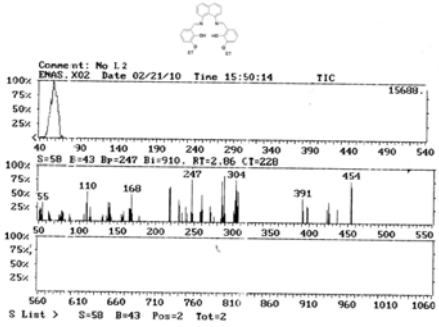
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