

Schiff Bases and Their La(III) Complexes: Conventional and Microwave-Assisted Synthesis, Physicochemical and Spectroscopic Analysis

Nur Husnina Nasaruddin¹, Shahrul Nizam Ahmad^{1*}, Hadariah Bahron¹,
Nor Mas Mira Abd Rahman² and Nor Saadah Mohd Yusof²

¹Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

²Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

*Corresponding author (e-mail: shahruln@uitm.edu.my)

Two lanthanum(III) Schiff base complexes, 2,2'-((1E,1'E)-((2,2-dimethylpropane-1,3-diyl)bis(azanylylidene))bis(methanylylidene))diphenollanthanum(III) [**La(AD1H)**] and 6,6'-((1E, 1'E)-((2,2-dimethylpropane-1,3-diyl)bis(azanylylidene))bis(methanylylidene))bis(2-methoxyphenol)lanthanum(III) [**La(AD1OMe)**] were successfully synthesized. The complexes were prepared by conventional reflux and microwave-assisted synthesis methods where a minimum amount of solvent was used, with a shorter reaction time for the latter. Both ligands and their lanthanum(III) complexes were characterized by spectroscopic and physicochemical analyses. The shift of $\nu(\text{C}=\text{N})$ to a higher frequency by 15-18 cm^{-1} indicated that the complexation to La(III) through the azomethine N was established. It was further supported through the shifting of the azomethine proton signal to higher chemical shifts with $\Delta\delta=0.19\text{-}0.23$ ppm. In addition, the shifting of the $n-\pi^*(\text{C}=\text{N})$ band in UV-Vis spectra with $\Delta\lambda= 2\text{-}16$ nm also indicated the involvement of azomethine nitrogen in the complexation.

Key words: Schiff base; lanthanum(III); 2,2-dimethyl-1,3-propanediamine; microwave-assisted synthesis

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Schiff bases are compounds with imine (C=N) functional group(s) that can be formed through condensation reactions between primary amines with either aldehydes or ketones. Schiff bases can easily be coordinated to various metal ions as chelating ligands, producing stable and sometimes brightly-coloured metal complexes with fascinating physical, mechanical, biological and catalytic properties [1]. Lanthanum is one of the lanthanide series elements that has been categorized as a light rare-earth element (LREE) [2] based on its atomic number that falls between 57 to 61 amu. La(III) complexes have become compounds of interest owing to their physiological activity and lower toxicity upon coordination with a ligand [3].

Green chemistry has become one of the main considerations in the synthesis of products, with particular attention given to create processes that minimize or eliminate the use and generation of waste as well as hazardous substances. The first principle of green chemistry, namely waste prevention, focuses on the prevention or minimisation of waste at every step of the process rather than cleaning up and treating the waste after it has been created. In line with this, microwave-assisted synthesis (MWS) can be employed to synthesize compounds as it can eliminate or minimize waste [6]. MWS is a clean, cost-effective and efficient synthetic method that reduces the

reaction time without compromising yield [5].

In fundamental terms, MWS utilizes microwave radiation to generate heat in chemical reactions [4]. The target molecules in polar solvents and reactant molecules are heated by high frequency microwave radiation, forcing them to vibrate and rotate in resonance with the applied microwave field. The heat is produced through frequent collisions and vibrations of the molecules. This results in an increased reaction rate, shortening the reaction time [4]. The MWS method uses tightly-sealed small reaction vessels that enable pressure to build-up as the solvent evaporates when heated, hastening the forward reaction.

The popularity of MWS has risen in the past two decades and reports on utilizing microwave irradiation as an alternative to the conventional heating methods are abundant [4] [6]. However, to the best of our knowledge, reports on the use of MWS for lanthanum(III) complexes are scarce. Therefore, this paper aims at reporting the synthesis and characterization of two Schiff bases and their lanthanum(III) complexes using two different methods, namely conventional reflux and MWS. The molecular structures of all compounds prepared using both methods were elucidated through elemental analysis, FTIR, ¹H NMR and UV-Vis analysis, and the results are compared and discussed.

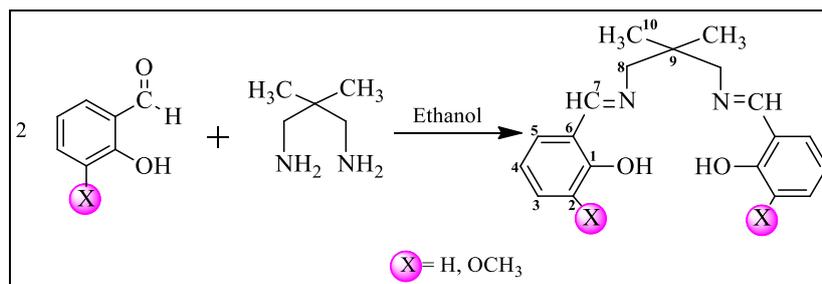


Figure 1. Conventional synthesis of Schiff bases

MATERIALS AND METHODS

All chemicals and reagents used in the synthesis were of analytical grade and procured from Sigma-Aldrich and Merck. The solvents for the synthesis of ligands and complexes were used without further purification.

1. Physicochemical and Spectroscopic Characterizations

The melting points of the synthesized compounds were determined using a Buchi Melting Point M-560 apparatus. The elemental analysis (CHN) was carried out using a Thermo Scientific Flash 2000 Elemental Analyser. The chemical structure of Schiff bases and lanthanum(III) complexes were elucidated through FTIR, ^1H NMR and UV-Visible spectroscopic analyses. FTIR spectra were recorded in the 400-4000 cm^{-1} range, using a Perkin-Elmer Spectrum One FTIR spectrometer with samples prepared using the standard KBr pellet technique. The proton NMR spectra of the Schiff bases and La(III) complexes were recorded in CDCl_3 and $\text{DMSO}-d_6$, respectively, using TMS as the internal standard, on a Bruker Varian-300 MHz NMR spectrometer (^1H NMR). Electronic absorption spectra were recorded at room temperature on a Perkin Elmer UV-Vis Lambda 35 spectrophotometer, in the range of 190 to 900 nm, using 1×10^{-4} M acetonitrile (MeCN) solution in a quartz cell.

2. Conventional Synthesis of Schiff bases

The synthesis protocol for both Schiff bases were adopted from Sakhare *et al.* [7] with several modifications. The Schiff base was synthesized by adding 10 mL hot ethanolic solution of 2,2-dimethyl-1,3-propanediamine (DMPD) (1 mmol) to 10 mL ethanolic solution of salicylaldehyde or 3-methoxysalicylaldehyde (2 mmol). The mixture was refluxed and stirred for 2 h (Figure 1). Then, the solution was cooled at room temperature. The yellow solid obtained was filtered off, washed with cold ethanol and air-dried.

2.1. AD1H

Yield: 91.6 %. Melting point: 96.4–96.8 °C. Elemental

percentages, analyzed as $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$: Found (Calc.) C 74.08 (73.52) H 7.27 (7.14) N 9.08 (9.03) %. IR bands (KBr pellet, cm^{-1}): $\nu(\text{C}=\text{N})$ 1630 (s), $\nu(\text{C}-\text{N})$ 1333 (w), $\nu(\text{C}-\text{O})$ 1277 (s), $\nu(\text{C}=\text{C})$ 1498 (m), $\nu(\text{C}-\text{H})\text{sp}^2$ 3064 (w), $\nu(\text{C}-\text{H})\text{sp}^3$ 2963 (w). ^1H NMR (300 MHz, CDCl_3): $\delta(\text{C}^1-\text{OH})$ 13.60 (s, 2H), $\delta(\text{HC}^7=\text{N})$ 8.34 (s, 2H), $\delta(\text{C}-\text{H}(\text{Ar}))$ 6.86-7.35 (m, 8H), $\delta(\text{H}_2\text{C}^8-\text{N})$ 3.49 (s, 2H), $\delta(\text{C}^{10}-\text{H}_3)$ 1.08 (s, 6H).

2.2. AD1OMe

Yield: 93.8%. Melting point: 113.2–113.8 °C. Elemental percentages, analysed as $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_4$: Found (Calc.) C 67.23 (68.09) H 7.07 (7.07) N 7.21 (7.56) %. IR bands (KBr pellet, cm^{-1}): $\nu(\text{C}=\text{N})$ 1630 (s), $\nu(\text{C}-\text{N})$ 1351 (w), $\nu(\text{C}-\text{O})$ 1252 (s), $\nu(\text{C}=\text{C})$ 1463 (s), $\nu(\text{C}-\text{H})\text{sp}^2$ 3061 (w), $\nu(\text{C}-\text{H})\text{sp}^3$ 2958 (m). ^1H NMR (300 MHz, CDCl_3): $\delta(\text{C}^1-\text{OH})$ 14.20 (s, 2H), $\delta(\text{HC}^7=\text{N})$ 8.34 (s, 2H), $\delta(\text{C}-\text{H}(\text{Ar}))$ 6.80-6.97 (m, 6H), $\delta(\text{H}_2\text{C}^8-\text{N})$ 3.51 (s, 2H), $\delta(\text{C}^{10}-\text{H}_3)$ 1.09 (s, 6H), $\delta(\text{Ar}-\text{OCH}_3)$ 3.93 (s, 6H).

3. Conventional Synthesis of Lanthanum(III) Complexes

The lanthanum(III) complexes (Figure 2) were synthesized by the conventional method as reported previously [8]. In a clean round bottom flask, AD1H or AD1OMe (1 mmol) was added to 10 mL ethanol. Then, 10 mL of ethanolic solution of $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (1 mmol) was added, and the mixture was stirred and refluxed for 4 h. The yellow precipitate produced was carefully filtered off, washed with a small amount of cold ethanol and air-dried.

3.1 La(AD1H)

Yield: 70.9%. Melting point: 231.7 °C (decomposed). Elemental percentages, analysed as $[\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2\text{La}(\text{2NO}_3)]$: Found (Calc.) C 41.77 (39.80) H 4.33 (3.87) N 9.96 (9.77) %. IR bands (KBr pellet, cm^{-1}): $\nu(\text{C}=\text{N})$ 1645 (s), $\nu(\text{C}-\text{N})$ 1385 (m), $\nu(\text{C}-\text{O})$ 1281 (s), $\nu(\text{C}=\text{C})$ 1475 (m), $\nu(\text{C}-\text{H})\text{sp}^2$ 3067 (w), $\nu(\text{C}-\text{H})\text{sp}^3$ 2966 (w), $\nu(\text{La}-\text{N})$ 571 (w), $\nu(\text{NO}_3)$ 1303 (s). ^1H NMR (300 MHz, DMSO): $\delta(\text{C}^1-\text{OH})$ 13.65 (s, 2H), $\delta(\text{HC}^7=\text{N})$ 8.57 (s, 2H), $\delta(\text{C}-\text{H}(\text{Ar}))$ 6.90-7.45 (m, 8H), $\delta(\text{H}_2\text{C}^8-\text{N})$ 3.49 (s, 2H), $\delta(\text{C}^{10}-\text{H}_3)$ 0.99 (s, 6H).

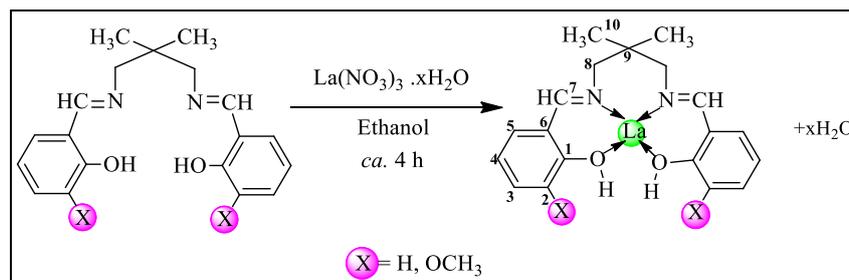


Figure 2. Conventional synthesis of lanthanum(III) complexes

3.2. La(AD1OMe)

Yield: 46.4%. Melting point: 259.3 °C (decomposed). Elemental percentages, analysed as $[C_{21}H_{26}N_2O_4La(3NO_3)]$: Found (Calc.) C 36.31 (36.27) H 3.86 (3.77) N 9.68 (10.07) %. IR bands (KBr pellet, cm^{-1}): $\nu(C=N)$ 1648 (s), $\nu(C-N)$ 1384 (w), $\nu(C-O)$ 1277 (s), $\nu(C=C)$ 1490 (m), $\nu(C-H)sp^2$ 3074 (w), $\nu(C-H)sp^3$ 2963 (w), $\nu(La-N)$ 620 (w), $\nu(La-O)$ 441 (w), $\nu(NO_3)$ 1311 (m). 1H NMR (300 MHz, DMSO): $\delta(C^1-OH)$ 13.89 (s, 2H), $\delta(HC^7=N)$ 8.54 (s, 2H), $\delta(C-H (Ar))$ 6.80-7.05 (m, 6H), $\delta(H_2C^8-N)$ 3.48 (s, 2H), $\delta(C^{10}-H_3)$ 0.98 (s, 6H), $\delta(Ar-OCH_3)$ 3.77 (s, 6H).

4. Microwave-Assisted Synthesis of Lanthanum(III) Complexes

The method was adopted from Ermis *et al.* [9] with some modifications. Both metal complexes were synthesized by the reaction of respective ligands with $La(NO_3)_3 \cdot xH_2O$ via a microwave-assisted synthesis method. The 1:1 molar ratio of ligand to metal salt in ethanolic solution (10 mL) was heated in the microwave reactor Monowave 450 (Anton Paar) for 8 min at 110°C, with a rotation speed of 600 rpm and an energy consumption of 169.9 kJ per reaction. The resulting precipitates were filtered off, washed with cold ethanol and air-dried.

4.1. MWS-La(AD1H)

Yield: 77.0%. Melting point: 223.7 °C (decomposed). Elemental percentages, analysed as $[C_{19}H_{22}N_2O_2La(2NO_3)]$: Found (Calc.) C 40.18 (39.80) H 3.99 (3.87) N 10.02 (9.77) %. IR bands (KBr pellet, cm^{-1}): $\nu(C=N)$ 1647 (s), $\nu(C-N)$ 1385 (w), $\nu(C-O)$ 1281 (s), $\nu(C=C)$ 1475 (s), $\nu(C-H)sp^2$ 3067 (w), $\nu(C-H)sp^3$ 2966 (w), $\nu(La-N)$ 572 (w), $\nu(NO_3)$ 1304 (s). 1H NMR (300 MHz, DMSO): $\delta(C^1-OH)$ 13.65 (s, 2H), $\delta(HC^7=N)$ 8.55 (s, 2H), $\delta(C-H (Ar))$ 6.88-7.47 (m, 8H), $\delta(H_2C^8-N)$ 3.49 (s, 2H), $\delta(C^{10}-H_3)$ 0.99 (s, 6H).

4.2. MWS-La(AD1OMe)

Yield: 88.9%. Melting point: 238.2 °C (decomposed). Elemental percentages, analysed as $[C_{21}H_{26}N_2O_4La(2NO_3)]$: Found (Calc.) C 40.19 (39.82) H 4.41 (4.14) N 9.08 (8.85) %. IR bands (KBr pellet, cm^{-1}):

$\nu(C=N)$ 1648 (s), $\nu(C-N)$ 1384 (w), $\nu(C-O)$ 1229 (s), $\nu(C=C)$ 1490 (m), $\nu(C-H)sp^2$ 3074 (w), $\nu(C-H)sp^3$ 2965 (w), $\nu(La-N)$ 620 (w), $\nu(La-O)$ 441 (w), $\nu(NO_3)$ 1311 (m). 1H NMR (300 MHz, DMSO): $\delta(C^1-OH)$ 13.89 (s, 2H), $\delta(HC^7=N)$ 8.53 (s, 2H), $\delta(C-H (Ar))$ 6.80-7.05 (m, 6H), $\delta(H_2C^8-N)$ 3.48 (s, 2H), $\delta(C^{10}-H_3)$ 0.98 (s, 6H), $\delta(Ar-OCH_3)$ 3.77 (s, 6H).

RESULTS AND DISCUSSION

1. Synthesis and Physicochemical Characterization

Two Schiff bases were successfully synthesized from 2,2-dimethyl-1,3-propanediamine (DMPD) and salicylaldehyde derivatives through conventional synthesis. Next, two lanthanum(III) complexes were prepared through conventional reflux and MWS methods. The synthesized Schiff bases and their La(III) complexes were characterized by melting point determination, elemental analysis (CHN), FTIR, 1H NMR and UV-Visible spectroscopy.

The syntheses of the Schiff bases and their lanthanum(III) complexes afforded yellow solids with more than 70% yield, except for La(AD1OMe). The lanthanum(III) complexes decomposed at high temperatures (223.7–259.3 °C). The percent yield and elemental analysis results of carbon, hydrogen and nitrogen for all compounds are presented in Table 1.

The experimental values of elemental analysis C, H, N for all compounds were in accord with the calculated values of the proposed structure. Based on the elemental analysis data, La(AD1H) and MWS-La(AD1H) were found to be compounds of similar chemical formula, where both appeared to possess two nitrate moieties. However, for the lanthanum(III) complexes of AD1OMe, different numbers of nitrate moieties were observed for the two compounds obtained from different synthesis methods. The compound obtained by the conventional synthesis method appeared to have three nitrate ions, whereas the product of the MWS method suggested the presence of only two nitrate ions. The low molar conductivity values of both compounds, 5.83 and 15.62 $\Omega^{-1} cm^2 mol^{-1}$, respectively, indicated that all the nitrate moieties in the compounds act as ligands, rather than counter ions.

Table 1. The experimental parameters and elemental analysis results of conventional reflux and microwave-assisted synthesis for the Schiff bases and their La(III) complexes.

Compound	Amount of solvent (EtOH)	Reaction time (min)	Percent yield (%)	Elemental Analysis % Calculated (Found)		
				C	H	N
AD1H	20 mL	120 min (Reflux)	91.6	73.52 (74.08)	7.14 (7.27)	9.03 (9.08)
La(AD1H).2NO₃	20 mL	240 min (Reflux)	70.9	39.80 (41.77)	3.87 (4.33)	9.77 (9.96)
MWS-La(AD1H).2NO₃	10 mL	8 min (Microwave)	77.0	39.80 (40.18)	3.87 (3.99)	9.77 (10.02)
AD1OMe	20 mL	120 min (Reflux)	93.8	68.09 (67.23)	7.07 (7.07)	7.56 (7.21)
[La(AD1OMe).3NO₃]	20 mL	240 min (Reflux)	46.4	36.27 (36.31)	3.77 (3.86)	10.07 (9.68)
MWS-La(AD1OMe).2NO₃	10 mL	8 min (Microwave)	88.9	39.82 (40.19)	4.14 (4.41)	8.85 (9.08)

The data in Table 1 indicates that the MWS reactions were completed in a much shorter time with relatively higher yields compared to the conventional method, as previously reported [4]. Reaction completion using the conventional method required 4 h (240 min), while the MWS method only took 8 min. Consequently, the consumption of electricity was much reduced for MWS and the need for circulating cooling water for the reflux condenser was eliminated. The yield of products increased by 6.1% for La(AD1H) and 42.5% for La(AD1OMe). The improvement in product yield as well as the reduction in reaction time has been previously reported by Kumari *et al.* [10]. In addition, 50% less solvent was used in the MWS method compared to conventional heating, which is a significant saving.

2. FTIR Spectroscopy

The IR spectra of the Schiff bases and their lanthanum(III) complexes are shown in Figures 3 and 4 while the significant data are listed in Table 2. The IR spectra of the ligands AD1H and AD1OMe exhibit a band at 1630 cm⁻¹ due to the azomethine $\nu(\text{C}=\text{N})$ group, in agreement with the value reported by Ahmad *et al.* [11]. Upon complexation, the band corresponding to the imine group in the Schiff bases was shifted to a considerably higher frequency in the range of 15–18 cm⁻¹ for their corresponding lanthanum(III) complexes obtained from both synthesis methods, suggesting the involvement

of the imine nitrogen in coordination with the metal ions [12]. The formation of the complexes is supported by the shifting of the $\nu(\text{C}-\text{N})$ to a higher frequency upon complexation. It was further supported by the appearance of a new peak in both the spectra of the La(III) complexes assigned to the $\nu(\text{La}-\text{N})$ observed at 571–620 cm⁻¹ (Figure 3(c)).

The $\nu(\text{C}-\text{O})$ band was observed as a strong peak at 1252–1277 cm⁻¹ in the spectra of both Schiff bases, in agreement with the value reported by Bahron *et al.* [13]. Similar bands were observed at a higher frequency, $\Delta\nu = 4$ cm⁻¹ in La(AD1H) and MWS-La(AD1H) as well as at a lower frequency, $\Delta\nu = 23$ –25 cm⁻¹ in La(AD1OMe) and MWS-La(AD1OMe). The large shifts in La(AD1OMe) and MWS-La(AD1OMe) suggest the involvement of phenol in the complexation (Figure 4(b)). In addition, the coordination was proven by the presence of a new band for La-O at 441 cm⁻¹, observed in La(AD1OMe) and MWS-La(AD1OMe) infrared spectra (Figure 4(c)). The nitrate ion that coordinates to the metal center in all La(III) complexes was observed through the peak at 1303–1311 cm⁻¹ [14]. The weak vibrations due to $\nu(\text{C}-\text{H})\text{sp}^2$ stretching in the aromatic ring of Schiff bases and La(III) complexes were seen at 3061–3074 cm⁻¹, in agreement with previous reports [13][14]. Meanwhile, the $\nu(\text{C}-\text{H})\text{sp}^3$ of methyl group of the aliphatic amine was present at 2958–2966 cm⁻¹, in agreement with the reported value by Matshwele *et al.* [17].

Table 2. FTIR data of Schiff bases and their La(III) complexes

Compounds	Wavenumber, ν (cm ⁻¹)							
	C=N	C-N	C-O (phenol)	La-N	La-O	NO ₃ (coordinated)	C-H sp ²	C-H sp ³
AD1H	1630 (s)	1333 (w)	1277 (s)	–	–	–	3064 (w)	2963 (w)
La(AD1H)	1645 (s)	1385 (w)	1281 (s)	571 (w)	–	1303 (s)	3067 (w)	2966 (w)
MWS-La(AD1H)	1647 (s)	1385 (w)	1281 (s)	572 (w)	–	1304 (s)	3067 (w)	2966 (w)
AD1OMe	1630 (s)	1351 (w)	1252 (s)	–	–	–	3061 (w)	2958 (m)
La(AD1OMe)	1648 (s)	1384 (w)	1227 (s)	620 (w)	441 (w)	1311 (m)	3074 (w)	2963 (w)
MWS-La(AD1OMe)	1648 (s)	1384 (w)	1229 (s)	620 (w)	441 (w)	1311 (m)	3074 (w)	2965 (w)

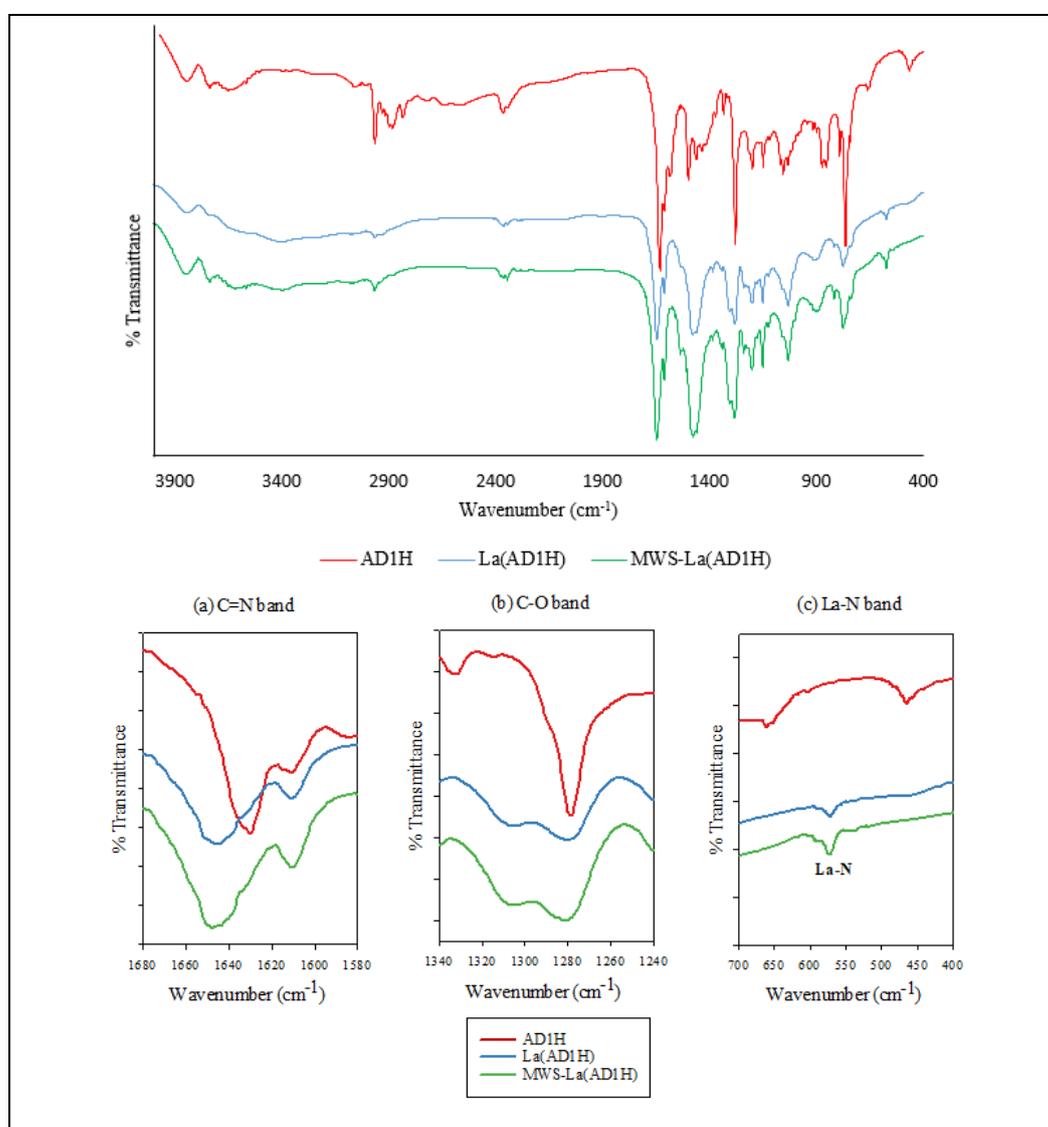


Figure 3. Significant bands in the IR spectra of AD1H, La(AD1H) and MWS-La(AD1H)

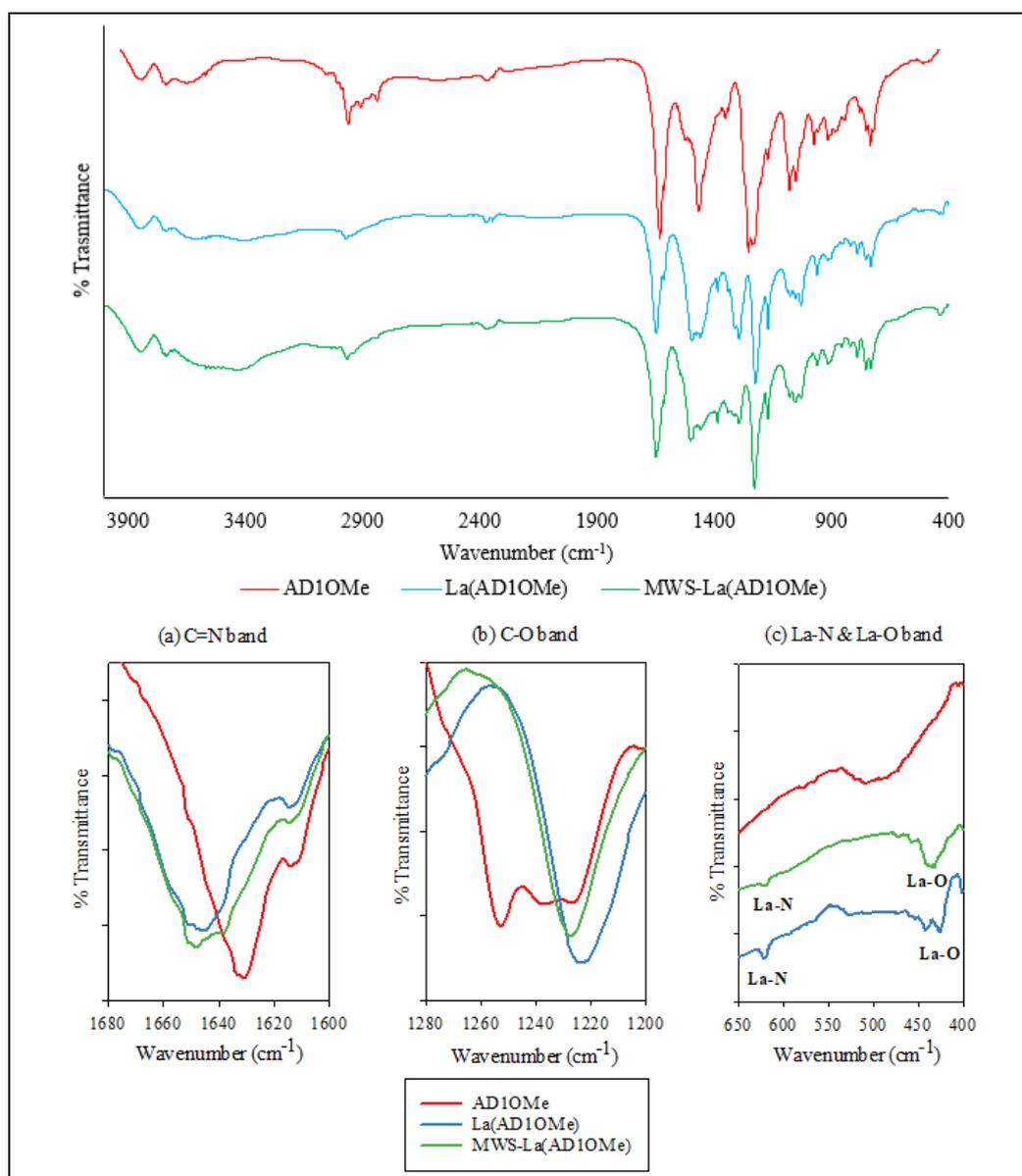


Figure 4. Significant bands in the IR spectra of AD1OMe, La(AD1OMe) and MWS-La(AD1OMe)

3. ¹H NMR Spectroscopy

The ¹H NMR of Schiff bases were recorded in CDCl₃ and the La(III) complexes in DMSO-*d*₆. The experimental ¹H NMR data are listed in Table 3 while the spectra are shown in Figures 5 and 6. In AD1H and AD1OMe, the phenolic proton peak was observed at 13.60 and 14.20 ppm, respectively. This phenolic proton (OH) was still present in both La(AD1H) and La(AD1OMe) spectra, however at different chemical shifts i.e. 13.65 and 13.89 ppm, respectively. A similar trend of shifts of this phenolic proton signal was observed for the MWS La(III) complexes. Based on Figure 6, there is a significant shift of this phenolic proton in La(AD1OMe) and MWS-La(AD1OMe), where the O-H was assumed to be bonded to the metal center

without the phenolic proton being deprotonated [18]. This bonding is possible due to the presence of lone pairs of electrons on the oxygen of the hydroxyl group. Therefore, a dative covalent bond seems to have been formed, where the lone pair of electrons is donated to the La(III) center.

Meanwhile, the azomethine protons, HC⁷=N appeared at 8.34 ppm for both Schiff bases. Upon complexation, the azomethine proton signal shifted upfield, with $\Delta\delta=0.19-0.23$ ppm. This shift indicates that the nitrogen is coordinated to the La(III) ion upon complexation [19]. In addition, the aromatic protons of these lanthanum(III) complexes were shifted slightly downfield, which can be attributed to the formation of a bond between the phenolic oxygen and the La(III) ion.

Table 3. Experimental ^1H NMR chemical shift δ (ppm) values for Schiff bases and their La(III) complexes

Compounds	Assignment, δ (ppm)					
	$\text{C}^1\text{-OH}$	$\text{HC}^7=\text{N}$	$\text{C}^2\text{-H (Ar)}$	$\text{N-C}^8\text{H}_2$	$\text{C}^{10}\text{-H}_3$	Ar-OCH_3
AD1H	13.60 (<i>s</i> , 2H)	8.34 (<i>s</i> , 2H)	6.86-7.35 (<i>m</i> , 8H)	3.49 (<i>s</i> , 4H)	1.08 (<i>s</i> , 6H)	–
La(AD1H)	13.65 (<i>s</i> , 2H)	8.57 (<i>s</i> , 2H)	6.90-7.45 (<i>m</i> , 8H)	3.49 (<i>s</i> , 4H)	0.99 (<i>s</i> , 6H)	–
MWS-La(AD1H)	13.65 (<i>s</i> , 2H)	8.55 (<i>s</i> , 2H)	6.88-7.47 (<i>m</i> , 8H)	3.49 (<i>s</i> , 4H)	0.99 (<i>s</i> , 6H)	–
AD1OMe	14.20 (<i>s</i> , 2H)	8.34 (<i>s</i> , 2H)	6.80-6.97 (<i>m</i> , 6H)	3.51 (<i>s</i> , 4H)	1.09 (<i>s</i> , 6H)	3.93 (<i>s</i> , 6H)
La(AD1OMe)	13.89 (<i>s</i> , 2H)	8.54 (<i>s</i> , 2H)	6.80-7.05 (<i>m</i> , 6H)	3.48 (<i>s</i> , 4H)	0.98 (<i>s</i> , 6H)	3.77 (<i>s</i> , 6H)
MWS-LaAD1OMe	13.89 (<i>s</i> , 2H)	8.53 (<i>s</i> , 2H)	6.80-7.05 (<i>m</i> , 6H)	3.48 (<i>s</i> , 4H)	0.98 (<i>s</i> , 6H)	3.77 (<i>s</i> , 6H)

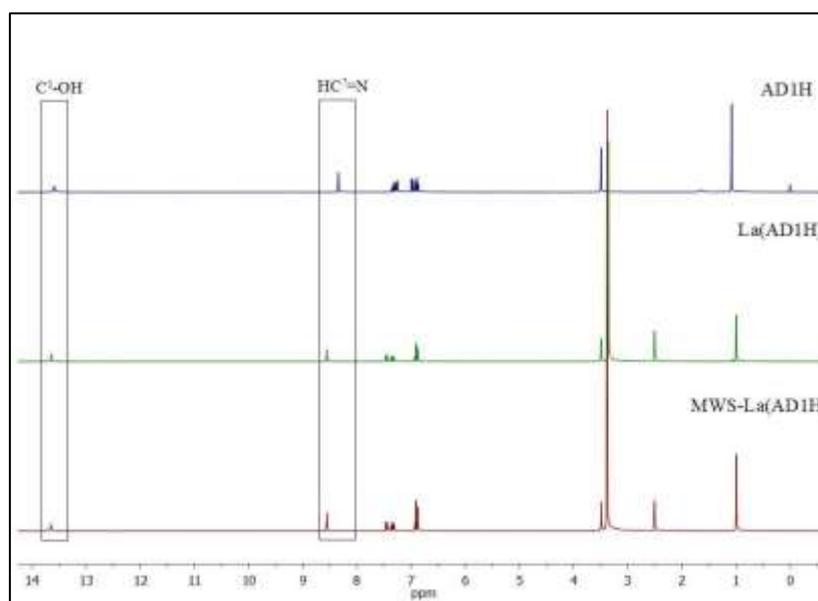


Figure 5. ^1H NMR spectra of AD1H, La(AD1H) and MWS-La(AD1H)

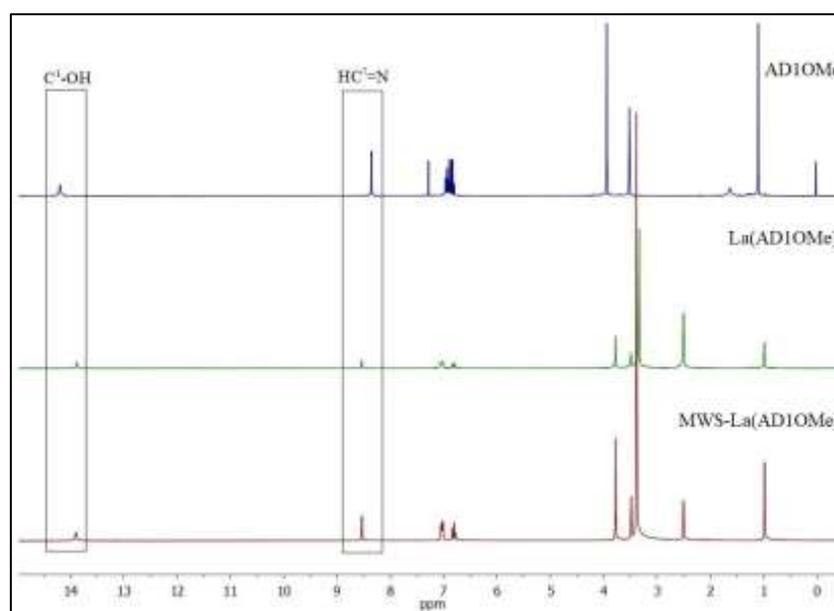


Figure 6. ^1H NMR spectra of AD1OMe, La(AD1OMe) and MWS-La(AD1OMe)

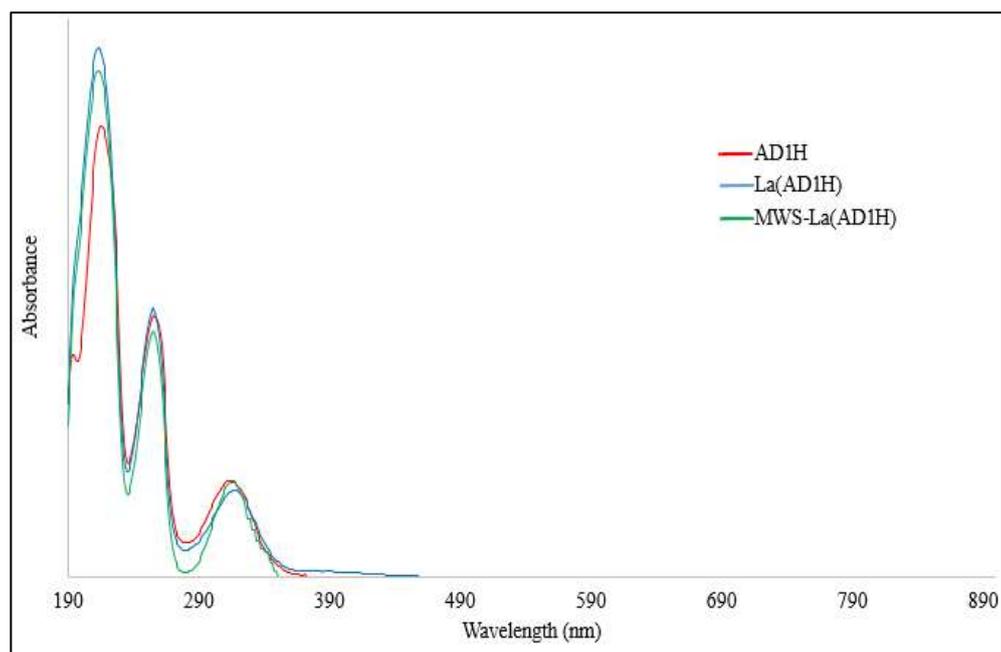


Figure 7. UV-Vis spectra of AD1H, La(AD1H) and MWS-La(AD1H)

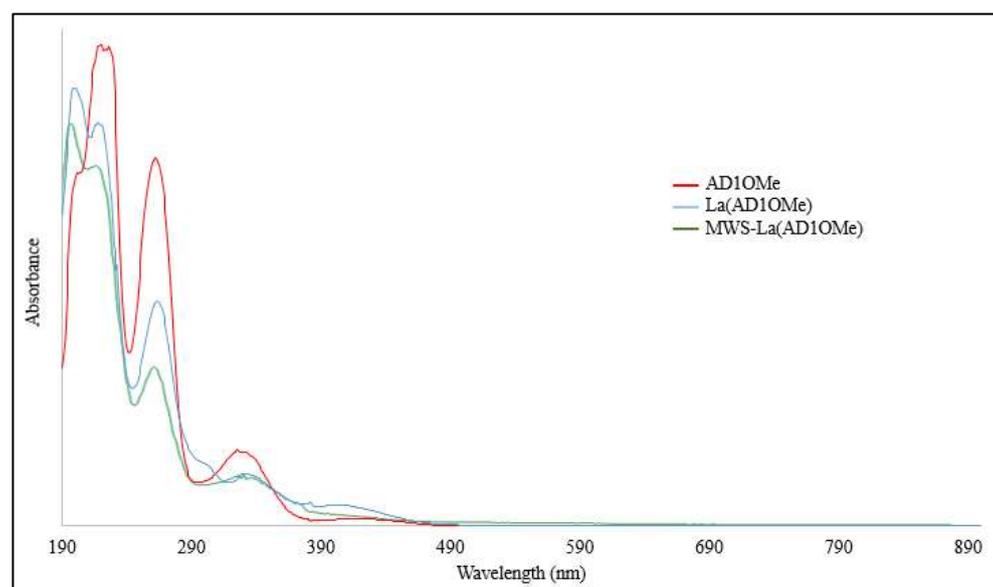


Figure 8. UV-Vis spectra of AD1OMe, La(AD1OMe) and MWS-La(AD1OMe)

Table 4. UV-Vis data of Schiff bases and their lanthanum(III) complexes

Compounds	$\pi \rightarrow \pi^*$ (C=C)	$\pi \rightarrow \pi^*$ (C=N)	$n \rightarrow \pi^*$ (imine)	Ligand to Metal Charge Transfer
AD1H	216 (19980)	256 (11408)	320 (4028)	–
La(AD1H)	216 (23407)	256 (11761)	322 (3742)	–
MWS-La(AD1H)	216 (22749)	256 (11284)	321 (4035)	–
AD1OMe	222, 228 (25090, 24990)	262 (18187)	328 (4655)	–
La(AD1OMe)	219 (20911)	268 (11165)	342 (3473)	–
MWS-La(AD1OMe)	220 (18553)	266 (10879)	345 (3458)	–

4. UV-Vis Absorption Spectroscopy

The Schiff bases and their lanthanum(III) complexes were analyzed using a Lambda 35-Perkin Elmer UV-Visible spectrometer within the range of 190 to 900 nm. The samples were prepared in acetonitrile with a concentration of 1×10^{-4} M. Figures 7 and 8 show the significant bands in the UV-Vis spectra of representative Schiff bases and lanthanum(III) complexes, while the data is tabulated in Table 4.

The spectra of the Schiff bases show three significant absorption bands for $\pi-\pi^*$ (benzene), $\pi-\pi^*$ (imine) and $n-\pi^*$ (imine). The first band in the range 216–228 nm was attributed to the $\pi-\pi^*$ (benzene), in accordance with the reported value by Alturqi *et al.* [20]. The azomethine chromophore $\pi-\pi^*$ and $n-\pi^*$ bands of both Schiff bases present at 256–262 nm and 320–328 nm, respectively. The wavelength, λ_{\max} , of $\pi-\pi^*$ is lower than that of $n-\pi^*$ because the energy needed for the electron to undergo excitation from π orbital to π^* orbital is higher than the energy required for the electron excitation from a non-bonding, n electron to π^* orbital.

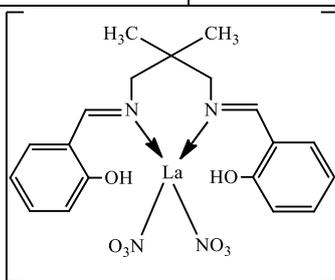
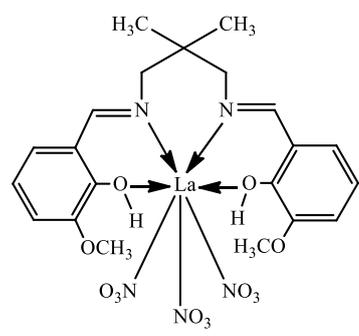
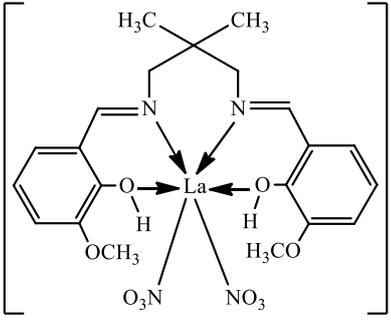
Upon complexation, there was a very small shift (or even no shift) involving $\pi-\pi^*$ (C=C), $\pi-\pi^*$ (C=C) and $n-\pi^*$ (C=N) bands. However, in La(AD1OMe) and MWS-La(AD1OMe), the $n-\pi^*$ (C=N) had clearly

shifted to higher wavelengths with $\Delta\lambda=14-16$ nm, indicating the coordination of the imine nitrogen to the La(III) ion. Besides, there was no significant absorption of the LMCT band (expected around 380–700 nm) in lanthanum(III) complexes due to the absence of $4f$ orbital electrons and the shielding effect of rare earth $4f$ orbital electrons [18]. As a lanthanum(III) complex is one of the lanthanide series elements, no absorption band of $f-f$ transition can be observed due to the fact that the $f-f$ bands are very weak [8].

5. Predicted structure and geometry of La(III) complexes

Lanthanum is considered a high-coordinate species which can have a coordination number of up to 12, as reported by Upadhyay *et al.* [12]. Therefore, La(III) complexes could display a wide variety of geometries. Since La(AD1H) and MWS-La(AD1H) have a coordination number of 6, the predicted geometry is octahedral. Meanwhile, La(AD1OMe) has a coordination number of 10, and its predicted geometry is bicapped square antiprism. On the other hand, MWS-La(AD1OMe) is predicted to possess square antiprism geometry since it has a coordination number of 8. Table 5 shows the predicted chemical structures and geometries of the La(III) complexes where the structures are proposed based on the physicochemical and spectroscopic analysis. The

Table 5. Chemical structures and predicted geometries of La(III) complexes

	Conventional synthesis product	MWS product
La(AD1H)	 <p>Coordination number = 6; Suggested geometry is Octahedral</p>	
La(AD1OMe)	 <p>Coordination number = 10; Suggested geometry is Bicapped square antiprism</p>	 <p>Coordination numbers = 8; Suggested geometry is Square antiprism</p>

total charge for La(AD1H), MWS-La(AD1H) and MWS-La(AD1OMe) is +1 since there are two coordinated nitrate groups to counter the +3 charge of the central lanthanum. Meanwhile, the La(AD1OMe) is a neutral uncharged species having three nitrate ions bonded to the La³⁺ metal center.

CONCLUSION

Both the Schiff bases and their lanthanum(III) complexes were successfully characterized through elemental analysis, IR, ¹H NMR and UV-Visible spectroscopy. Based on the reported data, both conventional and microwave synthesis methods afforded similar products of La(AD1H) with different yields. However, for La(AD1OMe) the different synthesis methods seemed to have caused the formation of slightly different products, where three nitrate ions were observed in the conventionally synthesised product while two nitrate ions were found in the MWS product. The shift of the azomethine peak in FTIR, ¹H NMR and UV-Vis, suggested the formation of lanthanum(III) complexes. The microwave-assisted method produced better percentage yields than the conventional method. MWS only needed 50% of solvent compared to the conventional method, and required a much shorter reaction time, with a very significant 96.7 % time saving for the synthesis the lanthanum(III) complexes.

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