Extraction of Toxic Metal Ions by Resorcin[4]arene Schiff Base Derivatives

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ABSTRACT

The present work reports the synthesis of eight new resorcin[4]arene Schiff base derivatives (2a–h) by reacting 2,6-dihydroxyacetophenone with different aliphatic aldehydes, followed by condensation with *n*-butylamine to give the final products in quantitative yields. All the synthesized Schiff base derivatives were characterized by spectroscopic techniques, such as ^{1}H-NMR, ^{13}C-NMR, IR, mass spectrometry and elemental analysis. Application of these Schiff base derivatives is shown in the extraction of some toxic cations, namely Ni^{2+}, Mn^{2+}, Hg^{2+}, Co^{2+}, and anion, namely $Cr_2O_7^{2-}$. The results showed higher extraction efficiency for Hg^{2+} compared to the other cations tested under identical experimental conditions. Furthermore, the extraction of the dichromate anion was higher with 2d under highly acidic conditions.

KEYWORDS

2,6-Dihydroxyacetophenone[4]arene, Schiff bases, cations, dichromate anion, solvent extraction.

1. Introduction

In supramolecular chemistry, the recognition of various species, such as anions, cations and neutral molecules, have been studied using several calixarene derivatives. The complexation ability of calix[4]arene molecules depend on their nature, conformation and the number of donor groups. Furthermore, calix[4]arene based receptors are known for their pre-designed cavities and are prepared by 'lower' and 'upper' rim functionalization.[1] In the recent era, the molecular recognition of anionic or cationic guest molecules by positively charged or electron-deficient neutral abiotic receptor molecules is an interesting area in supramolecular research. The hydrogen bonding interaction between an amine, amide or imide with an anion is widely used in anion receptors in calix[4]arenes.[2] Azines include two imine groups in the molecule and hence they act as potential ligands in the coordination chemistry.[3] The concept of Metal-Organic Frameworks (MOFs) in supramolecular chemistry has been extensively used as anion receptors.[4–10] Moreover, MOFs have been applied for drug delivery, as luminescent probes, sensors, and many more. These luminescent MOFs based sensors can attract guest molecules.[11] Resorcin[4]arenes are good receptors to attract anions and cations due to their flexible nature of ionophores with desired binding properties.[12] For the design and synthesis of molecular receptors, the chemical modification of N-ligating groups is very important.[13] Azocalix[4]arene has been synthesized, for the application of complexation, extraction and thermal studies.[14] The condensation reaction of an aldehyde or ketone with a primary amine is well-known because it generates an imine by the removal of water molecules.[15] The Schiff bases are widely useful for the formation of metal complexes and metal chelates in coordination chemistry.[16–24]

High toxicity effects of several metals have become a huge problem worldwide. Several toxic heavy metals, such as mercury, lead, cadmium and chromium, are continuously produced during industrial processes and are found in industrial wastewaters. The industrial processes in question are metal plating, battery manufacturing, smelting, petroleum refining, paint manufacturing, tanneries, pigment manufacturing, pesticides, etc.[25–28] Heavy metals are often present together with complex-forming organic compounds in wastewater.[29] When the extent of toxicity reaches threatening levels, it becomes essential to remove these metals from the water.[30] Several separation techniques are known for the extraction of metal ions to regulate the toxicity level.[31]

The binding properties of receptors have been examined by liquid-liquid extraction process and the extraction efficiency, selectivity, stoichiometry of complexation and extraction constants for the transition metal ions was determined.[32] Ions extraction have been reported with different calix[4]arene based nanoemulsions.[33,34] Recognition studies of some divalent toxic metals like, Cd^{2+}, Hg^{2+} and Pb^{2+} has been reported with a functionalized calix[n]arene using liquid-liquid extraction method.[35] Schiff bases of calix[4]arene have been applied for the extraction of anions and cations.[36] Our research group reported the synthesis of various 2,6-dihydroxyacetophenone[4]arene derivatives and their use for the recognition of different amino acids.[37]

In the present work, 2,6-dihydroxyacetophenone[4]arene derivatives were synthesized (Scheme 1) with good yield and were characterized by NMR, as well as by other spectroscopic techniques. 2,6-Dihydroxyacetopheone[4]arene having an acetyl group at the *ortho* position reacts with *n*-butylamine to give the Schiff base derivatives. Selected toxic metals were extracted from water samples with these macrocyclic Schiff bases.

2. Experimental

2.1. Materials and Methods

All the chemicals and solvents used in this study were of lab reagent grade and used without further purification. The aldehyde derivatives were purchased from Sigma Aldrich (St. Louis, MO, US). Monitoring of the reaction was carried out by thin-layer chromatography (TLC), using aluminium-backed silica gel 60 F254 plates (Merck, Germany). Melting points were determined by programmable Veego melting point apparatus.

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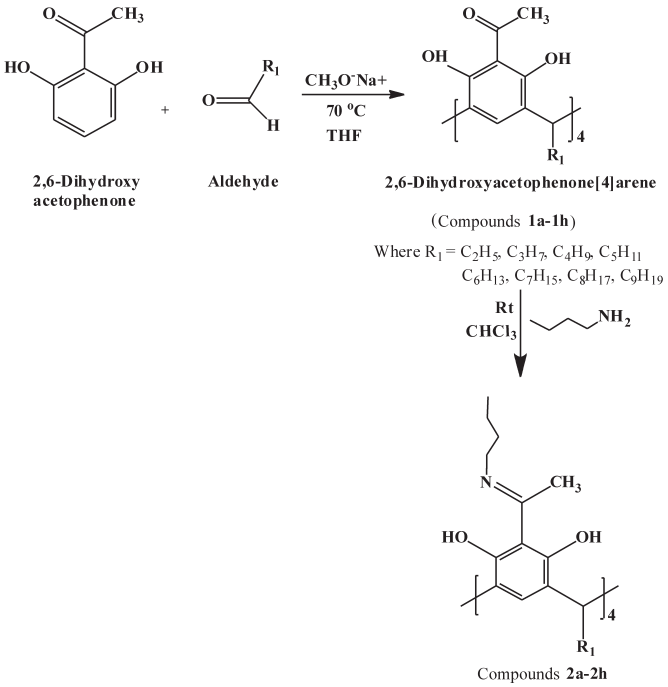

Scheme 1
Formation of resorcin[4]arene Schiff base derivatives.

^{1}H-NMR ($CDCl_3$) and ^{13}C-NMR ($CDCl_3$) spectra were recorded on a Bruker Avance (400 MHz) spectrometer. IR spectra were recorded on Perkin Elmer FT-IR 377 spectrometer using the KBr pellets method. Mass spectra were acquired using Waters Xevo G2-XS QTof Quadrupole Time-of-Flight Mass Spectrometry. Elemental analysis was carried out using EURO VECTOR EA3000 CHNS-O Analyzer. The UV absorption spectra were recorded on Jasco V-630 UV-Visible spectrophotometer (Tokyo, Japan).

2.1.1. *Preparation of 2,6-Dihydroxyacetophenone[4]arene Derivatives* (**1a**–**1h**)

The derivatives of 2,6-dihydroxyacetophenone[4]arene were synthesized (Scheme 1) using a previously published method.[37] Briefly, 2,6-dihydroxyacetophenone (0.500 g, 3.289 mmol) and aliphatic aldehyde (3.289 mmol) were dissolved in 20 mL of tetrahydrofuran (THF). 0.1 g (1.85 mmol) sodium methoxide was added, and the reaction mixture was refluxed with constant stirring for 72 h. The completion of the reaction was checked by TLC using ethyl acetate and hexane (3:7) solvent mixture (Rf 0.21). The reaction mixture was cooled to room temperature, and the solvent was evaporated under vacuum. The crude product obtained was dissolved in 25 mL of methanol, and few drops of acetic acid were added. A yellow precipitate formed. The solution containing the precipitate was stirred at 0–5 °C for 30 min. The product was filtered and washed with cold methanol. It was purified by column chromatography using ethyl acetate and hexane and dried at 40–45 °C. All the synthesized compounds were characterized by IR, ^{1}H- and ^{13}C-NMR and mass spectrometry.

2.1.2. *Preparation of Resorcin[4]arene Schiff Base Derivatives* (**2a**–**2h**)

Synthesis of 15-(1-(butylimino)ethyl)-35,55,75-tris(1-(butylimino)ethyl)-2,4,6,8-tetraethyl-1,3,5,7 (1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54,56,74,76-octol (**2a**)

1.00 g (1.30 mmol) of compound **1a** and 2.05 mL (20.8 mmol) of *n*-butylamine were dissolved in 20 mL of chloroform. The reaction mixture was stirred for 24 h at room temperature. The completion of the reaction was checked by TLC (hexane:ethyl acetate, 7:3). At the end of the reaction, 25 mL of water was added to the reaction mixture to enable liquid-liquid extraction. The aqueous layer was extracted twice with 20 mL chloroform. The separated organic layers were combined and dried with anhydrous magnesium sulphate, which was then filtered off. The solvent was evaporated in a rotatory evaporator under vacuum at 40 °C. The oily product obtained was treated with hexane and methanol to get a solid product, which was filtered and washed twice with methanol. The light red product was dried in an oven at 60 °C.

Yield: 78.12 %, m.p.: 220 °C, M.W: 989, ^{1}H-NMR (400 MHz in $CDCl_3$), δ: 12.21 (s, 8H, Ar-OH), 7.26 (s, 4H, Ar), 4.41 (t, 4H, J = 8.0 MHz, -CH-), 3.46 (t, 8H, J = 13.6 MHz, -CH_2N), 2.20 (q, 8H, J = 7.6 MHz, -CH_2), 2.62 (s, 12H, -CH_3), 1.68 (m, 8H, J = 7.2 MHz, -CH_2), 1.44 (m, 8H, J = 16.8 MHz, -CH_2), 0.96 (t, 24H, J = 4.0 MHz, -CH_3). Anal. calcd. for $C_{60}H_{84}N_40_8$ (%):C, 72.84; H, 8.56; N, 5.66; O, 12.94. Found: C, 72.81; H, 8.55; N, 5.65; O, 12.92.

The other derivatives of the Schiff base were synthesized following the same procedure by changing the respective compounds (**1b**–**1h**) with different amount of *n*-butylamine, 1.91 mL (19.39 mmol), 1.79 mL (18.16 mmol), 1.68 mL (17 mmol), 1.59 mL (16 mmol), 1.50 mL (15.25 mmol), 1.67 mL (17 mmol), 1.35 mL (13.73 mmol), respectively.

Synthesis of 15-(1-(butylimino)ethyl)-35,55,75-tris(1-(butylimino)ethyl)-2,4,6,8-tetrapropyl-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54,56,74,76-octol (**2b**)

Yellowish orange. Yield: 79.36 %, m.p.: 199 °C, M.W: 1045, ^{1}H-NMR (400 MHz in$CDCl_3$), δ: 12.20 (s, 8H, Ar-OH), 7.26 (s, 4H, Ar), 4.53 (t, 4H, J = 8.0 MHz, -CH-), 3.46 (t, 8H, J = 6.8 MHz, -CH_2N), 2.13 (q, 8H, J = 22.4 MHz, -CH_2), 2.60 (s, 12H, -CH_3), 1.68 (m, 8H, J = 6.8 MHz, -CH_2), 1.40 (m, 16H, J = 33.2 MHz, -CH_2-CH_2-), 1.38 (m, 24H, -CH_3). Anal. calcd. for $C_{64}H_{92}N_40_8$ (%): C, 73.53; H, 8.87; N, 5.36; O, 12.24. Found: C, 73.52; H, 8.85; N, 5.34; O, 12.22.

Synthesis of 15-(1-(butylimino)ethyl)-35,55,75-tris(1-(butylimino)ethyl)-2,4,6,8-tetrabutyl-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54,56,74,76-octol (**2c**)

Dark yellow. Yield: 80.64 %, m.p.: 247 °C, M.W: 1102, ^{1}H-NMR (400 MHz in $CDCl_3$), δ: 12.21 (s, 8H, Ar-OH), 7.26 (s, 4H, Ar), 4.50 (t, 4H, J = 8.0 MHz, -CH-), 3.47 (t, 8H, J = 6.8 MHz, -CH_2N), 2.14 (q, 8H, J = 14.8 MHz, -CH_2), 2.62 (s, 12H, -CH_3), 1.66 (m, 8H, J = 7.2 MHz, -CH_2), 1.45 (m, 24H, J = 7.2 MHz, -CH_2-CH_2-), 0.92 (t, 24H, J = 7.6 MHz, -CH_3). Anal. calcd. for $C_{68}H_{100}N_40_8$ (%): C, 74.14; H, 9.15; N, 5.09; O, 11.62. Found: C, 74.11; H, 9.14; N, 5.08; O, 11.61.

Synthesis of 15-(1-(butylimino)ethyl)-35,55,75-tris(1-(butylimino)ethyl)-2,4,6,8-tetrapentyl-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54,56,74,76-octol (**2d**)

Dark orange. Yield: 81.96 %, m.p.: 215 °C, M.W: 1158, ^{1}H-NMR (400 MHz in $CDCl_3$), δ: 12.20 (s, 8H, Ar-OH), 7.36 (s, 4H, Ar), 4.49 (t, 4H, J = 7.6 MHz, -CH-), 3.48 (t, 8H, J = 6.8 MHz, -CH_2N), 2.14 (q, 8H, J = 6.0 MHz, -CH_2), 2.60 (s, 12H, -CH_3),1.67 (m, 8H, J = 7.2 MHz, -CH_2), 1.43 (m, 32H, J = 14.8 MHz, -CH_2-CH_2-), 1.36 (m, 24H, -CH_3), ^{13}C-NMR (400 MHz, $CDCl_3$): δ[ppm] = 13.68, 14.25, 19.18, 20.11, 22.84, 28.21, 31.11, 33.37, 33.74, 44.26, 107.79, 126.67, 176.78, MS: m/z = 1157.68 $[M]^+$, positive ionization mode m/z = 1158.68, IR (KBr) ν/cm^{-1}: 3744.34 (O-H str.), 3611.98 (N-H), 2932.07 (-CH_2-), 1556.26 (C=C), 805.68 (C=C). Anal. calcd. for $C_{72}H_{108}N_40_8$ (%): C, 74.70; H, 9.40; N, 4.84; O, 11.06. Found: C, 74.68; H, 9.39; N, 4.83; O, 11.04.

Synthesis of 15-(1-(butylimino)ethyl)-35,55,75-tris(1-(butylimino)ethyl)-2,4,6,8-tetrahexyl-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54,56,74,76-octol (**2e**)

Light orange. Yield: 81.80 %, m.p.: 214 °C, M.W: 1214, ^{1}H-NMR (400 MHz in $CDCl_3$), δ: 12.19 (s, 8H, Ar-OH), 7.25 (s, 4H, Ar), 4.49 (t, 4H, J = 7.6 MHz, -CH-), 3.45 (t, 8H, J = 6.8 MHz, -CH_2N), 2.14 (q, 8H, J = 6.4 MHz, -CH_2), 2.59 (s, 12H, -CH_3), 1.63 (m, 8H, J = 14.4 MHz, -CH_2), 1.41 (m, 48H, J = 22 MHz, -CH_2-CH_2-), 1.28 (t, 24H, -CH_3), ^{13}C-NMR (400 MHz, $CDCl_3$): δ[ppm] = 13.69, 14.14,.19.77, 20.12, 22.75, 28.45, 29.78, 31.12, 32.05, 33.10, 33.71, 44.27, 107.79, 128.70, 176.76, MS: m/z = 1213.78 $[M]^+$, positive ionization mode m/z = 1214.78, IR (KBr) ν/cm^{-1}: 3735.21 (O-H str.), 3678.35 (N-H), 2928.68 (-CH_2-), 1549.01 (C=C), 819.48 (C=C). Anal. calcd. for $C_{76}H_{116}N_40_8$ (%): C, 75.21; H, 9.63; N, 4.62; O, 10.55. Found: C, 75.20; H, 9.61; N, 4.60; O, 10.52.

Synthesis of 15-(1-(butylimino)ethyl)-35,55,75-tris(1-(butylimino)ethyl)-2,4,6,8-tetraheptyl-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54,56,74,76-octol (**2f**)

Reddish yellow. Yield: 82.60 %, m.p.: 160 °C, M.W: 1270, ^{1}H-NMR (400 MHz in $CDCl_3$), δ: 12.19 (s, 8H, Ar-OH), 7.24 (s, 4H, Ar), 4.49 (t, 4H, J = 9.2 MHz, -CH-), 3.46 (t, 8H, J = 13.6 MHz, -CH_2N), 2.14 (q, 8H, J = 6.0 MHz, -CH_2), 2.60 (s, 12H, -CH_3), 1.65 (m, 8H, J = 21.2 MHz, -CH_2), 1.45 (m, 40H, J = 14.8 MHz, -CH_2-CH_2-), 1.38 (m, 24H, -CH_3), ^{13}C-NMR (400 MHz, $CDCl_3$): δ[ppm] = 13.67, 14.16, 19.75, 20.11, 22.72, 28.47, 30.04, 31.12, 31.96, 33.10, 33.71, 44.25, 107.79, 128.70, 176.75. MS: m/z = 1269.99 $[M]^+$, positive ionization mode m/z = 1050.30, IR (KBr) ν/cm^{-1}: 3743.71 (O-H str.), 3616.47 (N-H), 2927.98 (-CH_2-), 1552.08 (C=C), 809.33 (C=C). Anal. calcd. for $C_{80}H_{124}N_40_8$ (%): C, 75.67; H, 9.84; N, 4.41; O, 10.08. Found: C, 75.65; H, 9.82; N, 4.40; O, 10.05.

Synthesis of 15-(1-(butylimino)ethyl)-35,55,75-tris(1-(butylimino)ethyl)-2,4,6,8-tetraoctyl-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54,56,74,76-octol (**2g**)

Orange. Yield: 83.33 %, m.p.: 210 °C, M.W: 1326, ^{1}H ^{1}H-NMR (400 MHz in $CDCl_3$), δ: 12.19 (s, 8H, Ar-OH), 7.25 (s, 4H, Ar), 4.49 (t, 4H, -CH-), 3.46 (t, 8H, -CH_2N), 2.62 (s, 12H, -CH_3CO), 2.15 (q, 8H, -CH_2), 1.66 (m, 8H, -CH_2NH), 1.40 (m, 56H, J = 7.2 MHz, -CH_2-CH_2-), 0.90 (m, 24H, J = 14 MHz, -CH_3), ^{13}C-NMR (400 MHz, $CDCl_3$): δ[ppm] = 13.69, 14.18, 19.77, 22.76, 28.48, 29.45, 29.81, 30.10, 31.12, 31.97, 33.08, 33.70, 44.27, 107.79, 128.71, 176.76. MS: m/z = 1326.00 $[M]^+$, positive ionization mode m/z = 1270.89. IR (KBr) ν/cm^{-1}: 3732.99 (O-H str.), 3678.35 (N-H), 2926.38 (-CH_2-), 1548.63 (C=C), 819.48 (C=C). Anal. calcd. for $C_{84}H_{132}N_40_8$ (%): C, 76.09; H, 10.03; N, 4.23; O, 9.65. Found: C, 76.05; H, 10.01; N, 4.22; O, 9.62.

Synthesis of 15-(1-(butylimino)ethyl)-35,55,75-tris(1-(butylimino)ethyl)-2,4,6,8-tetranonyl-1,3,5,7(1,3)-tetrabenzenacyclooctaphan-14,16,34,36,54,56,74,76-octol (**2h**)

Reddish orange. Yield: 84.74 %, m.p.: 206 °C, M.W: 1382, ^{1}H-NMR (400 MHz in $CDCl_3$), δ: 12.19 (s, 8H, Ar-OH), 7.25 (s, 4H, Ar), 4.49 (t, 4H, -CH-), 3.45 (t, 8H, -CH_2N), 2.14 (q, 8H, -CH_2), 2.61 (s, 12H, -CH_3), 1.65 (m, 8H, -CH_2), 1.41 (m, 64H, J = 7.2 MHz, -CH_2-CH_2-), 0.92 (m, 24H, J = 7.2 MHz, -CH_3), ^{13}C-NMR (400 MHz, $CDCl_3$): δ[ppm] = 13.68, 14.17, 19.75, 20.12, 22.75, 28.48, 29.43, 29.75, 29.88, 30.09, 31.13, 32.02, 33.09, 33.69, 44.28, 107.80, 128.72, 176.75. MS: m/z = 1381.01 $[M]^+$, negative ionization mode m/z = 1380.84, IR (KBr) ν/cm^{-1}: 3742.82 (O-H str.), 3615.76 (N-H), 2927.48 (-CH_2-), 1544.48 (C=C), 810.34 (C=C). Anal. calcd. for $C_{88}H_{140}N_40_8$ (%): C, 76.47; H, 10.21; N, 4.05; O, 9.26. Found C, 76.46; H, 10.20; N, 4.03; O, 9.25.

2.2. Analytical Procedure for Extraction Study

A solution of Ni^{2+}, Mn^{2+}, Hg^{2+}, Co^{2+} and Na^+ was prepared from the acetate and sulphate salts of these metal ions. Cation solutions were prepared at a concentration of 1×10^{-4} M, while the $Cr_2O_7^{2-}$ anion solution of sodium dichromate was prepared at a concentration of 1×10^{-5} M. Anion extraction experiment was done by changing the pH (1.0–5.0) of the solution using 0.01 M HCL/0.01 M KOH solution.[35,36] The standard solution (1×10^{-3} M) of resorcin[4]arene Schiff base ligands were prepared in CH_2Cl_2. In the analytical experiment, 10 mL solution of the cations were extracted with 10 mL ligand solution. For the extraction of dichromate anion, 10 mL of 1×10^{-5} M was extracted with 1×10^{-3} M ligand solution in a glass stoppered tube. Initially, the solution mixture was mechanically shaken for 2 min and then magnetically stirred for an hour in the thermostat at 25 °C. The solution was then transferred into a separating funnel and kept for 30 min for phase separation. Thereafter, the layers were separated, and the concentration of the cations in the aqueous phase was determined spectrophotometrically. Similarly, a blank experiment was also performed in the absence of a Schiff base, which showed no absorbance/extraction of the cations/anions. The percentage of extraction was calculated by using Equation 135,36, and the results are listed in Tables 1–3.

$$E\ \% = \frac{(A_0 - A)}{A_0} \times 100 \quad (1)$$

where, A_0 = Initial concentration of cations/anions solution before the extraction and A = final concentration of cations/anions solution after the extraction.

Table 1 Extraction of different metal cations with Schiff base derivative **2h**.

	% Extraction of metal cations with Schiff base derivative **2h**				
Metal cations:	Co^{2+}	Hg^{2+}	Mn^{2+}	Ni^{2+}	Na^+
% Extraction	24.82	32.50	12.64	6.57	12.03

Concentration of metal cations = 1×10^{-4} M.
Concentration of ligands = 1×10^{-3} M.

Table 2 Extraction of Hg^{2+} ion with Schiff base derivatives (**2a**–**2h**).

	% Extraction of Hg^{2+} ion with Schiff base derivatives **2a**–**2h**							
Ligands:	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**
% Extraction	36.03	39.47	37.00	26.68	36.98	38.72	29.37	32.50

Concentration of metal cations = 1×10^{-4} M.
Concentration of ligands = 1×10^{-3} M.

3. Result and Discussion

The present work aimed to synthesize new resorcin[4]arene derivatives which can extract toxic cations and dichromate ion from the aqueous medium. 2,6-Dihydroxyacetophenone[4]arene Schiff base ligands were prepared to extract Ni^{2+}, Mn^{2+}, Hg^{2+}, Co^{2+}, Na^+ ions. In our previous work, we synthesized and characterized several 2,6-dihydroxyacetophenone[4]arene derivatives (**1a**–**1h**).[37] Synthesis of these Schiff base derivatives of resorcin[4]arene was accomplished by reacting, **1a**–**h** with *n*-butylamine in the chloroform solvent by eliminating four water molecules. In the reaction, the ketone group of 2,6-dihydroxyacetophenone[4]arene reacts with the amine groups

Table 3 Extraction of dichromate anion with different Schiff base derivatives at various pH values.

Ligands	% Extraction of dichromate anion at different pH values				
	pH 5	pH 4	pH 3	pH 2	pH 1
2a	02.85	05.34	08.09	10.76	13.36
2b	01.07	03.92	11.95	16.11	22.52
2c	02.52	03.56	04.62	08.12	13.59
2d	02.72	09.22	11.51	17.31	22.83
2e	05.04	12.09	13.89	16.77	19.28
2f	06.02	07.79	08.09	12.45	14.66
2g	03.58	04.92	09.46	13.06	16.34
2h	01.81	04.31	07.06	10.13	13.72

Concentration of metal anions = 1×10^{-5} M.
Concentration of ligands = 1×10^{-3} M.

to create the Schiff base derivatives. All the Schiff bases were produced in excellent yield, had stable structures and were soluble in common organic solvents.

Furthermore, Schiff base derivatives were characterized by ^{1}H- and ^{13}C-NMR spectra in $CDCl_3$ and DMSO-d_6. The spectral data of compounds are listed in the supplementary material. The δ value of 8 hydroxyl group is shifted at around 12 ppm for all compounds because of the Schiff base formation. The δ value of four -CH_2 chain of *n*-butylamine are observed at approximately 0.90, 1.46, 1.68, 3.48 ppm, respectively. The δ value of alkyl chain of amine group appeared around 3.70 ppm for all Schiff base derivatives. The formation of the macrocyclic ring of resorcin[4]arene was confirmed by the characteristic peak of bridge proton as a triplet between 4 and 4.5 ppm.

Because of the presence of azomethine nitrogen atom on the Schiff base compounds, they were effectively applied for the extraction of anions and cations. Chromate and dichromate anions are present in soil and water, which contains chromium(VI), a cancer-causing agent in humans.[1,35] Compounds **2a**–**2h** were dissolved in dichloromethane for extracting the selected cations/anions. The extraction of dichromate anion by the ligands was measured at different pH values and effectively extraction by Schiff base compounds was observed. The results of the extraction studies are given in Tables 1–3. The results of different cationic extractions with compound **2h** are mentioned in Table 1. Based on the results in Table 1, the extraction of Hg^{2+} was higher compared to other cations tested. As the Hg^{2+} has greater electronegativity[38] compared to the other tested metal ions, it was effectively extracted with 2,6-dihydroxyacetophenone[4]arene Schiff bases under identical experimental condition. The resulting data of the Hg^{+2} extraction with all the Schiff base derivatives (**2a**–**2h**) are given in Table 2.

Due to hydrogen bonding the dichromate anions possess the oxide of $HCr_2O_7^-/Cr_2O_7^{2-}$.[38] Dichromate ion extraction experiment was performed with ligands by changing the pH value of the dichromate solution from pH 1.00–5.00 and the resulting data show that the percentage extraction increased with decrease in the pH of the solution (Table 3).

From the resulting data, it can be concluded that at the lower pH value, the dichromate anion aqueous solution is protonated and formed $HCr_2O_7^-$. The di-anionic system of $Cr_2O_7^{2-}$ has more free energy of hydration than the mono-anion of $HCr_2O_7^-$.[39] When the $HCr_2O_7^-$ is moved from the aqueous phase into the organic phase, there is a little loss in hydration energy.[39] At lower pH values, the better extraction of chromate ion was observed because of the protonation of the nitrile nitrogen to form a dication.[35] An additional explanation of the dichromate anion extraction at lower pH value is due to the formation of $NaHCr_2O_7$.[35] The advantage of the imine nitrogen is that it gets protonated and helps to extract chromate into the dichloromethane. The ligand effectively extracts the chromate ion from the aqueous solution at low pH because of the free energy of hydration of the alkylammonium ion is less than that of the sodium ion.[39] The optimum result of extraction is found at the lowest pH 1.0 because the dichromate anion can exist in $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ forms that dimerize to generate the dominate Cr(IV) form.[39]

However, under alkaline conditions extraction of dichromate ion in dichloromethane was not possible due to lack of protonation of the nitrile nitrogen. Furthermore, under highly acidic conditions $Na_2Cr_2O_7$ gets converted into $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ by the following ionization process.[36]

$$H_2CrO_7 \rightleftharpoons H^+ + HCr_2O_7^- \quad (2)$$
$$HCr_2O_7^- \rightleftharpoons H^+ + Cr_2O_7^{-2}$$

Anion extraction of A^{n-} through the receptor LH^{n+} occurs as evident from the following equation.[39]

$$n(LH^{n+})org + nA_{aq}^{n-} \rightleftharpoons [(LH^{n+})n, A_n^{n-}]_{org} \quad (3)$$

The K_{ex} for the above equation can be expressed as

$$K_{ex} = \frac{[(LH^{n+})n, A_n^{n-}]_{org}}{[(A^{n-}]_{aq}^n [(LH^{n+}]_{org}^n} \quad (4)$$

From Equation 4 the value of K_{ex} for dichromate ion with ligand **2h** was 5.95.

4. Conclusion

In summary, eight new resorcin[4]arene Schiff bases have been prepared in quantitative yields using different derivatives of 2,6-dihydroxyacetophenone[4]arene. All the compounds were successfully characterized by spectroscopic techniques to confirm their structures. The metal extraction experiments displayed that resorcin[4]arene Schiff base compounds act as good extractants for all the tested cations Ni^{2+}, Mn^{2+}, Hg^{2+}, Co^{2+}, Na^+ and $Cr_2O_7^{2-}$ anion. The Hg^{2+} cation displays the highest percentage extraction compared to other cations tested. Further, the extraction of the dichromate ion was greater at lower pH. This can be attributed to the conversion of $Na_2Cr_2O_7$ into $HCr_2O_7^-$ and $Cr_2O_7^{2-}$, which improved the extraction efficiency. Finally, the results obtained in the study may provide further scope for the extraction of other toxic metals from wastewater. Additionally, these resorcin[4]arene Schiff Base derivatives may serve as an important intermediates/building blocks for the construction of various supramolecular architectures.

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Conflict of interest

The authors report no conflict of interest.

Supplementary Material

Supplementary information is provided in the online supplement.

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Extraction of Toxic Metal ions by Resorcin[4]arene Schiff base derivatives

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Spectral Data of Compounds

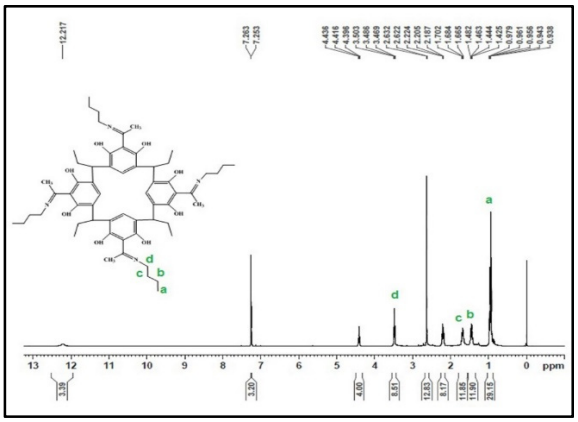
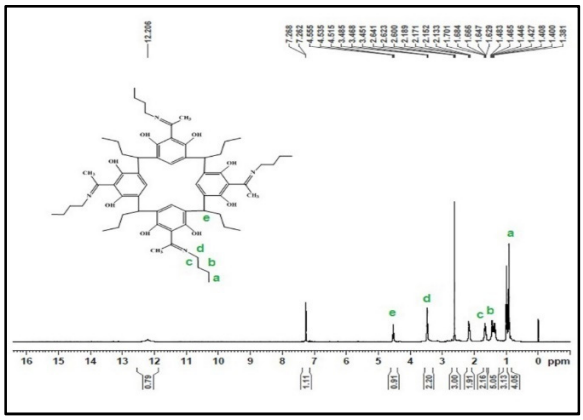


Figure 1 ^{1}H-NMR Spectral Data of compound **2a**



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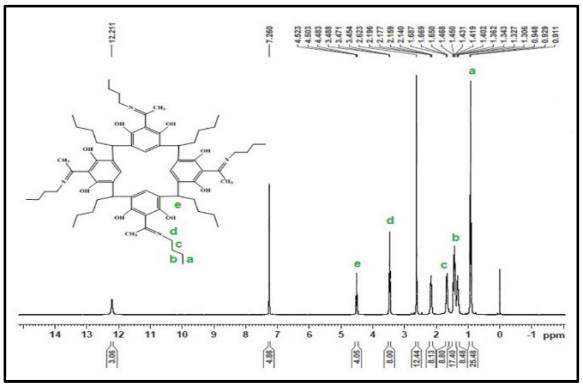

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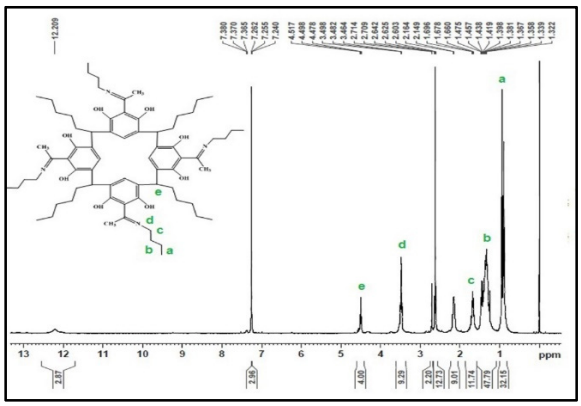


Figure 4. ^{1}H-NMR Spectral Data of compound **2d**

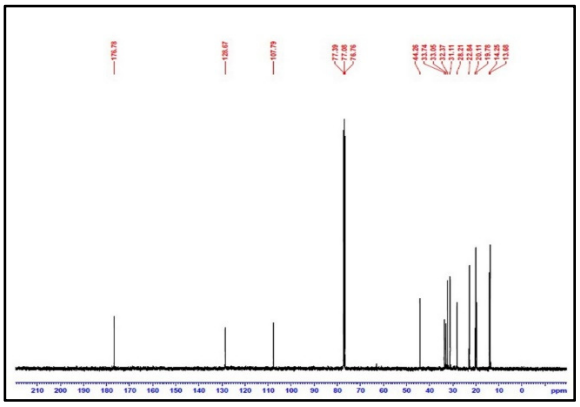
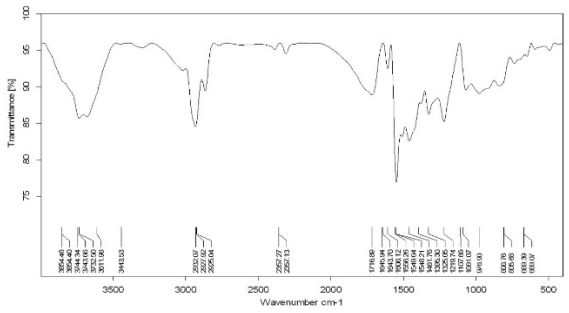


Figure 5. ^{13}C-NMR Spectral Data of compound **2d**



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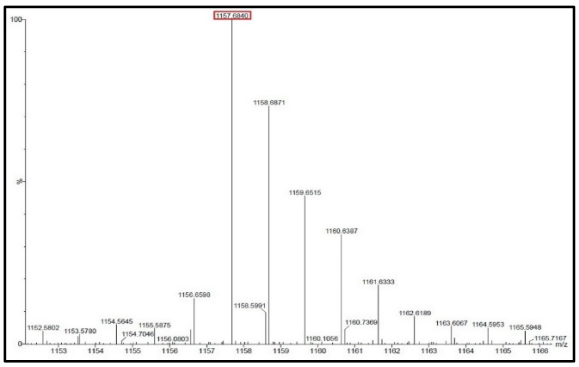

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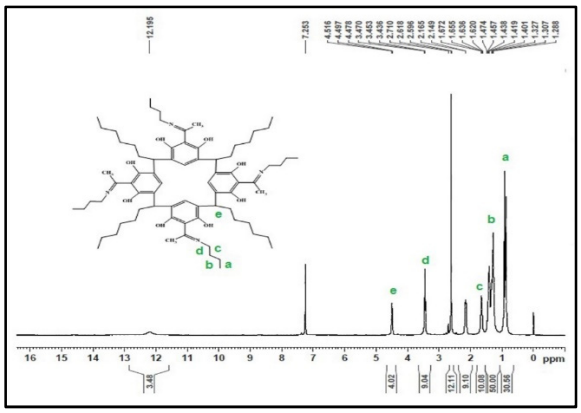
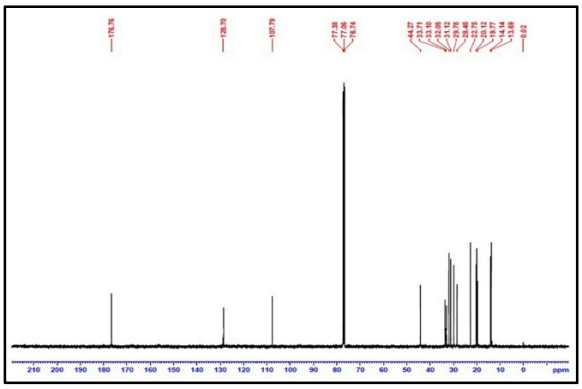


Figure 8. ^{1}H-NMR Spectral Data of compound **2e**



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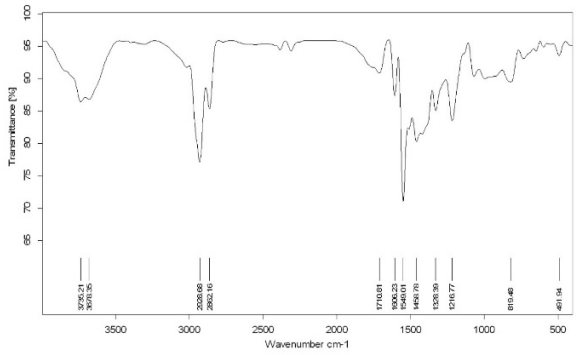

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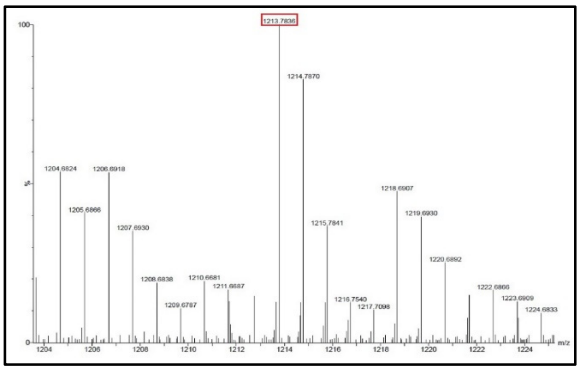

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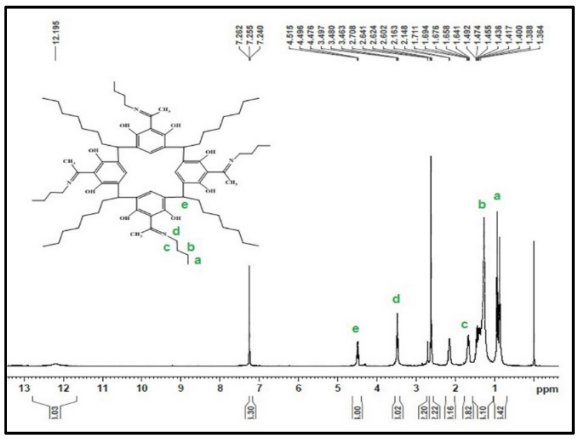

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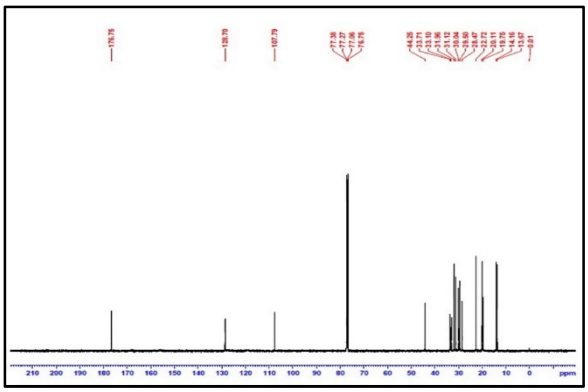

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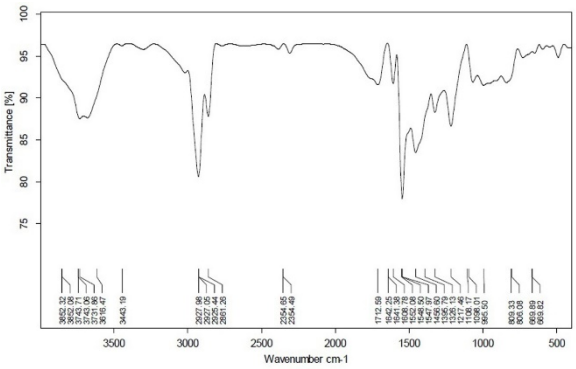

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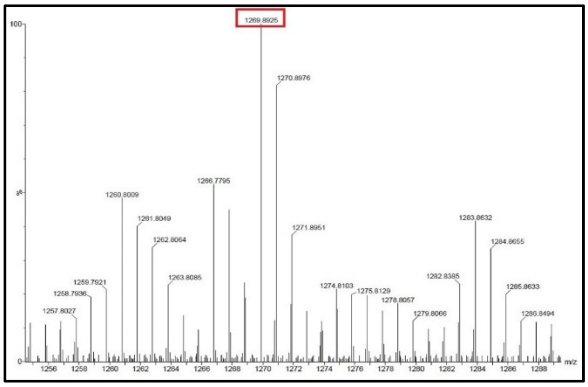

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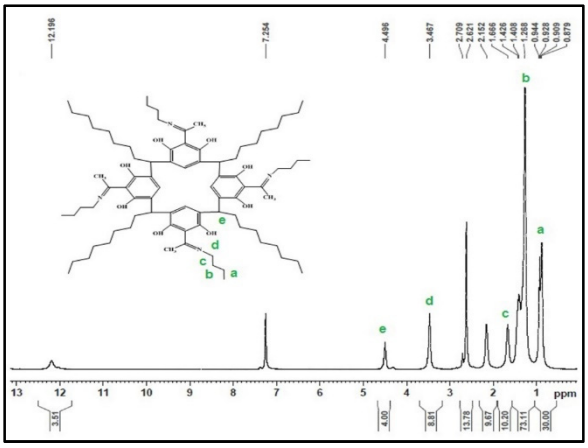


Figure 16. ^{1}H-NMR Spectral Data of compound **2g**

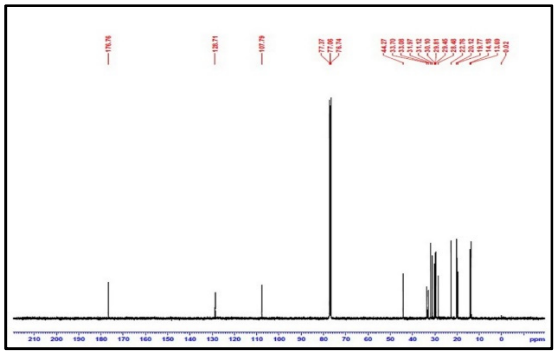
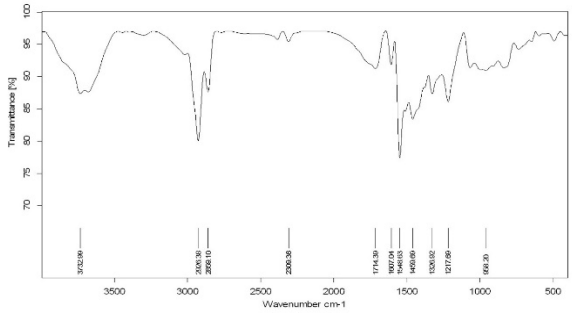


Figure 17. ^{13}C-NMR Spectral Data of compound **2g**



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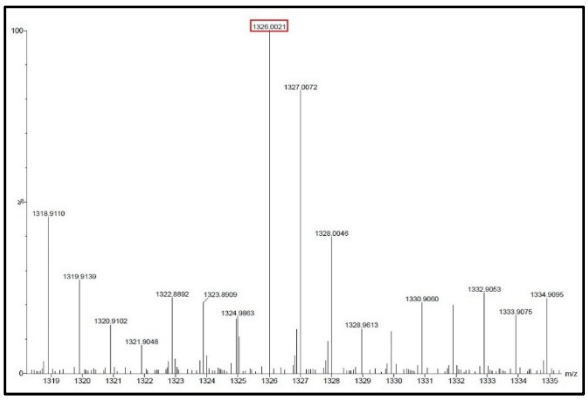

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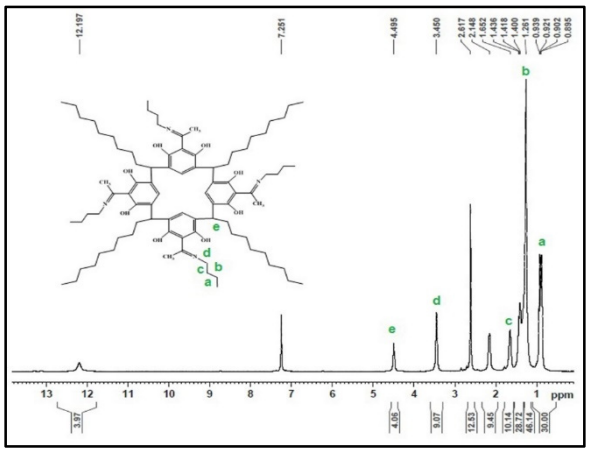

Figure 20. ^{1}H-NMR Spectral Data of compound **2h**

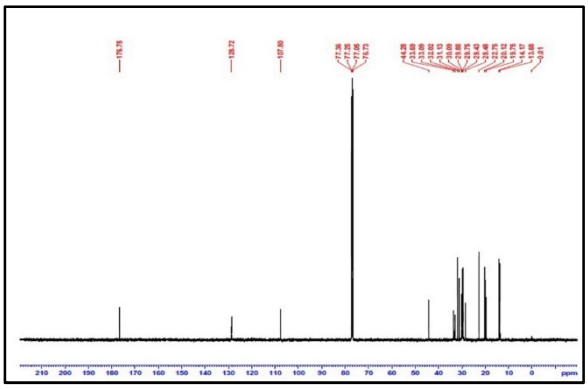

Figure 21. ^{13}C-NMR Spectral Data of compound **2h**

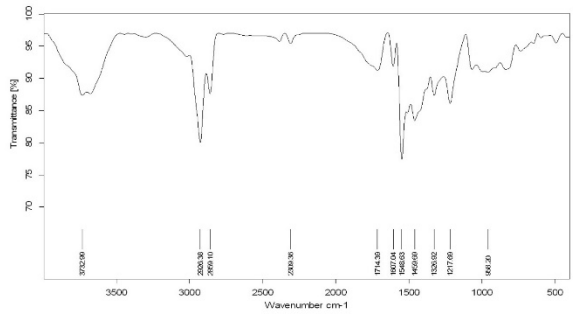

Figure 22. IR Spectral Data of compound **2h**

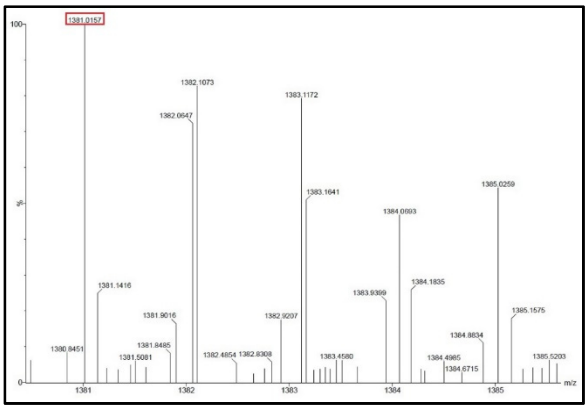

Figure 23. Mass Spectral Data of compound **2h**