Indian Journal of Chemistry
Vol. 64, April 2025, pp. 399-410
DOI: 10.56042/ijc.v64i4.16270

Innovative syntheses of benzoxazines with improved thermal and mechanical performance

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Received 07 January 2025; accepted (revised) 26 March 2025

Thermosetting resins are a type of material that is widely used in the industry, especially due to their high mechanical strength, flame retardant qualities and thermal stability. One such type of thermosetting resin is Benzoxazines. The conventional method of synthesis requires catalysts and solvents which makes the process complex. The goal of this research was to develop a modernized solvent free method for the synthesis of various types of benzoxazines *via* a Mannich reaction, and also examining the linkage between serotonin levels and factors such as the population characteristics of an individual when diagnosing colorectal cancer. In this study, two benzoxazines monomers are used, containing Schiff bases and bulky hand groups. These monomers are created *via* a copolymerization process with amine, phenol and paraformaldehyde. The chemical structures of the resulting compounds were characterized using Fourier Transform Infrared (FTIR) spectroscopy, as well as ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy. The structural conversion accompanied by the enhancement of the thermal and mechanical properties of the benzoxazine structures was visualized by the distinct absorption band located at 1709 cm^{-1}. Moreover, the benzoxazine displayed a greater yield than what was obtained previously confirming the successful process structure formation. The novel solvent devoid synthesis process for benzoxazines aids in making the manufacturing good more straightforward and also enables the creation of material with specific properties enhanced for various engineering purposes. Further investigations into serotonin physiology in tumors may give new ideas for treatment of colorectal cancer.

Keywords: Benzoxazine, Pyridine heterocyclic group, Schiff-Base, Mannich reaction, Aromatic aldehyde

Thermosetting resins are widely used in various industries, including automotive, aerospace, and construction. The requirement for these resources is being felt more and more. The operation of thermosets, however, may be costly, as it includes the use of reinforcement, fillers, pigments, and various additives[1]. Phenolic resin represents a group of materials characterized by fantastic physical features, such as firm mechanical strength, dimensional stability to different solvents, and fire retardance, and also others. Much due to the distinct properties of this family of thermosets, they have been used widely in many branches of industry including devices for high technology and aerospace. Even though it does have its benefits, the glass type has its limitations like brittleness, short shelf life, and eventually acid or base catalyst residues. Thus, this search for replacement of phenolic resins[2] that operate without the author endured disadvantages led to the development of a new addition-cure phenolic system called polybenzoxazine. This system has been the focus of some research woks due to its outstanding thermal and flame retardant performance not only but extremely mechanical properties too[3]. At the beginning of 1940, the duo in the University of Toronto Cope and Holly[4] managed to synthesize benzoxazines with the solvent method. During the research, Riess and coauthors[5] focused on the construction of the nonfunctional heterocyclic compounds of this category. Although synthesized in the late 1940s, great advantages have been uncovered about the polybenzoxazine effect only in the last several years scientifically[6,7]. Above all, the outstanding compound of polybenzoxazine provides the main ability to tailor cured materials to a wide range of applications[8]. The newly synthesized resins are highly particular with many advantageous features. These include minimal volumetric change upon curing, eliminating the need for a strong acid catalyst during the process. Additionally, no byproducts are released during curing, and the resins have low water absorption. In certain polybenzoxazine-based materials, the glass transition temperature (Tg) is significantly higher than the cure temperature. The resins also exhibit high char yield, excellent resistance to chemicals and UV light, and demonstrate thermal and dimensional stability. Furthermore, they possess superior electrical properties[9-14].

Materials scientists often synthesize benzoxazine monomers using phenol, formaldehyde, and amine (aliphatic or aromatic)[15], as starting materials, either through solution or solvent-less methods. A solvent-less method was initially reported by Ishida[16], different types of benzoxazine monomers can offer extra sites for polymerization, which can influence the curing process based on the groups involved. By customizing the benzoxazine monomer, one can achieve polymeric materials with the desired properties.

Experimental Section

Materials

4-Bromobenzaldehyde from (SIGMA-ALDRICH/ Germany), Phenol and Absolute methanol from(THOMAS-BAKER/India), Terephthalaldehyde and 4-Amino phenol from (MERCK – Schuchardt/ Germany), P-hydroxyacetophenone, ammonium acetate, glacial acetic acid, and hydrochloric acid from (HiMedia /India), Thioglycolic acid (Tokyo chemical industry co. ltd), Sulfuric acid (Sd fine- CHEMLimited / India, Paraformaldehyde (BDH/England).

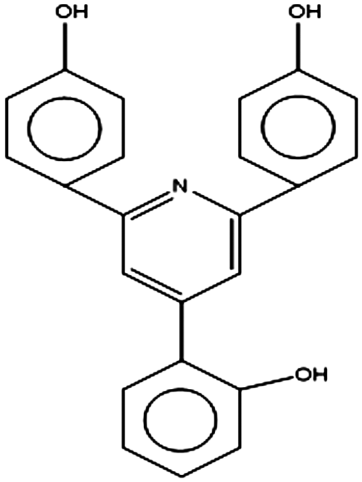
Instruments

Fourier Transform Infrared (FTIR) spectroscopyof type FT-IR-8400S supplied by the company Brüker, Germany, Department of Chemical Engineering - University of Al- Qadisiyah is used in the study. ^{1}H NMR spectra were registered utilizing a Bruker, Ultra Shield 400 Mhz, spectrometer (Switzerland) using DMSO being a solvent, at the [University of Tehran in Iran. Oven Burning, K & K Scientific suppler, Korea., Hot-platestirrer, ModelL-81, Labinco, The Netherlands. Vacuum Drying Oven k-vo27, K&K Scientific suppler, Korea, Degree of fusion (Melting Points) were measured using the pipeline and a lattice Stuart smp30 melting point apparatus.

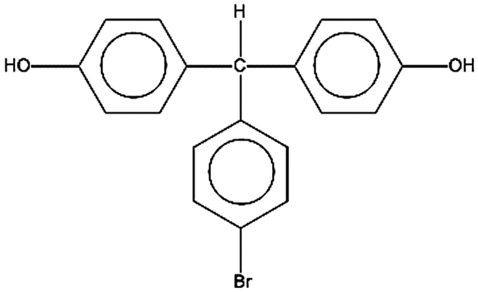
Synthesis of phenols compounds

Synthesis of (PHE1)

In a round-bottomed flask (150 ml) equipped with a reflux condenser, a mixture of (Salicylaldehyde) ((8.1mmol)), P-hydroxyacetophenol ne" (24.3 mmol), "ammonium acetate (97.3 mmol), and glacial acetic acid (20 ml) was refluxed at 140-142°C for 2hs. Upon cooling, crystals separated, which were filtered and washed first with acetic acid (50%) and then with cold ethanol," after that dried at 60ºC under vacuum. The structure of PHE1 is shown in Scheme 1.



Scheme 1 — Structure of(PHE1)



Scheme 2 — Structure of(PHE2)

Synthesis of (PHE2)

To solution, 0.1 M from (60%: 40%) sulfuric acid in methanol (12ml, H_2SO_4+8ml, Methanol), phenol (2 gm, 20.1 mmol) and 4-Bromo benzaldehyde (1.5 gm, 8.1mmol) were added (Scheme 2 and Table 1). The mixture underwent reflux at a temperature of 120°C for duration of 10 hours while being continuously stirred. After the reaction was completed, the solvent was eliminated using a vacuum.

Synthesis of amino compounds

Synthesis of (AM1)

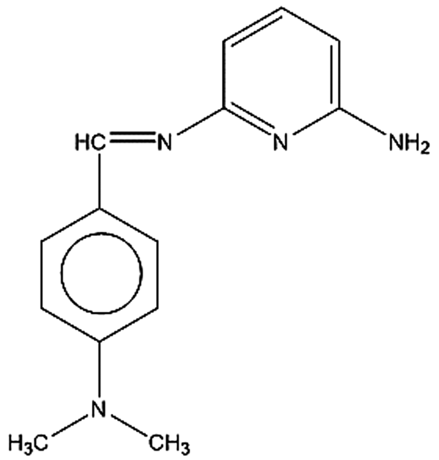
To produce this monomer (Scheme 3), 3gm (20.1 mmol) of 4-(Dimethylamino) benzaldehyde is combined with 1.1gm (10.07 mmol) of (2.6-diaminopyridine) in 15ml of methanol (Table 2). Add 4-

Table 1 — Synthesis of phenols (PHE1 and PHE2).

Monomers	Substance		Weight	Yield	Color	m.p/°C
	aldehyde	*Weight gm/mmol*	*gm*	(%*wt*)		
PHE1	Salicylaldehyde	0.988gm (8.1mmol)	2.5gm	91	deep purple	118-135
PHE2	4- bromo benzaldehyde	1.5gm (8.1mmol)	1.1gm	73	deep yellow	165-193

Table 2 — Synthesis of [AM1, AM2]

Monomers	Substance		Weight	Yield	Color	m.p/°C
	aldehyde	*weight*	*gm*	(%*wt*)		
AM1	4-(Dimethylamino) benzaldehyde	3gm (20.1 mmol)	2.3gm	85	deep brown	*Liquid*
AM2	Terpathaldehyde	1.5 gm (11.19)	4.2gm	84	deep brown	*Liquid*



Scheme 3 — Structure of(AM1)

5 drops of glacial acetic acid. The mixture was heated under reflux at 120 ºC for a period of 3 hours. Later, the solid was filtered and then purified by recrystallization using methanol. After filtering the precipitate, it was recrystallized using methanol. Finally, the monomer was dried in vacuum desiccators

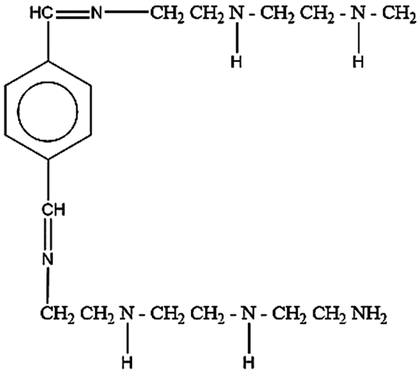
The other diamino compound (Scheme 4) was prepared through the same procedure as above using Triethylenetetramine in association with terephthaldehyde.

Results and Discussion

Synthesis and Characterization of phenols compounds

Synthesis and characterization of (PHE1)

The synthesis of (PHE1) involves the condensation from one mole of Salicylaldehyde with two moles of p-hydroxy acetophenone (Fig. 1). Under specific conditions, the reaction takes place at a temperature of 140-142°C for a period of 2 hours, with the presence of ammonium acetate and glacial acetic acid. Afterwards, the monomer was analyzed using FTIR analysis.



Scheme 4 — Structure of (AM2)

FTIR spectrum of (PHE1)

Fig. 2 displays the FTIR spectrum from (PHE1), revealing significant Absorption bands at (3386 cm^{-1}) corresponding to the presence of the (–OH group), (3150cm^{-1}) indicating the aromatic –CH stretching, absorption bands at approximately (1691, 1666 cm^{-1}) representing the (C=C) bonds of the aromatic rings, and (1596cm^{-1}) indicating the (C=N) bonds of the heteroaromatic ring. Additionally, there is a (C-O) bond observed at (1064 cm^{-1})[18-20].

^{1}H NMR spectrum of (PHE1)

^{1}H NMR spectrum of (PHE1) shown in Fig. 3 reveals that the major signal at δ 1.5–2.1 ppm is characteristic of DMSO-d6 as solvent.

Synthesis and characterization of (PHE2)

The synthesis of (PHE2) involves the condensation reaction between a single molecule of 4-bromobenzaldehyde and two molecules of phenol

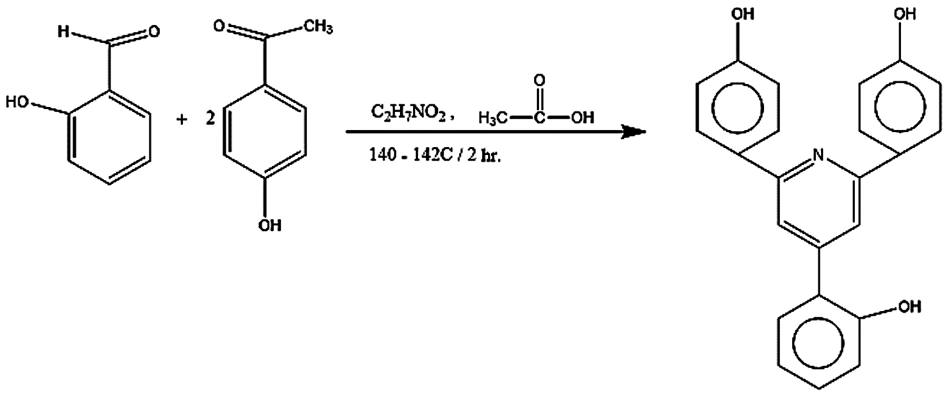


Fig. 1 — Synthesis of (PHE1)

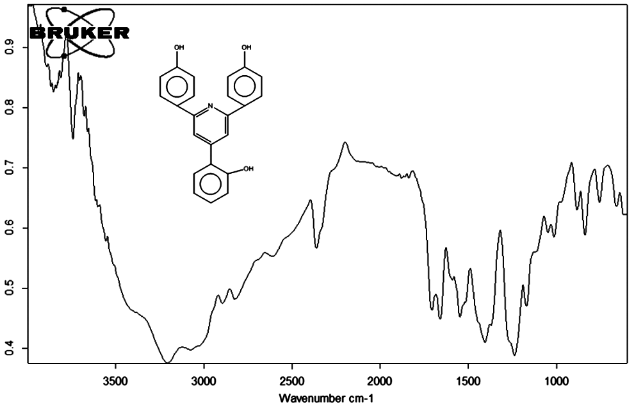


Fig. 2 — FTIR spectra of (PHE1)

(Fig. 4). This reaction takes place in the presence of methanol and sulfuric acid at a temperature of 120°C for duration of 10 hours. The resulting monomer was then characterized using FTIR analysis.

FTIR spectrum of (PHE2)

The FTIR spectrum of (PHE62), as depicted in Fig. 5, reveals the existence of absorption bands at (3480 cm^{-1}) corresponding to the (–OH) group, (3055 cm^{-1}) corresponding to the (aromatic–CH stretching), and (2954 cm^{-1}) corresponding to the (aliphatic–CH stretching). Additionally, absorption bands at (1570, 1488 cm^{-1}) indicate the presence of (C=C) in the aromatic rings, while absorption bands at (601 cm^{-1}) correspond to (C–Br)[18-20].

^{1}H NMR spectrum of (PHE2)

The ^{1}H NMR spectrum from (PHE2) is depicted in Fig. 6, revealing the assigned chemical shifts as follows: DMSO at δ (2.5) ppm, C–H group at δ (0.8–1.4) ppm (s,1H), (Ar–H) group at (6.3-7.5) ppm (12H), and (s,2H ,2OH) group at δ (7.9-8.0). These assignments have been supported by earlier studies[18-20].

Synthesis and characterization from (AM1)

The synthesis of (AM1) involves the condensation of one mole of 2,6-diaminopyridine with one mole of 4- Dimethylaminobenzaldehyde in the presence of methanol for a duration of 3 hours (Fig. 7). The resulting monomer was then characterized using FTIR analysis.

FTIR spectrum from (AM1)

The FTIR spectrum from (AM4*Schiff-base*) depicted in (Fig. 8) indicates the presence of absorption bands at (3400cm^{-1}) to (–NH$_2$ group), (3100cm^{-1}) to (aromatic –CH stretching), (2916cm^{-1}) to (aliphatic –CH stretching), absorption bands around (1604, 1589cm^{-1}) show (C=C) of the aromatic rings, and (1550, 1535cm^{-1}) to heteroaromatic ring (C=N), absorption band at 1020Cm^{-1} show up the presence of C-N, absorption band at 2820cm^{-1} show the presence of C-CH$_3$[18-20].

^{1}H NMR spectrum of (AM1)

The ^{1}H NMR spectrum of AM1 Schiff-base in Fig. 9 exhibits distinct peaks. There is a double peak ranging from 2.2 to 2.6 δ ppm, corresponding to 6H of CH$_3$. Another doublet peak is observed at (3.723 δ ppm), representing 4H of NH$_2$. Additionally, a multiplet peak is seen from (6.6 to 7.7 δ ppm), indicating 7H of phenyl and hetero rings. Lastly, a singlet peak is observed at 9.6 δ ppm, representing 2H of the CH=N Schiff_base group. This information is supported by earlier studies[18-20].

Synthesis and characterization of (AM2)

The synthesis of (AM2) involves the condensation of one mole of Terapthaldehyde with one mole of triethylenetetramine with existence of methanol for duration of 3 hours (Fig. 10). The resulting monomer was then characterized using FTIR analysis.

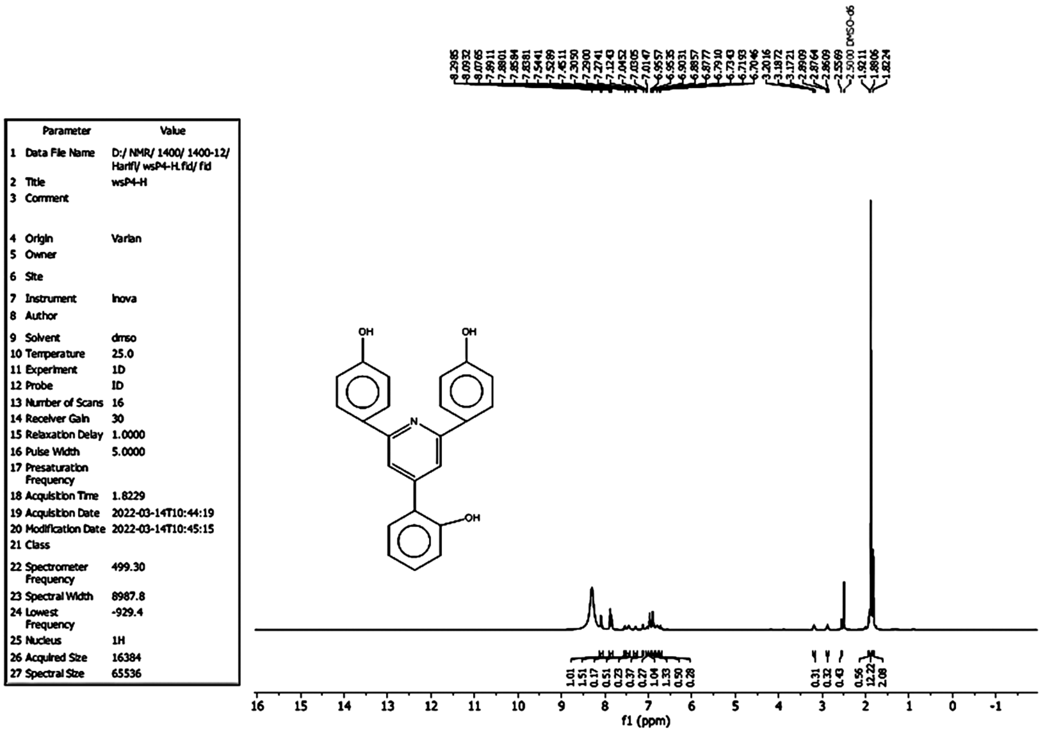


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Fig. 3 — ^{1}H NMR spectra from (PHE1)

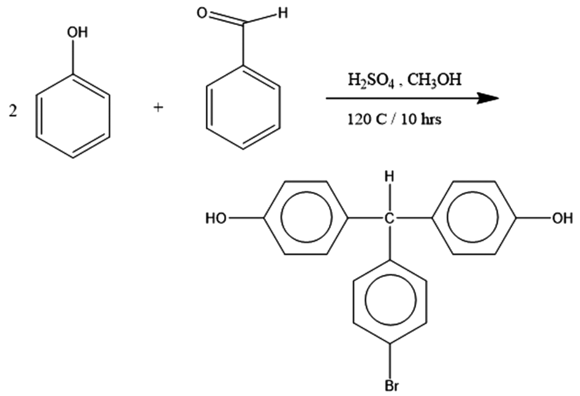


Fig. 4 — Synthesis of (PHE2)

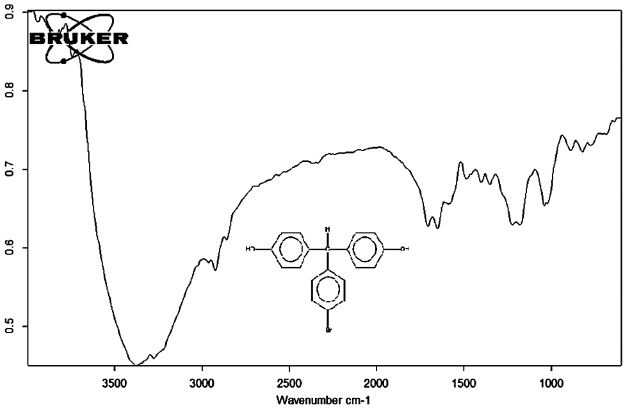


Fig. 5 — FTIR spectra of (PHE1)

FTIR spectrum of (AM2)

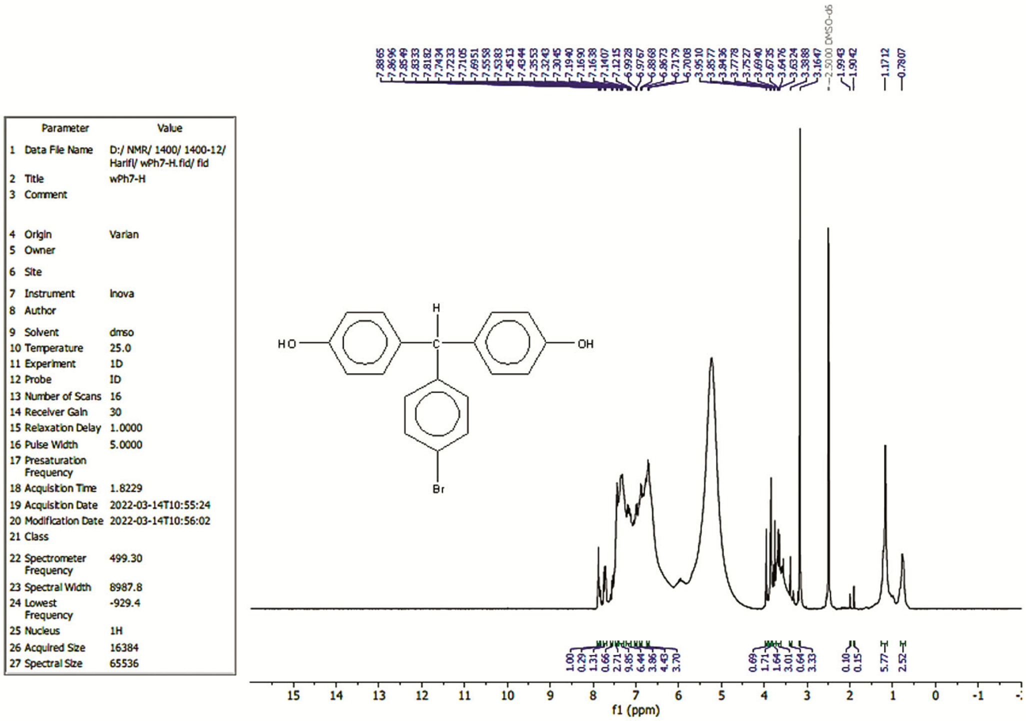
The AM2 (Schiff-base) FTIR spectrum, depicted in Fig. 11, reveals several absorption bands indicating the existence of different functional groups. The absorption bands at 3400 cm^{-1} correspond to the –NH$_2$ group, while the bands at 3100cm^{-1} represent the aromatic –CH stretching. Additionally, the aliphatic –CH stretching is observed at 2916 cm^{-1}. The absorption bands at 1604 cm^{-1} and 1589 cm^{-1} point to the presence of C=C bonds in the aromatic rings, while the bands at 1550 cm^{-1} and 1535 cm^{-1} correspond to the heteroaromatic ring (C=N). Furthermore, the absorption band at 1020 cm^{-1} signifies the presence of C-N bonds, and the band at 2820 cm^{-1} indicates the presence of C-CH$_3$ groups. Notably, the spectrum also displays two characteristic bands at 3494 cm^{-1} and 3392 cm^{-1}, which correspond to the N-H asymmetrical and symmetrical stretching vibrations, respectively[18-20].

^{1}H NMR spectrum of (AM2)

The ^{1}H NMR spectrum of AM2 in Fig. 12 exhibits distinct peaks.

^{13}C NMR spectrum of (AM2)

^{13}C NMR spectrum of (AM2) is illustrated in Fig. 13. The third signals from olefinic and aromatic



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12	Probe	ID
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27	Spectral Size	65536

Fig. 6 — ^{1}H NMR spectra from (PHE1)

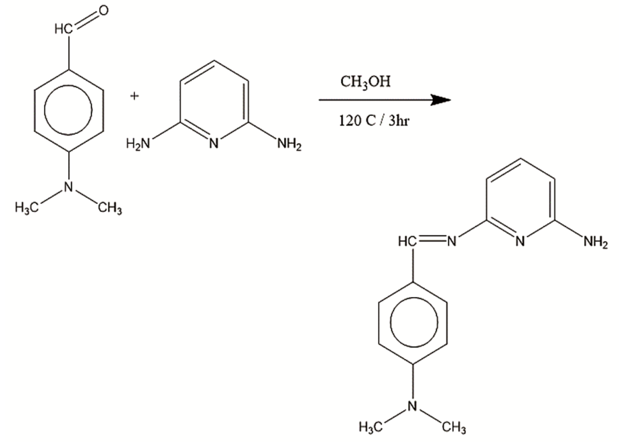

Fig. 7 — Synthesis of [AM1]

carbons appear in the four regions between 110-131ppm. The doublet signals of Carbon related to heteroatoms C-N appear in the region 48-52 ppm. Signals of Carbon related to heteroatoms appear at 42 ppm; of (CH_2-N).The doublet signal of Carbon related to azomethine appear at 153-167ppm; of (CH=N).[18-20]

Synthesis and characterization of benzoxazine(1)

Benzoxazines were synthesized simply by the reaction between PHE2, AM2, and paraformaldehyde in the presence of toluene at 110°C for 6 hours (Fig. 14).

FTIR spectra of benzoxazine(1)

Fig. 15 exhibits the Fourier Transform Infrared (FTIR) spectra of benzoxazine(1), showcasing different absorption bands linked to benzoxazines. The aforementioned bands, with wavenumbers of 1495, 1370, 1229, 1035, and 946 cm^{-1}, are indicative of the presence of disubstituted benzene rings. Furthermore, the spectrum demonstrates absorption bands at 1228 cm^{-1}, which correspond to the asymmetric stretching of C–O–C bonds, 1366 cm^{-1}, corresponding to the wagging of CH2 bonds, the antisymmetric stretching of Ar-O-C bonds, the symmetric stretching of C-O-C bonds, and the vibration mode originating from cyclic substituted benzene rings. In addition, the presence of benzoxazine (C–O–C) can be detected at a wavenumber of 1232 cm^{-1}, –CH_2 at 1375 cm^{-1}, and the stretching of the benzene ring at 913 cm^{-1} and 1491 cm^{-1}. The absorption bands that are particularly noteworthy are as follows: (3100 cm^{-1}) for the stretching of aromatic –CH bonds, (2916 cm^{-1}) for the stretching of aliphatic –CH bonds, (3435 cm^{-1}) for the stretching of –OH groups, (1604, 1589 cm^{-1}) for the (C=C) bond in the aromatic rings, and (1550, 1535 cm^{-1}) for the stretching of heteroaromatic ring rings (C=N). Furthermore, the presence of an absorption band at 2820 may be attributed to the aromatic compound N-CH_3. The validity of these findings is supported by earlier studies[18-20].

^{1}H NMR spectrum of benzoxazine(1)

The benzoxazine(1) ^{1}H NMR spectrum, as shown in Fig. 16, displays distinct resonances. The singlet resonances at 3.63 ppm and 4.36 ppm correspond to the characteristic protons present in the oxazine ring, specifically -C-CH_2-N- and -O-CH_2-N-, in succession. Additionally, it was noted that a multiplicity at 6.6 ppm is attributed to the protons in the aromatic ring. Additionally, a doublet at δ (9.7-9.9 ppm) was assigned to (1H, OH), a doublet at δ (7.3-7.4 ppm) was assigned to (2H, CH=N Schiff-base group), and a doublet at δ 2.5-3.8 ppm was assigned to (6H, N-CH3). These assignments were supported by references[18-20].

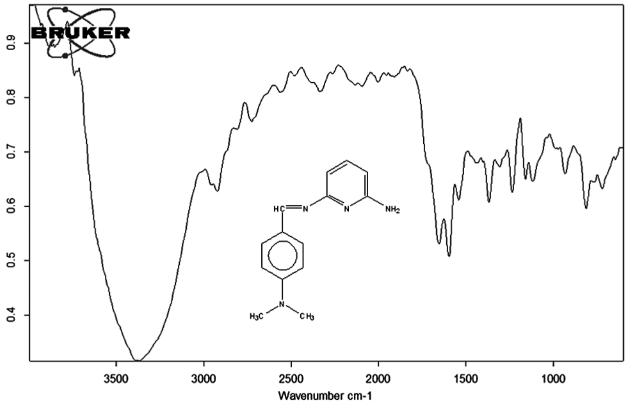

Fig. 8 — FTIR spectra of (AM1)

Synthesis and characterization of benzoxazine(2)

Benzoxazines were synthesized simply by the reaction between PHE1, AM1, and paraformaldehyde in the presence of toluene at 110ºC for 6 hours (Fig. 17).

FTIR spectra of benzoxazine(2)

Fig. 18 displays the FTIR spectra of benzoxazine (2), revealing distinct absorption bands at specific wavenumbers. These bands, namely (1495, 1370, 1229, 1035, and 946 cm^{-1}) correspond to the disubstituted benzene rings. Moreover, there are absorption bands at 1228 cm^{-1} (asymmetric stretching of (C–O–C), 1366 cm^{-1} (CH_2 wagging), (Ar-O-C) antisymmetric stretching, (C-O-C) symmetric stretching, and vibration from cyclic substituted benzene rings[17]. Noteworthy absorption bands also include benzoxazine(C–O–C) at 1232 cm^{-1}, –CH_2 at 1375 cm^{-1}, and benzene ring stretching at 913 cm^{-1} and 1491 cm^{-1}. The wavenumbers 3100 cm^{-1} and 2916cm^{-1} indicate aromatic –CH stretching and aliphatic –CH stretching, respectively. The presence of –NH_2 is indicated by an absorption

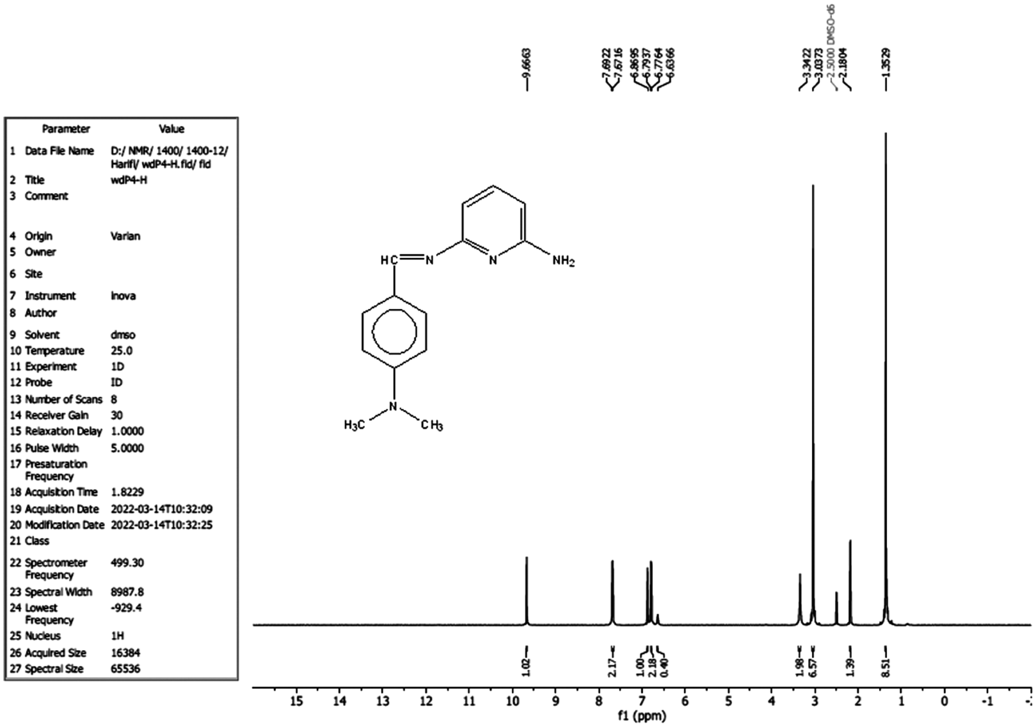

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Fig. 9 — ^{1}H NMR spectra from (AM1)

band at 3350 cm^{-1}, while an absorption band at 3480 cm^{-1} suggests the presence of an –OH group. The absorption bands around 1440 cm^{-1} indicates existence of C=C bonds in the aromatic rings, and the wavenumbers 1604 cm^{-1} correspond to the heteroaromatic ring (C=N). These findings are supported by references[18-20].

^{1}H NMR spectrum of benzoxazine (2)

The benzoxazine (4) compound, as shown in Fig. 19, displays two singlet resonances in its ^{1}H NMR spectrum. These resonances, observed at 4.63 ppm and 5.36 ppm, can be attributed to the characteristic protons present in the oxazine ring, specifically -C-CH_2-N- and -O-CH_2-N-, in succession. The multiplet observed at 6.6 ppm is assigned to the protons of the aromatic ring. Furthermore, a singlet at (δ 7.2 - 7.8 ppm) corresponds to (6H, NH_2), while a doublet at δ (8.1-8.4 δ ppm) corresponds to (2H, CH=N Schiff-base group). These assignments have been supported by references[18-20].

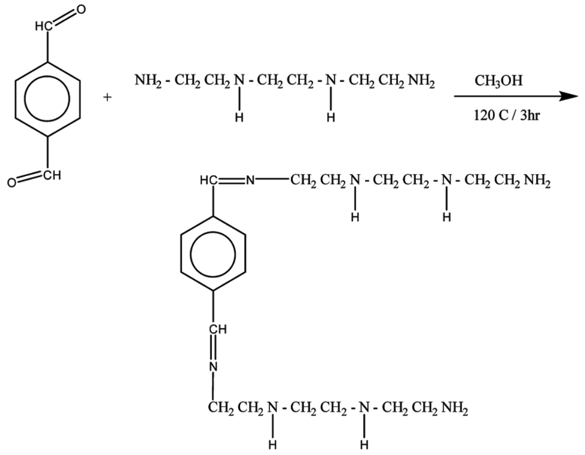

Fig. 10 — Synthesis of (AM2)

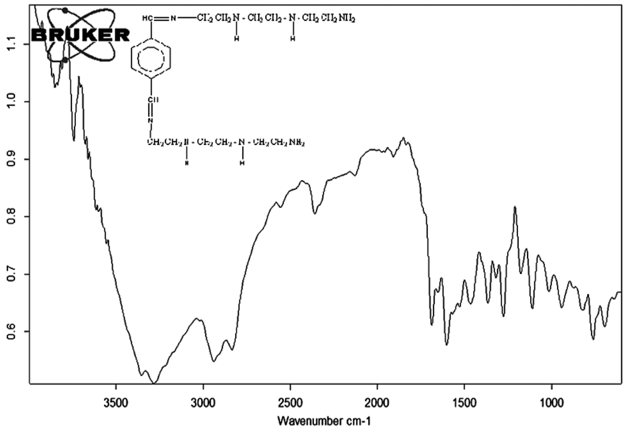

Fig. 11 — FTIR spectra of (AM2)

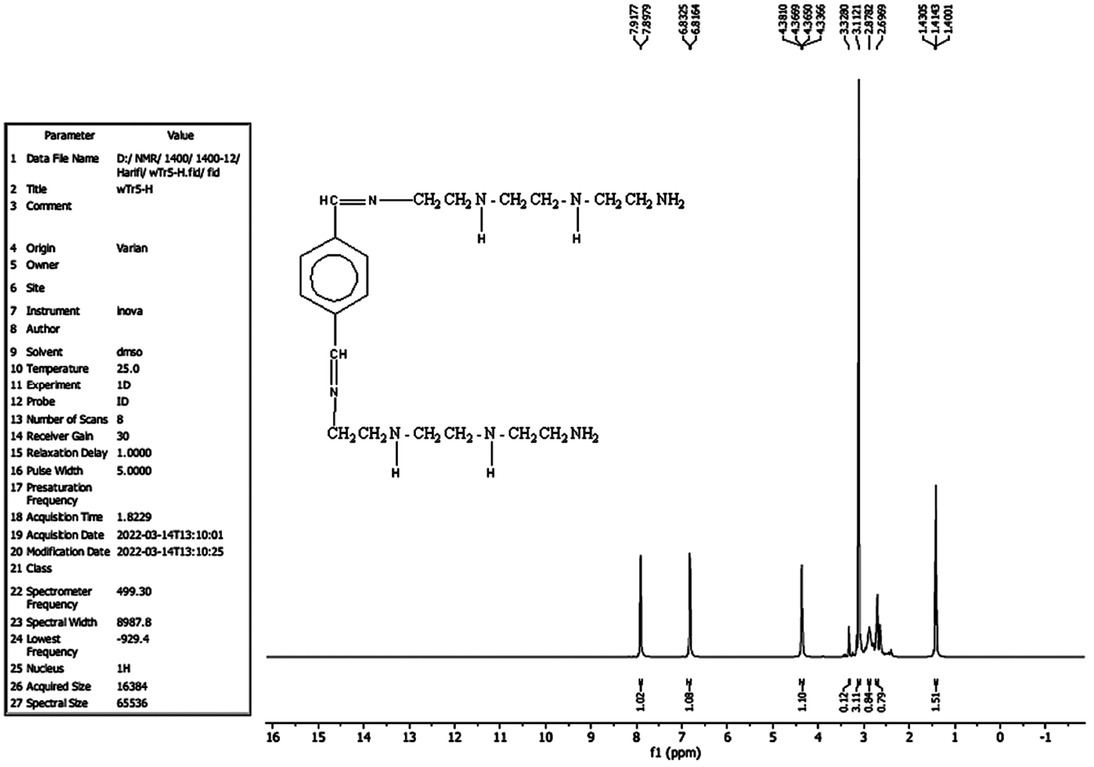

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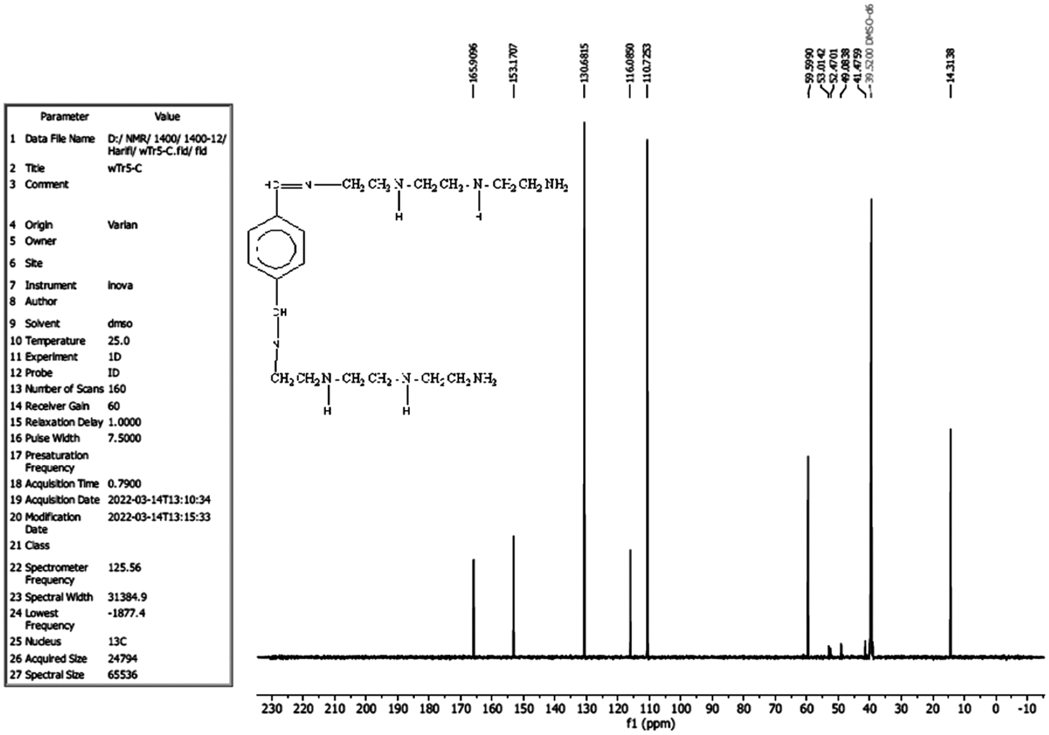
Fig. 12 — ^{1}H NMR spectra of (AM2)



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19	Acquisition Date	2022-03-14T13:10:34
20	Modification Date	2022-03-14T13:15:33
21	Class	
22	Spectrometer Frequency	125.56
23	Spectral Width	31384.9
24	Lowest Frequency	-1877.4
25	Nucleus	13C
26	Acquired Size	24794
27	Spectral Size	65536

Fig. 13 — ^{13}C NMR spectra of (AM2)

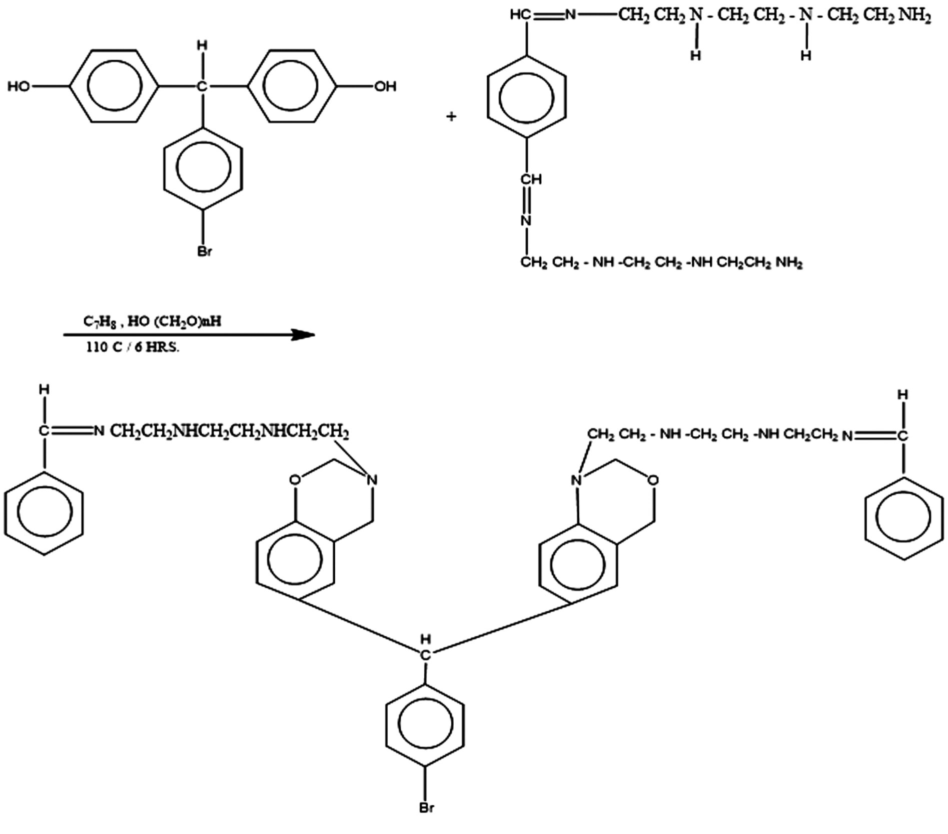


Fig. 14 — Synthesis of benzoxazine(1)

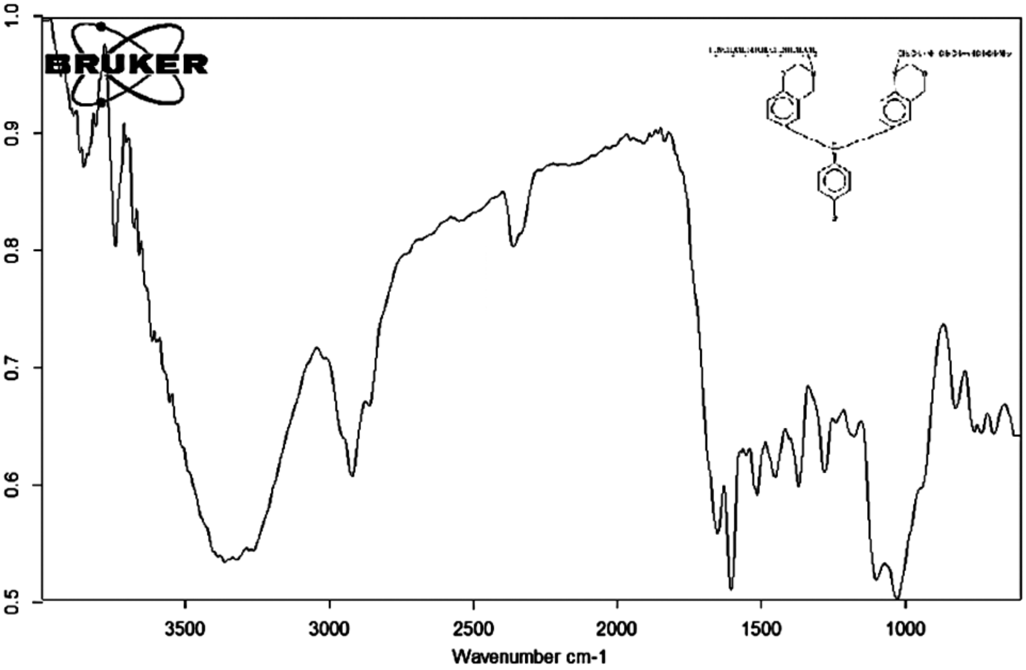
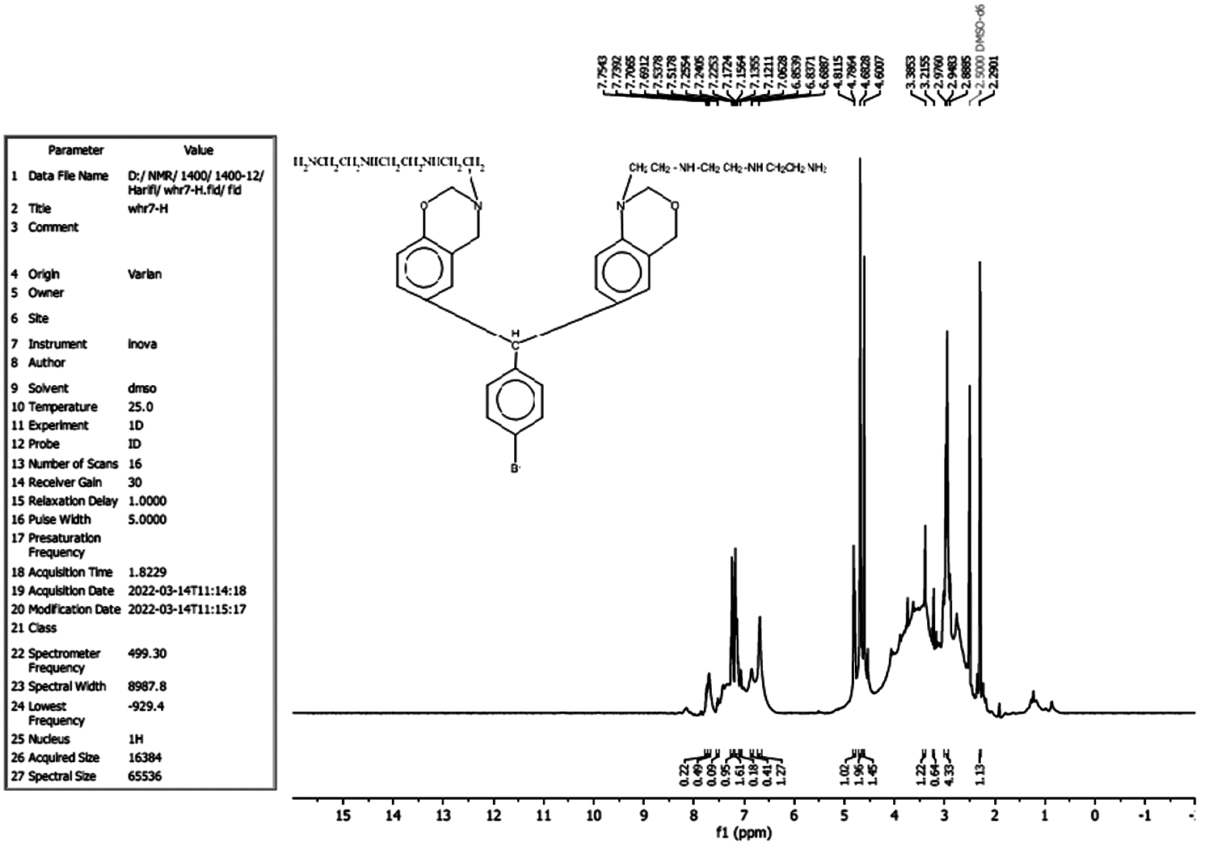


Fig. 15 — FTIR spectra of (BZ1)



	Parameter	Value
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2	Title	whr7-H
3	Comment	
4	Origin	Varian
5	Owner	
6	Site	
7	Instrument	inova
8	Author	
9	Solvent	dmso
10	Temperature	25.0
11	Experiment	1D
12	Probe	ID
13	Number of Scans	16
14	Receiver Gain	30
15	Relaxation Delay	1.0000
16	Pulse Width	5.0000
17	Presaturation Frequency	
18	Acquisition Time	1.8229
19	Acquisition Date	2022-03-14T11:14:18
20	Modification Date	2022-03-14T11:15:17
21	Class	
22	Spectrometer Frequency	499.30
23	Spectral Width	8987.8
24	Lowest Frequency	-929.4
25	Nucleus	1H
26	Acquired Size	16384
27	Spectral Size	65536

Fig. 16 — ^{1}H NMR spectra of (BZ1)

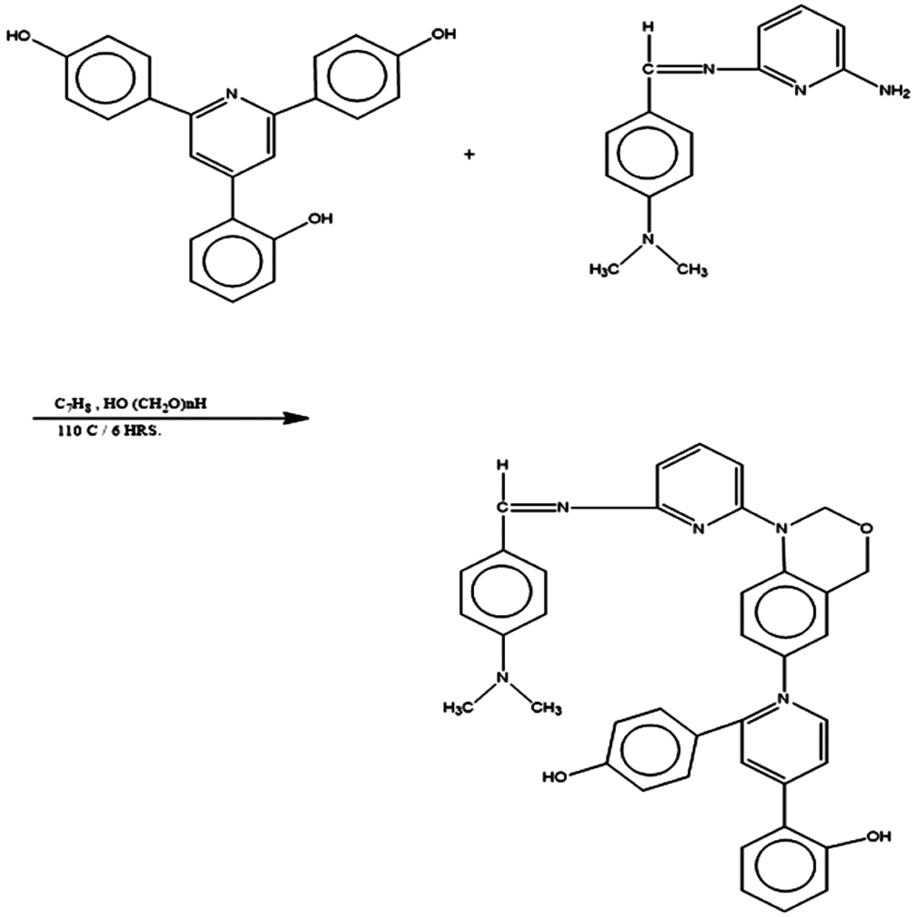


Fig. 17 — Synthesis of (BZ2)

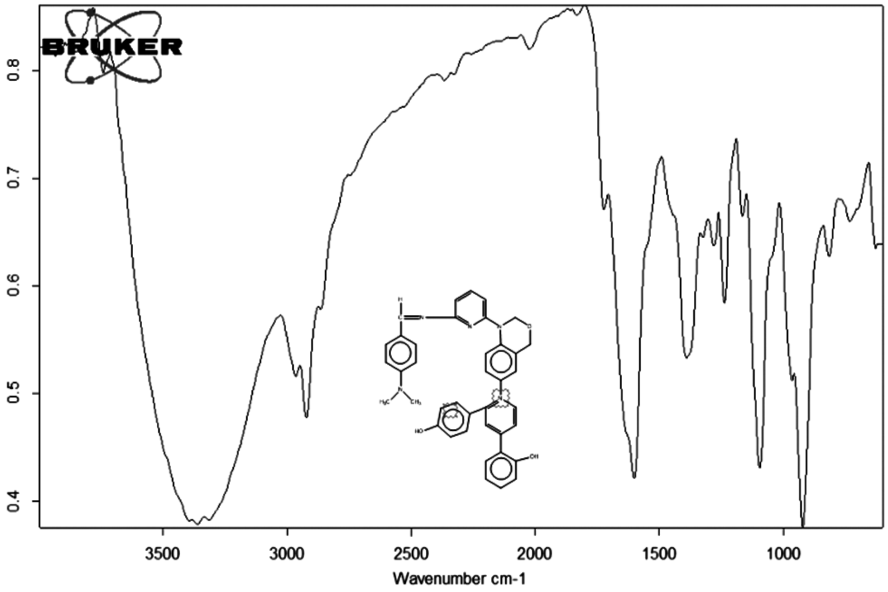
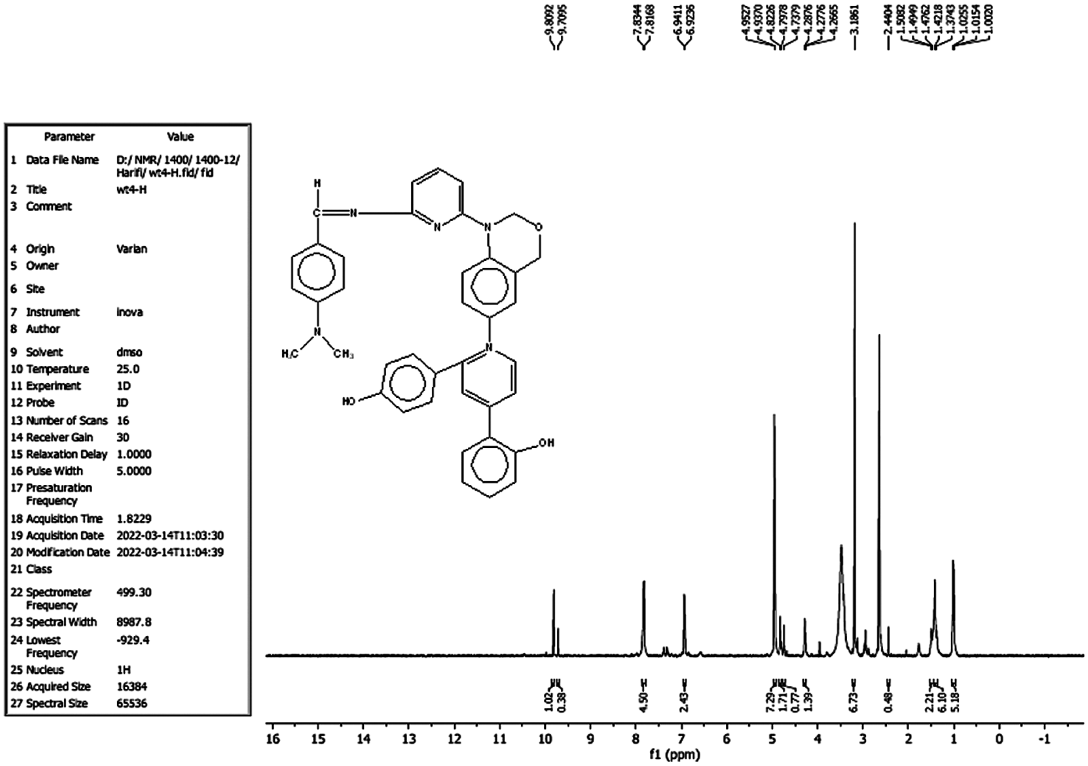


Fig. 18 — FTIR spectra of (BZ2)



Parameter	Value
1 Data File Name	D:/ NMR/ 1400/ 1400-12/ Harifi/ wt4-H.fid/ fid
2 Title	wt4-H
3 Comment	
4 Origin	Varian
5 Owner	
6 Site	
7 Instrument	inova
8 Author	
9 Solvent	dmso
10 Temperature	25.0
11 Experiment	1D
12 Probe	ID
13 Number of Scans	16
14 Receiver Gain	30
15 Relaxation Delay	1.0000
16 Pulse Width	5.0000
17 Presaturation Frequency	
18 Acquisition Time	1.8229
19 Acquisition Date	2022-03-14T11:03:30
20 Modification Date	2022-03-14T11:04:39
21 Class	
22 Spectrometer Frequency	499.30
23 Spectral Width	8987.8
24 Lowest Frequency	-929.4
25 Nucleus	1H
26 Acquired Size	16384
27 Spectral Size	65536

Fig. 19 — ^{1}H NMR spectra of (BZ2)

Conclusions

Two distinct benzoxazines were synthesized, and their structures were validated by employing FTIR, ^{1}H, and ^{13}C NMR methods. Aside from getting good yields of benzoxazines, we also managed to figure out the structure of bis benzoxazine from the aromatic segment that connects the two benzoxazine units. The most heat-resistant benzoxazine was the one with a phenyl group substituted into the pyridine ring. Some research suggests that adding a larger substituent at the 4-position of the pyridine ring of the diamine improves both solubility and thermal stability.

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