



# SYNTHESIS AND CHARACTERIZATION OF SOME BENZIMIDAZOLE DERIVATIVES FROM 4-BENZOYL-O – PHENYLENE DIAMINE

Sara Mustafa Naeem<sup>[a]\*</sup>, M. Shakir Magtoof<sup>[b]</sup>

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**Abstract:** This study is concerned with Synthesis and identification were performed on a new Benzimidazole derivatives produced from 4-Benzoyl-o-phenylenediamine. These compounds were made by reacting 4- Benzoyl-o-phenylenediamine with an appropriate aromatic aldehyde by microwave or heating a solution of the reactants under reflux. Synthetic compounds were identified using FIT-IR spectra, 1H NMR, and 13C NMR.

**Keywords:** heterocyclic, benzimidazole, 4-Benzoyl-o-phenylenediamine, aromatic aldehyde, Green Synthesis

[a]. Department of Chemistry, Science College, University Thi-Qar, Thi-Qar, 64001, Iraq

[b]. Department of Chemistry, Science College, University Thi-Qar, Thi-Qar, 64001, Iraq

\*Corresponding Author

E-mail: xxxxx

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## INTRODUCTION

Heterocyclic compounds are cyclic compounds that have one or more atoms of another atom in their rings in addition to carbon.[1] [2] Benzimidazole (figure 1.1) is a combination of benzene and an imidazole ring.[3]

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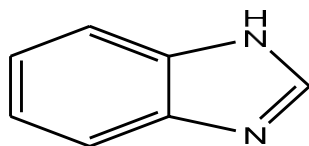
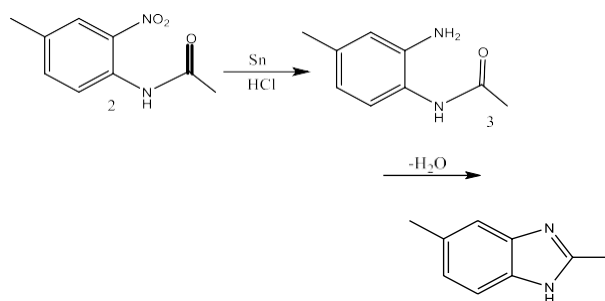


Figure (1.1): Benzimidazole

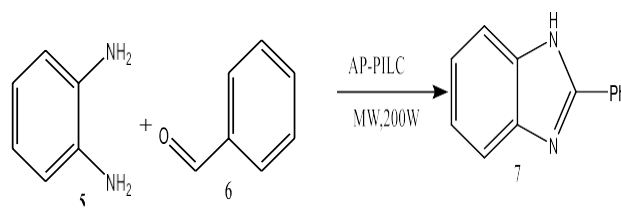
The benzimidazole nucleus performs a vital role in the production of bioactive derivatives that are used to treat a variety of disorders.[4] Compounds containing benzimidazole nucleus display tremendous biological activities including antibacterial,[5] antifungal,[6]antioxidant,[7]antiviral,[8]anti-tubercular, [9] anti-inflammatory, [10] anti-diabetic, [11] analgesic, [12] and insecticidal agents. [13] Hoebrecker synthesized the first benzimidazole by reducing and dehydrating 2-nitro-4-methylacetanilide in order to produce 2,5-dimethylbenzimidazole.[14] (Scheme1).

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Scheme (1-1): Hoebrecker prepared Benzimidazole

R.Azzallou et al. reported a quick and simple technique for producing 2- arylbenzimidazole from o-phenylenediamine and aldehyde during Green Synthesis of Benzimidazole Derivatives, utilizing a little amount of a modified Moroccan clay surfactant catalyst.[15] [16] straightforward, clean, inexpensive, and selective protocol for the production of benzimidazole substituted was offered by the heterogeneous reaction condition.[17]



Scheme (1-2): Al-PILC-catalyzed 2- substituted benzimidazole synthesis with microwave radiation.

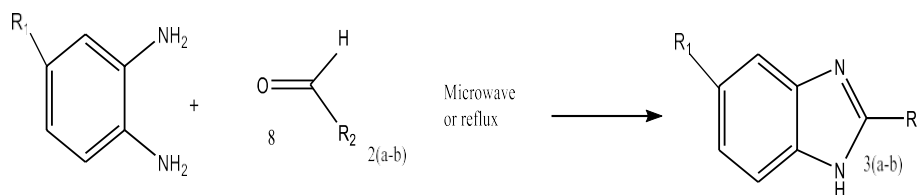
## MATERIALS AND METHODS

The chemicals were supplied from Flurouchem and Sigma Aldrich. Frigidaire Company purchased the microwave that was used in the experiments. All melting points were calculated using Stuart SMP3 in an open capillary tube and were uncorrected. The silica Gel used for TLC was purchased from Merk. TLC spots were visualized using Iodine. FT-IR spectra for the synthesized compounds were recorded on KBr disc in the region (600-4000) cm<sup>-1</sup> by using "Perkin Elmer, tensor 27 (Bruker)" in the Labs of chemistry department, Science College, Thi-Qar University. Proton Nuclear magnetic spectra <sup>1</sup>HNMR and <sup>13</sup>CNMR spectra were recorded on Bruker by College of Education for Pure Sciences at Basrah University.

## Experimental

Benzimidazoles were obtained by simple condensation of Diamines as 4-Benzoyl-o-phenylenediamine and appropriate aromatic aldehyde or carboxylic acids in the solid phase solvent free and under microwave irradiation without catalyst.

To enhance the reaction conditions, various levels of microwave irradiation were used. Another way was via refluxed with a catalyst on a magnetic stirrer for many hours. Microwave reactions take less time than reflux reactions with easier reaction conditions (without a solvent or a catalyst). TLC was used to maintain track of the reaction's progress, and the final product was filtered, cleaned, dried, and purified using a suitable solvent. The general reaction was shown in (Scheme 2).



**Scheme (2-1): general reaction of Benzimidazole derivatives synthesis**

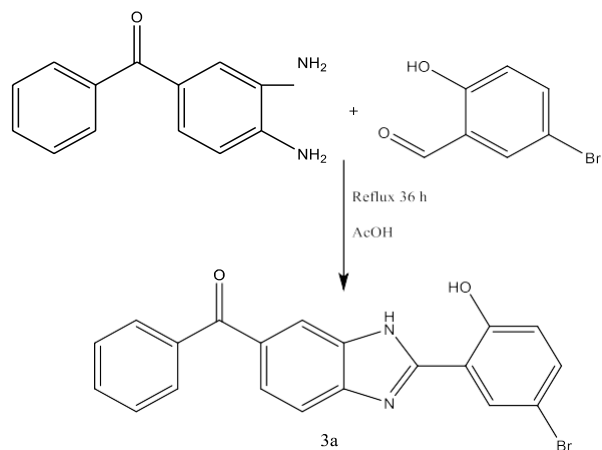
**Table (2-1): compound of benzimidazole**

compound	R1	R2
3a		
3b		

### Synthesis of (2-(5-bromo-2-hydroxyphenyl)-1H-benzo[d]imidazole-6-yl)(phenyl)methanone (3a)

4-Benzoyl-o-phenylenediamine (0.84g) was dissolved in ethanol 20mL with 5-Bromo salicylaldehyde (0.80g,

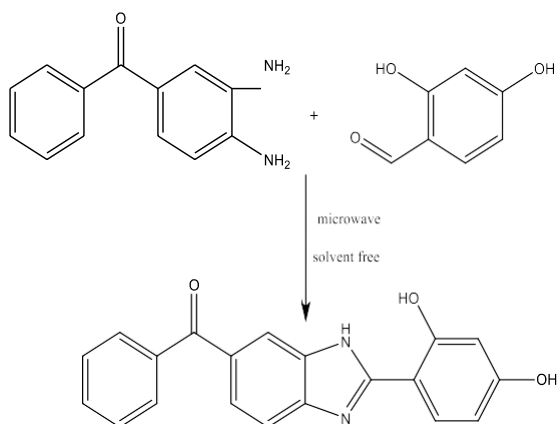
0.00397mole) with a drops of CH<sub>3</sub>COOH. The mixture was heated under reflux for 36h.



**Synthesis of (2-(2,4-dihydroxyphenyl)-1H-benzimidazol-5-yl)(phenyl)methanone (3b)**

1g of 4-Benzoyl-o-phenylenediamine was milled with 2,4-dihydroxy benzaldehyde (0.65g, 0.00470 mole) in Evaporating

dish at room temperature, then the mixture was placed in the microwave for (40 min, 80W). TLC monitored the progress of the reaction per 5 min



**Table (2-2)** shows the Physical properties of compounds

no	Molecular formula	Color	M.Wt g/mol	Yield	m.poC	Eluent	R.F (cm)
a3	C <sub>20</sub> H <sub>13</sub> BrN <sub>2</sub> O <sub>2</sub>	White powder	393.24	39.2%	110-112	3:7 EtOAc: Hexane	0.77
b3	C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>	Reddish brown crystals	330.34	45.16%	145	3:7 EtOAc: Hexane	0.48

## RESULTS AND DISCUSSION

Different Benzimidazole derivatives are produced. All compounds synthesized were purified by recrystallization with a suitable solvent and then dried. The chemicals generated have been identified based on their physical properties and spectral analysis, such as FT-IR, <sup>1</sup>H-NMR, and <sup>13</sup>CNMR spectrum. For <sup>1</sup>H-NMR, dimethyl sulfoxide (DMSO-d<sub>6</sub>) was used as a solvent at a chemical shift of 2.5 ppm. In <sup>13</sup>C-NMR, DMSO-d<sub>6</sub> was also used with signal (39.33- 40.58) ppm.

Characterization of (2-(5-bromo-2- hydroxyphenyl)-1H-benzo[d]imidazol-6- yl) (phenyl) methanone (3a) showed bands at 3091, 3063, and 3041 cm<sup>-1</sup> for the stretching vibration of C-H aromatic, as well as a new band at 1655, 1610 cm<sup>-1</sup> for the stretching vibration of the C=N group. In addition, the spectrum shows another band at 1562 cm<sup>-1</sup>, which is the stretching vibration of the C=C group of the aromatic ring. Because of this, absorption bands at a frequency of 1275 cm<sup>-1</sup> (C-O).

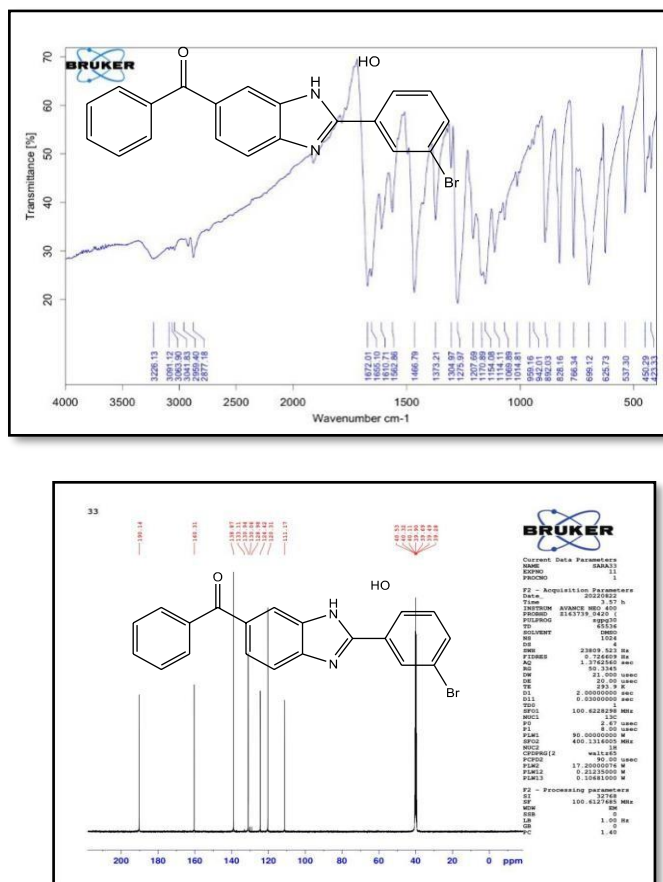


Figure (3-1): FT-IR spectrum of compound (3a)

<sup>1</sup>H-NMR spectrum of compound 3a, Figure (3-2) Showed signals, overall integration equal to 12H, in addition to OH.

According to the following chemical shifts in (ppm):10.19 (s, 1H, OH), 7.69- 6.95(aromatic proton).

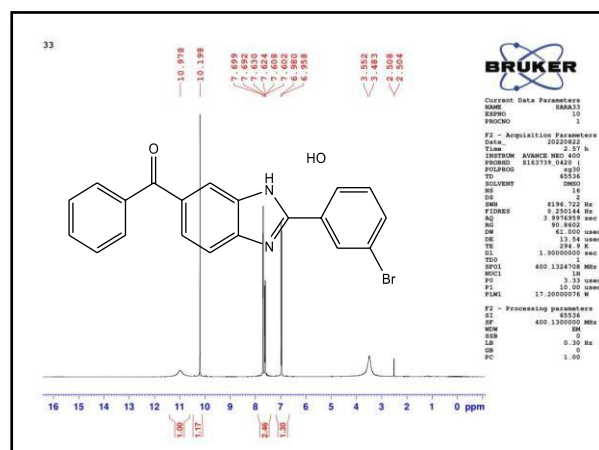


Figure (3-2): <sup>1</sup>H-NMR spectrum of compound (3a)

The results were seen in the <sup>13</sup>C-NMR spectrum of compound (3a): 190.14 due to C=O, 160.31 belong to C=N, 138.87, 133.11, 130.94, 130.06, 128.98, 124.42, 120.31, and 111.17 belong to aromatic C=C. Figure (3-3): <sup>13</sup>C-NMR spectrum of compound (3a)

### 3.2 Characterization of (2-(2,4-dihydroxyphenyl)-1H-benzimidazol-5-yl)(phenyl)methanone (3b)

The FT-IR of Benzimidazole derivative (3b), Figure (3-4) were characterized by appearance of C=N group bands at 1631 cm<sup>-1</sup> and band at 3129 cm<sup>-1</sup> respectively which corresponding to the stretching vibration of CH. band at 1498 cm<sup>-1</sup> respectively demonstrated to the stretch band (C=C) of aromatic rings.

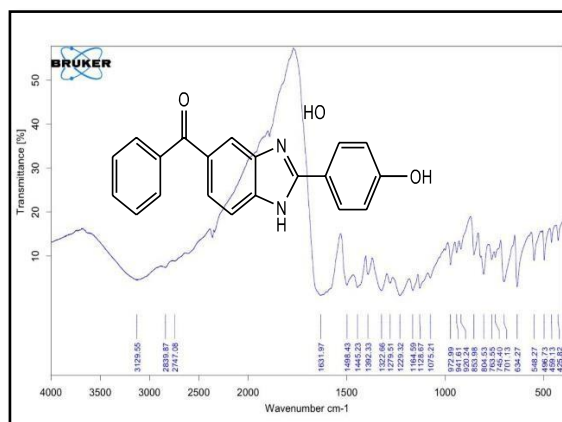


Figure (3-4): FT-IR spectrum of compound (3b)

<sup>1</sup>H-NMR spectrum of compound 3b, Figure (3-5) Showed signals, overall integration equal to 11H, in addition to 2(OH). According to the following chemical shifts in (ppm): 10.93,

10.70 (d, 1H, OH), also 9.92 (s, 1H, OH), 7.74- 7.52 (aromatic proton), also 6.42-6.33 due Ar-H.

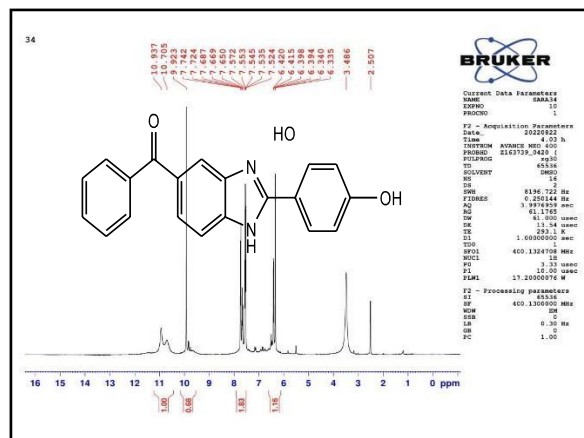


Figure (3-5): <sup>1</sup>H-NMR spectrum of compound (3b)

The results was shown in the <sup>13</sup>C-NMR spectrum of compound (3b):196.29, 191.47 due to carbonyl group of ketone, 165.64, 163.72, and 162.00 belong to carbon of Benzimidazole ring. 157.47 attributed to carbon of azomethine (CH=N), 137.45,

133.33, 133.14, 130.07 and 129.01 belong to aromatic ring also observed band at 115.66, 115.35, 115.02, 112.50, 109.10, 102.93, 102.82, 102.65 due to aromatic C=C.

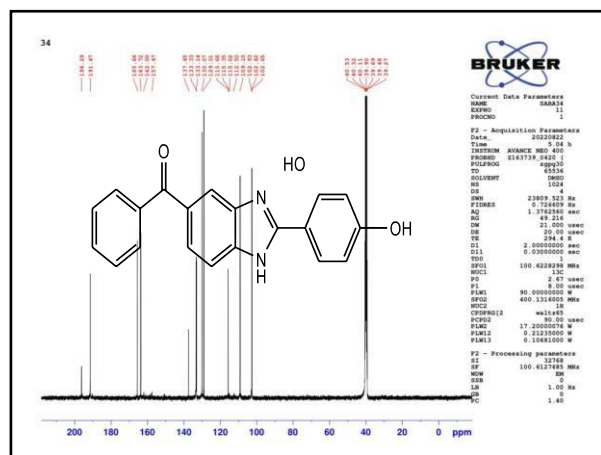


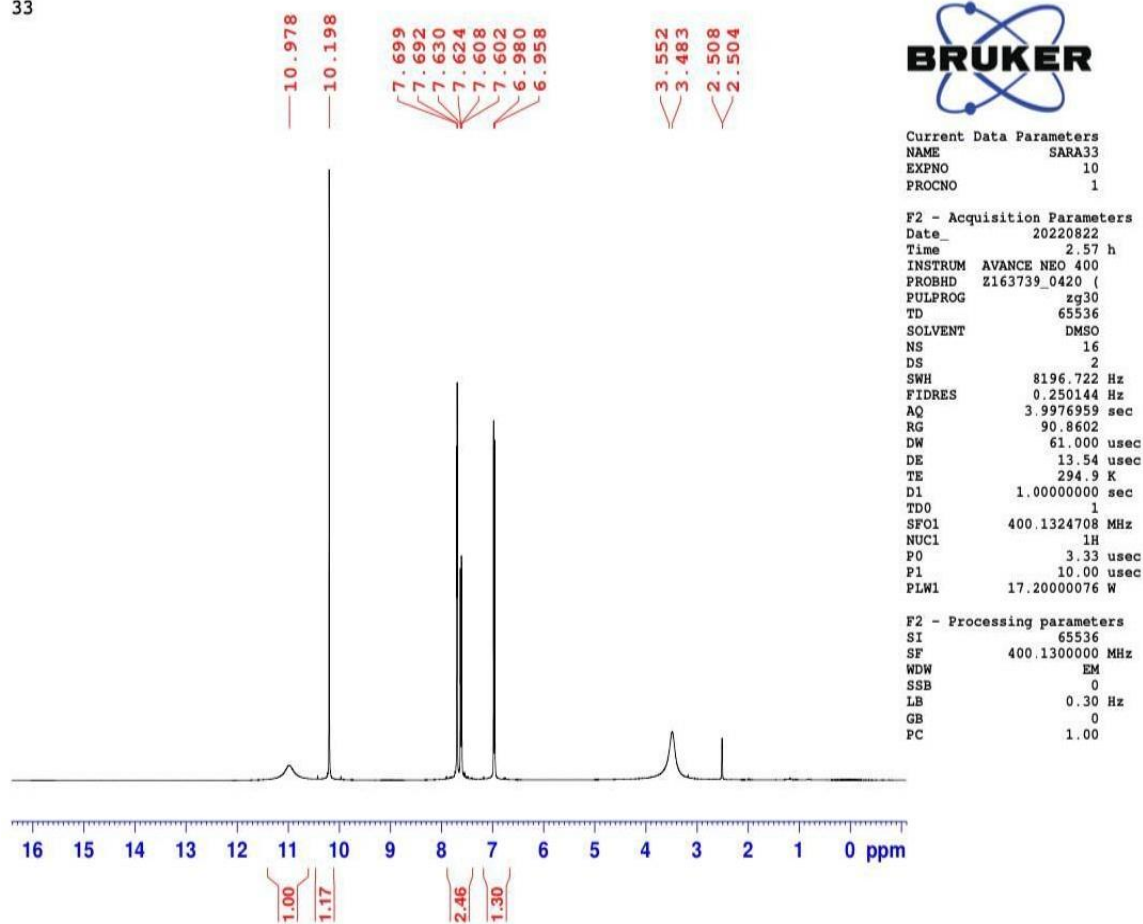
Figure (3-6): <sup>13</sup>C-NMR spectrum of compound (3b)

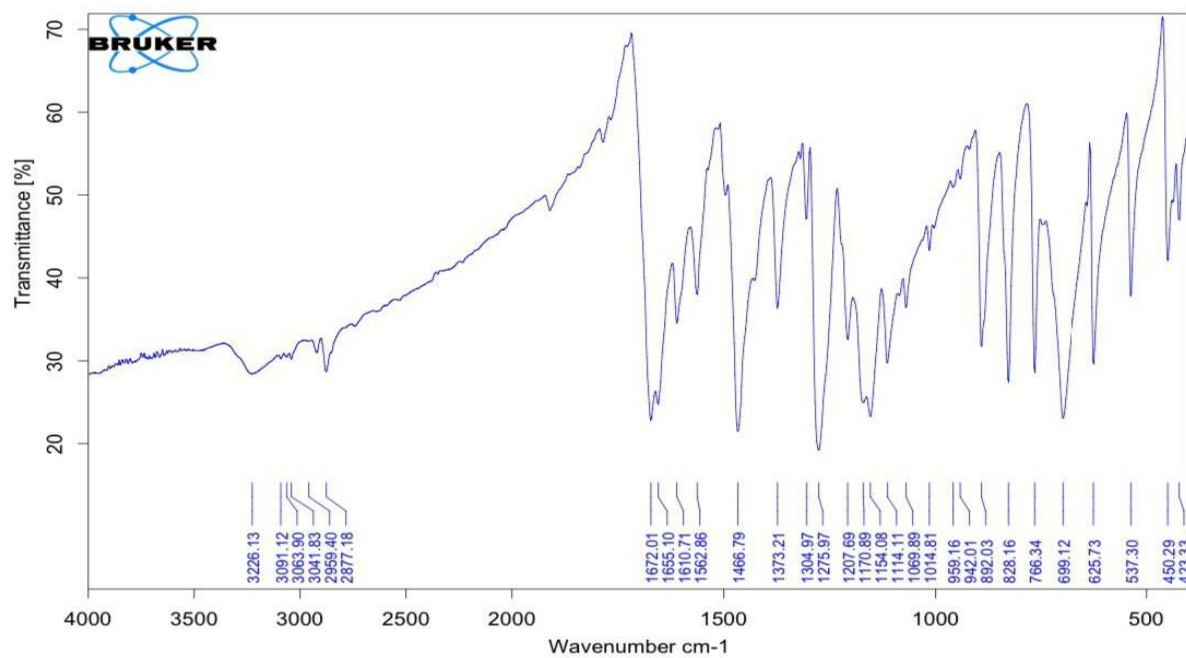
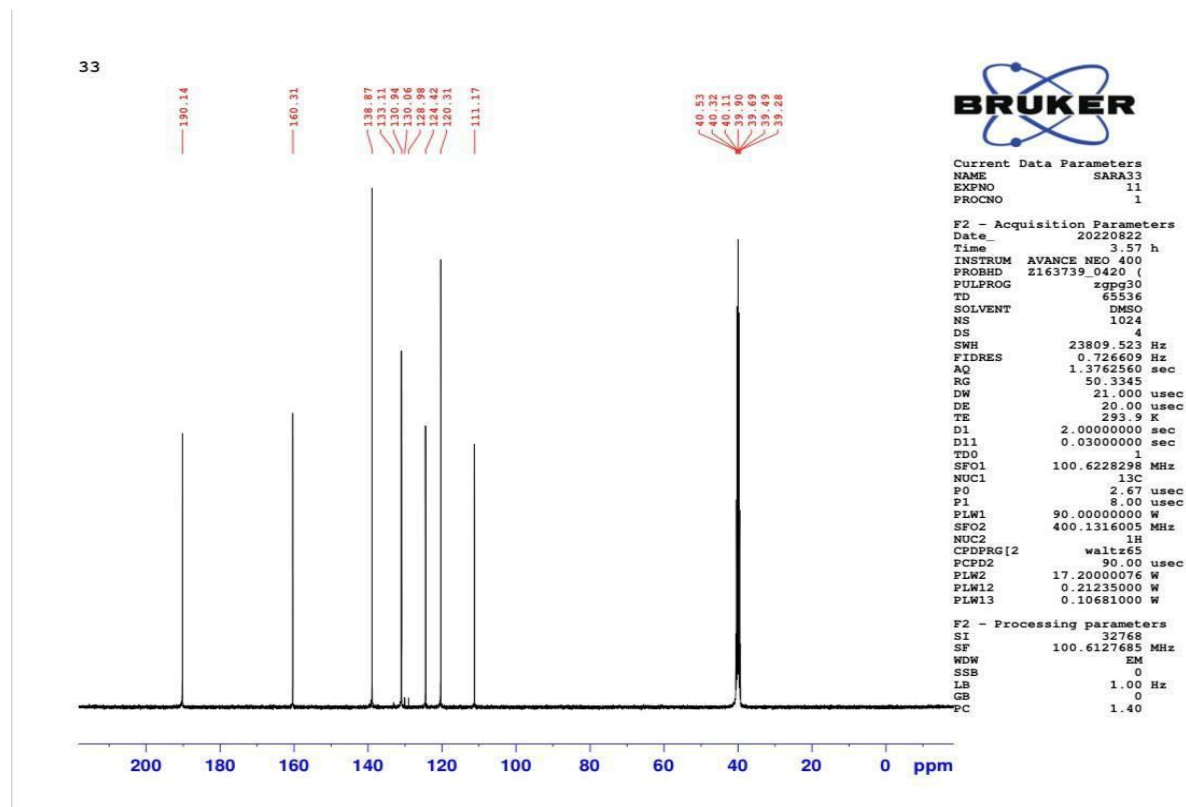
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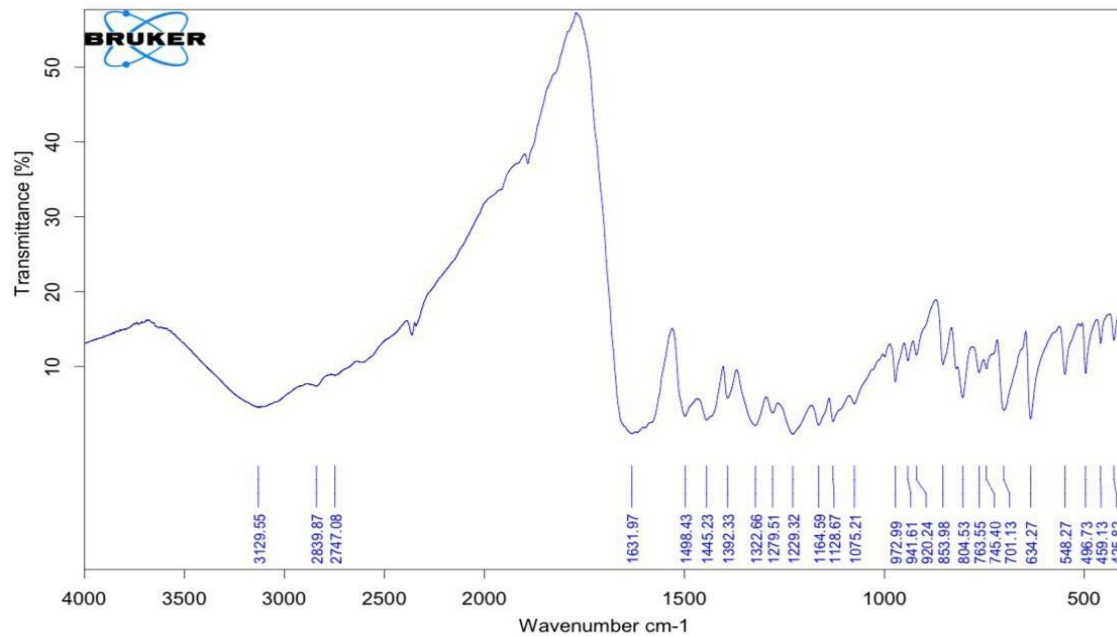
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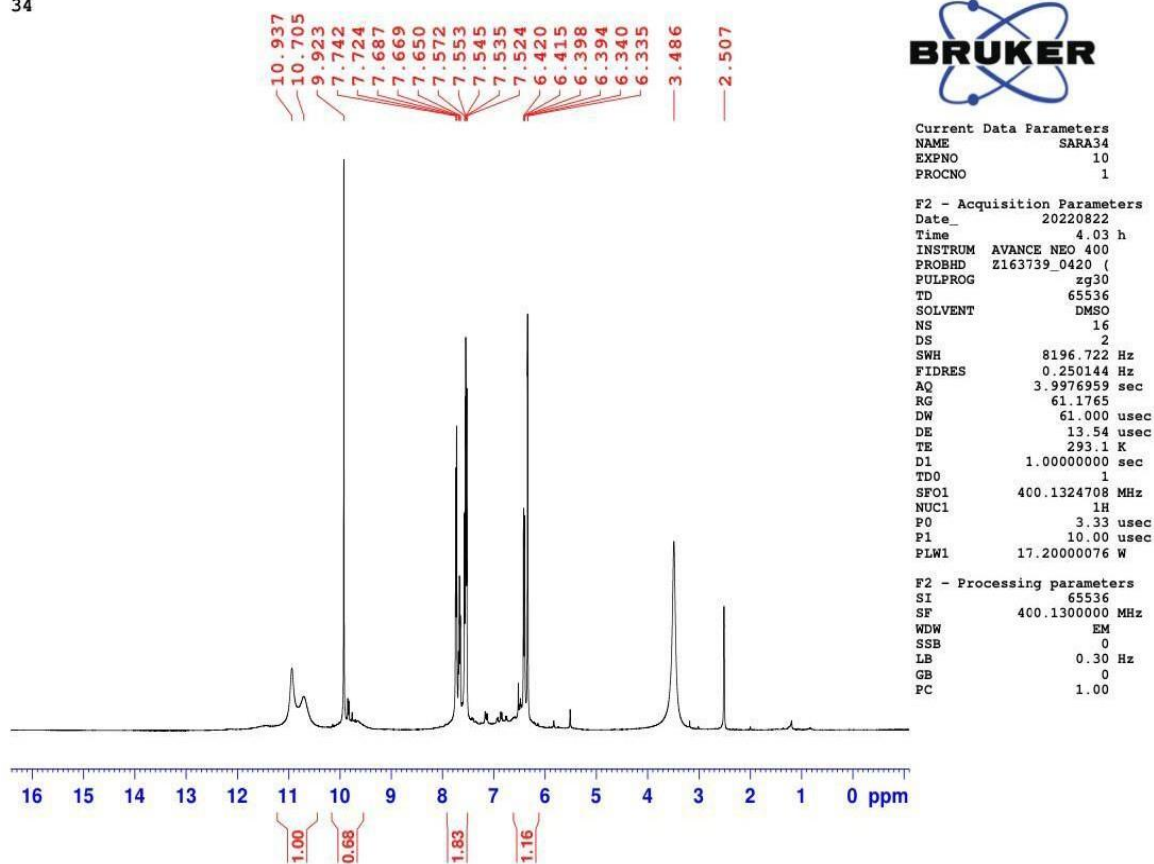








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