

# Synthesis and Characterization of New 1,2,4-Triazole Derivatives Form 2-Naphthol

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## Abstract

In this work 1,2,4-triazole derivatives were synthesized from [4-(2-hydroxy naphthyl)diazenyl]benzoic acid [N1] then converted to [4-(2-hydroxy naphthyl)diazenyl] benzoate [N2] which reacted with thiosemicarbazide and then cyclization by using sodium hydroxide. Then different alkyl halides like (methyl iodide, allyl chloride, propargyl chloride and benzyl chloride) were added to [4-(2-hydroxy naphthyl)diazenyl]-4H-1,2,4-triazole-3-thiol [N4] that led to alkylation of thiol to afforded compounds [N5] – [N8]. These compounds were characterized by the following techniques: FT-IR, and <sup>1</sup>H, <sup>13</sup>C NMR spectroscopies, and elemental analysis C.H.N.S. The physical properties of prepared compounds were studied.

**Keywords:** 2-Naphthol, Azo dyes, 1,2,4-Triazole and Alkyl halides

## 1- Introduction

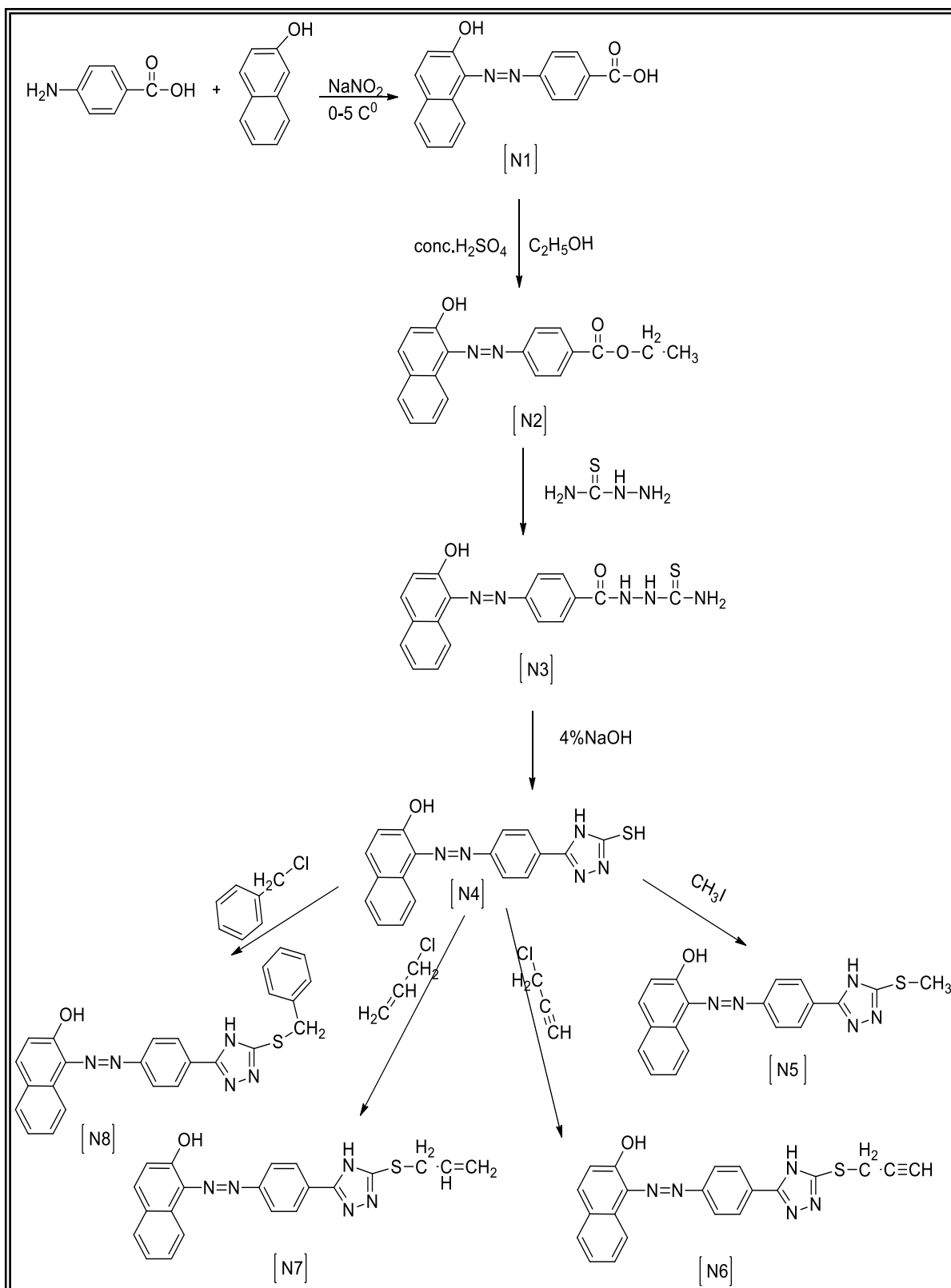
Azo dyes is one of the most important classes of organic compounds, characterizes by presence –N=N– in their structure [1][2][3]. These compounds have wide application in food, pharmaceutical, cosmetic, and analytical chemistry, due to their physico-chemical properties [4].

1,2,4-Triazoles and their derivatives are one of heterocyclic compounds characterized by a five-membered ring containing two carbons and three nitrogen atoms [5]. 1,2,4-Triazole rings are typically planar 6 $\pi$ -electron aromatic systems and extensive research has been carried out in this domain [6][7].

Triazole an important bioactive compounds that are associated with large biological activities [8], also 1,2,4-triazoles occupy a special place in the field of medicinal and pharmaceutical chemistry [9][10] as well as in industry.

Organosulfur chemistry is one of the most important and valuable branches of in organic synthesis. These compounds containing C-S bond in particular sulfides have a long and rich history as excellent intermediates in organic chemistry [11][12][13][14]. Thioethers are very efficient and valuable compounds in various areas such as medicine, pharmaceutical, bio-chemistry, agriculture, industry, heterocyclic chemistry and biological processes [15][16][17][18][19][20]. In the field of agriculture, it can be indicated to chlorbense that widely applied as pesticide [21].

The thiols (RSH) and alkyl halides (RX) are useful, available and valuable reagents that are widely used in the various fields in particular chemistry laboratory and industry processes. Some characters of thiols and alkyl halides such as being cheap and available have caused that organic chemists to use these compounds for the synthesis of sulfides in large scale [22]. For these reasons, in present work we have prepared some new thiol derivatives [N4-N8] as shown in scheme 1.



Scheme 1: preparations route of compounds [N1-N8]

## 2-Materials and methods

**Materials and instruments:** All used chemicals are highest purity available. 2-Naphthol, 4-amino benzoic acid, thiosemicarbazide, sodium hydroxide, sulfuric acid, hydrochloric acid, methyl iodide, allyl chloride, propargyl chloride and benzyl chloride from.

FT-IR, Micro Analysis (C.H.N),  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were used for characterization of the prepared compounds. Melting point, and physical properties were recorded.

### Preparation of compounds [N1-N8]:

(a) **Preparation of [4-(2-hydroxy naphthyl)diazenyl]benzoic acid [N1]:** Dissolve (0.01 mole, 1.37 g) of p-amino benzoic acid in (10 ml) distill water and (5 ml) HCl, keep the temperature at (0  $^{\circ}\text{C}$ ), the solution was then cooled to (0  $^{\circ}\text{C}$ ) and maintained under this temperature, then add  $\text{NaNO}_2$  which dissolve in (10 ml) distill water as drop wise, leave the reaction for (15) min. This diazonium solution was add as drop wise to coupling component solution which prepared by mixing (0.01 mole, 1.44g) of  $\beta$ -naphthol in absolute ethanol and (1 g) of sodium hydroxide in (100 ml) distill water, the precipitate then filter and washed with water many time.

Yield: 94% , $R_f$  0.66 (Hexane:DCM)( 3:2), m.p. 290-292  $^{\circ}\text{C}$ , Elemental analyses for  $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$  C, 70.21; H, 4.10; N, 9.58; Found: C,70.22; H, 3.95; N, 9.79.

**IR ( $\nu, \text{cm}^{-1}$ ):** 3360.33 (O-H), 3064.5 (C-H<sub>Ar.</sub>), 1718 (C=O<sub>carboxylic acid</sub>), 1677 (N=N)

**$^1\text{H-NMR}$  ( $\delta$ , ppm):** 6.745 (H<sub>5</sub>, Ar-H ), 6.764 (H<sub>6</sub>, Ar-H), 7.461(H<sub>10</sub>, Ar-H ), 7.485 (H<sub>7</sub>, Ar-H), 7.880 (H<sub>2</sub>, H<sub>4</sub>, Ar-H ), (, Ar-H), 8.028 (H<sub>3</sub>, H<sub>1</sub>, Ar-H ), 8.047 (H<sub>11</sub>, Ar-OH), 13 (H<sub>12</sub>, COOH)

**$^{13}\text{C-HNMR}$  ( $\delta$ , ppm):** 117.78 (C<sub>4</sub>, Ar-C), 122.20 (C<sub>6</sub>, Ar-C), 125.97 (C<sub>15</sub>, Ar-C), 127.27 (C<sub>11</sub>, Ar-C), 128.53(C<sub>8</sub>, Ar-C), 129.65 (C<sub>10</sub>, Ar-C), 129.99 (C<sub>3</sub>, C<sub>7</sub>, Ar-C), 130.16 (C<sub>13</sub>, Ar-C), 131.54 (C<sub>9</sub>, C<sub>12</sub>, C<sub>13</sub>, Ar-C), 133.16 (C<sub>2</sub>, Ar-C), 142.61 (C<sub>14</sub>, Ar-C.) 147.02 (C<sub>16</sub>, Ar-C), 67.19 (C<sub>5</sub>, Ar-C). 176.44 (C<sub>1</sub>, C=O)

### (b) Preparation of [4-(2-hydroxy naphthyl)diazenyl] benzoiate [N2]:

To solution of (0.01 mole, 2.92 g) of compound [1] in (100 ml) absolute ethanol was added (15 ml) concentrated sulfuric acid as dropwise, the mixture was refluxed for overnight. The reaction content was poured into ice-water mixture, the precipitate was filtered and washed with water two time. Yield:92%,  $R_f$  0.64 (Hexane:DCM)( 3:3), m.p. 142-144  $^{\circ}\text{C}$ , Elemental analyses for  $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_3$  C, 71.25 ; H, 5.0; N, 8.75; Found: C,71.29; H, 5.20; N, 8.91:

**IR ( $\nu, \text{cm}^{-1}$ ):** 3400.73 (O-H), 3080 (C-H<sub>Ar.</sub>), 2950, 2860 (C-H<sub>alph.</sub>), 1711(C=O<sub>ester</sub>), 1603.71(N=N), 1563.98 (C=C<sub>Ar.</sub>)

**$^1\text{H-NMR}$  ( $\delta$ , ppm):** 1.347 (3H<sub>1</sub>, CH<sub>3</sub> ), 2.509 (2H<sub>2</sub>, CH<sub>2</sub>), 7.485(H<sub>9</sub>, Ar-H ), 7.585 (H<sub>8</sub>, Ar-H), 7.729 (H<sub>12</sub>, Ar-H ), 7.729(H<sub>7</sub>, H<sub>10</sub>, Ar-H), 7.747 (H<sub>11</sub>, Ar-H ), 7.932(H<sub>4</sub>, H<sub>6</sub>, Ar-H ), 8.046 (H<sub>3</sub>, H<sub>5</sub>, Ar-H ), 8.49(H, Ar-OH).

**$^{13}\text{C-HNMR}$  ( $\delta$ , ppm):** 14.67 (C<sub>1</sub>, CH<sub>3</sub>), 61.21 (C<sub>2</sub>, CH<sub>2</sub>), 130.08 (C<sub>6</sub>, C<sub>8</sub>, Ar-C), 130.64 (C<sub>12</sub>, Ar-C), 130.76 (C<sub>11</sub>, Ar-C), 131.38(C<sub>13</sub>, Ar-C), 131.56(C<sub>17</sub>, Ar-C), 133.16(C<sub>10</sub>, Ar-C), 133.19 (C<sub>9</sub>, H<sub>5</sub>, Ar-C), 142.76 (C<sub>14</sub>, Ar-C), 142.96 (C<sub>15</sub>, Ar-C), 147.09 (C<sub>4</sub>, Ar-C), 147.22 (C<sub>16</sub>, Ar-C), 165.61(C<sub>7</sub>, Ar-C), 167.20 (C<sub>8</sub>, Ar-C), 177.01 (C<sub>3</sub>, C=O).

**(c) Preparation of [4-(2-hydroxy naphthyl)diazenyl] -2-carboxylic thiosemicarbazide [N3]:**

A mixture of thiosemicarbazide (0.01 mole, 0.91g) and (0.01 mole, 3.2 g) compound [N2] in absolute ethanol was refluxed overnight, the solvent was evaporated and the solid was recrystallized by ethanol.

Yield: 85%,  $R_f$  0.54 (Petroleum ether:CHCl<sub>3</sub>)(4:2), m.p. 186-188 °C, Elemental analyses for C<sub>18</sub>H<sub>15</sub>N<sub>5</sub>O<sub>2</sub>S C, 60.67; H, 4.21; N, 19.66; S, 8.76; Found: C,60.86; H, 4.15; N, 19.87; S, 8.84.

**IR(v,cm<sup>-1</sup>)**, 3295.25 (O-H), 3256.84,3187.25(N-H), 1618.09 (C=O<sub>amide</sub>), 1520 (N=N), 1162 (C=S), 1520 (C=C<sub>Ar.</sub>)

**<sup>1</sup>H-NMR (δ, ppm)**: 1.981 (H<sub>2</sub>,NH-C=S), 4.6 (H<sub>14</sub>,Ar-H), 6.7(H<sub>3</sub>, NH-C=O ), 7.607 (H<sub>9</sub>, Ar-H), 7. 108 (H<sub>10</sub>, Ar-H ) 7.620 (H<sub>11</sub>, Ar-H ), 7. 635 (H<sub>12</sub>, Ar-H ) 7.648(H<sub>13</sub>, Ar-H), 7.829 (H<sub>4</sub>, Ar-H ), 7.838 (H<sub>6</sub>, Ar-H ), 7.845 (H<sub>8</sub>, Ar-H ), 7.949(H<sub>5</sub>, Ar-H). 7. 957 (H<sub>7</sub>, Ar-H ) 7. 960 (H<sub>1</sub>, N-H<sub>2</sub> )

**<sup>13</sup>C-HNMR (δ, ppm)**: 117.79 (C<sub>5</sub>, Ar-C), 117.81 (C<sub>7</sub>, Ar-C), 122.12 (C<sub>15</sub>, Ar-C), 123.98 (C<sub>11</sub>, Ar-C), 125.98 (C<sub>9</sub>, Ar-C), 126.11(C<sub>10</sub>, Ar-C), 127.31(C<sub>13</sub>, Ar-C), 128.54(C<sub>18</sub>, Ar-C), 128.69 (C<sub>12</sub>, Ar-C), 129.21 (C<sub>4</sub>, Ar-C), 130.02 (C<sub>8</sub>, Ar-C), 130.53 (C<sub>14</sub>, Ar-C), 131.55 (C<sub>3</sub>, Ar-C), 133.14 (C<sub>17</sub>, Ar-C). 124.18 (C<sub>16</sub>, Ar-C), 167.00 (C<sub>6</sub>, Ar-C), 177.03 (C<sub>2</sub>, C=O). 181.68 (C<sub>1</sub>, C=S).

**(d) Preparation of [4-(2-hydroxy naphthyl)diazenyl]-4H-1,2,4-Triazole-3-thiol [N4]:**

A mixture of [N3] (0.01 mole, 3.56g) and 4% NaOH solution (20 ml) refluxed for (4) hours, then neutralize with 30% HCl solution, the precipitate was filtered and washed with water, and then recrystallization by ethanol.

Yield:89 %,  $R_f$  0.62 (Petroleum ether:CHCl<sub>3</sub>) (4:2), m.p. 266-268 0 °C, Elemental analyses for C<sub>12</sub>H<sub>13</sub>N<sub>5</sub>OS C, 45.71; H, 4.12; N, 22.22; S, 9.22; Found: C,45.82; H, 4.22; N, 22.37; S, 9.35.

**IR (v,cm<sup>-1</sup>)**: (O-H), 3366.23 (N-H), 3050 (C-H<sub>Ar.</sub>), 2662.78-2542.80 (S-H), 1671.74 (C=C<sub>Ar.</sub>),1601.27(N=N).

**<sup>1</sup>H-NMR (δ, ppm)**: 1.227 (H<sub>11</sub>, SH ), 6.8 (H<sub>13</sub>,Ar-OH), 7.5(H<sub>6</sub>, C-Arm.), 7.8 (H<sub>5</sub>, Ar-H), 7.91(H<sub>7</sub>, Ar-H ),7.93 (H<sub>1</sub>, Ar-H ), 7.95(H<sub>3</sub>, Ar-H), 8.1 (H<sub>2</sub>, Ar-H ), 8.13(H<sub>4</sub>, Ar-H ), 8.15 (H<sub>8</sub>, Ar-H ), 8.2(H<sub>9</sub>, Ar-H), 8.5 (H<sub>12</sub>,N-H ).

**<sup>13</sup>C-HNMR (δ, ppm)**: 117.93 (C<sub>5</sub>,C<sub>7</sub>,C<sub>11</sub> Ar-C), 122.18 (C<sub>17</sub>, Ar-C), 125.76 (C<sub>8</sub>,C<sub>4</sub>, Ar-C), 127.16 (C<sub>11</sub>, Ar-C), 128.52 (C<sub>14</sub>, Ar-C), 129.65(C<sub>15</sub>, Ar-C), 129.98(C<sub>10</sub>, Ar-C), 130.50(C<sub>16</sub>, Ar-C-), 131.47 (C<sub>3</sub>, Ar-C), 133.20 (C<sub>9</sub>, Ar-C), 142.37 (C<sub>6</sub>, Ar-C), 146.85 (C<sub>2</sub>, C<sub>1</sub>, C=N),167.49 (C<sub>18</sub>, Ar-C).

**(e) Preparation of [4-(2-hydroxy naphthyl)diazenyl]-3-alkyl sulfanyl-4H-1,2,4-Triazole [N5-N8]:**

Compound [N4](0.001 mole, 0.348 g) was dissolve in a mixture of (3.5 ml ) ethanol and 10% NaOH (3ml). Alkyl halides(0.01 mole) [(0.06 ml) methyl iodide, (0.08 ml) allyl chloride, (0.07 ml) propargyl chloride and (0.11 ml) benzyl chloride] respectively was added and the solution was sonicated for (45 min), then add (7ml) distill water and extracted with DCM.

Yield:78%,  $R_f$  0.78 (Hexane:ethylacetate) (3:3), m.p. 317-319 °C, Elemental analyses for compound [N5] C, 47.41; H, 4.126; N, 21.27; S, 8.86; Found: C,47.44; H, 4.35; N, 21.27; S, 8.91.Yield:77,  $R_f$  0.71 (Petroleum ether:CHCl<sub>3</sub>) (4:2), m.p. 350-352 °C. Elemental analyses for compound [N6] C, 70.98; H, 4.78; N, 19.71; 8.26; Found: C,71.11; H, 4.95; N, 19.85; S, 8.38.Yield: 78%,  $R_f$  0.73

(Hexane:ethylacetate) (3:1), m.p. 312-314 °C. Elemental analyses for compound [N7] C, 71.38; H, 4.24; N, 19.83; 8.31; Found: C,72.44; H, 4.41; N, 19.99; S, 8.44. Yield: 79%,  $R_f$  0.52 (Hexane:ethylacetate) (3:3), m.p. 321-323 °C, Elemental analyses for compound [N8] C, 68.64; H, 4.34; N, 16.01; S, 7.32 Found: C,68.64; H, 4.21; N, 16.23; S, 7.42.

**N5 : IR ( $\nu, \text{cm}^{-1}$ ):** 3412.67 (O-H), 3279.25 (N-H), 3165.01 (C-H<sub>Ar.</sub>), 2980.62 (C-H<sub>alph.</sub>), 1686.37 (C=C<sub>Ar.</sub>), 1636.24 (N=N).

**<sup>1</sup>H-NMR ( $\delta$ , ppm):** 1.340 (3H<sub>1</sub>, CH<sub>3</sub>), 4.5 (H<sub>13</sub>, Ar-OH), 6.770 (H<sub>12</sub>, C-Arm.), 7.3 (H<sub>2</sub>, N-H), 7.469 (H<sub>9</sub>, Ar-H), 7.483 (H<sub>8</sub>, Ar-H), 7.587 (H<sub>4</sub>, Ar-H), 7.714 (H<sub>3</sub>, Ar-H), 7.728 (H<sub>6</sub>, Ar-H), 7.843 (H<sub>7</sub>, Ar-H), 8.036 (H<sub>4</sub>, Ar-H), 8.047 (H<sub>5</sub>, Ar-H).

**<sup>13</sup>C-HNMR ( $\delta$ , ppm):** 13 (C<sub>1</sub>, CH<sub>3</sub>), 129.5 (C<sub>6</sub>, C<sub>7</sub>, C<sub>13</sub> Ar-C), 129.6 (C<sub>14</sub>, C<sub>11</sub>, Ar-C), 129.8 (C<sub>5</sub>, C<sub>8</sub>, Ar-C), 129.9 (C<sub>16</sub>, Ar-C), 130.2 (C<sub>12</sub>, Ar-C), 135.5 (C<sub>10</sub> Ar-C), 135.6 (C<sub>15</sub>, Ar-C), 136.3 (C<sub>4</sub>, Ar-C), 136.7 (C<sub>9</sub>, Ar-C), 137.5 (C<sub>2</sub>, C=N), 138.1 (C<sub>3</sub>, C=N), 146.85 (C<sub>17</sub>, Ar-C), 167.49 (C<sub>18</sub>, Ar-C).

**N6: IR ( $\nu, \text{cm}^{-1}$ ):** 3323.83 (N-H), 3045.05 (C-H<sub>Ar.</sub>), 2974 (C-H<sub>alph.</sub>), 2098.81 (C=C<sub>alph.</sub>), 1594.39 (C=N), 1544.01 (N=N).

**<sup>1</sup>H-NMR ( $\delta$ , ppm):** 1.616 (2H<sub>3</sub>, CH<sub>2</sub>), 6.88 (2H<sub>1</sub>, CH<sub>2</sub>), 6.9 (2H<sub>2</sub>, CH<sub>2</sub>), 7.3 (H<sub>15</sub>, Ar-OH), 7.469 (H<sub>5</sub>, C-H), 7.51 (H<sub>4</sub>, N-H), 7.65-8.83 (H<sub>8</sub>-H<sub>14</sub> Ar-H), 7.97 (H<sub>6</sub>, Ar-H), 7.98 (H<sub>7</sub>, Ar-H).

**<sup>13</sup>C-HNMR ( $\delta$ , ppm):** 53 (2C<sub>3</sub>, CH<sub>2</sub>), 105.30 (2C<sub>1</sub>, CH<sub>2</sub>), 118.91 (C<sub>7</sub>, C<sub>11</sub>, Ar-C), 118.96 (C<sub>8</sub>, C<sub>10</sub>, Ar-C), 121.59 (C<sub>17</sub>, Ar-C), 122.65 (C<sub>12</sub>, Ar-C), 128.84 (C<sub>10</sub> Ar-C), 128.85 (C<sub>15</sub>, Ar-C), 128.87 (C<sub>15</sub>, C<sub>16</sub>, Ar-C), 130.43 (C<sub>6</sub>, <sub>19</sub>Ar-C), 134.24 (C<sub>13</sub>, Ar-C), 138.85 (C<sub>18</sub>, Ar-C), 141.39 (C<sub>2</sub>, Ar-C), 145.55 (C<sub>12</sub>, Ar-C), 145.90 (C<sub>21</sub>, Ar-C), 149.49 (C<sub>9</sub>, Ar-C), 149.79 (C<sub>5</sub>, C=N), 168.97 (C<sub>4</sub>, C=N).

**N7: IR ( $\nu, \text{cm}^{-1}$ ):** 3408.01 (O-H), 3277.49 (N-H), 3165.85 (C-H<sub>alkyne.</sub>), 2990 (C-H<sub>alph.</sub>), 2241.57 (C=C), 1686.12 (C=N), 1636.93 (C=C<sub>Ar.</sub>), 1548.64 (N=N).

**<sup>1</sup>H-NMR ( $\delta$ , ppm):** 1.615 (H<sub>1</sub>, CH), 3.3 (2H<sub>2</sub>, CH<sub>2</sub>), 6.7 (H<sub>14</sub>, OH), 7.31 (H<sub>10</sub>, OH), 7.33 (H<sub>13</sub>, C-H), 7.5 (H<sub>9</sub>, Ar-H), 7.6 (H<sub>8</sub>, Ar-H), 7.62 (H<sub>4</sub>, Ar-H), 7.63 (H<sub>7</sub>, Ar-H), 7.64 (H<sub>11</sub>, Ar-H), 7.95 (H<sub>5</sub>, Ar-H), 7.96 (H<sub>7</sub>, Ar-H), 7.98 (H<sub>12</sub>, Ar-H),

**N8: IR ( $\nu, \text{cm}^{-1}$ ):** 3400 (O-H), 3249.20 (N-H), 3054.80 (C-H<sub>Ar.</sub>), 2981.0 -2932.17 (C-H<sub>alph.</sub>), 1596.61 (C=C<sub>Ar.</sub>), 1551.25 (N=N)

**<sup>1</sup>H-NMR ( $\delta$ , ppm):** 5.4 (H<sub>18</sub>, Ar-OH), 6.8 (H<sub>7</sub>, NH), 7.35 (H<sub>1</sub>, Ar-H), 7.45 (H<sub>3</sub>, Ar-H), 7.46 (H<sub>5</sub>, C-H), 7.51 (H<sub>2</sub>, Ar-H), 7.52 (H<sub>4</sub>, Ar-H), 7.65 (H<sub>17</sub>, Ar-H), 7.66 (H<sub>13</sub>, Ar-H), 7.75 (H<sub>14</sub>, Ar-H), 7.77 (H<sub>12</sub>, Ar-H), 8.01 (H<sub>8</sub>, Ar-H), 8.11 (H<sub>11</sub>, Ar-H), 8.17 (H<sub>9</sub>, Ar-H), 8.18 (H<sub>10</sub>, Ar-H), 8.31 (H<sub>16</sub>, Ar-H),

### 3- Result and Discussion

The structure of synthesized compounds [N1-N8] has been characterized by FT-IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra, and elemental analysis. The data of these measurements were presented in table 1,2.

The IR spectrum of compound [N1] exhibit a new absorption band at 1504.68 cm<sup>-1</sup> corresponding to N=N and disappearance absorption band at 3458.98-3360.45 cm<sup>-1</sup> for NH<sub>2</sub>. <sup>1</sup>HNMR show single signal at (13) ppm for hydrogen of carboxylic acid and peaks at (6.5-8.5) for hydrogen of aromatic ring. The IR spectrum for compound [N2] show disappearance of C=O of carboxylic acid at 1711 cm<sup>-1</sup> and appearance C=O of ester at 1718 cm<sup>-1</sup>, <sup>1</sup>HNMR show appearance signals at (1.347, 2.509) ppm for hydrogen's of ester, and disappearance peak of carboxylic acid. For compound [N3],

the IR spectra show absence absorption band at  $1718\text{ cm}^{-1}$  for  $\text{C}=\text{O}_{\text{ester}}$  and appear new absorption band at for  $\text{C}=\text{O}_{\text{amid}}$  at  $1618\text{ cm}^{-1}$ ,  $^1\text{HNMR}$  show a single signal at (1.981, 6.7) ppm for hydrogen of NH and disappearance peak of hydrogen of ester. compound [N3] which upon ring closure with NaOH gave compound [N4] which exists in tautomeric thiol-thione equilibrium, as indicated by  $\text{C}=\text{S}$  stretching band at  $1207.73\text{ cm}^{-1}$  and S-H stretch at  $2662.78$  and  $2542.80\text{ cm}^{-1}$ ,  $^1\text{HNMR}$  show a single signal at (1.227) ppm for hydrogen of thiol and disappearance peak of NH. Methylation of compound [N4] to give compound [N5] show disappearance peak of stretch S-H at  $2662.78$  and  $2542.80$  and appearance  $\text{C}-\text{H}_{\text{aliphatic}}$  at  $2980.62\text{ cm}^{-1}$ ,  $^1\text{HNMR}$  show disappearance a single signal for hydrogen of thiol and appearance peak of aliphatic hydrogen at (1.340) and appearance single signal for hydrogen of NH at (7.3) ppm. The IR spectrum of alkylation of triazole by allyl chloride exhibit a new absorption band at  $1594\text{ cm}^{-1}$  for  $\text{C}=\text{C}_{\text{alkene}}$  and disappearances thiol group,  $^1\text{HNMR}$  show a single signal at (6.88, 6.9) ppm for hydrogen of  $\text{C}=\text{C}$ . Compound [N4] upon alkylation with propargyl chloride gave compound [N7] which show appearance and at ( $2241.57$ )  $\text{cm}^{-1}$  for  $\text{C}-\text{C}_{\text{triple bond}}$  and absence of thiol group at ( $2662.78, 2542.80$ )  $\text{cm}^{-1}$ .  $^1\text{HNMR}$  show a single signal at (1.615) ppm for hydrogen of hydrogen of  $\text{CH}_{\text{alkyne}}$ . The IR spectrum for Compound [N8] show appear new peak at for  $\text{C}-\text{H}_{\text{aliphatic}}$  and disappearance peak for stretch S-H of compound [N4] at ( $2662.78, 2542.80$ ).  $^1\text{HNMR}$  show signal at (2990) ppm for  $\text{C}-\text{H}_{\text{aliph.}}$ .

### UV-Vis spectroscopy

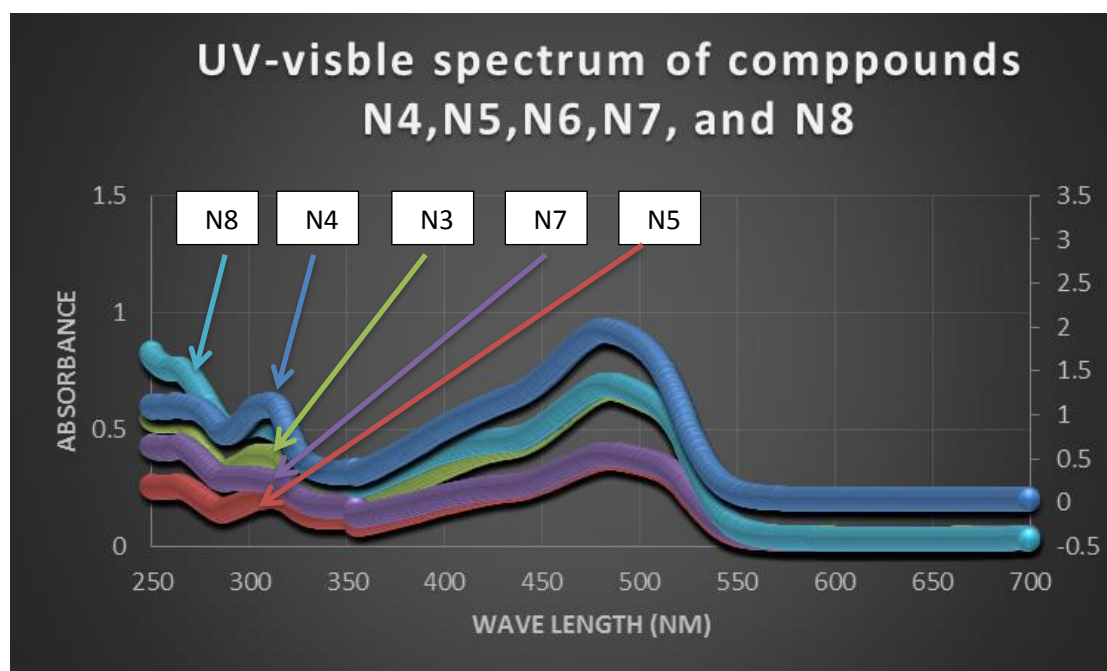


Figure 1; UV-Vis spectra of compounds [N4-N8], recorded in  $\text{CH}_3\text{OH}$  ( $1 \times 10^{-4}$  M)

The UV-Vis spectra of compounds N5-N8 displayed broad CT bands with end-absorptions reaching closely into the near infrared in comparison with compound N4 reflecting the effective of conjugation (Figure 1). Red shift (bathochromically shifted) occurred in  $\text{CH}_3\text{OH}$  (between 5 - 6 nm).



### Fluorescence spectroscopy

The photo physical behavior was qualitatively investigated by fluorescence spectroscopy recorded in  $1 \times 10^{-5}$  M solution in  $\text{CH}_3\text{OH}$ . It can be seen that the allyl [N6] and methyl group [N5] plays an important role in modulating the fluorescence properties of the 1,2,4-Triazole unit as shown in figure 2, the fluorescence of [N7] is quenched strongly compared to 1,2,4-Triazole [N4].

Quenching for [N5]= 236

Quenching for [N6]= 115

Quenching for [N7]= 15

Quenching for [N8]= 18

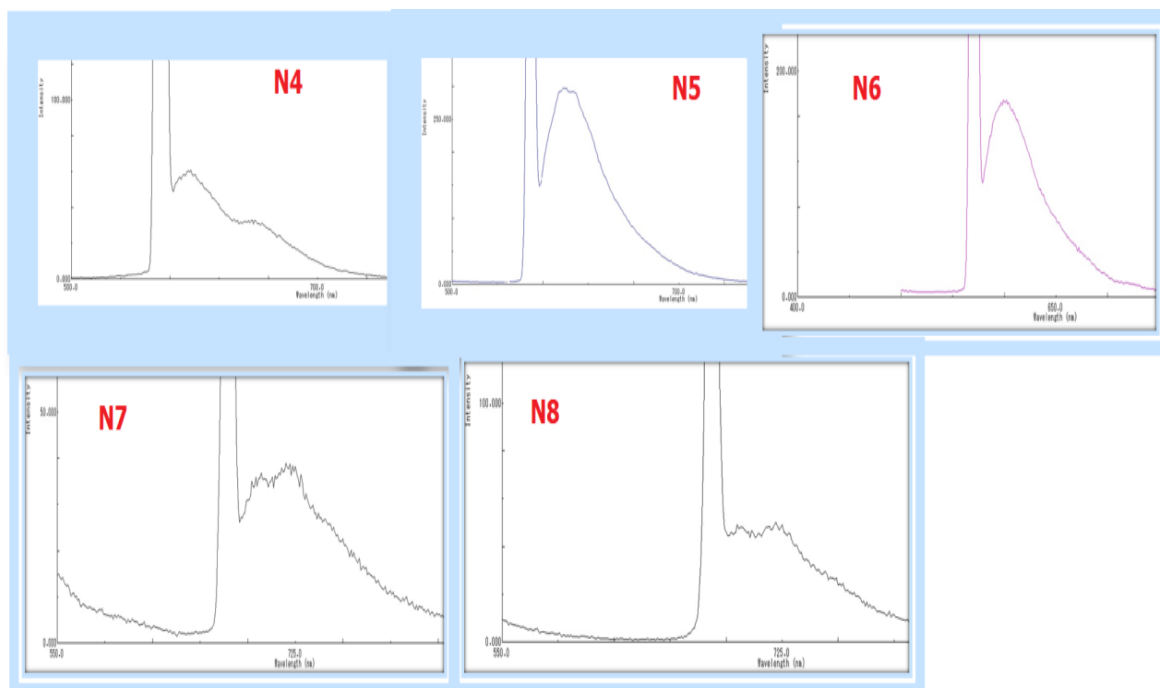


Figure 2. Fluorescence spectra of compounds [N4-N8] recorded in  $\text{CH}_3\text{OH}$  ( $1 \times 10^{-5}$  M).

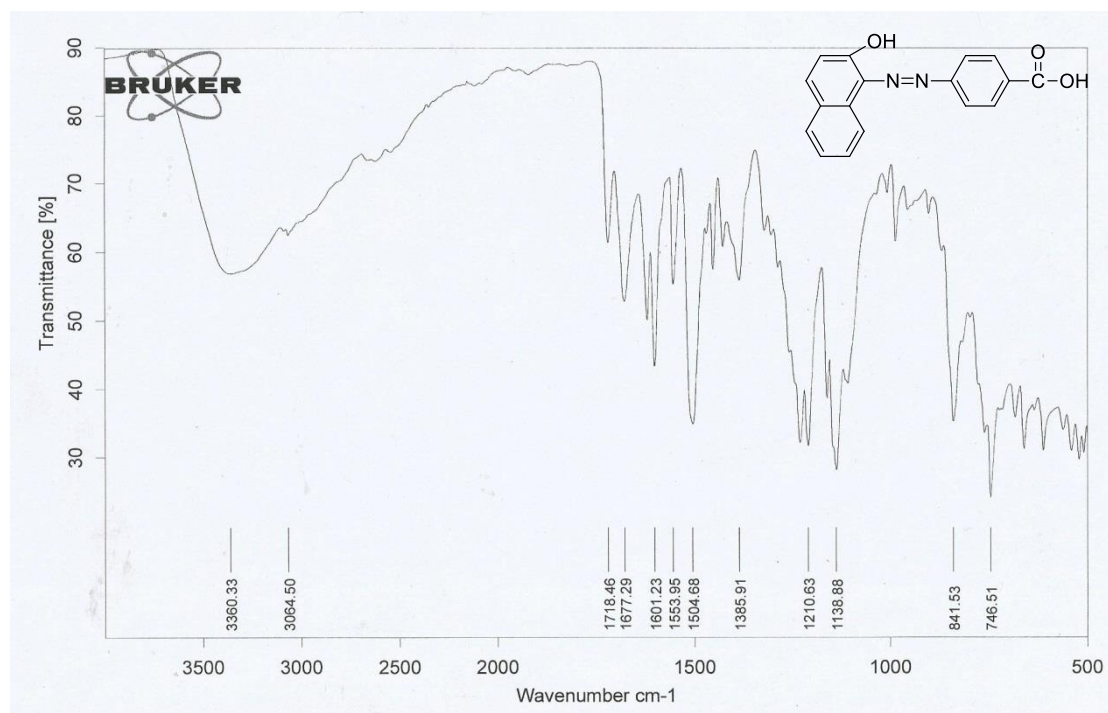


Figure 3: FTIR spectrum for prepared compound [N1]

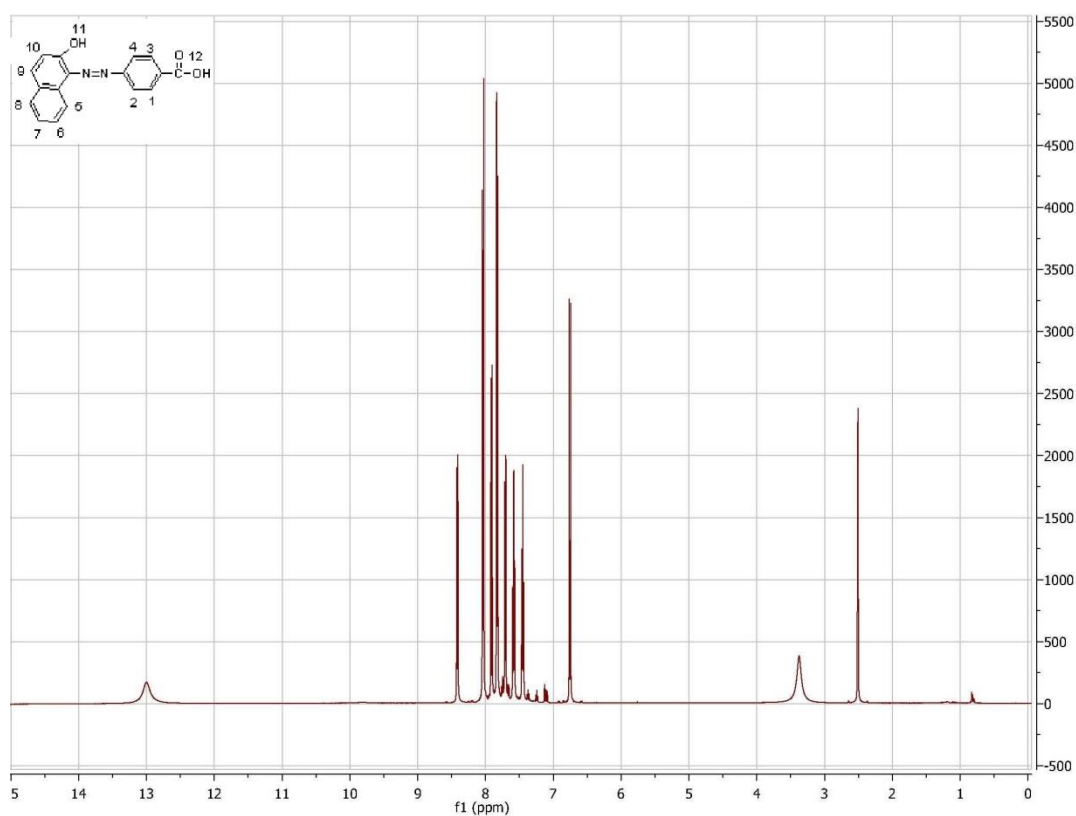


Figure 4: <sup>1</sup>H-NMR spectrum for prepared compound [N1]



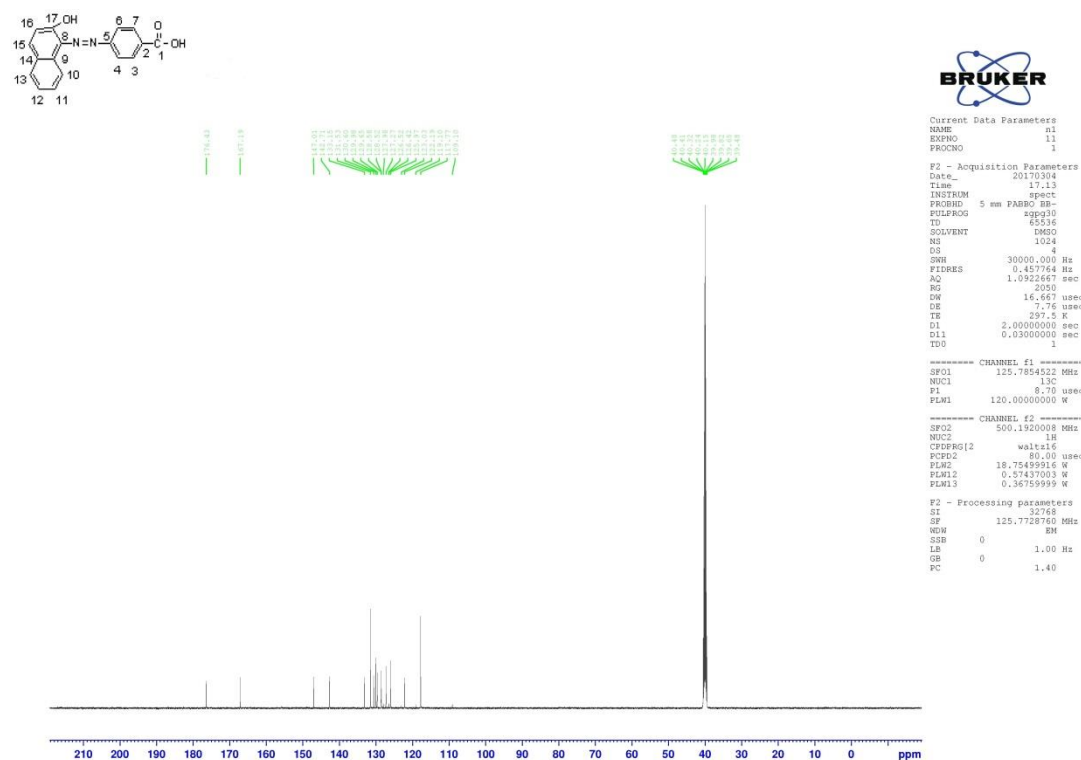


Figure 5: <sup>13</sup>C-NMR spectrum for prepared compound [N1]

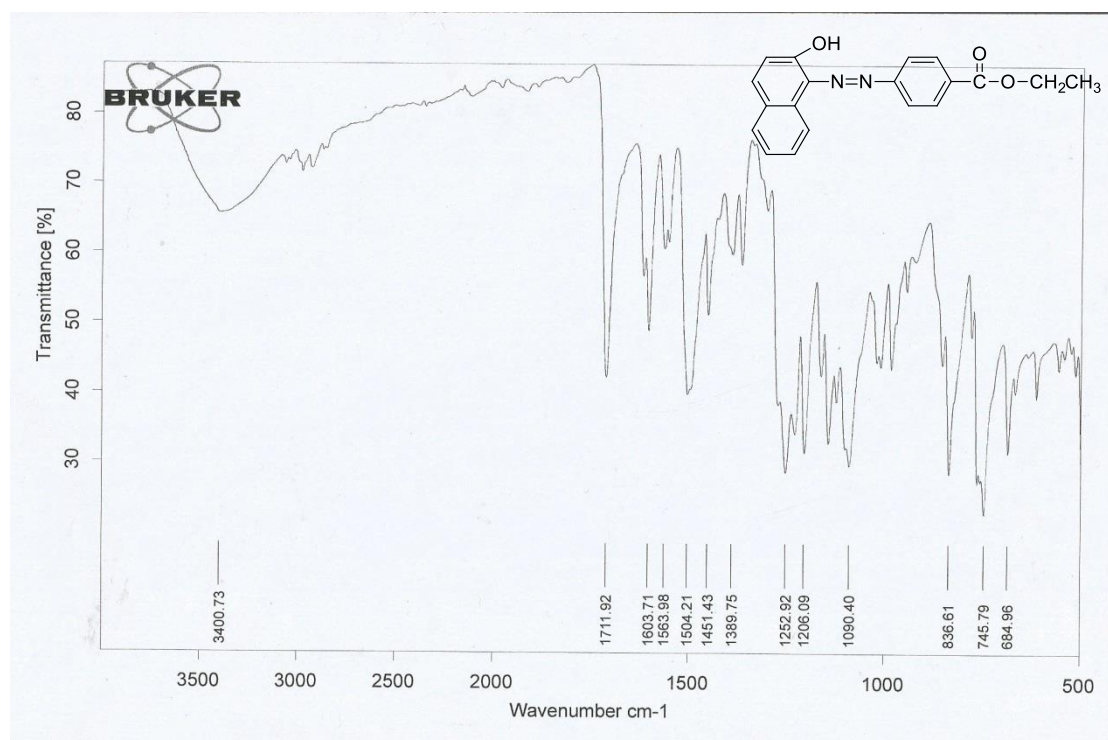


Figure 6: FTIR spectrum for prepared compound [N2]

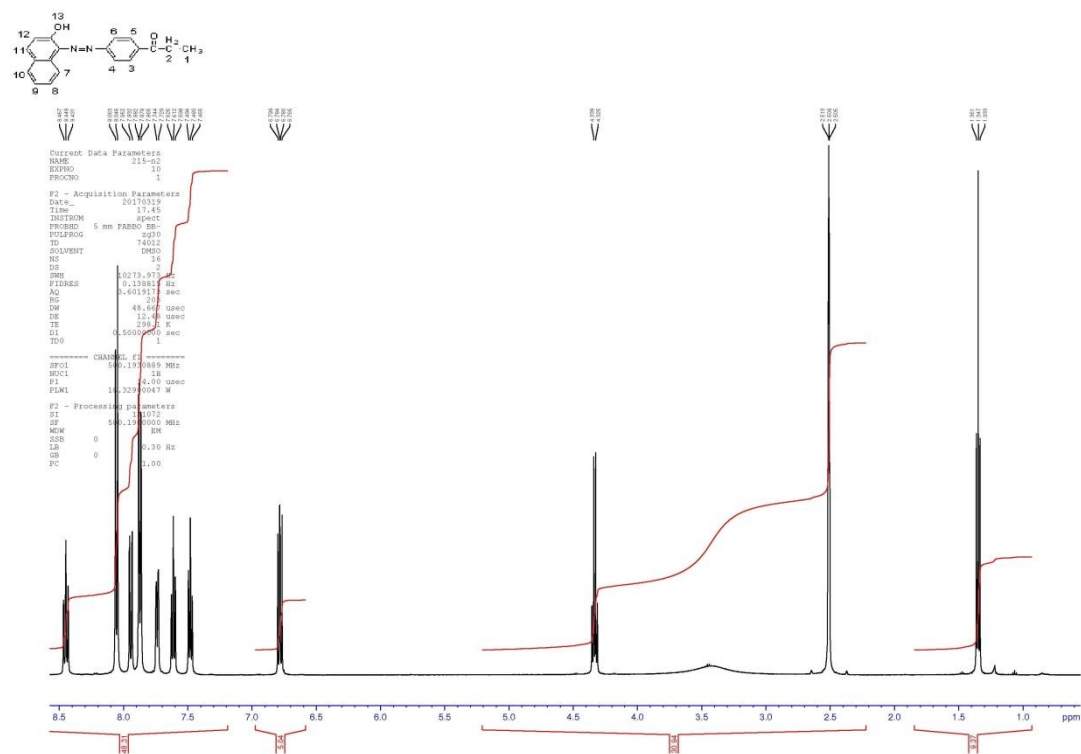


Figure 7: <sup>1</sup>H-NMR spectrum for prepared compound [N2]

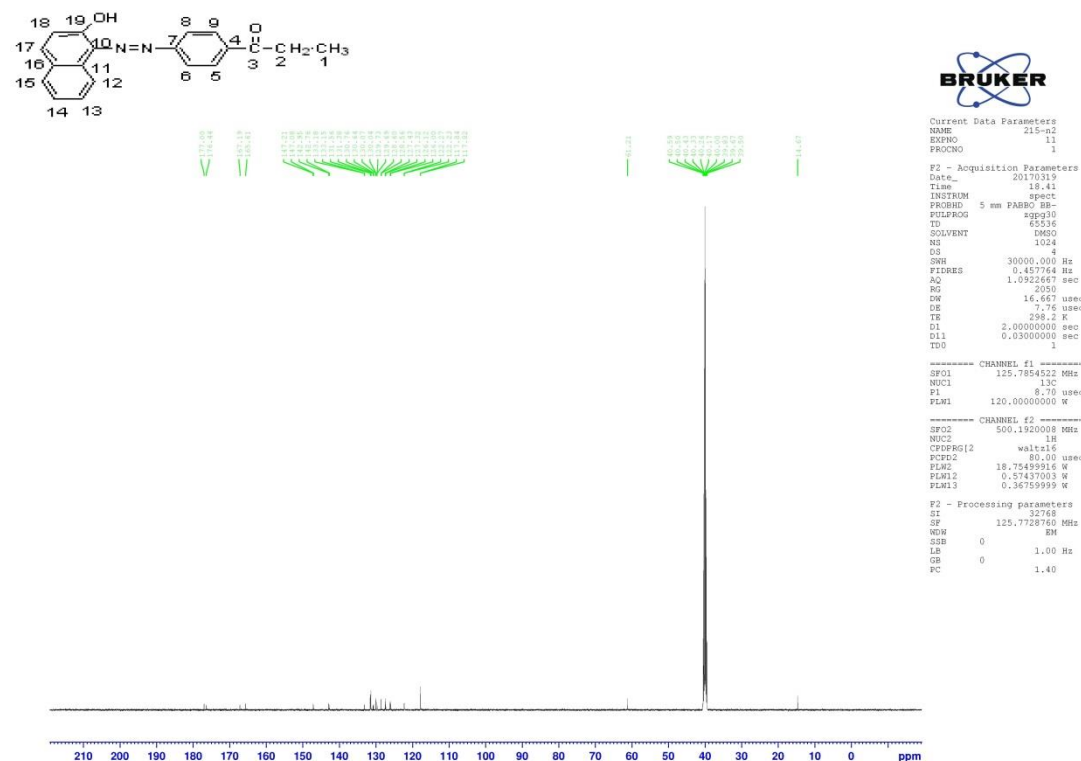


Figure 8: <sup>13</sup>C-NMR spectrum for prepared compound [N2]

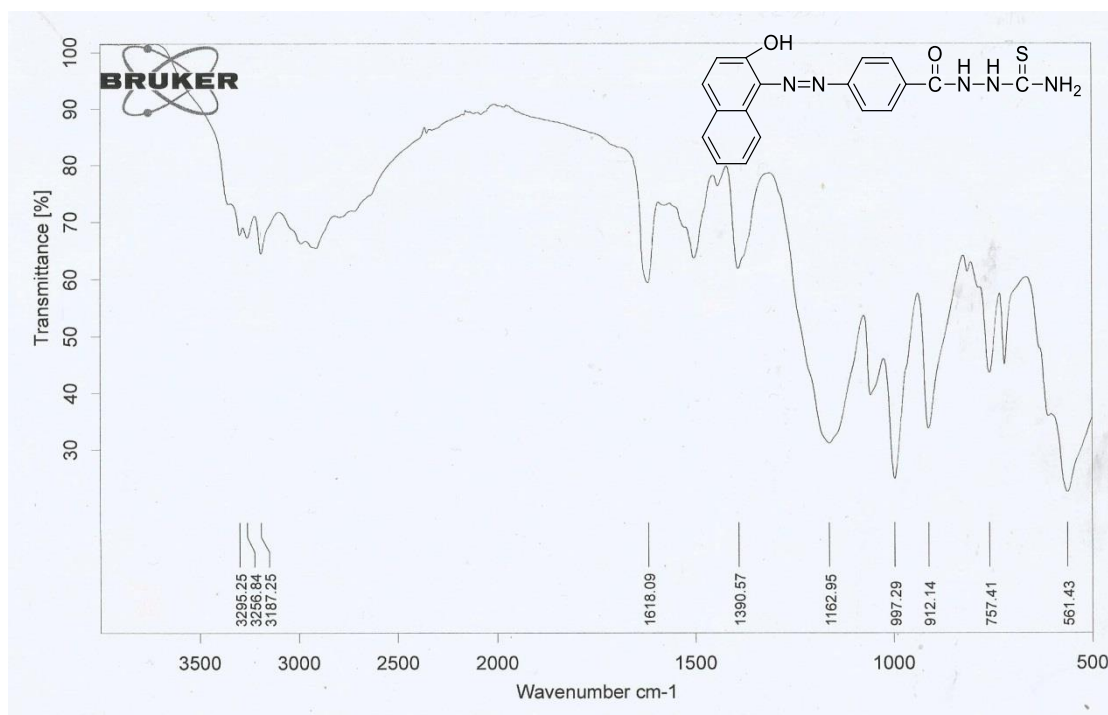


Figure 9: FTIR spectrum for prepared compound [N3]

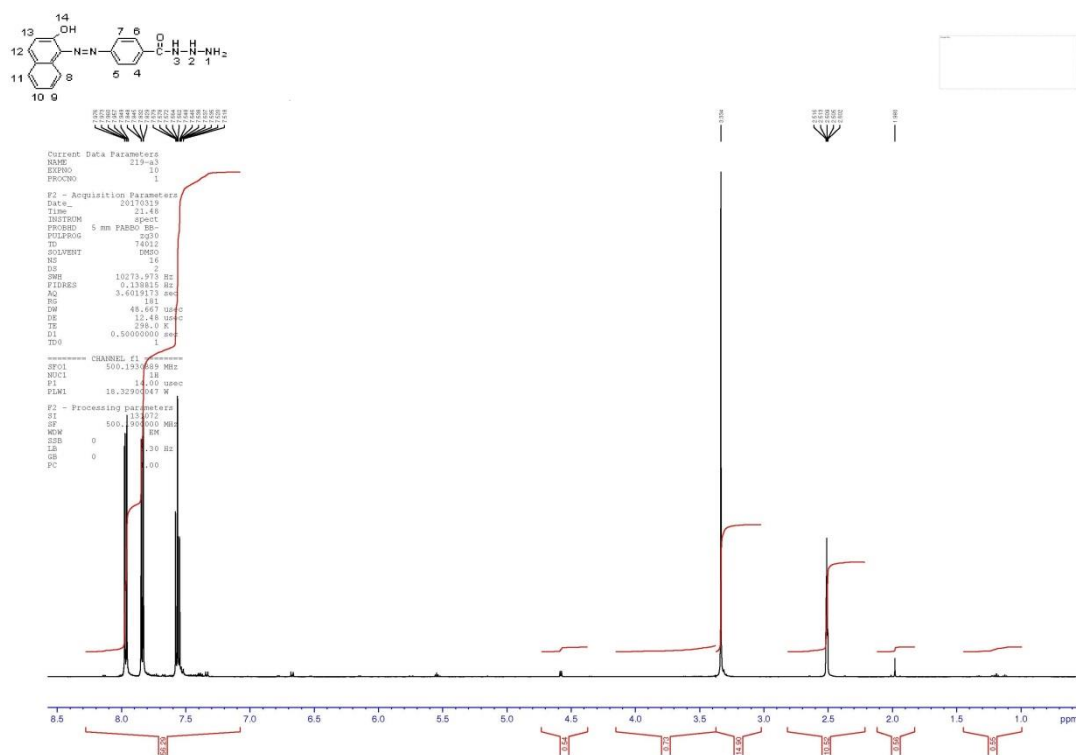


Figure 10: <sup>1</sup>H-NMR spectrum for prepared compound [N3]

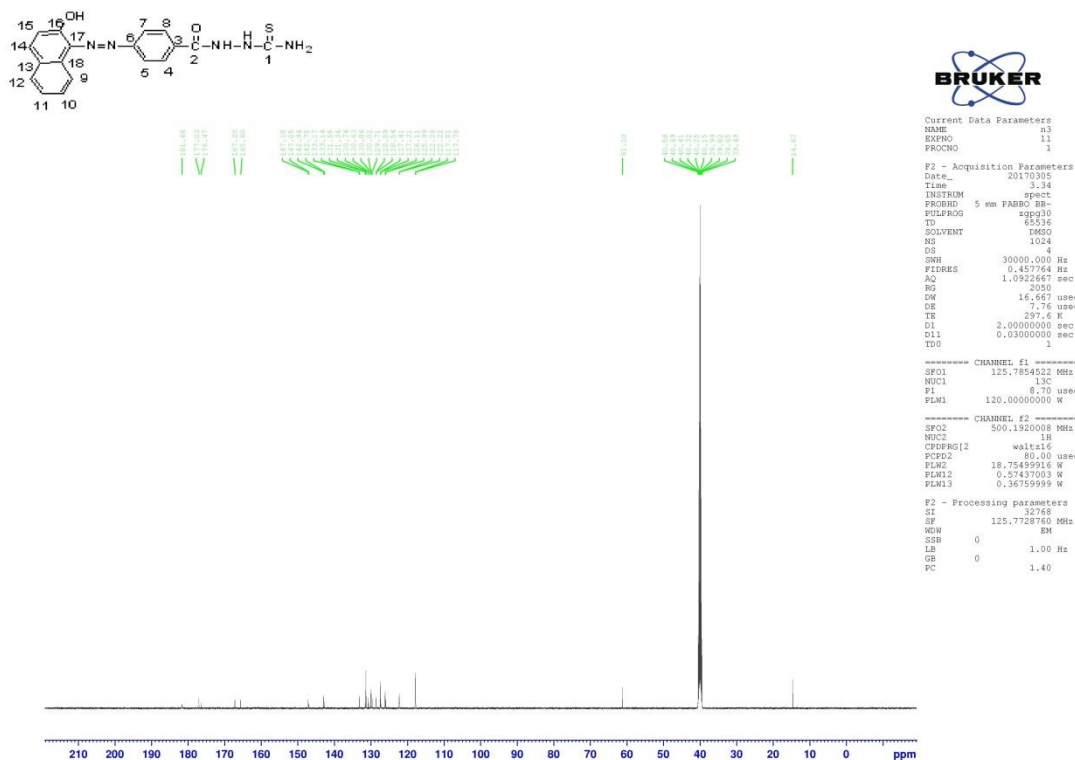


Figure 11: <sup>13</sup>C-NMR spectrum for prepared compound [N3]

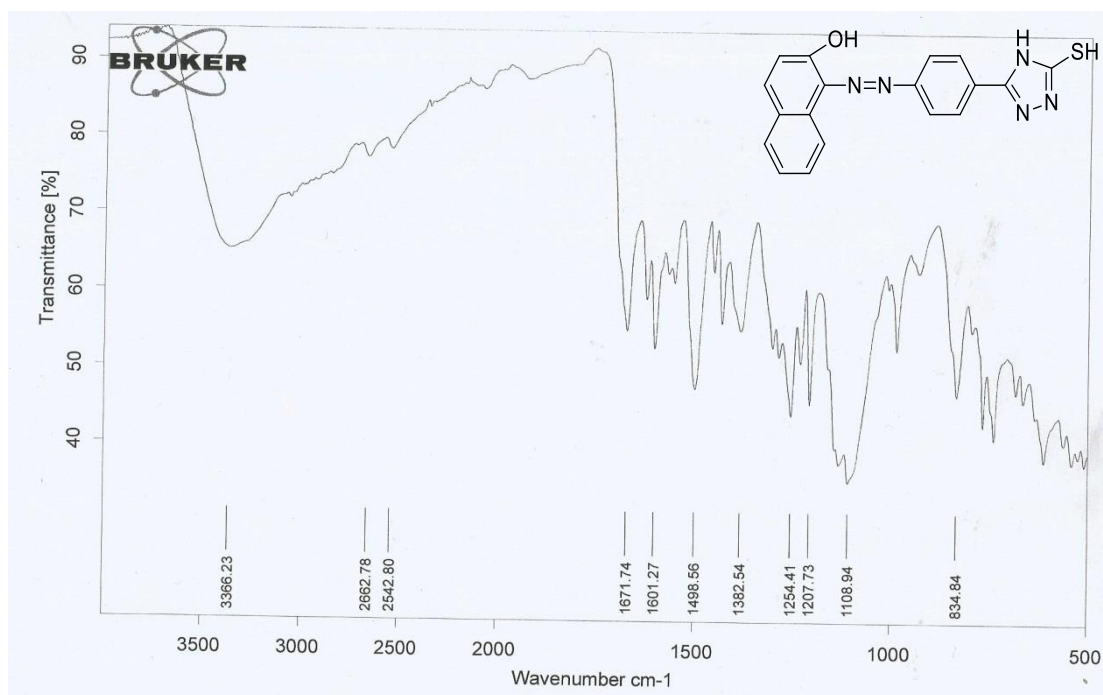


Figure 12: FTIR spectrum for prepared compound [N4]

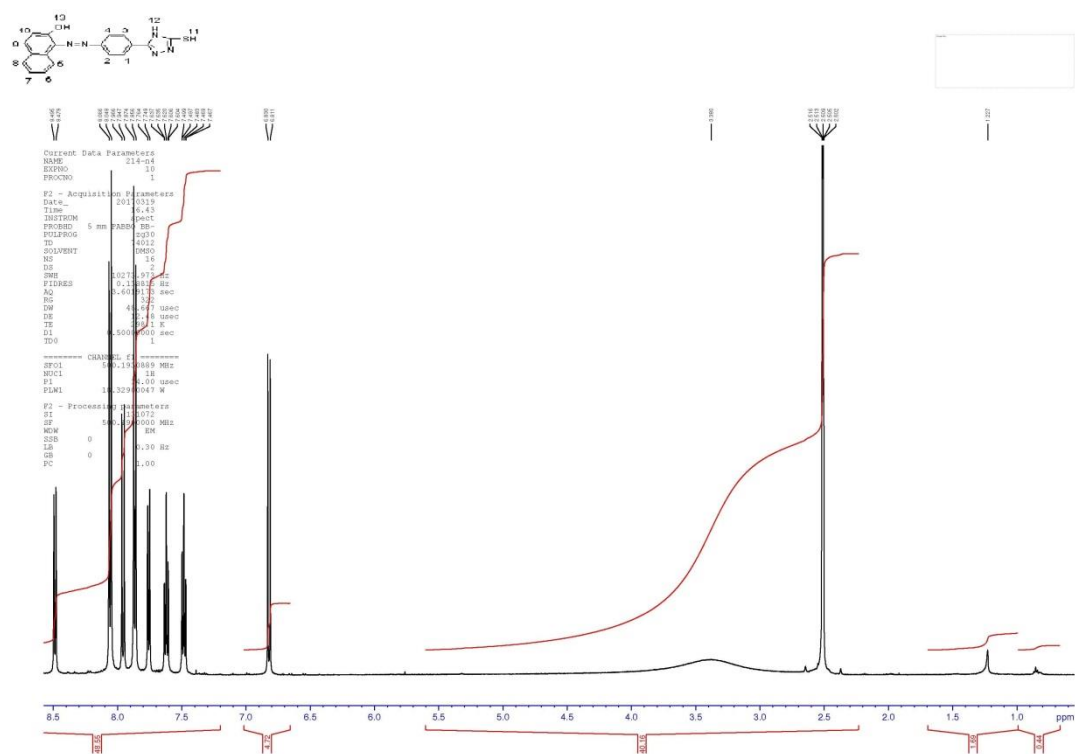


Figure 13: <sup>1</sup>H-NMR spectrum for prepared compound [N4]

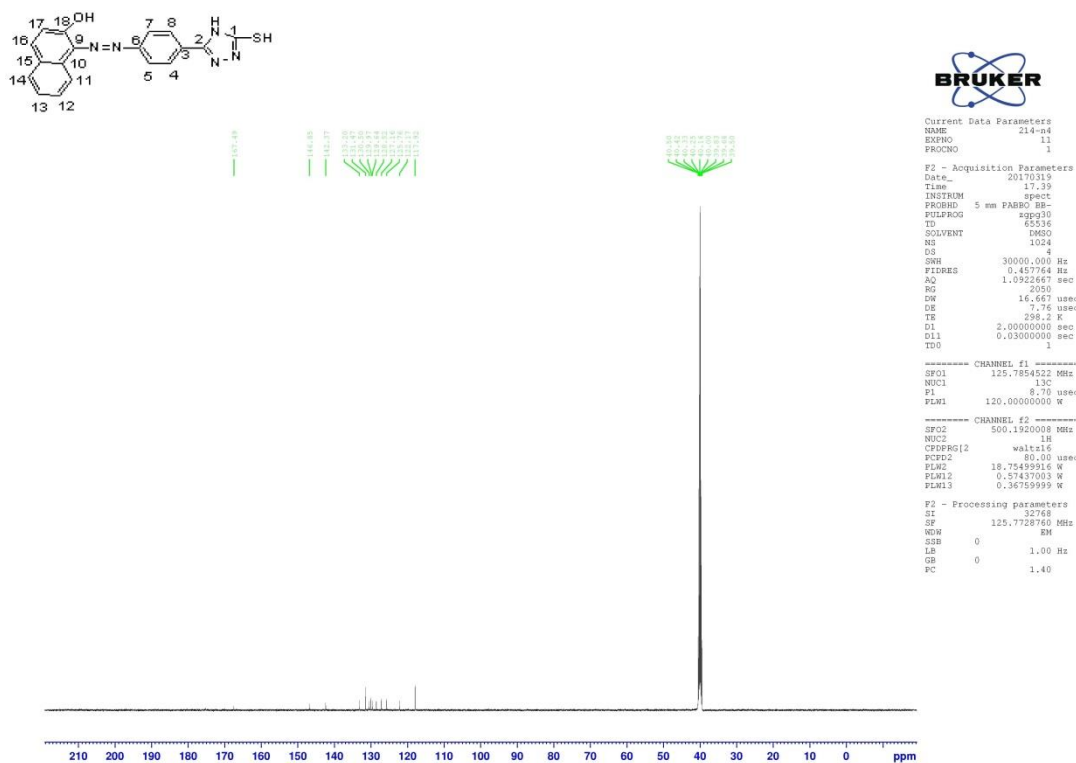


Figure 14: <sup>13</sup>C-NMR spectrum for prepared compound [N4]

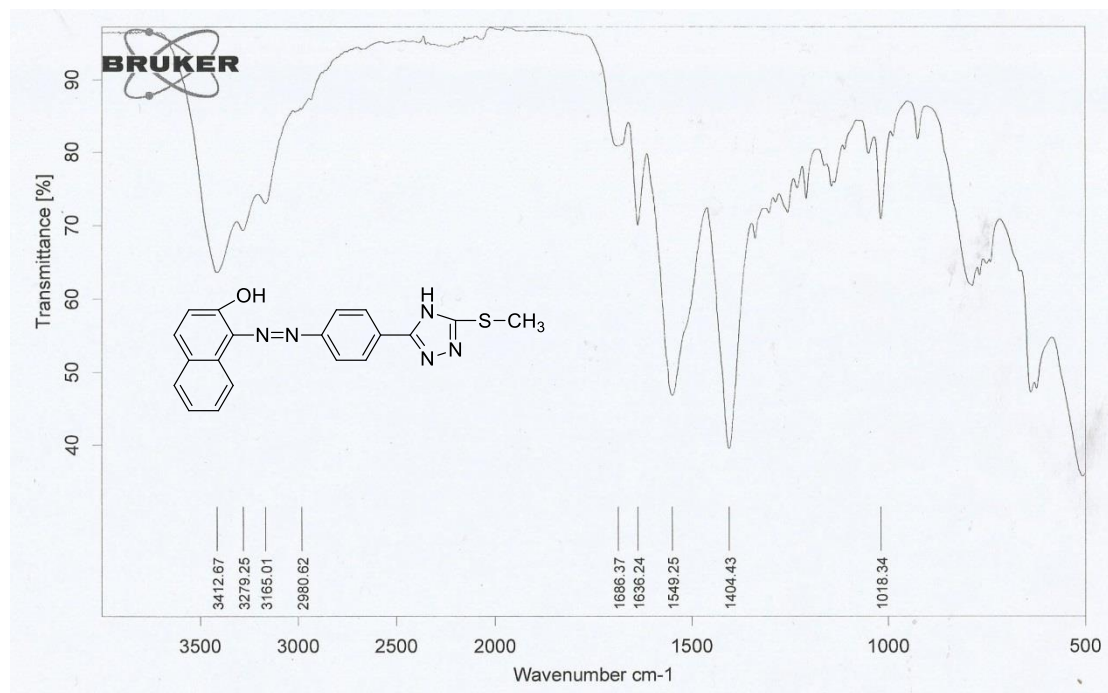


Figure 15: FTIR spectrum for prepared compound [N5]

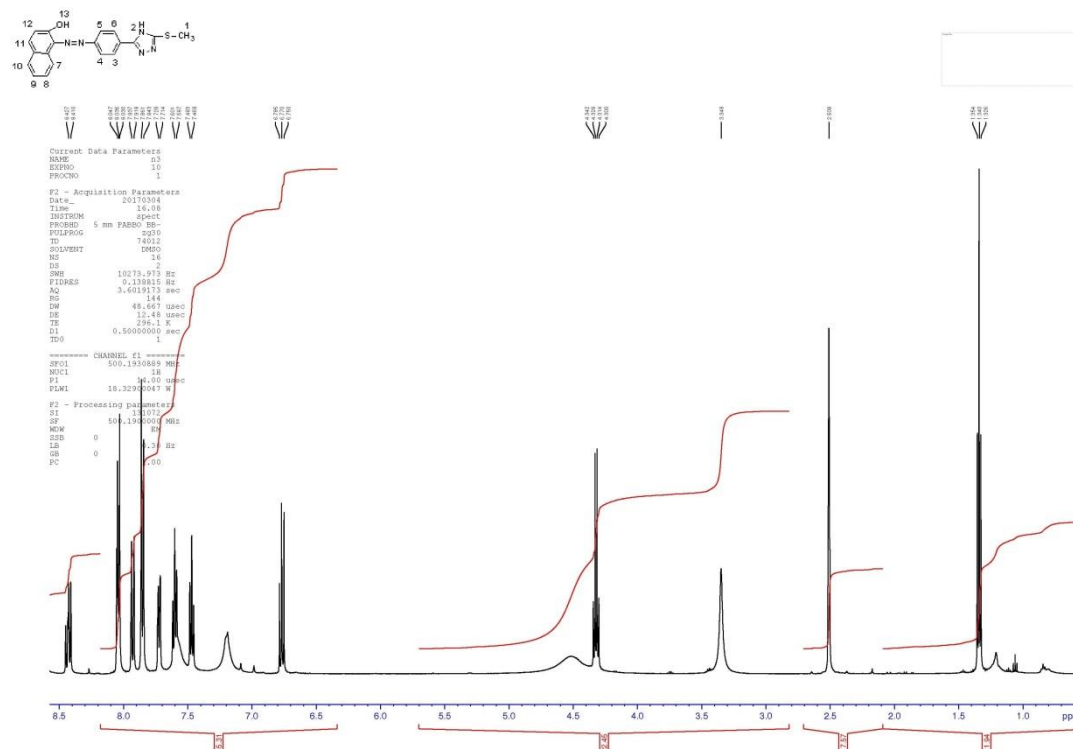


Figure 16: <sup>1</sup>H-NMR spectrum for prepared compound [N5]



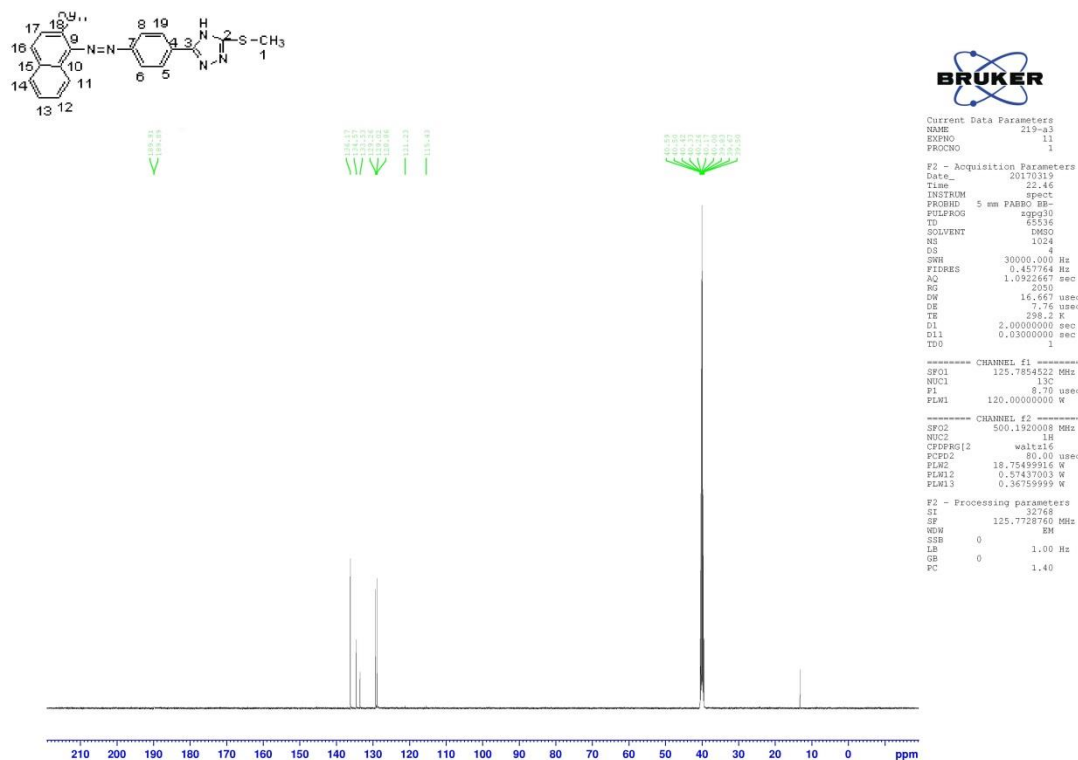


Figure 17: <sup>1</sup>H-NMR spectrum for prepared compound [N5]

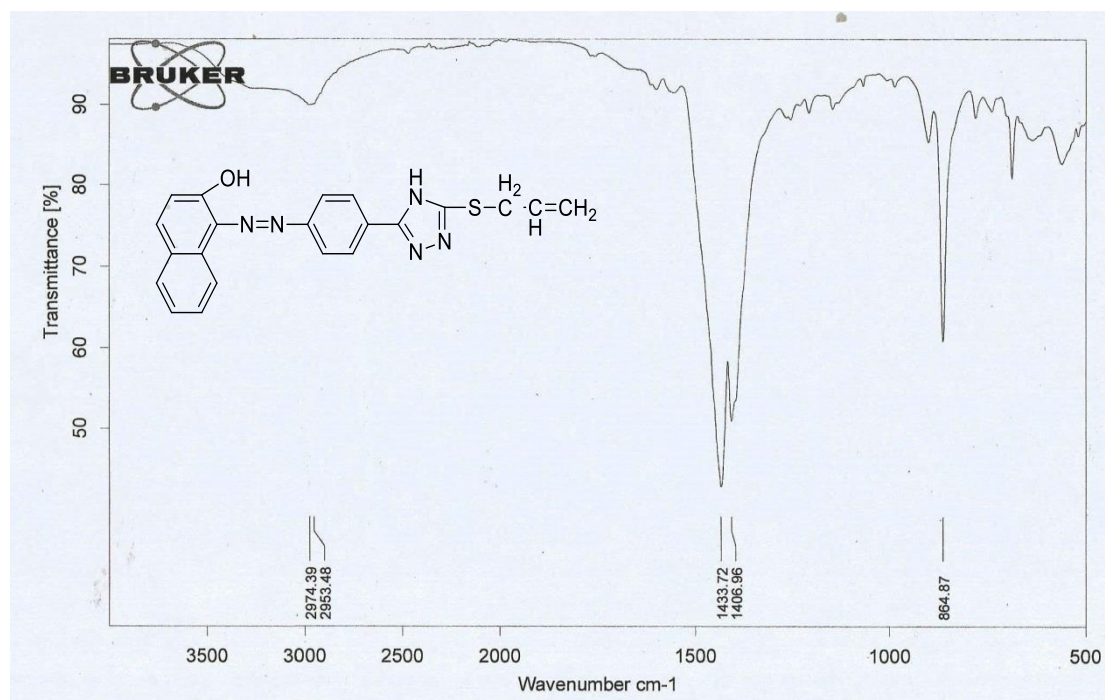


Figure 18: FTIR spectrum for prepared compound [N6]

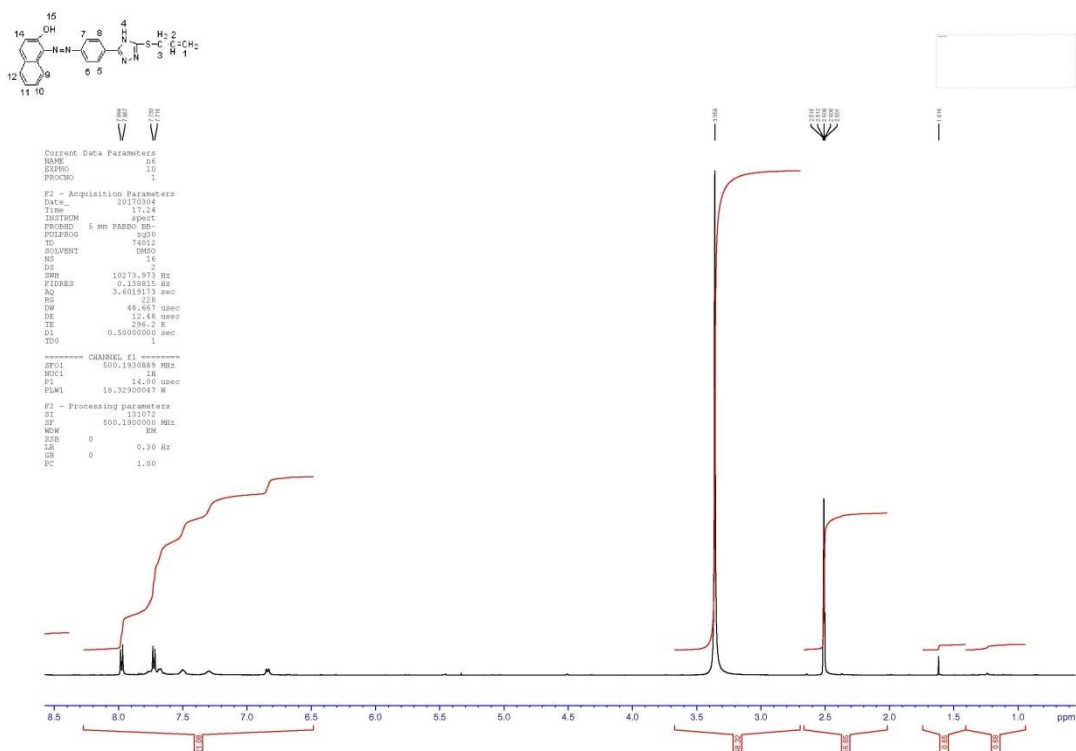


Figure 19: <sup>1</sup>H-NMR spectrum for prepared compound [N6]

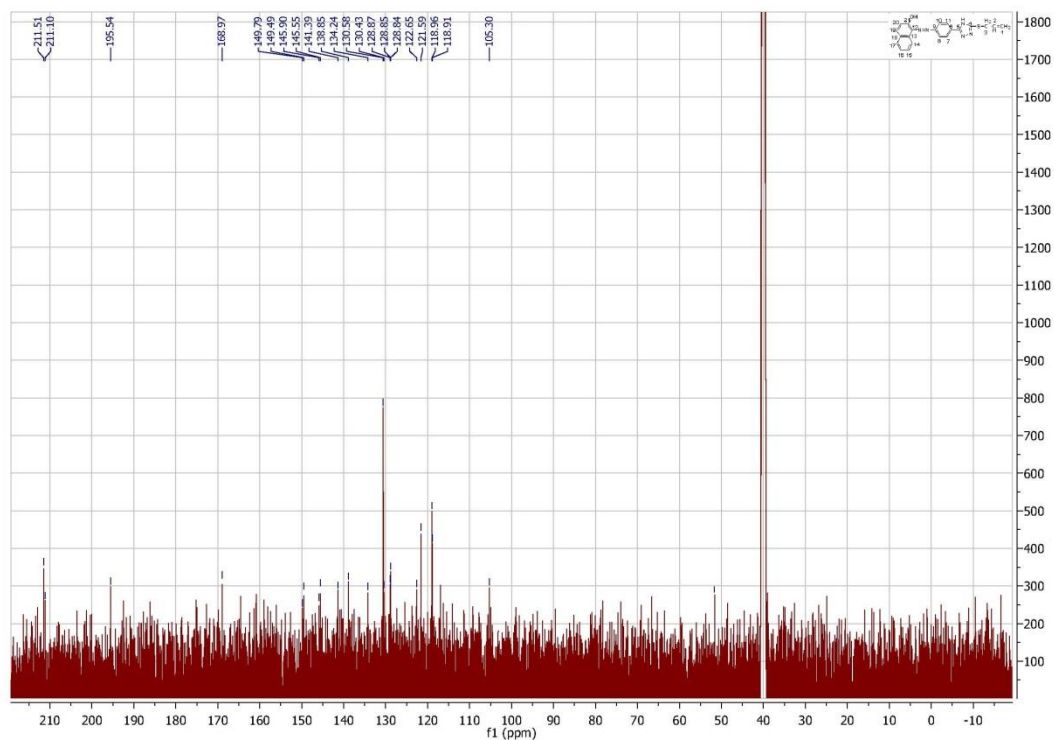


Figure 20: <sup>13</sup>C-NMR spectrum for prepared compound [N6]

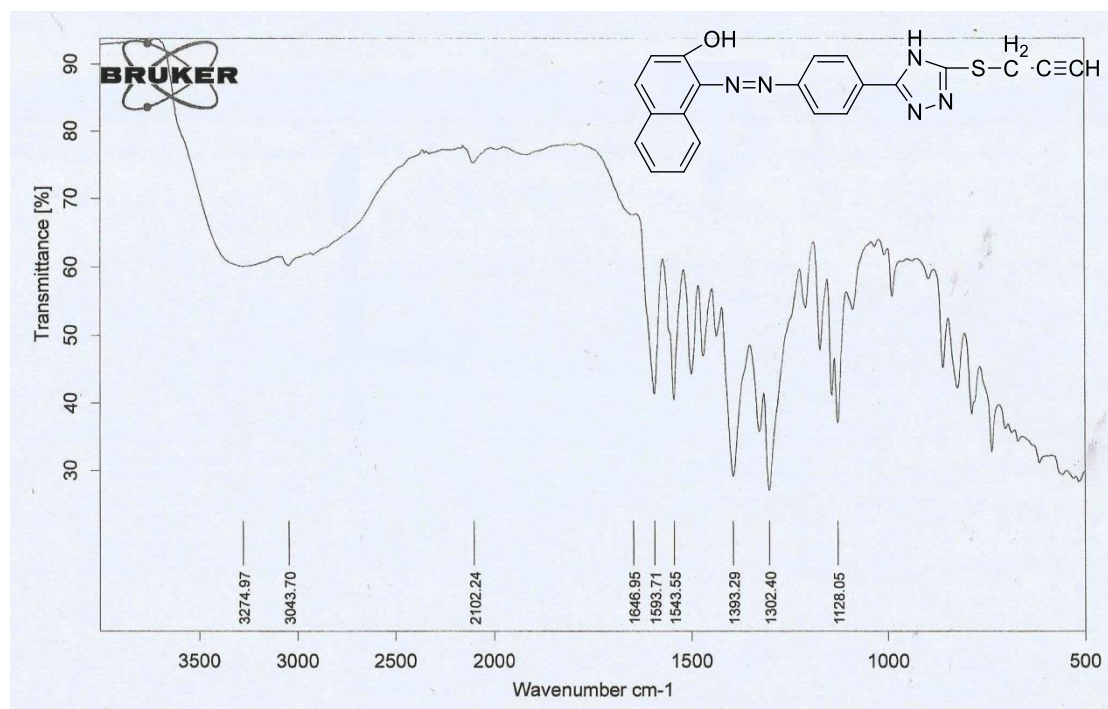


Figure 21: FTIR spectrum for prepared compound [N7]

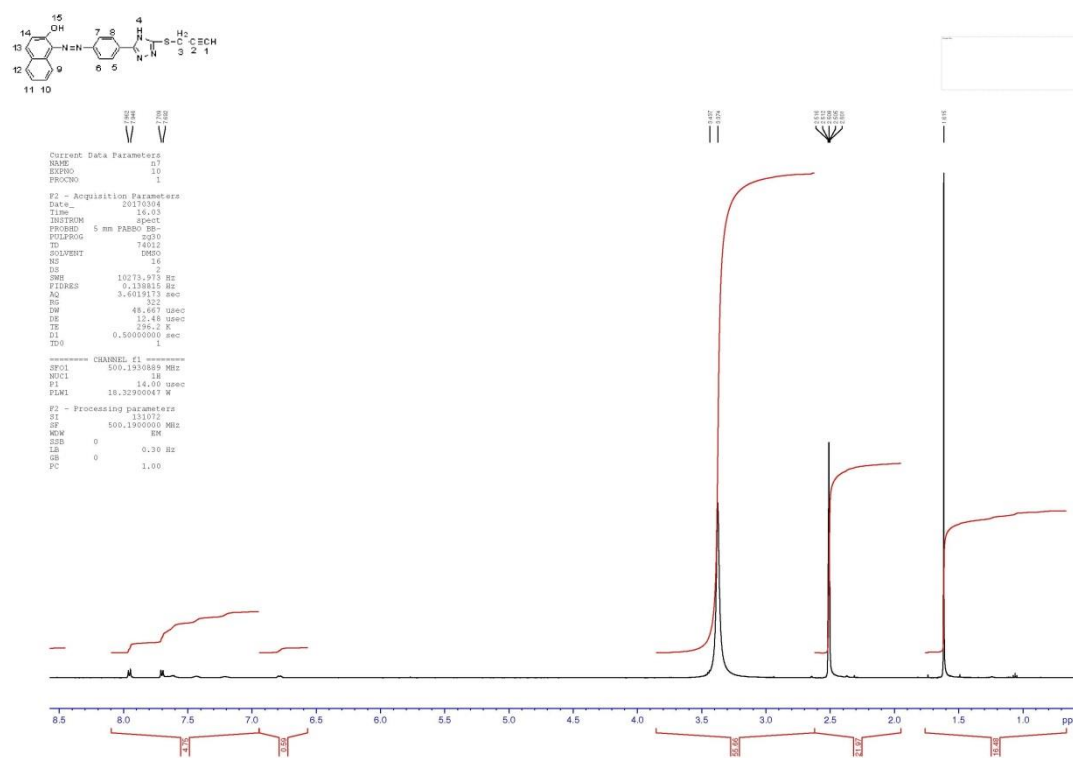


Figure 22: <sup>1</sup>H-NMR spectrum for prepared compound [N7]

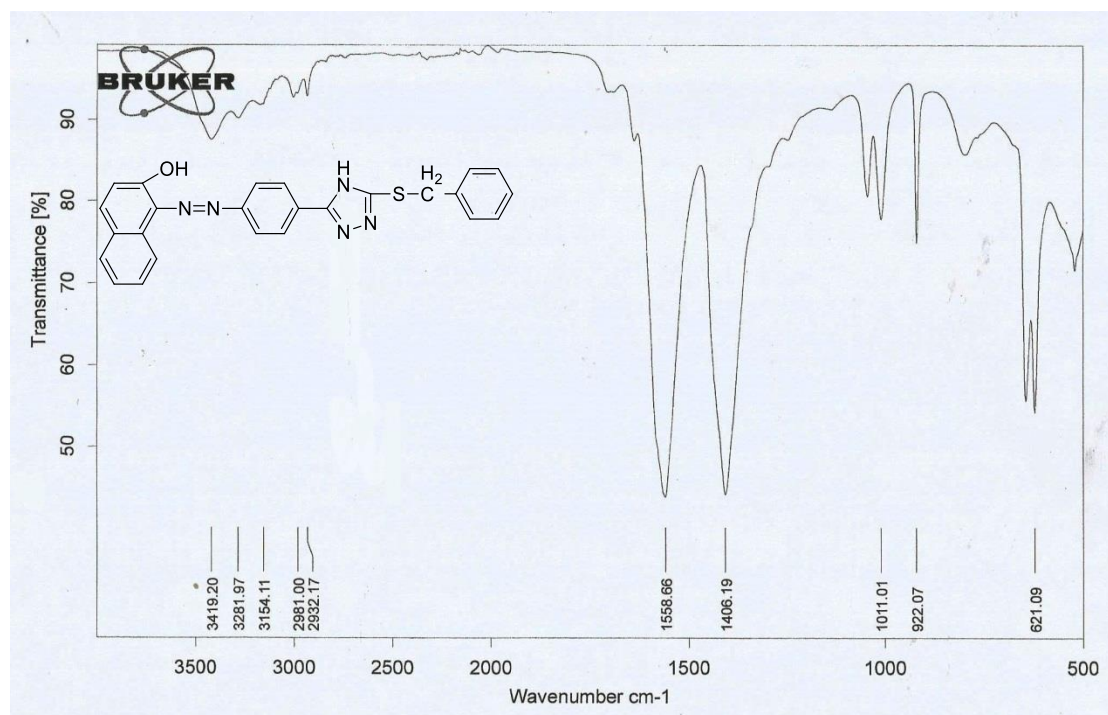


Figure 23: FTIR spectrum for prepared of compound [N8]

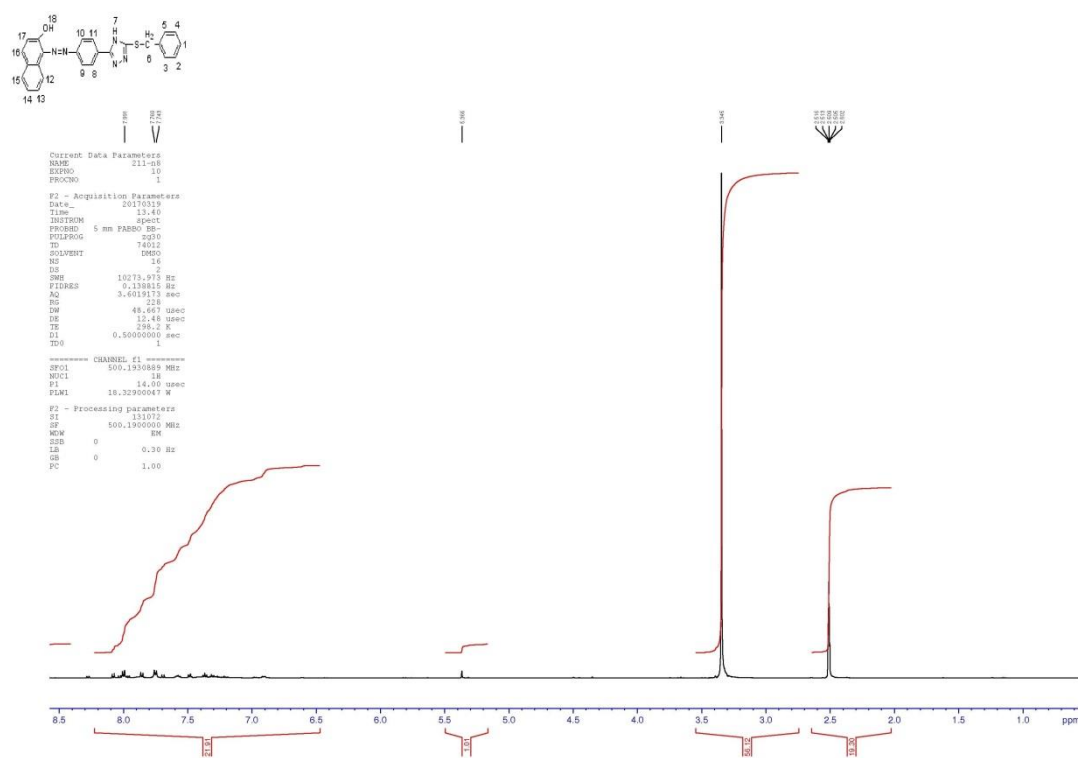


Figure 24: <sup>1</sup>H-NMR spectrum for prepared compound [N8]

## 4-Conclusions

1,2,4-Triazole derivatives were synthesized from the reaction of ester compound with thiosemicarbazide and then cyclization using sodium hydroxide. A range of new 1,2,4-triazole system have successfully been synthesized by sonication process incorporating methyl, allyl, propargyl and benzyl functionalities and their physical properties have been investigated.

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## الخلاصة

في هذا البحث تم تحضير مشتقات 4,2,1-تريازول من 4- [إيزو(2-هايدروكسي نثايل)] حامض البنزويك [N1] والتي حولت الى بنزوات 4- [إيزو(2-هايدروكسي نثايل)] [N2]. المركب [N2] يتم تفاعله مع الثايوسيمي كاريزايد وبعد ذلك تم غلقه بواسطة هيدروكسيد الصوديوم ليعطي 4,2,1 - تريازول. تم اضافة هاليدات الكيل مختلفة (يوديد المثل، كلوريد الاليل، كلوريد البروبرجايل وكلوريد البنزائل) الى 4-إيزو(2-هايدروكسي نثايل) [4,2,1-تريازول] [N4] باستعمال جهاز الامواج الصوتيه (sonicator) لغرض الكلة التريازول لينتج المركبات [N5-N8]. وقد شخصت المركبات المحضرة الجديدة بواسطة الاشعة تحت الحمراء ، الرنين النووي المغناطيسي ، والتحليل الطيفي للأشعة فوق البنفسجية المرئية تقنيات تحليل العناصر .

الكلمات المفتاحية: 2-هايدروكسي نثايل، 4,2,1 - تريازول، هاليدات الكيل