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Abstract

In this study, 2-amino-spiro[benzo]thiophene derivatives were prepared using the Gewald method. Subsequently, monoazo dyes were synthesized via conventional diazotization method, with 2-indanone or 1,3-indandione compounds as preferred coupling components. The chemical structures of the monoazo dyes have been characterized using several spectroscopic methods (FT-IR, 1H-NMR, 13C-APT NMR). The tautomeric forms of the dyes were discussed, and it was concluded that the hydrazo form is the dominant tautomer.

Keywords: 2-Aminothiophene, Spiro[benzo]thiophene, Azo dyes, Heterocyclic components

INTRODUCTION

Primary aromatic amine compounds are used in the synthesis of diazonium compounds. Several different methods can be applied for the synthesis of aromatic diazonium compounds. The selection of the method to be applied is influenced by the solubility or basic character of primary amines. Additionally, a strong acidic environment is preferred during the reaction to prevent the formation of by-products (such as triazines, etc.)[1]. Due to the azo chromophore group in their structure, diazonium compounds are colorful compounds and are mostly referred to as azo dyes. In fact, azo dyes constitute the largest class of synthetic dyes. The incorporation of a heterocyclic component in the diazo or coupling moiety of dyes positively affects their fastness properties. Some research suggests that azo dyes modified with heterocyclic structures exhibit bioactive properties[2-4]. In the literature, many different azo dyes containing various heterocyclic structures have been reported, such as thiophene[5], pyrazole[6], thiazole[7], pyrimidine[8], coumarin[9], indole[10], barbituric acid[11], etc. It has been reported that, in addition to their beneficial uses in various fields[12-14], azo compounds containing heterocyclic components exhibit toxicological and mutagenic properties, posing a risk to health[15].

Thiophene-based azo dyes, with a history spanning approximately 70 years, have been obtained in a wide range of colors with the presence of various chromophore groups[16]. Studies have shown that the durability properties of thiophene-based azo dyes are superior to many carbocyclic azo dyes. The observed changes with the addition of different substituents to the thiophene skeleton have been quite valuable for understanding the structure-activity relationship[17].

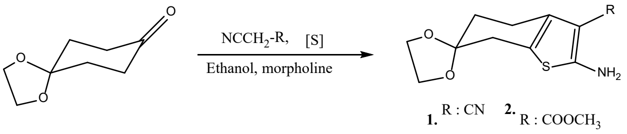
When we examine studies on thiophene-based azo compounds, we realize their potential applications in various fields such as heat- and light-resistant dyes[18-21], diverse biological activities[22-24], solar cells and non-linear optics[25-26], corrosion inhibitors[27-28], and more. Therefore, in this study, we synthesized two new azo compounds by diazotizing 2-aminothiophene derivatives and coupling them with 2-indanone and 1,3-indandione compounds. In the further stages of our research, the applications of the newly synthesized azo compounds will be investigated, with a priority given to their biological activities, and their evaluation as useful products will be ensured.

MATERIAL AND METHODS

For the determination of melting points, a capillary tube was used, and the Gallenkamp apparatus (without any adjustments) was employed. Infrared spectra (4000-400 cm-1) were acquired utilizing a Thermo Nicolet 6700 FT-IR spectrometer equipped with Attenuated Total Reflectance. For nuclear magnetic resonance spectra, the Bruker AVANCE III instrument (400 MHz for ^{1}H-NMR; 100 MHz for ^{13}C-NMR) and TMS as an internal standard were used. All reagents (Sigma-Aldrich) employed without additional purification.

2.1 Synthesis of amine compounds (1,2).

2-amino-4,7-dihydro-5H-spiro[benzo[b]thiophene-6,2'-[1,3]dioxolane]-3-carbonitrile (1) and methyl 2-amino-4,7-dihydro-5H-spiro[benzo[b]thiophene-6,2'-[1,3]dioxolane]-3-carboxylate (2) were synthesized based on the method outlined in the literature[29-34]. In this reaction, malononitrile (0.66 g, 0.01 mol) was used for compound 1, while methylcyanoacetate (1.00 g, 0.01 mol) for compound 2. Additionally, 1,4-dioxaspiro[4.5]decan-8-one, sulfur and morpholine were added in equimolar amounts. The reaction mixture was stirred at room temperature in absolute ethanol (15 ml). Due to the exothermic nature of the reaction, the temperature increased to 50°C. The reaction ended after 72 hours with the formation of a thick precipitate. The product formed after pouring the reaction mixture into water was collected by filtration. It was then purified by recrystallization (via EtOH) (Scheme 1).



Scheme 1. Synthesis demonstration of amine compounds (1: 2-amino-4,7-dihydro-5H-spiro[benzo[b]thiophene-6,2'-[1,3]dioxolane]-3-carbonitrile; 2: methyl 2-amino-4,7-dihydro-5H-spiro[benzo[b]thiophene-6,2'-[1,3]dioxolane]-3-carboxlate).

2.2 Diazotization procedure

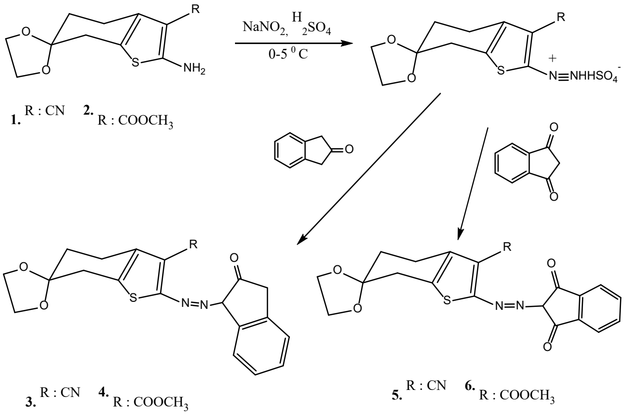
While dry $NaNO_2$ (0.138g, 0.002 mol) was added gradually to concentrated H_2SO_4 (1.1 ml), the reaction temperature rose to 65°C. Then, it was cooled to around 5°C, and with continuous stirring, CH_3COOH (20 ml) was added dropwise. Throughout this process, care was taken to ensure that the temperature did not exceed 15°C. Then, the reaction mixture (0-5°C) was added dropwise with compound 1 (0.472 g, 0.002 mol) or compound 2 (0.538 g, 0.002 mol) and continued to stir at same temperature for 2 h, thereby ensuring the formation of diazonium salt. The excess nitric acid was removed from the solution using urea. Diazonium salt solutions can only remain stable for short periods and at low temperatures. Therefore, immediate coupling reaction should be ensured following the synthesis. The reaction scheme for this experimental stage is illustrated in Scheme 2.

2.3 Coupling procedure

For coupling solution, 2-indanone (0.266 g, 0.002 mol) (or 1,3-indandione (0.292 g, 0.002)) was dissolved in a mixture containing CH_3COOH (10 ml), H_2O (5 ml) and CH_3COONa (5 g). The temperature was lowered by an ice-bath and then was slowly dripped in to the diazonium solution with vigorous stirring. The pH was modified using an aqueous 10% CH_3COONa. The reaction was terminated after 2 h, and the temperature was allowed reach to ambient temperature. The crude coupling product was separated and purified by recrystallization (DMF-water)[35] (Scheme 2).

The physical and spectral data of obtained compounds were shown in Table 1.

Additional, the spectrum graphics of compounds (S1-S12) are given in Supplementary
Material.



Scheme 2. Synthesis demontstration of diazonium compounds (**3-6**).

Table1. Physical and spectral data of diazonium compounds (**3-6**)

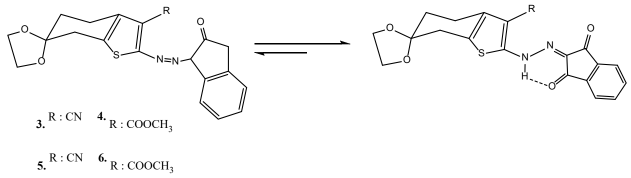
Compound number, Yield, Color, m.p. (°C)	FT-IR (ū, cm^{-1})	^{1}H-NMR (λ, ppm)	^{13}C-APT (λ, ppm)
3 68% Yellow 250-252	3257 (N-H) 3085 (Ar-H) 2962-2895 (Aliph. C-H) 2221 (C≡N) 1662 (C=O)	9.65 (s, 1H, NH) 7.98-7.94 (d, 1H, J= 7.40, Hz, Ar-H) 7.52 (d, 1H, Ar-H) 7.47-7.43 (m, j= 7.40 Hz, 2H, Ar-H) 4.09 (s, 4H, CH_2) 3.79 (s, 2H, CH_2) 2.91 (s, 2H, CH_2) 2.87-2.84 (t, 2H, j= 6.38 Hz, CH_2) 2.01-1.98 (t, 2H, J= 6.38 Hz, CH_2)	Pozitive amplitude : 161.96, 147.50, 131.41, 127.89, 126.06, 113.69, 107.50, 94.47, 64.80, 34.29, 30.58, 23.14 Negative amplitude : 132.84, 132.06, 129.77, 129.77
4 60% Dark yellow 204-205	3177 (N-H) 3082 (Ar-H) 2987-2903 (aliph. C-H) 1676 and 1658 (2 C=O)	12.34 (s, 1H, NH) 7.86 (t, 1H, Ar-H) 7.58-7.48 (m, 3H, Ar-H) 4.06 (s, 4H, CH_2) 3.94 (s, 3H, CH_3) 3.76 (s, 2H, CH_2) 3.06-3.02 (t, 2H, J= 6.38 Hz, CH_2) 2.93 (s, 2H, CH_2) 1.99-1.96 (t, 2H, J=6.38 Hz, CH_2)	Pozitive amplitude : 166.81, 163.81, 148.30, 134.01, 131.60, 130.13, 125.01, 112.24, 108.41, 64.84, 38.83, 35.01, 31.72, 25.23 Negative amplitude : 132.76, 131.12, 126.99, 51.44
5 55% Pale brown 238-240	3201 (N-H) 3084 (Ar-H) 2962-2899 (aliph. C-H) 2212 (C≡N) 1679 and 1621 (2C=O)	12.39 (s, 1H, NH) 8.27-8.22 (t, 1H, J= 7.20 Hz, Ar-H) 7.94-7.89 (t, 1H, J= 7.20 Hz, Ar-H) 7.84-7.75 (dt, 2H, Ar-H) 3.99 (s, 4H, CH_2) 2.83 (s, 2H, CH_2) 2.64 (t, 2H, CH_2) 1.87 (t, 2H, CH_2)	Pozitive amplitude: 165.60, 148.00, 146.80, 131.06, 130,11, 125.70, 113.76, 107.46, 94.09, 63.70, 33.60, 30.31, 22.31. Negative amplitude : 134.64, 131.35, 129.27, 124.19
6 58% Brown 125-127	3349 (N-H) 3082 (Ar-H) 2960-2878 (aliph. C-H) 1716, 1667 and 1615 (3C=O).	11.93 (s, 1H, NH) 7.82 (t, 1H, Ar-H) 7.49-7.38 (m, 3H, Ar-H) 4.06 (s, 4H, CH_2) 3.86 (s, 3H, CH_3) 3.05-3.02 (t, 2H, J= 6.42 Hz, CH_2) 2.87 (s, 2H, CH_2) 1.98-1.95 (t, 2H, J=6.42 Hz, CH_2)	Pozitive amplitude: 166.99, 162.90, 148.29, 133.68, 131.72, 124.36, 130.20, 111.93, 107.85, 38.75, 35.09, 31.98, 25.23. Negative amplitude : 132.12,130.01, 127.63

[3] 2-((2-oxo-2,3-dihydro-1H-inden-1-yl)diazenyl)-4,7-dihydro-5H-spiro[benzo[b]thiophene-6,2'-[1,3]dioxolane]-3-carbonitrile

[4] Methyl 2-((2-oxo-2,3-dihydro-1H-inden-1-yl)diazenyl)-4,7-dihydro-5H-spiro[benzo[b]thiophene-6,2'-[1,3]dioxolane]-3-carboxylate

[5] 2-((1,3-dioxo-2,3-dihydro-1H-inden-2-yl)diazenyl)-4,7-dihydro-5H-spiro[benzo[b] thiophene-6,2'-[1,3]dioxolane]-3-carbonitrile

[6] Methyl 2-((1,3-dioxo-2,3-dihydro-1H-inden-2-yl)diazenyl)-4,7-dihydro-5H-spiro[benzo[b] thiophene-6,2'-[1,3]dioxolane]-3-carboxylate



3. R : CN 4. R : $COOCH_3$

5. R : CN 6. R : $COOCH_3$

Scheme 3. Tautomeric form of diazo compounds.

CONCLUSION

Amine compounds were synthesized by the Gewald's method, based on the ketone compounds 1,4-dioxaspiro[4.5]decan-8-one. The preparation of diazonium compounds of amino thiophene compounds differs considerably from aniline-derived compounds. For this reason, it is necessary to be extremely careful when preparing diazonium salts of these compounds. Synthesis of compounds with high yields is possible when the relevant literature is followed. It was observed that the compounds obtained as a result of the interlocking of 1 and 2 amine compounds with 2-indanone and 1,3-indandione preferred the hydrazo form due to the low area of the NH groups (Scheme 3).

The fact that the NH peak in the docked compounds is at (3-6), 9.65, 12.34, 12.39, 11.93 ppm, respectively, indicates that the compounds are in the form of hydrazo. The aromatic peaks of the compounds were detected in the range of 7.98-7.43 ppm for compound no. 3, and in the range of 7.86-7.48 ppm for compound no. 4, in the range of 8.27-7.75 ppm for compound no. 5, in the range of 7.82-7.38 ppm for compound no. 6. The CH_2 group between the two oxygens of the compounds was observed as a singlet of 4.09, 4.06, 3.99 and 4.06 ppm, respectively. Additionally, the CH_3 group belonging to the ester group was observed 3.94 ppm for substance 4 and 3.86 ppm for substance 6. It was observed that the CH_2 group, which was not hydrogen in its neighbor in the aliphatic ring structure, was divided into triplets at (3-6), 3.79 ppm, 2.93 ppm, 2.83 ppm, 2.87 ppm, respectively, and the neighboring CH_2 groups were split into triplets at 2.86 ppm, 3.04 ppm, 2.64 ppm, 3.02 ppm, and the other CH_2 group was at 1.99 ppm, 1.98 ppm, 1.87 ppm, 1.97 ppm.

The compounds are present in the hydrazo tautomer on the ^{13}C-APT NMR spectrum.

In the ^{13}C-APT NMR spectrum of the compounds, it was observed that the carbon peaks of the non-hydrogen C and CH_2 groups with two hydrogen atoms on them came out at positive amplitude. Carbons in the indanone ring and with hydrogen atom on it have been observed in the spectrum ^{13}C-APT at negative amplitude and in the range of 134.64 to 124.19 ppm.

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Supplementary Material

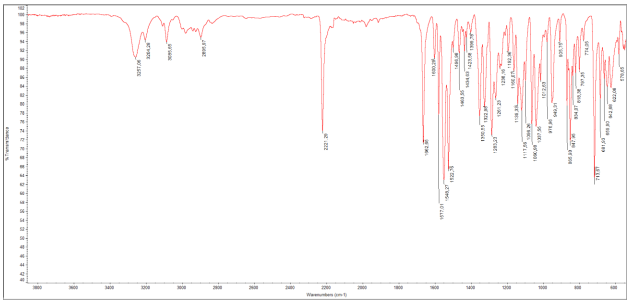

Figure S1. FT-IR spectrum of compound 3

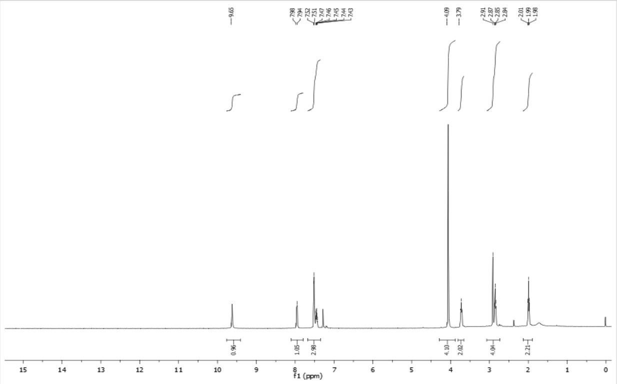

Figure S2. ^{1}H-NMR spectrum of compound 3

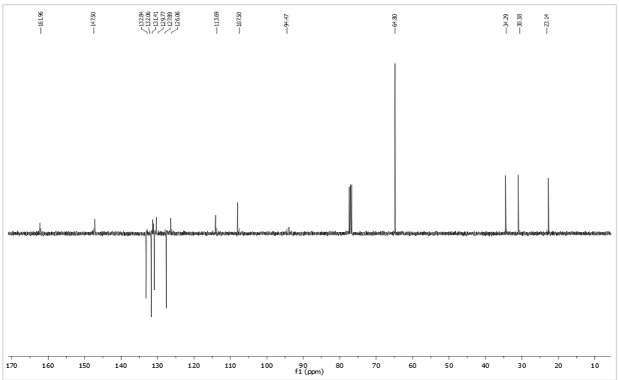

Figure S3. ^{13}C-NMR APT spectrum of compound 3

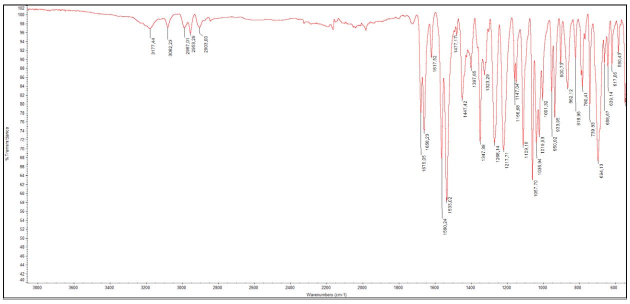

Figure S4. FT-IR spectrum of compound 4

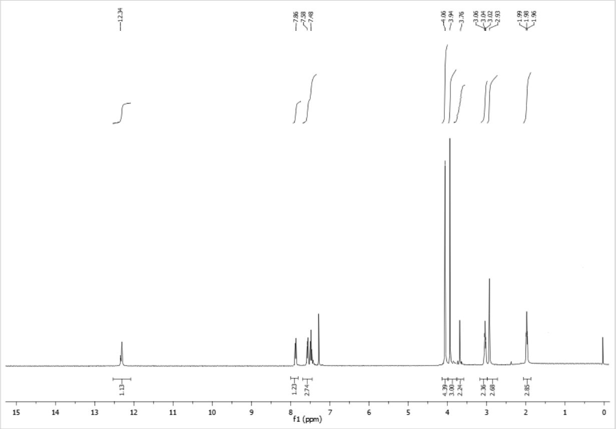

Figure S5. ^{1}H-NMR spectrum of compound 4

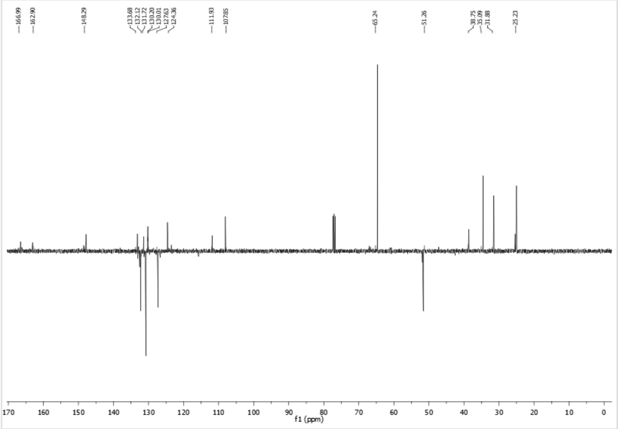

Figure S6. ^{13}C-NMR APT spectrum of compound 4

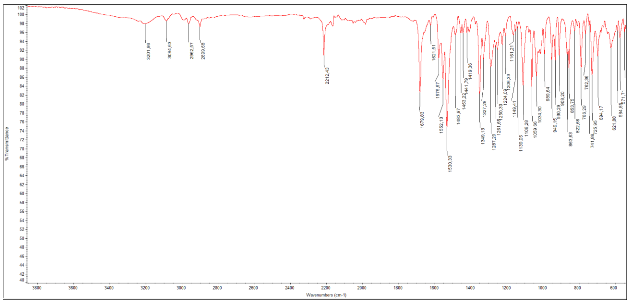

Figure S7. FT-IR spectrum of compound 5

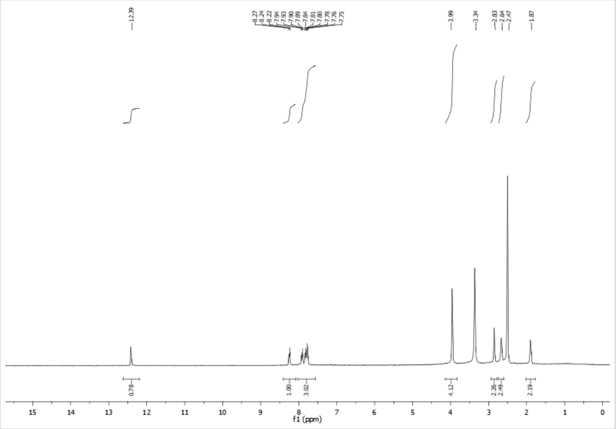

Figure S8. ^{1}H-NMR spectrum of compound 5

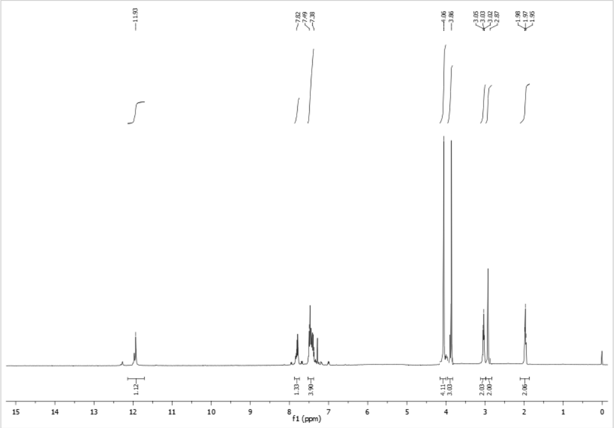

Figure S11. ^{1}H-NMR spectrum of compound 6

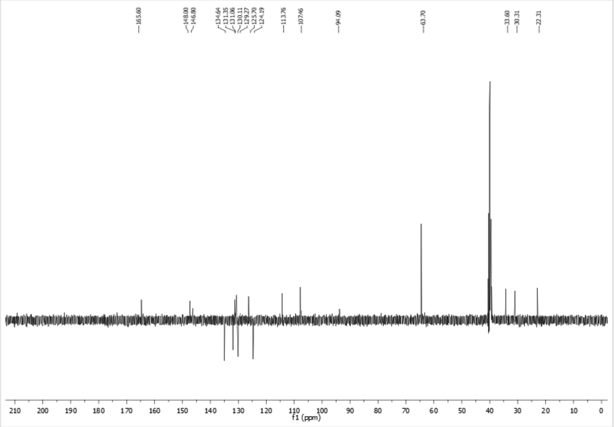

Figure S9. ^{13}C-NMR APT spectrum of compound 5

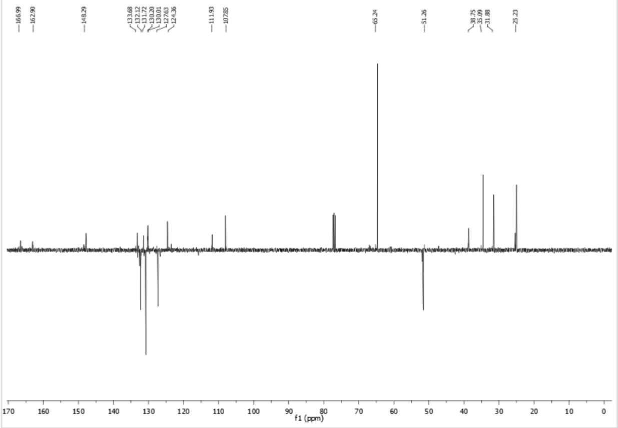

Figure S12. ^{13}C-NMR APT spectrum of compound 6

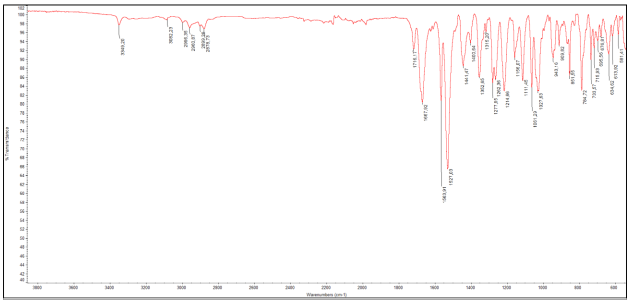

Figure S10. FT-IR spectrum of compound 6