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Synthesis of Pyrazoles and Pyrazolones Moiety from diazonium salt of 1,3,4-thiadiazole

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Abstract

The diazonium salt of [2,2'-bi(1,3,4-thiadiazole)]-5,5'-diamine (BTD) and 5-(1-phenylprop-1-en-2-yl)-1,3,4-thiadiazol-2-amine (PTA) was coupled with ethyl acetoacetate, ethyl benzoylacetate and benzylacetone to give the corresponding diazo compounds under basic media. These products were allowed to react with hydrazine hydrate and phenylhydrazine under conventional method to give pyrazole and pyrazolone derivatives in high yields.

Introduction

Heterocyclic compounds have acquired more importance in recent years because of the broad pharmacological activities[1]. Pyrazole and Pyrazolone derived from [2,2'-bi(1,3,4-thiadiazole)]-5,5'-diamine (BTD) and 5-(1-phenylprop-1-en-2-yl)-1,3,4-thiadiazol-2-amine PTA with 2-amimo- 1,3,5-thiadiazole have a particular value due to both their wide spectrum of biological activity and their wide ranging utility as synthetic tools in the design of various bioactive molecules[2].

Pyrazolone is a five-membered lactam ring which contains two nitrogens and a ketone in the same molecule. The chemistry of pyrazolone compounds were started by knorr in 1883 and reported the first pyrazolone derivative and followed by other methods[3]. The pronounced synthetic utility of heterocycles in the area of pharmaceuticals, dyes and pigment[4], technology and natural products Pyrazolone or BTD and PTA derivatives are important series of heterocyclic compounds, which have been shown to have diverse biological properties such as cytotoxic, anti-inflammatory[5], antimicrobial[6], antioxidant[7], antifungal[7], antiviral[8], antitumor[9], analgesic[10].

The approach reported here deals with the synthetic of some new pyrazolones start in 1,3-dicarbonyl compound such as benzoylacetone ethylacetoacetate and ethylbenzoylacetate after coupled with BTD and PTA and then reacted with hydrazine or phenylhydrazine to give Pyrazole and pyrazolone derivatives using simple methodology ,i.e. conventional and benign multicomponent procedure.

Materials and Methods

Melting point were determined on a Stuat melting apparatus SMP30 Infrared spectra were recorded on a Bruker, FT-IR Ultra-Violet spectra were recorded on Shimadzu UV – 1650 pc, UV-Visible spectrophotometer, Japan, using chloroform as a solvent. ^{1}HNMR and ^{13}C-NMR, 400.20MHz, Bruker BioSpin GmbH, Iran.

Synthesis of [2,2'-bi(1,3,4-thiadiazole)]-5,5'-diamine (1)[11].

The 0.2 mole of thiosimemicabazide was placed in a round bottom flask (100 mL), then a small amount of potassium hydroxide was used, dissolved in (2 mL) distilled water, (0.1 mole) of oxalic acid was added, then (6 mL) of concentrated sulfuric acid was added in the form batches, then the mixture reflux for eight hours, after which the mixture is cooled, filtered, and recrystallized by absolute ethanol to give a yellow precipitate, its melting point is (241 ^{0}C), its chemical formula is $C_4H_4N_6S_2$, and its molecular weight is 200.24 g/mol.

Synthesis of 5-(1-phenylprop-1-en-2-yl)-1,3,4-thiadiazol-2-amine (2)[12], [13].

In a beaker (0.04 mole) of thiosemicarbazide was dissolved in (20 mL) of absolute ethanol, a small amount of sodium acetate was added to it and then added slowly to a round bottom flask contain (0.04 mole) of ⍰-methyl cinnamaldehyde was dissolved in (20 mL) of absolute ethanol, , and then the mixture was refluxed for four hours, then it was cooled and the precipitate, which was recrystallized, was filtered using absolute ethanol, to give melting point (174-176 ^{0}C) and the formula is $C_{11}H_{13}N_3S$ and its molecular weight is (219.3g/mole). (0.1 mole) of thiosemicarbazone compounds were dissolved in (20 mL) of dry dioxane, and (0.002 mole) of iodine and (0.004 mole) of potassium carbonate were added to it, then the mixture was refluxed for four hours, after which the solution was concentrated under a sieve pressure, then it was cooled and the formed precipitate was filtered. The solution, which was recrystallized from absolute ethanol, to give a melting point (110 – 111 ^{0}C) and molecular formula $C_{11}H_{11}N_3S$, and its molecular weight is 217.29 g/mol.

Synthesis of compounds (3-8)[4].

A well stirred solution of BTD or PTA (1) (2.00g, or 2.17g, 0.01 mole) are respectively in conc. HCl (6 mL) and 4 mL H_2O are cooled in ice-bath and diazotized with the solution of $NaNO_2$ (0.70g, 10.2 mole) in (10 mL H_2O). The cold diazonium solution was added slowly to a well stirred of benzoylacetone (3.24g, 0.02 mole) or ethylbenzoylacetate (3.84g, 0.02 mole) or ethylacetoacetate (2.6g, 0.02 mole) in absolute ethanol (25 mL) containing sodium acetate (1.64g, 0.02 mole). The reaction mixture was stirred for another 2 h. The crude product was filtered off, dried well and recrystallized from appropriate solvent to give corresponding compounds (3-8).

Synthesis of compounds (9-14)[14]–[17].

A solution of hydrazine hydrate or (0.10g, 0.002 mol.) in ethanol (15 mL) was added dropwise to the corresponding ketoester compounds (.0546g, 0.001 mole) comp. (3) or (0.482g, 0.001 mole) (4) or (0.606g 0.001mole) (5) or (0.390g 0.001mole) (6) or (0.358g 0.001mole) (7) or (0.420g 0.001 mole) (8). The mixture was refluxed for 3 hrs. The precipitate was filtered, which was recrystallized from appropriate solvent. The solid product was filtered and dried., that yield for the physical properties in Tables (1,2).

Synthesis of compounds (15-20)[15]–[17].

We followed the same procedure for the preparation of compound (9-14). A solution of phenylhydrazine (0.216g, 0.002mole) in ethanol (15 mL) was added dropwise to the corresponding – ketoester compounds (3-8), (0.001 mole) in a 25mL, round bottom flask. The mixture was refluxed for 3 hrs. The precipitate was filtered which was recrystallized from appropriate solvent. The solid product was filtered and dried., that yield for the physical properties in Tables (1,2).

Results and Discussion

In this paper the intermediate 1,3-dicarbonyl compounds (3-8), used for synthesis of pyrazole and pyrazolone diazines derivatives pyrazole was synthesized from 1,3-diketone also pyrazolone was obtained from these compounds but one of carbonyl is ester, (9-20) scheme (1) were prepared by the coupling of diazonium salts for compounds (1-2) with benzoylacetone, ethylbenzoyl acetate and ethylacetoacetate in an alkaline medium to get wide spectrum of colours compounds.

The diazonium salts of [2,2'-bi(1,3,4-thiadiazole)]-5,5'-diamine and 5-(1-phenylprop-1-en-2-yl)-1,3,4-thiadiazol-2-amine have been found to be easy to couple with 1,3-diketone. Since, [2,2'-bi(1,3,4-thiadiazole)]-5,5'-diamine and 5-(1-phenylprop-1-en-2-yl)-1,3,4-thiadiazol-2-amine possessing electron-donating group give excellent yields. All compounds in FTIR, show constant peaks such as (N=N, C=N, C-S and C-H_{ali}) in range absorptions (1483-1527, 1593-1643, 1157-1177, 2881-2937 cm^{-1}) respectively for example figures 1-4, FTIR spectrum of compounds (1, 2, 7, 19). So (λ max) for all compounds are in range (333-367nm) n- π^* transitions[18].

The compounds (3-8) which show the range absorptions υ cm^{-1} at 1665- 1712 cm^{-1} (C=O), (C=O) (ester), and at 1605-1672 cm^{-1} due to (C=C) for compounds (2 and 6-8). 3023-3151 cm^{-1} (Ar-H) for compounds (2-4 and 6-8)[19] . The compounds (9-20) can be split into two parts through the reaction of compounds (1 and 2) with hydrazine and phenylhydrazine, part one compounds which react with hydrazine hydrate are (9- 14) show range absorptions υ cm^{-1} at 1707-1720 cm^{-1} (C=O) unconjugated amide for compounds (10, 11 and 13, 14) where this peak disappear in compounds (9 and 12) and at 1613-1623 cm^{-1} due to (C=C) for compounds (12-14), 3023,3125 cm^{-1} (Ar-H) for compounds (9, 10 and 12-14), and at 3275-3367 cm^{-1} due to (N-H) for compounds (10, 11, 13 and 14)[20].

Part two compounds which react with phenylhydrazine for synthesis of pyrazolone derivatives (15-20) show range absorptions υ cm^{-1} at 1647-1658 cm^{-1} (C=O) conjugated amide for compounds (16, 17 and 19, 20) where this peak disappear in compounds (15 and

18) because these compounds are not esters[21]. 1623-1632 cm^{-1} due to (C=C) for compounds (16 -20), 3021,3123 cm^{-1} (Ar-H) for compounds (15-20), and at 3327-3373 cm^{-1} due to (N-H) for compounds (16, 17, 19 and 20).

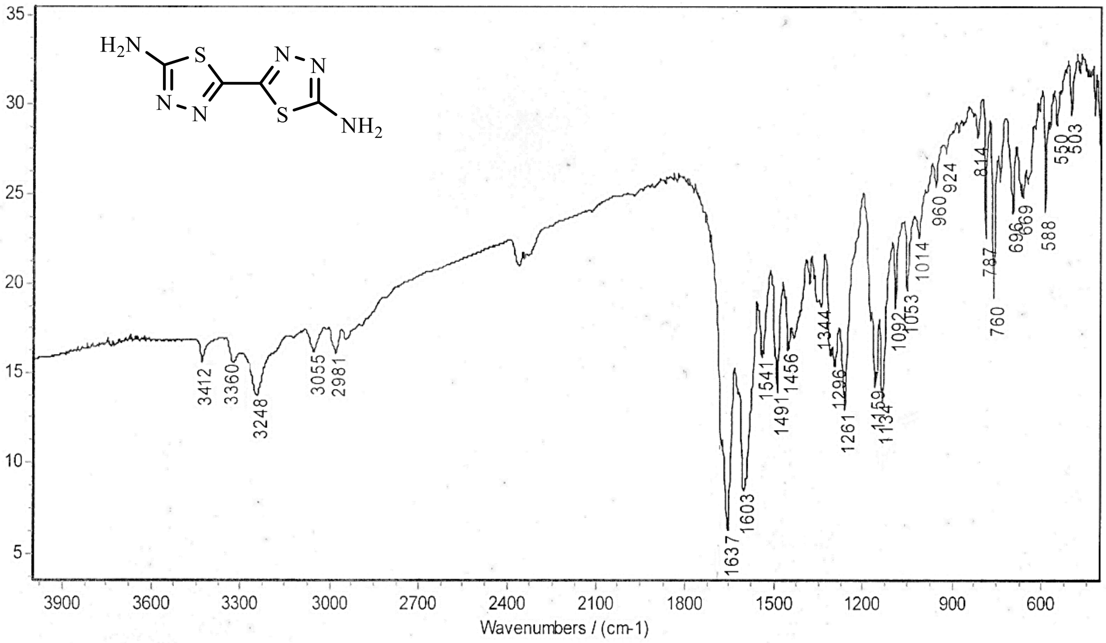


Fig. 1. *FTIR spectrum for compound (1).*

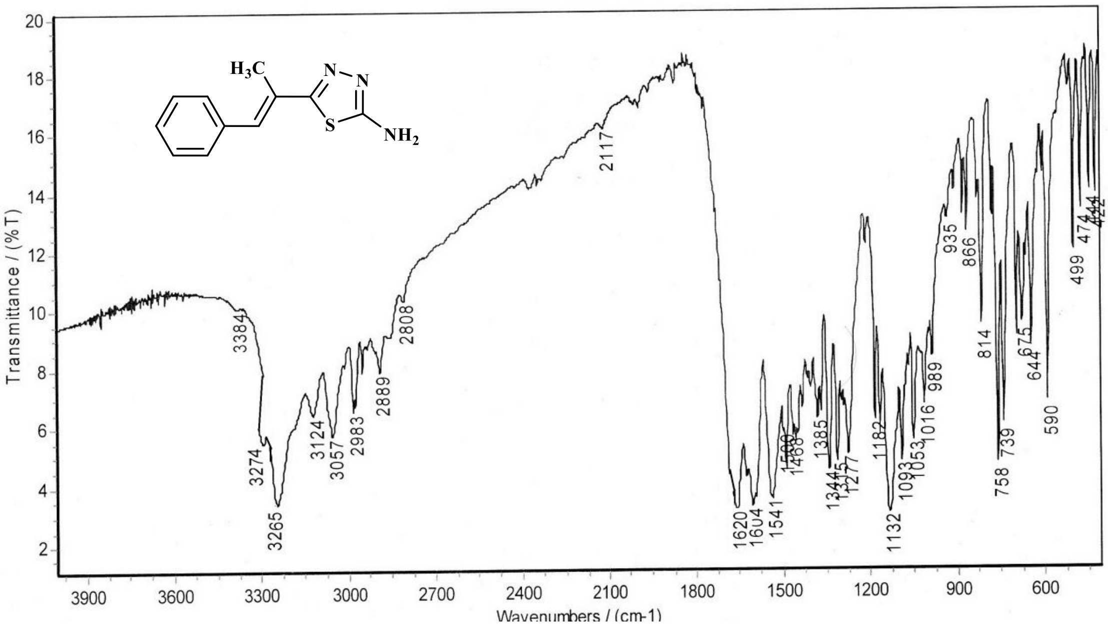


Fig. 2. *FTIR spectrum for compound (2).*

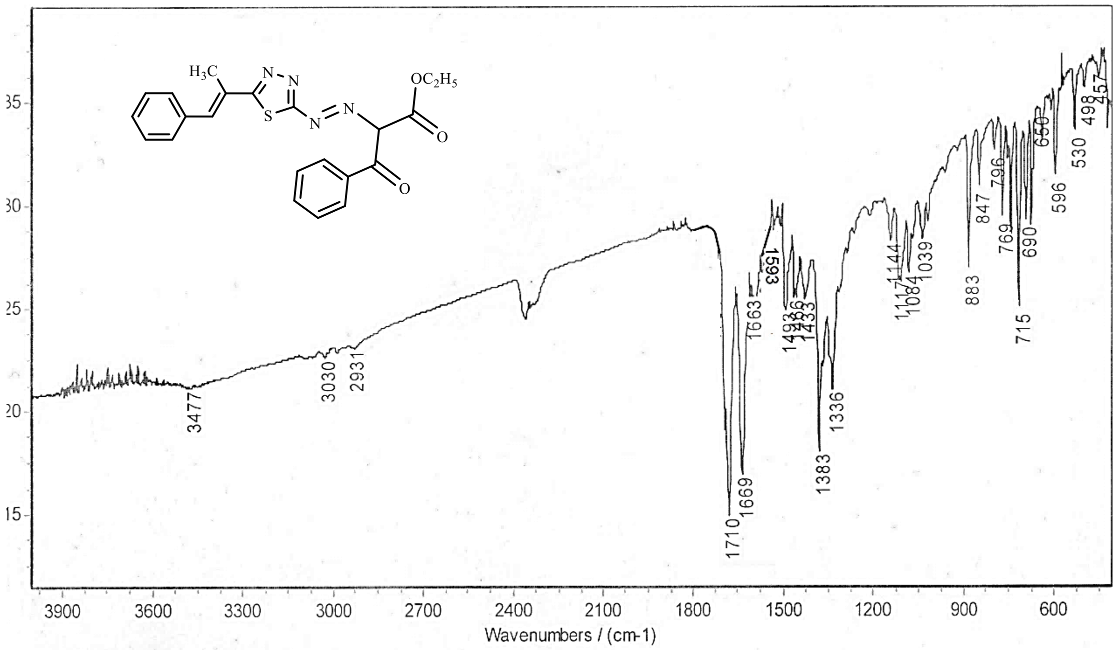


Fig. 3. *FTIR spectrum for compound (7).*

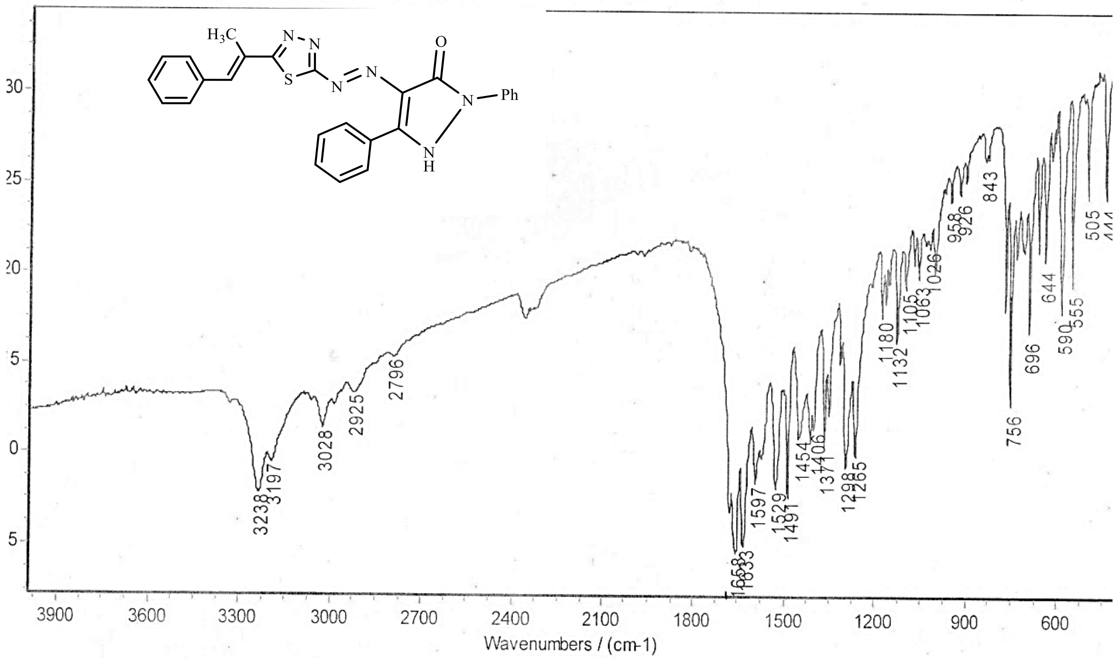


Fig. 4. *FTIR spectrum for compound (19).*

We note that the compounds showed high yields and excellent colors, which indicates the purity of materials, and this confirmed by the FTIR and HNMR spectrum, which gives the correct structure, as some products contain an N-H bond close to the carbonyl group, and leads to hydrogen bonding between them, but in other compounds they are distant especially, those formed by the reaction of phenylhydrazine due to the benzene ring as they give the stable structure because of the closeness of the rings which leads to electronic induction and thus leads to the instability of the compound. Physical and spectral data are listed in Table (1,2).

The structural formulas of the compounds (1, 2, 7, 19) were verified by other spectroscopic methods. By using (DMSO-d6) as solvent, the nuclear magnetic resonance spectrum (^{1}H-NMR) showed significant and clear peaks, figures (5-8) ^{1}HNMR and ^{13}C-NMR spectrums for compounds (1and 2). The types of peaks and their locations are confirmed in Table (3) in detail.

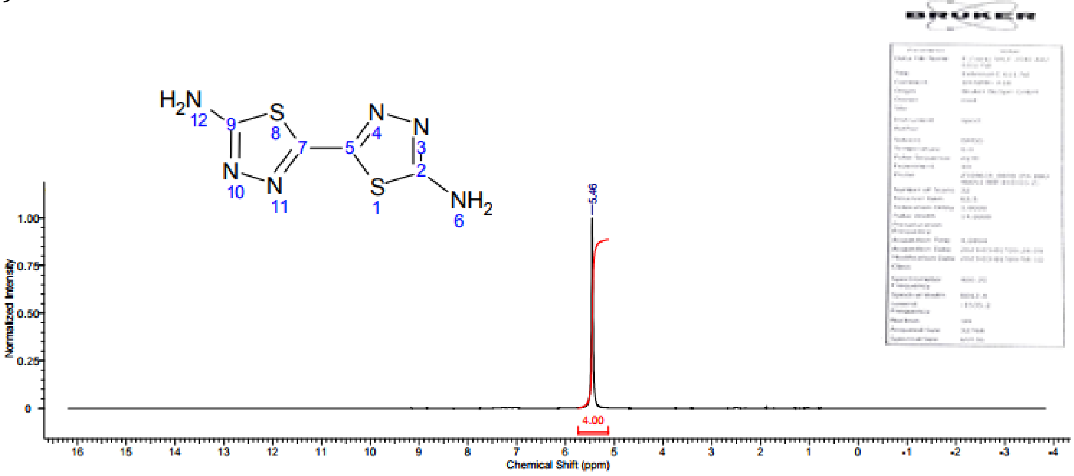


Fig. 5. *^{1}HNMR spectrum for compound (1).*

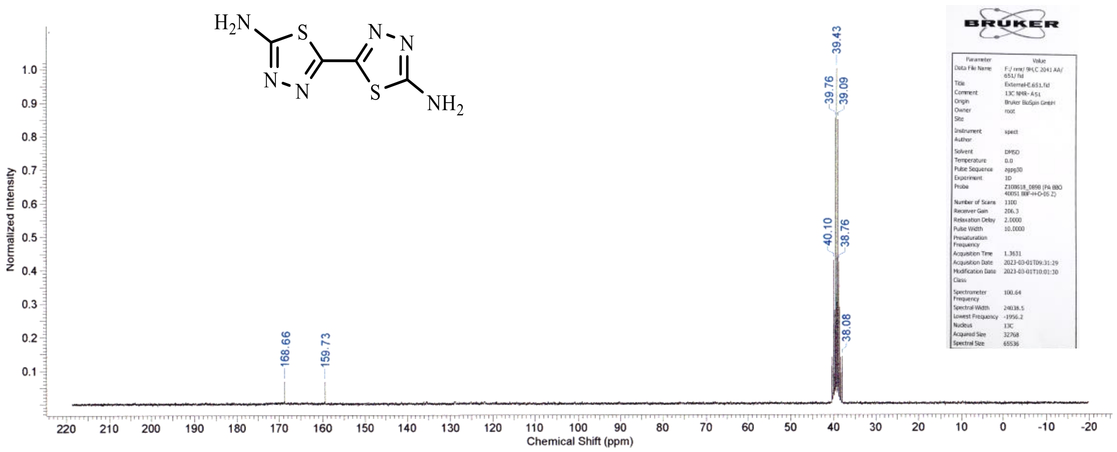


Fig. 6. *^{13}C-NMR spectrum for compound (1).*

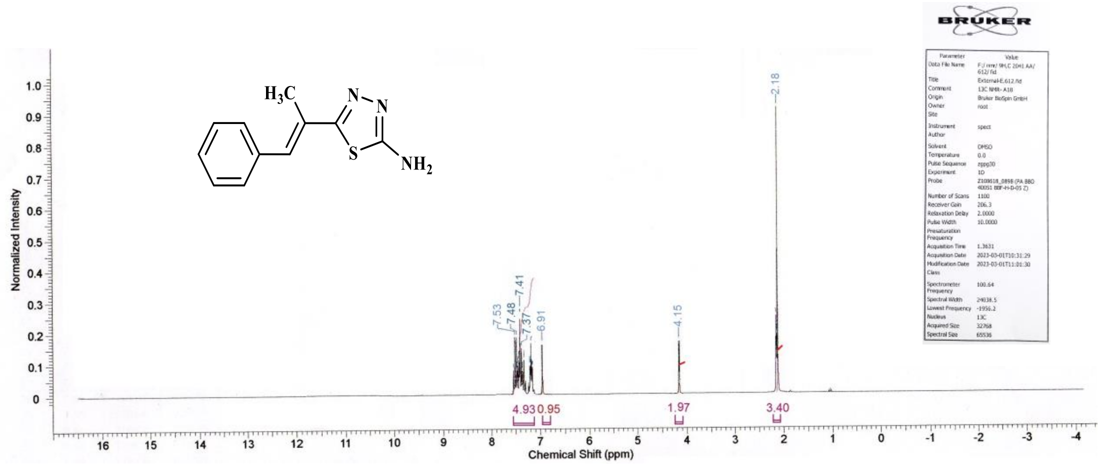


Fig. 7. *^{1}HNMR spectrum for compound (2).*

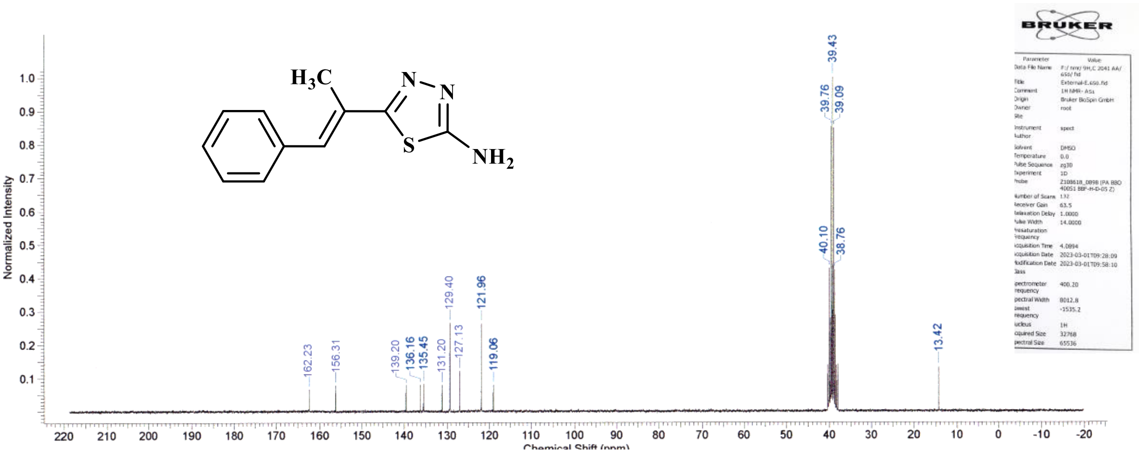


Fig. 8. *^{13}C-NMR spectrum for compound (2).*

The (^{1}H-NMR) spectrum of the compound (7) figure (9) using (DMSO-d6) as a solvent showed a triplet peak at the range (1.21ppm -1.27ppm) returning to three protons of the methyl ester group and a quartet peak at the range (4.24ppm-4.32ppm) belong to the two protons of the methylene ester group[22]. The spectrum also showed a weak peak singlet at the site (3.32ppm) belong to the proton (1,3- diketone) at its bonding site with the azo group (-N=N-) this indicates that the reaction has occurred, and singlet peak at (6.91 ppm) belong to the (H of alkene), proton of CH_3 appear at (2.18 ppm) and the protons of the aromatic rings appear at the range (7.37ppm -7.53ppm)[23].

In the measurement of (^{13}C-NMR) figure (10), the spectrum showed clear peaks of the structure recording in table (4).

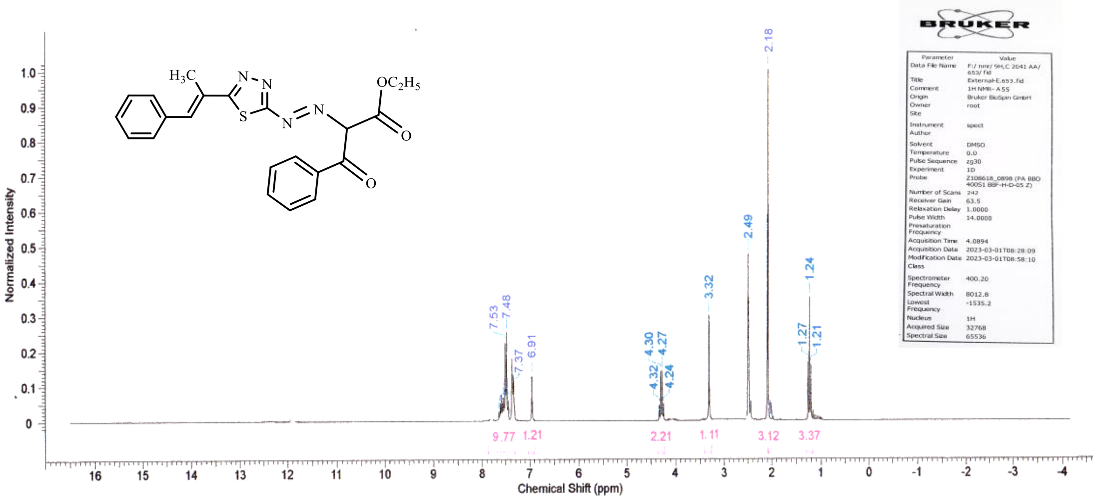
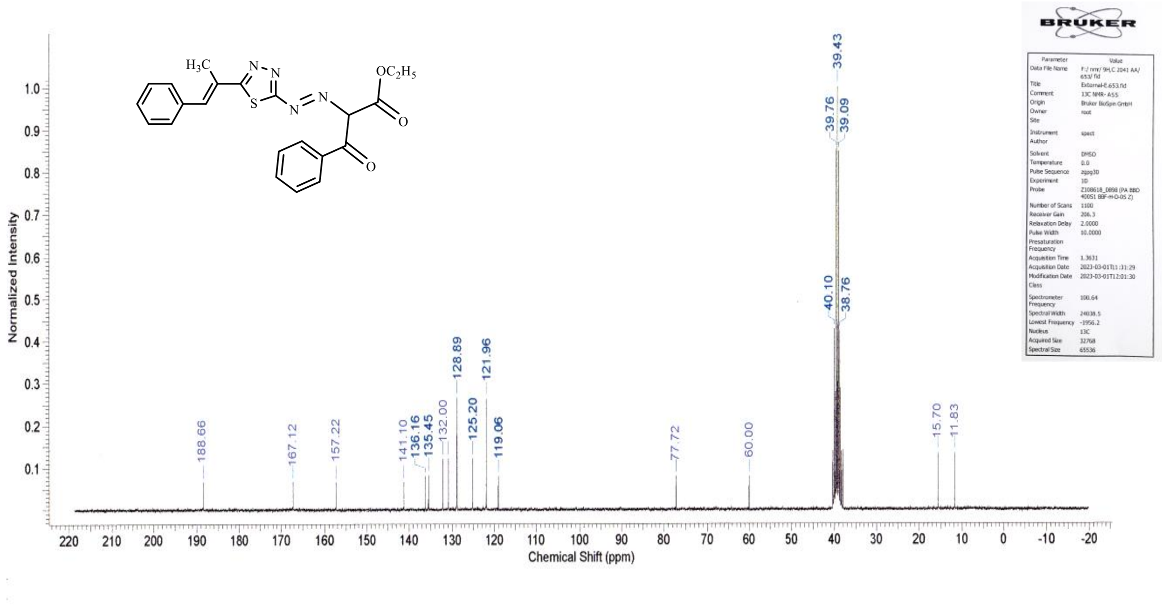


Fig. 9. *^{1}HNMR spectrum for compound (7).*



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Experiment	1D
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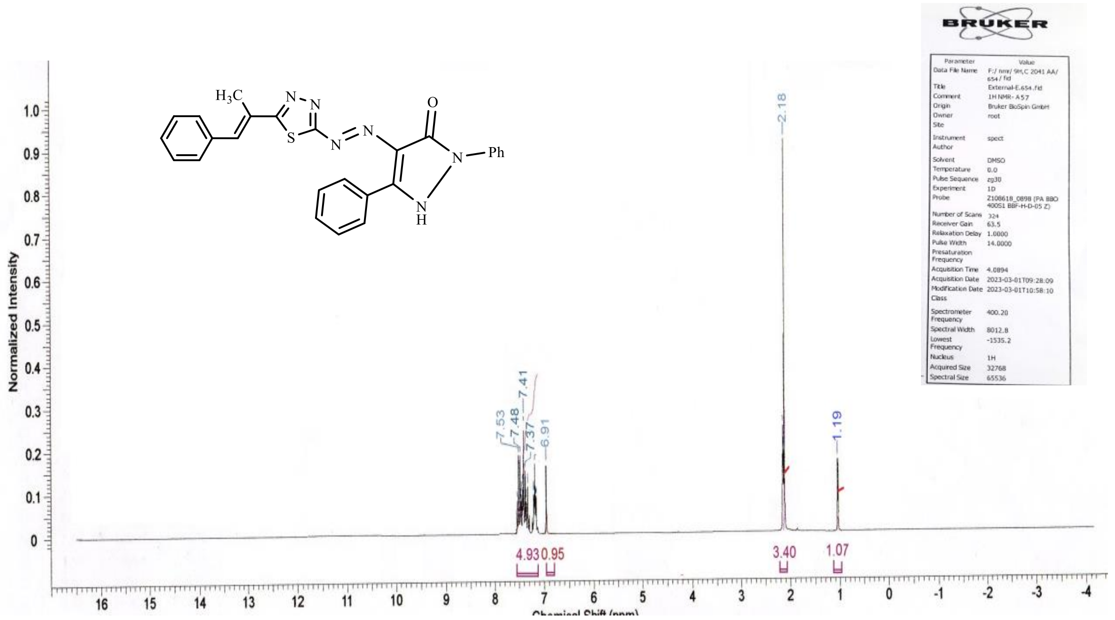
Spectral Size	65536

Fig. 10. *^{13}C-NMR spectrum for compound (7).*

The compound (19) was chosen in carrying out the other measurements. By using (DMSO-d6) as a solvent, the nuclear magnetic resonance spectrum (^{1}H-NMR) Table (3) showed a weak peak at the site (1.19 ppm) returning to the proton of the group (NH) in the new ring, and showed strong peak at site (2.18ppm) returning to three protons for each of the methyl group (CH_3 bonded to alkene), also H of alkene appear at (6.91ppm) and at the end of the spectrum appear peaks of protons of the aromatic rings at the range (7.32ppm- 7.82ppm). It is noted from the spectrum that the two peaks of ethyl group have disappeared, which is evidence of the formation of pyrazolone ring figure (11) ^{1}HNMR spectrum.[24], [25]. The (^{13}C-NMR) is listed in table (4) and figure (12) refer to compound (19).



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Site	
Instrument	spect
Author	
Solvent	DMSO
Temperature	0.0
Pulse Sequence	zg30
Experiment	1D
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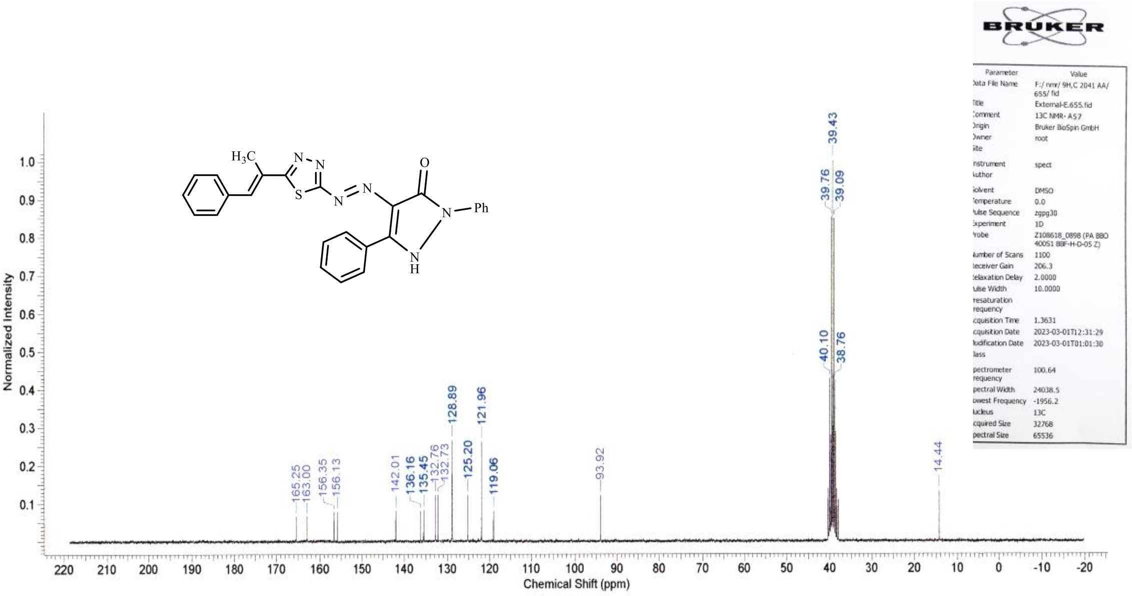
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

Fig. 11. *^{1}HNMR spectrum for compound (19).*



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cquisition Date	2023-03-01T12:31:29
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lass	
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owest Frequency	-1956.2
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pectral Size	65536

Fig. 12. *^{13}C-NMR spectrum for compound (19).*

Table 1: Physical data of compounds (1-20).

Comp. No	Solvent	Color	m.p. ˚C	M.F	Yield %
1	ether	Pale yellow	240 -241	$C_4H_4N_6S_2$	93
2	ethanol	yellow	110 -111	$C_{11}H_{11}N_3S$	85
3	ethanol	orange	265-267	$C_{24}H_{18}N_8O_4S_2$	88
4	ethanol	red	287-288	$C_{26}H_{22}N_8O_6S_2$	78
5	ether	brown	277-279	$C_{16}H_{18}N_8O_6S_2$	79
6	ethanol	red	182-183	$C_{21}H_{18}N_4O_2S$	67
7	Pet. ether	yellow	133-134	$C_{22}H_{20}N_4O_3S$	86
8	dioxane	yellow	177-178	$C_{17}H_{18}N_4O_3S$	77
9	ethanol	yellow	224-225	$C_{24}H_{18}N_{12}S_2$	92
10	benzene	orange	254-256	$C_{22}H_{14}N_{12}O_2S_2$	89
11	ethanol	Pale yellow	263-265	$C_{12}H_{10}N_{12}O_2S_2$	86
12	ether	brown	222-224	$C_{21}H_{18}N_6S$	79
13	ether	red	170-172	$C_{20}H_{16}N_6OS$	65
14	Pet. ether	red	193-95	$C_{15}H_{14}N_6OS$	63
15	Pet. ether	yellow	235-237	$C_{36}H_{26}N_{12}S_2$	79
16	ethanol	yellow	217-219	$C_{34}H_{22}N_{12}O_2S_2$	83
17	ethanol	orange	231-233	$C_{24}H_{18}N_{12}O_2S_2$	87
18	dioxane	orange	241-243	$C_{27}H_{22}N_6S$	90
19	ethanol	yellow	159-161	$C_{26}H_{20}N_6OS$	76
20	ethanol	red	205-207	$C_{21}H_{18}N_6OS$	79

Table 2: FT-IR Spectral data of compounds (1-20).

Comp. No	IR cm^{-1} , KBr									U.V. $CHCl_3$ λmax
	N-H	Ar-H	C-H ali.	C=O unco. ami.	C=O conj. amid	C=O, C=O est.	C=C	N=N	C=N, C-S	
1	3412, 3360								1637, 1163	335
2	3265, 3274	3151	2925				1605		1620, 1175	323
3		3026	2872			1667, ——		1487	1627, 1177	341
4		3147	2911			1673, 1712		1483	1622, 1157	346
5			2887			1665, 1705		1493	1597, 1172	351
6		3132	2884			1687, ——	1672	1492	1597, 1172	327
7		3031	2881			1669, 1710	1663	1491	1593, 1167	333
8		3047	2913			1669, 1705	1607	1495	1597, 1161	339
9		3117	2911					1507	1643, 1165	353
10	3324	3125	2903	1715				1515	1633, 1157	357
11	3333		2907	1720				1521	1629, 1163	361
12		3125	2911				1613	1523	1597, 1163	359
13	3275	3035	2907	1707			1620	1523	1620, 1170	357
14	3367	3023	2903	1707			1625	1523	1605, 1177	365
15		3076	2937				1622	1525	1623, 1161	367
16		3025	2917		1654		1632	1527	1632, 1161	361
17		3021	2905		1647		1627	1527	1621, 1169	364
18		3057	2907				1625	1487	1605, 1163	359
19		3123	2915		1658		1631	1489	1621, 1157	352
20		3121	2911		1652		1623	1483	1603, 1163	354

Table 3: ^{1}H-NMR Spectral data of compounds (1, 2, 7, 19).

Comp No.	N-H	CH_3-CH=C	CH_3CH_2	CH_3CH_2	C-H alkene	C-H	Ar-H
1	5.45,s, ($2NH_2$)	——	——	——	——	——	——
2	4.15,s, (NH_2)	2.18,s. (CH_3)	——	——	s, 6.91	——	7.37-7.53 (m, 5H)
7	——	2.18,s. (CH_3)	1.21-1.27 (t, CH_3)	4.24-4.32 (q, CH_2)	s, 6.91	s, 3.32	7.37-7.53 (m, 10H)

19	1.19,s, (NH)	2.18,s. (CH_3)	——	——	s, 6.91	——	7.32-7.82 (m, 15H)

Table 4: ^{13}C-NMR Spectral data of compounds (1, 2, 7, 19).

Comp No.	=C-*CH_3	=CH C=N	*CH_3CH_2 N=*C- *C=N	CH_3 *CH_2 H_2N-*C=N	C-N=N-CH	C=O Ph-$C_{pyr..}$	Ar-C	C=O est.	C=O Pyraz.
1	——	——	—— 168.66	—— 159.73	——	—	——	—	——
2	131.20, 13.42	129.40 156.31	_______	—— 162.23	——	——	127- 139	—	——
7	132.0, 15.7	131.81 157.22	11.83 ——	60.0 ——	157.22, 77.72	188.66	127- 141	167.12	——
19	132.73, 14.44	132.76 156.35	—— ——	——	156.13, 93.92	— 165.25	119- 142	——	163.0

Conclusions: The diazotized method has been used in this work to synthesis of pyrazole and pyrazolone from 1,3-dicarbonyl derivatives, then reacted with hydrazine or phenylhydrazine. This method is more important to the reduction of environmental impacts compared to preparing diazonium salts which is prepared from amino thiadiazole, with easy reaction to give high yields of five membered ring compounds. Characteristics of the final product including FTIR ^{1}HNMR, 13C-NMR indicate the configuration of the required compounds.

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تشييد البايرازول والبايرازولون من ملح الديازونيوم لـ 4،3،1-ثياديازول

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تفاعلات الأضافة الحلقية، البايرازولون، ملح الديازونيوم، والثايادايازول.

معلومات المؤلف

الايميل:

الخلاصة:

ملح الديازونيوم لـ [2،2'- ثنائي(4,3,1-ثايادايازول)] - 5،5'-ثنائي أمين (BTD) و 5- (1-فنيل بروب-1-ين-2- يل)-4,3,1-ثايادايازول-2-أمين (PTA) ةالتي تم أزدواجها مع أسيتو أسيتات الأثيل, بنزوايل أسيتات الأثيل وبنزوايل أسيتون لإعطاء مركبات الديازو المقابلة تحت الوسط القاعدي. تم السماح لهذه النواتج بالتفاعل مع الهيدرازين المائي والفينيل هيدرازين بالطريقة التقليدية لإعطاء مشتقات البايرازول والبايرازولون بنسب نواتج عالية.