

SYNTHESIS & IDENTIFICATION OF BIS-(AZ-COMPOUNDS) VIA ALKYLATION OF DIMETHYL MALONATE

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ABSTRACT

In this paper, dimethyl malonate has been used to the reaction with P -formal benzaldehyde forming the corresponding bis(Dimethyl malonate) which ciclyze with di amine compounds to produce bis { (5, 6, 7) –membered of di aze cycles }, & some of them reacts with different amino compounds to produce corresponding bis substituted. The structures of the synthesized compounds have been confirmed by (FT.IR - spectra, H.NMR -spectra, C.H.N - analysis) & melting points.

INTRODUCTION

Di alkyl malonate is important class of compounds is several field of organic chemistry such as alkylation of carbonyl 1, 2 compounds , incorporation with heterocyclic compounds to produce pharmaceutical compounds which have a wide range of pharmacological properties 3-5in pharmaceutical chemistry field , because of the number & the significance of these applications, many methods 6, 7 have been reported for the preparation of these compounds in the last years (diazolidine, diazine, diazepam) 8-11. Di nitrogen (di az)-containing heterocyclic compounds 12, 13 have received considerable attention due to their biological activity which represented as anti tumer, anti viral, anti fungal, anti cancer, analgesic, anti-Hiv, anti microbial etc. In recent years, chemistry of di az compounds developed very fast due to the discovery of the diverse biologically active (diazolidine, diazine, diazepam) derivatives 14, 15 [1].

EXPERIMENTAL

All chemical used from BDH & sigma -company, FT.IR -spectra were recorded on shimadzu 8300, Kbr - disk., H.NMR -spectra & (C.H.N) -analysis were recorded in Maliesia , the melting points were determined by digital -electrothermal 9300 LTD , UK .

Synthesis of compounds - 1, 2

A mixture of P -formal benzaldehyde (0.1 mole) reacted with di methyl malonate (0.2 mole) in basic medium of sodium hydroxide (10%) with mechanical stirr at room temperature for (4hrs) , the precipitate was filtered & recrystallized to yield 88% of compounds 1 , which (0.1 mole) reacts according to procedures [2-9] with (0.1 mole) of methylene di amine under reflux for (3hrs) in presence of absolute ethanol, the precipitate was filtered & recrystallized to give 89% of compounds 2.

Synthesis of compounds - 3- 6

The synthesis of these compounds was carried out according literature [2-9], a mixture of compound 2 (0.01 mole) with one of (0.01 mole) from (hydrazine, methylene di amine, guanidine, ethylene di amine) respectively were heated under reflux for (5hrs) in presence of absolute ethanol, the precipitate was filtered & recrystallized to yield (87, 85, 87, 89) % of compounds 3-6 respectively.

Synthesis of compounds - 7- 9

According to procedure [9], a mixture of compounds 2 (0.01 mole) with one of {(0.02 mole) from (2 -amino thiophene, 2 -aminothiazole) (0.01 of aniline)} respectively were refluxed for (5-6 hrs) in presence of absolute ethanol, the precipitate filtered recrystallized to yield (85, 87, 88) % of compounds 7-9 respectively.

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Synthesis of compound - 10

A mixture of equimolar (0.01 mole) of compound 9 with hydrazine were reacted under reflux for (4hrs) & stirr, precipitate was filtered & dried, recrystallized to yield 86 % of compound 10 [10-15].

RESULTS & DISCUSSION

The formation of compound 1 as starting compound proceed via reaction between dimethyl malonate with di aldehyde compound such as P-formal benzaldehyde, then compound 1 reacts with diamine compounds such as (methylene diamine, hydrazine, guanidine, ethylene diamine to yield cyclic compounds 2-6, & compound 2 reacts with primary amine compounds in one side or two side from compound 2 to yield compounds 7-10.

All these compounds characterized by I.R -spectra, (C.H.N)-analysis, melting points & some of them by H.NMR -spectra :

The I.R -spectra, showed an absorption band at (3026-3095) cm⁻¹ due to (CH=C) of alkene in all

compounds 1-10 for formation of double bond of alkene , absorption band at (1728) cm⁻¹ due to carbonyl of ester group(2) (CO-O-) in compounds 1, 2 which disappeared one of them & appeared other bands such as {(1660 - 1696), (3278 - 3478)} due to {(carbonyl of amide CO-NH), (amine of amide NH -CO)}(2) respectively in compounds 3-10, & other bands are summarized in (Table 1) & (Figures 1-10) .

The H.NMR -spectra showed important peaks at δ (6.40-6.60) due to proton of (CH=C) alkene in all compounds , peaks at δ (10.03-10.28) due to (NH-CO) proton of amide(2) in compounds 2, 3, 8, 9 peaks at δ (3.85 ,4.30) due to protons of methyl group in ester (-COOCH₃) in compounds 2, 9 respectively, peaks at δ (3.35-3.62) due to protons of methylene (15) in cycle (NH-CH₂-NH) in compounds 2, 3, 8, 9, & other signals of functional groups show in the following, (Table 1).

The (C.H.N)-analysis & melting points, the experimental data were good results with calculated data, all these data & physical properties in (Table 1).

Table 1. (FT.IR) -data (cm⁻¹) of compounds- 1-10

Comp. No.	(Only important frequency)			
	(CO) carbonyl of amide	(NH) of amide	(CH=C)	Other groups
1	----	----	3048	(CO-O-)carbonyl of ester :1728
2	1660	3482	3046	(CO-O)carbonyl of ester: 1714
3	1695	3299	3091	-----
4	1696	3290	3070	-----
5	1688	3312	3080	(C=N) :endocycle : 1537 ,(NH ₂) :3478 .
6	1691	3492	3091	-----
7	1696	3317	3091	(C-S) in thiophene ring :676 ,1271
8	1686	3278	3081	(C-S) in thiophene ring :675 , 1211 , (C-N) in thiophene ring :1168
9	1682	3478	3026	(CO-O-) carbonyl of ester :1728
10	1688	3278	3095	(NH ₂) : 3300 .

Table 2. H.NMR (δ ppm) of some Compounds

Comp. No.	H.NMR _(DMSO) ((Only important peaks))			
	(NH) of amide	(CH=C)	methylene of (NH-CH ₂ -NH)	Other peaks
2	10.04	6.60	3.62	4.30(COOCH ₃)methyl of ester
3	10.10 , 10.28	6.40 ,6.66	3.50	----
8	10.08 , 10.22	6.45	3.55	7.35 (proton of thiazol ring)
9	10.24 , 10.03	6.50	3.35	3.85 (COOCH ₃)methyl of ester

Table 3. Physical properties & (C.H.N) -analysis of Compounds -1-10

Comp. No.	M.F	M.p (+2)C°	Name of compounds	Calc./ Found		
				%C	&H	%N
1	C ₁₈ H ₁₈ O ₈	162	1-{(1',4'-phenyl)-tetra methyl -bis (2 -ene - propanoate)} .	59.668	4.972	---
				59.421	4.763	---
2	C ₁₇ H ₁₆ O ₆ N ₂	189	1-{2-(diazane-4,6-dione)styrene}-3-dimethyl-2-ene-propanoate	59.302	4.651	8.139
				59.188	4.44	8.09
3	C ₁₅ H ₁₂ O ₄ N ₄	194	2-(diazane-4,6-dione)-2- (diazolidine-3,5-dione)-4- ethene-1-styrene .	57.692	3.846	17.948
				57.38	3.67	17.71
4	C ₁₆ H ₁₄ O ₄ N ₄	198	2,2-bis(diazane-4,6-dione)-4- ethene -styrene .	58.895	4.294	17.177
				58.625	4.13	17.05



5	$C_{16}H_{13}O_4N_5$	220	2-(diazine-4,6-dione-2-amino)-2-(diazane-4,6-dione)-4- ethene styrene .	56.637 56.37	3.384 3.601	20.64 20.41
6	$C_{17}H_{16}O_4N_4$	208	2-(diazepane-5,7-dione)-2- (diazane-4,6-dione)-4-ethene- styrene .	60.00 59.93	4.705 4.44	16.470 16.25
7	$C_{23}H_{18}O_4N_4$ S_2	241	(1,4-phenyl)-2-(diazane -4,6-dione)-ethene-2-bis (thiophene amide) ethene .	57.740 57.51	3.765 3.56	11.715 11.54
8	$C_{21}H_{16}O_4N_6$ S_2	284	(1,4-phenyl)-2-(diazane -4,6-dione)-ethene-bis (thiazole amide) ethene .	52.5 52.31	3.33 3.20	17.50 17.27
9	$C_{22}H_{19}O_5N_3$	273	(1,4-phenyl)-2-(diazane -4,6-dione)-ethene-2-(phenyl amide)-3-methyl-1-ene -propanoate .	65.18 65.04	4.69 4.43	10.37 10.27
10	$C_{21}H_{19}O_4N_5$	259	(1,4-phenyl)-2-(diazane-4,6-dione)-ethene-2-(phenyl amide)-3-hydrizo-3-one -1-propane .	62.22 62.10	4.69 4.29	17.28 17.15

Fig 1. FT.IR of compound-1

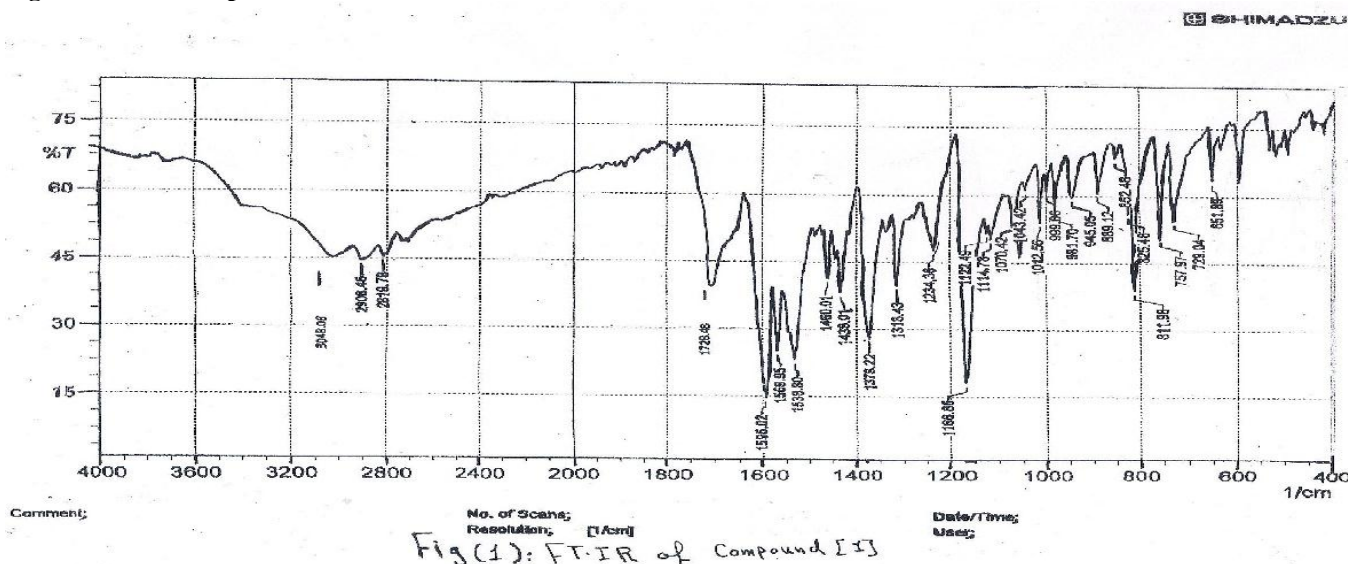


Fig 2. FT.IR of compound-2

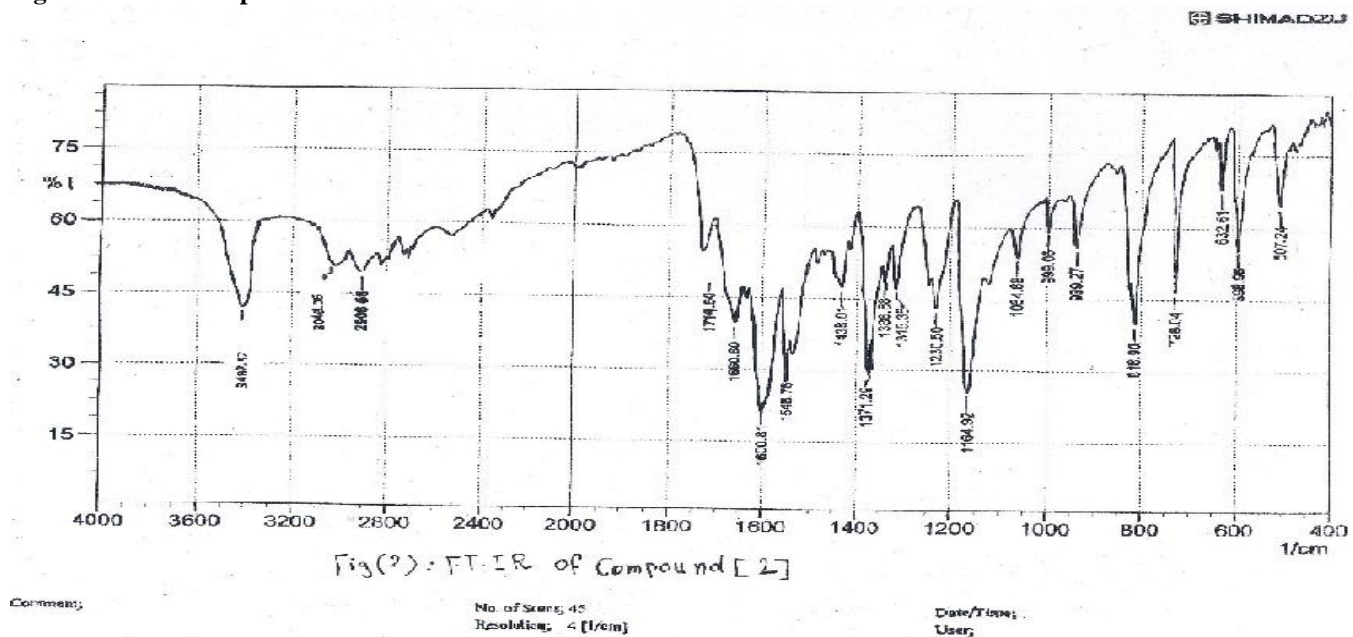


Fig 3 . FT.IR of compound-3

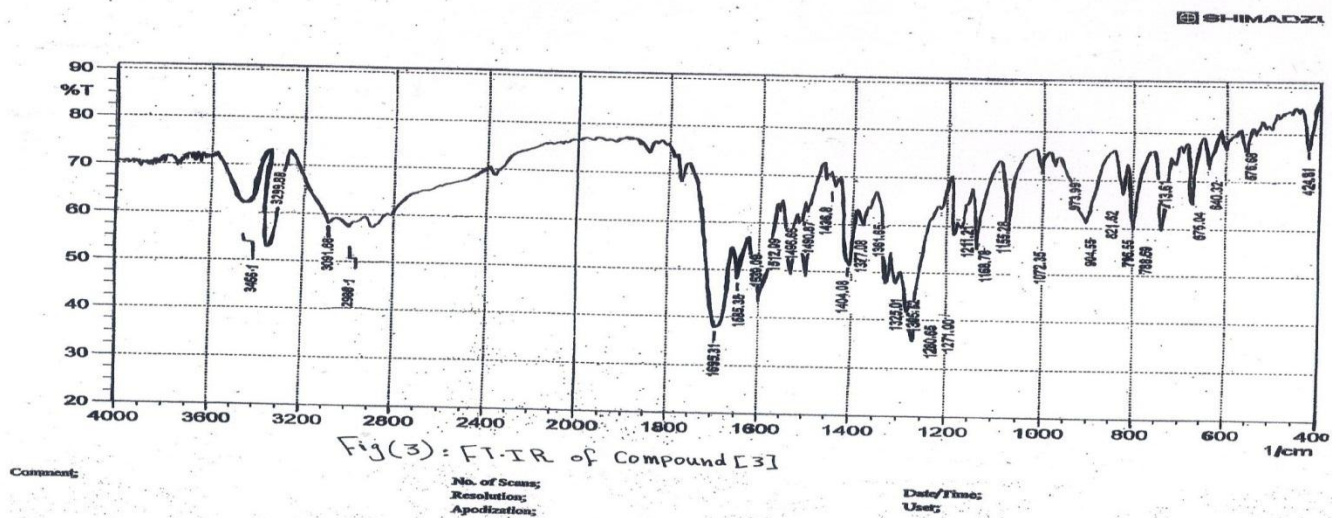


Fig 4 . FT.IR of compound-4

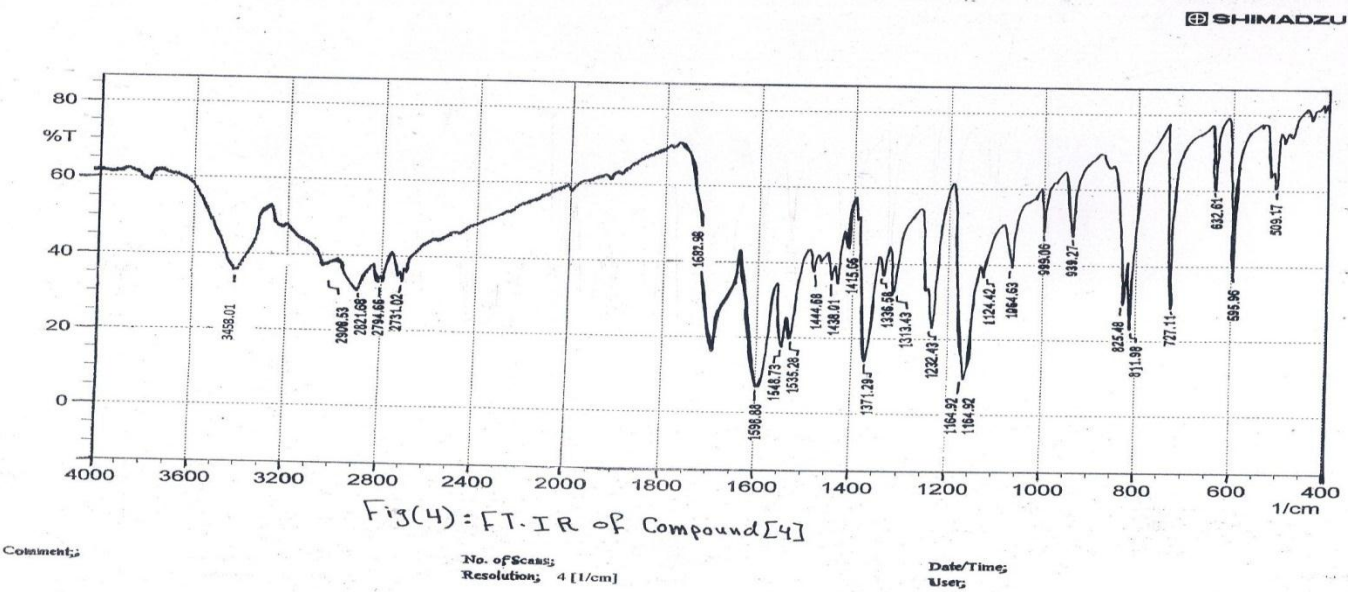


Fig 5. FT.IR of Compound- 5

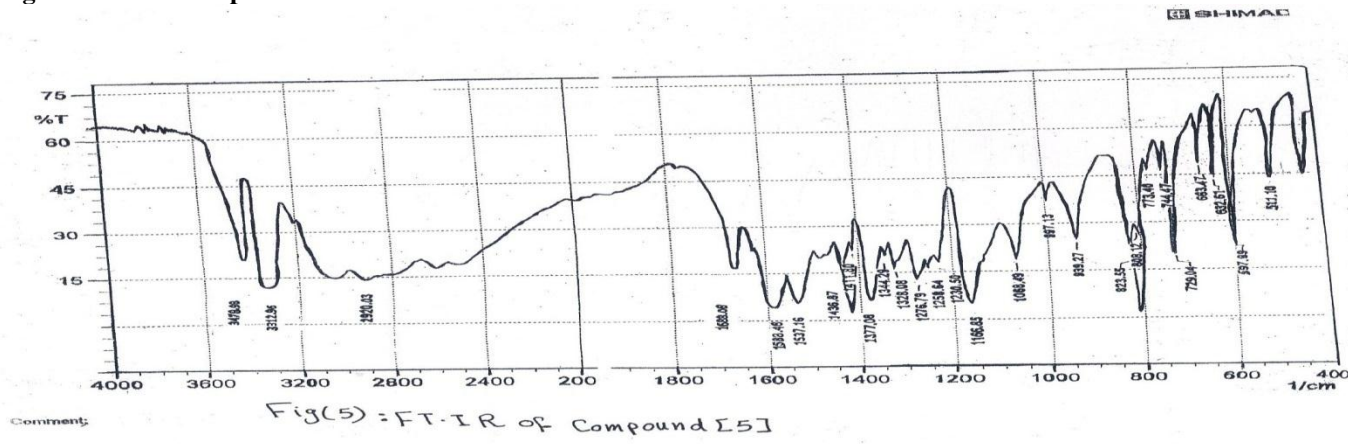


Fig 6. FT-IR of Compound-6

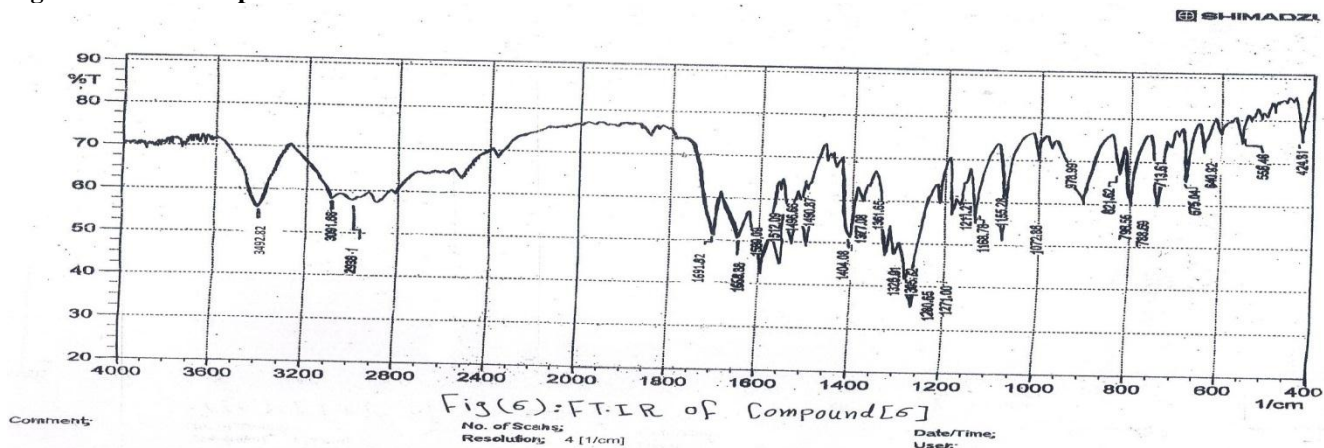


Fig 7. FT-IR of Compound-7

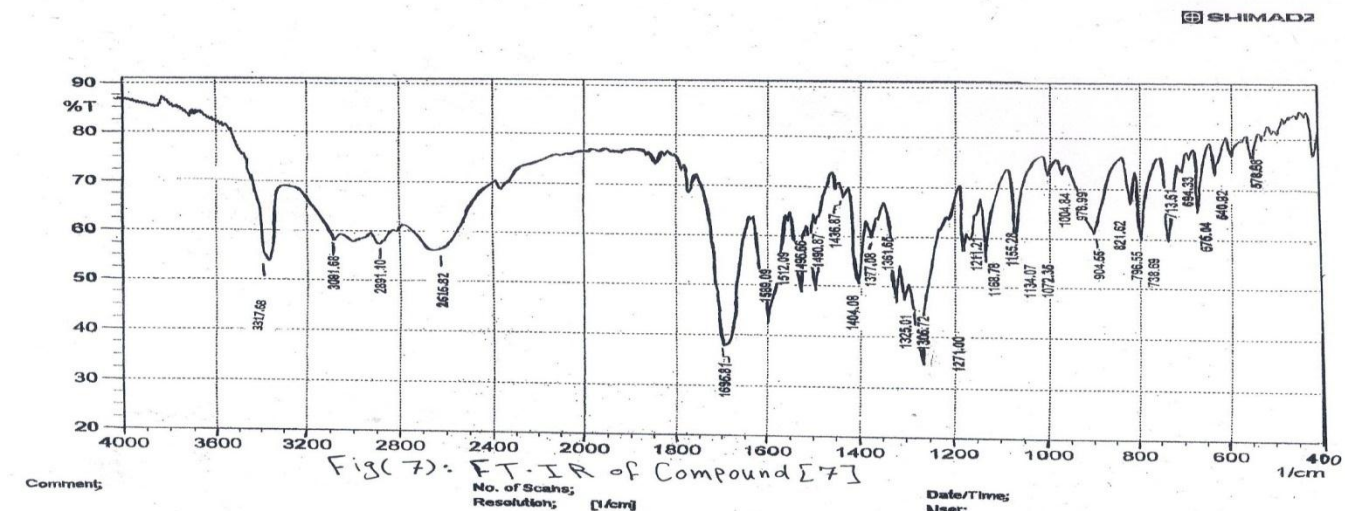


Fig 8. FT-IR of Compound-8

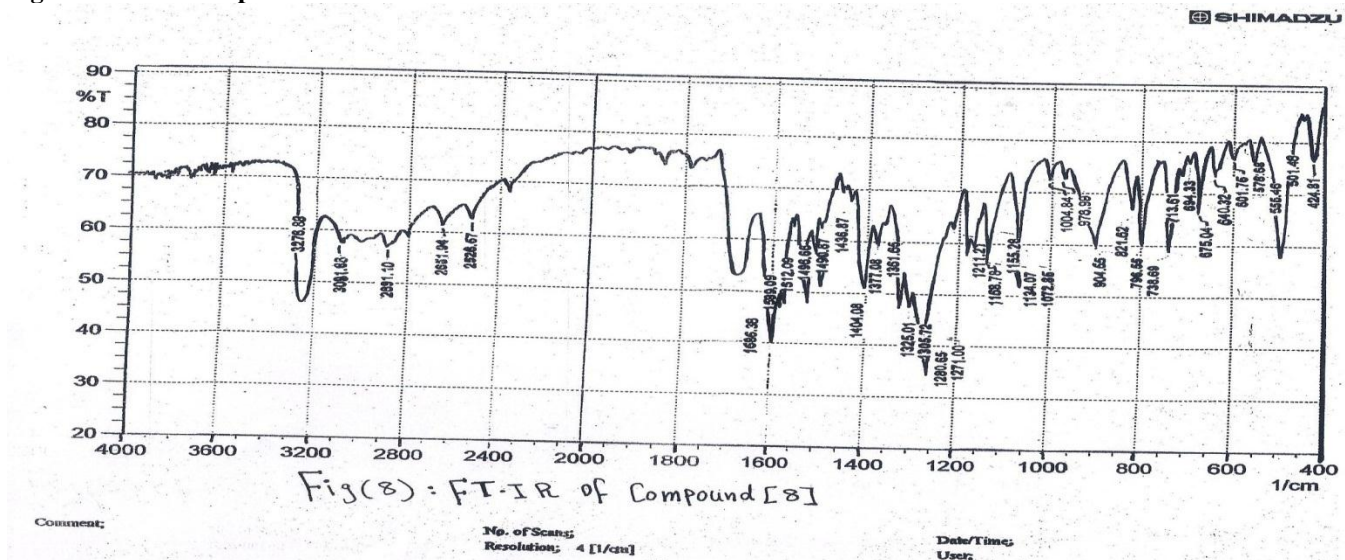
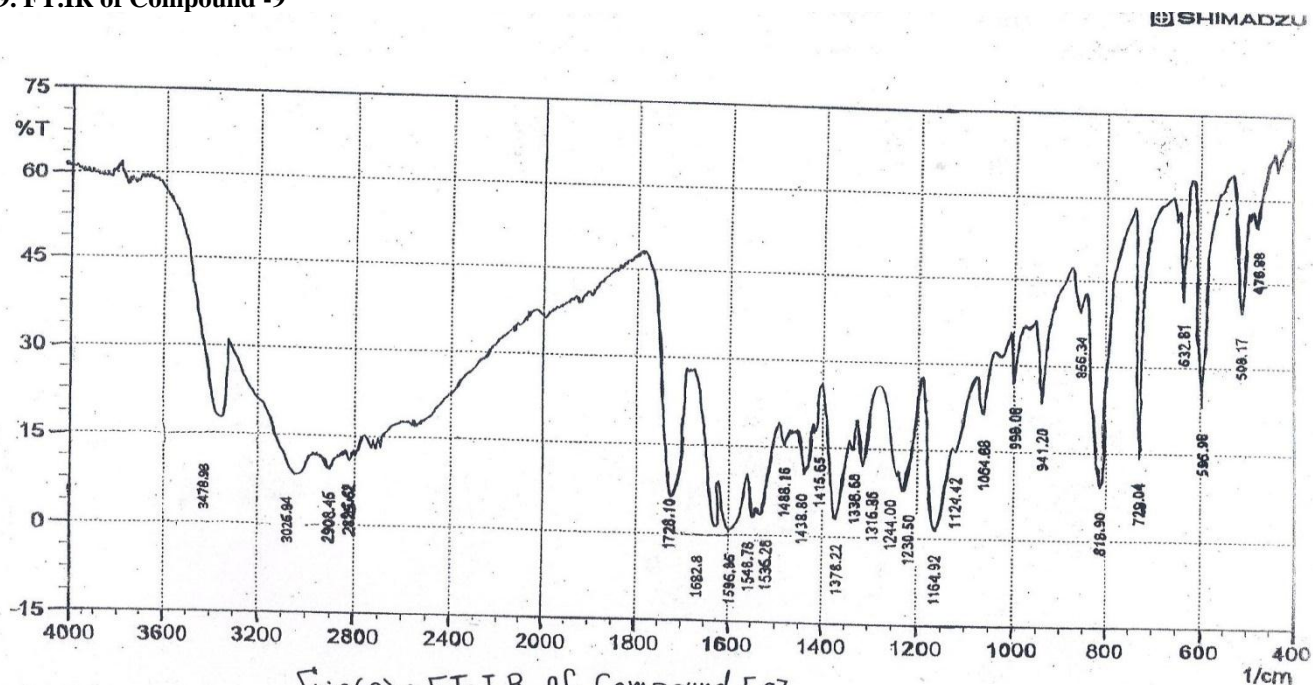


Fig 9. FT-IR of Compound -9



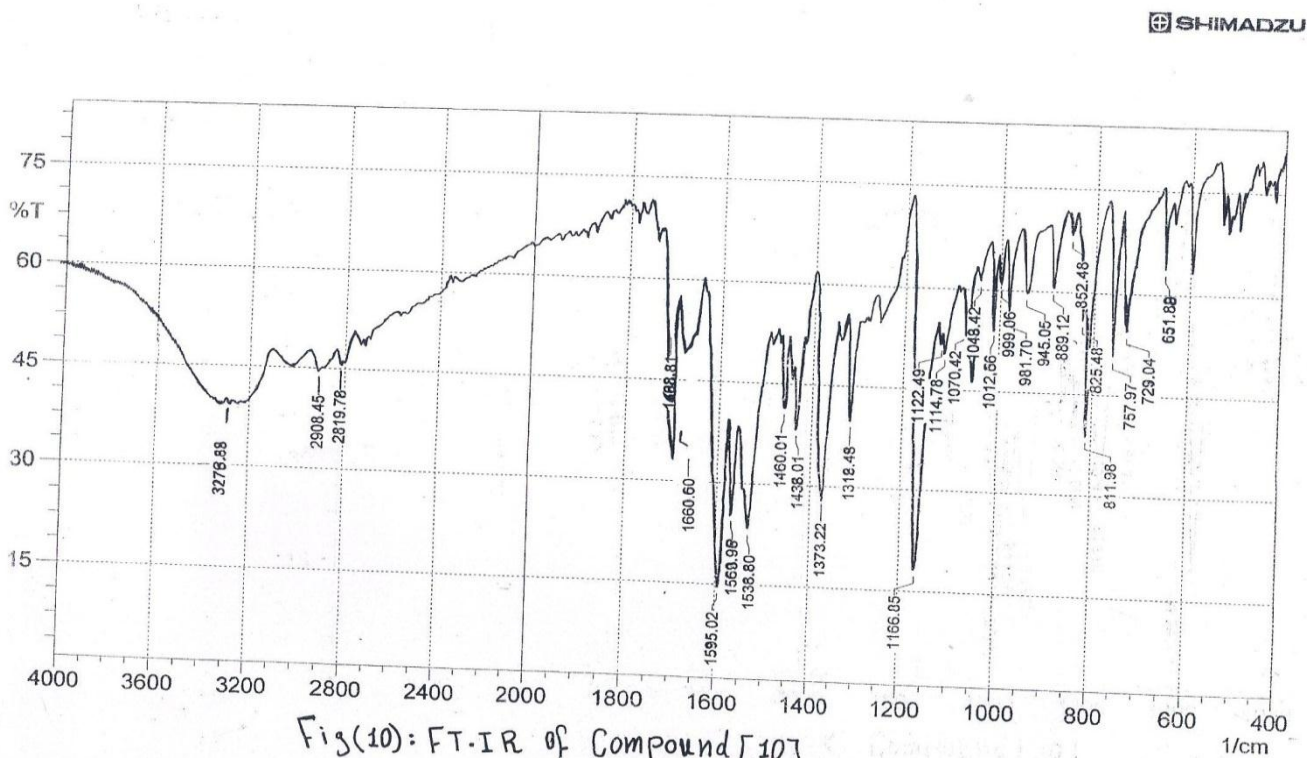
Fig(9) : FT-IR of Compound [9]

Comment:

No. of Scans;
Resolution; [1/cm]

Date/Time;
User;

Fig 10. FT-IR of Compound-10



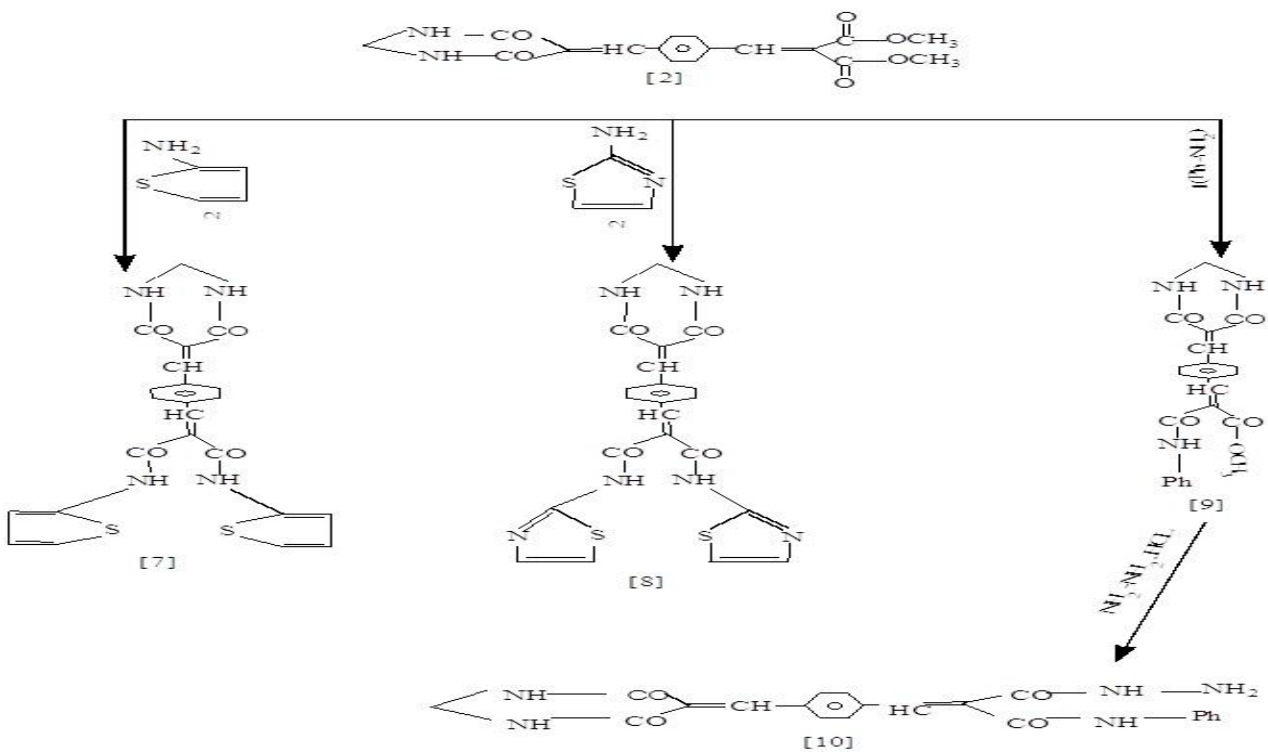
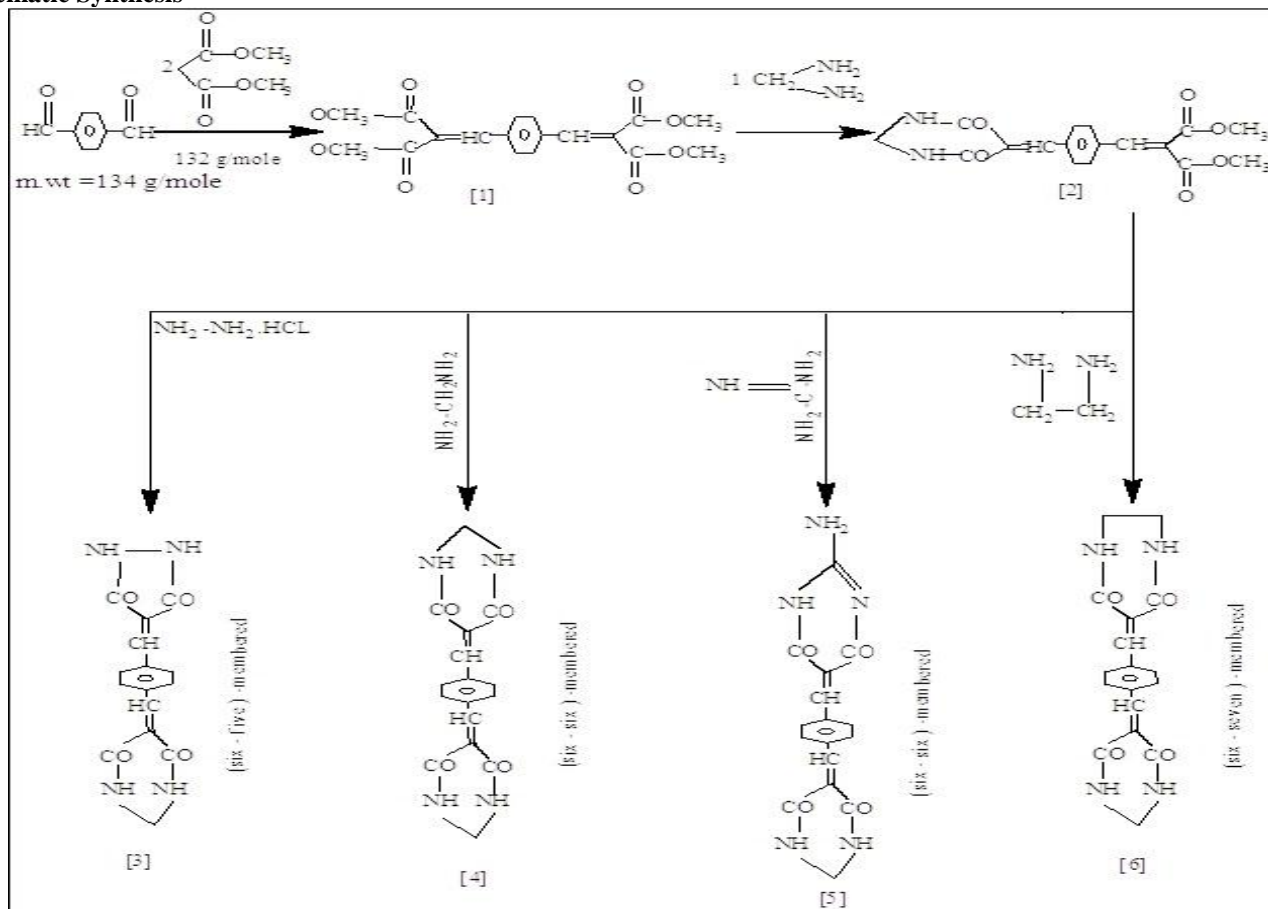
Fig(10): FT-IR of Compound [10]

Comment:

No. of Scans; 45
Resolution; 4 [1/cm]

Date/Time;
User:

Schematic Synthesis



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