Synthesis and Spectroscopic Investigation of Some New Chalcones and their transformation to pyrazoline derivatives

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Abstract

A series of a new chalcone derivatives (2a-i) containing benzyloxy moiety have been synthesized on the basis of base catalyzed claisen –Schmidt condensation in high yields from the reaction of the prepared starting material 3-(4-cholrobenzyloxy) paraldehyde (1)with different substituted acetophenones. The prepared chalcones were treated with hydrazine hydrate according to the Michael addition reaction to obtain new pyrazoline deivatives (3a-i). Finally the structures of the synthesized compounds were elucidated by using spectral methods such as; FT-IR, ^{1}H-nm, ^{13}C-nmr and ^{13}C- Dept 135 spectra.

Introduction

Chalcones (1,3-diaryl-2-propen-1-ones) are α,β-unsaturated aromatic ketones, constitute a class of naturally occurring and synthetic compounds belonging to the flavonoid family(Buckingham,1994) which synthesized by the base catalyzed Claisen-Schmidt condensation reaction(Mirjalal *et al*., 20008), and considered as a very useful precursor for the preparation of different important heterocyclic compounds like ; pyridines(Kolosov *et al.*, 2007), pyrimidines (Munawar *et al.*, 2008 and Prasad *et al.*,2008), thiazepines(Cherkupally *et al.*, 2008), isoxazoles(Al-Issa *et al.*,2008) (Mustafa *et al.*, 2003), and pyrazolines(Spivey *et al*., 2000; Guo *et al*., 2002; Azarifar *et al*., 2002; Goda *et al*.,2003 and Patel *et al*., 2004) . pyrazolines are the five membered heterocyclic compounds with two adjacent nitrogen atoms (Buchmeiser, 2003) would prepared by the Michael addition reaction(Otera, 2000) .

Chalcone and pyrazoline derivatives are found to possess a broad spectrum of biological activity, such as anti-malarial (Kenyon *et al.*,1995), anti-bacterial (Asiri *et al*.,2009), anti-oxidative (Arty *et al.*,2000), anti-fungal (Prasad *et al*.,2008), anti-inflammatory (Al-Hajjar, 2007), anti-hipatotoxic (Khan *et al.*,2006), anti-plasmodial(Liu *et al*., 2004), anti-tumor (Abunada *et al.*,2008), anti-mitotic (Fdward *et al.*,1990), anti-aldos reductase (Babin

et al.,1982), anti-trichomonal (Oyedapo *et al*., 2004), anti-prostate, anti-colon cance (Zhou *et al*., 2006), anti-histamic (Sridevi *et al*., 2009), anti-microbial(Srinivasa *et al.*, 2007) anti-hypertensive, anti-depressant (Zhang *et al.*,2007), anti-viral activities (Hajos, 2002) (Alam *et al*., 2005), Also chalcones can be used as eco-friendly bio-pesticides (Nalwar *et al.*, 2009).

The present investigation describes the synthesis and spectroscopic studies of some new chalcones and their transformations to pyrazoline derivatives.

Experimental

Melting points were determined using an Electrothermal melting point apparatus, IR spectra were recorded on a Bio-rad Merlin FT-IR spectroscopy Mod FTS 3000, using KBr disc. ^{1}H-NMR and C^{13}-NMR and ^{13}C-DEPT 135 spectra were recorded on a Bruker(300MHz) with TMS as internal reference in(Jordon) .

1-Synthesis of 3-(4-chlorobenzyloxy)benzaldehyde(1) (Ching *et al*.,2008)
A mixture of 3-hydroxy-benzaldehyde (12.2gm, 0.1mol), 4-chlorobenzylchloride (18.3 gm, 0.12 mol) and anhydrous K_2CO_3 (27.6 gm, 0.2 mol), in ethanol (100 ml - 96%) was refluxed with stirring for 6 hours. When the reaction is completed, the cooled solution poured into water, solid materials immediately was obtained. The product filtered off, washed several times with water and cold ethanol, dried and recrystallized from ethanol to obtain white crystals of 3-(4-chlorobenzyloxy)benzaldehyde (1) ($C_{14}H_{11}ClO_2$), m.p. (47-48 ^{0}C), and in the yield of (23 gm , 93%). IR (cm^{-1}); 1679 (C=O), 1594 (C=C), 1275 and 1182 (C-O-C).
^{1}H-NMR**:** 5.1(s, 2H, H_5); 7.26(d, 1H, H_{11}); 7.38(s, 4H, $H_{2,2`3,3`}$); 7.48(m, 3H, $H_{7,9,10}$);
9.98 (s, 1H, H_{12}). ^{13}C-NMR: 69.42: C_5; 113.12:C_7; 122.15: C_{11}; 123.95:C_9; 128.83:$C_{2,2`,3,3`}$;
130.2:C_{10}; 134.02:$_{C1}$; 134.85:C_8; 137.87:C_4; 159.08:C_6; 191.94:C_{12}.
^{13}C-DEPT: -69.42: C_5; 113.12:C_7; 122.15: C_{11}; 123.95:C_9; 128.83:$C_{2,2`,3,3`}$; 130.2:C_{10}; 191.94:C_{12}.

2- Synthesis of chalcones: 3[3(4-chlorobenzyloxy) phenyl]-1-(substitutedphenyl) -2-propene-1-one (2 a-i)(Patil *et al*.,2007)
Chalcones (2a-i) were synthesized by dissolving 3-(4-chlorobenzyloxy)-benzaldehyde (1) (1.48 gm, 0.006 mol) in ethanol (15ml - 96%), and added to the solution of an appropriate substituted acetophenones (0.006 mol) in ethanol (15 ml - 96%) and (12 ml) of 4% ethanolic sodiumhydroxide. The mixture was stirred at room temperature for (1-5 min.) until the formation of pale yellow crystals of chalcone, then kept the solution at room temperature for (1-2 hrs.). Chalcone crystals were separated by suction

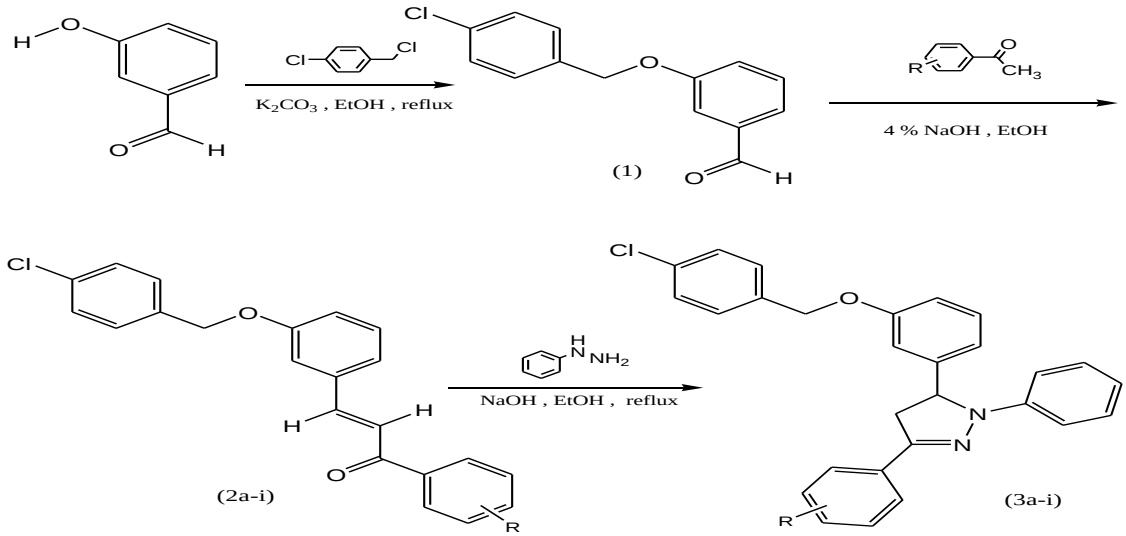
filteration, washed with ethanol and water to neutralize, dried and purified by recrystalization from ethanol or xylene as a suitable Solvents, table(1).

3-Synthesis of pyrazolines 5[3(4-chlorobenzyloxy)phenyl]1-phenyl -3(substituted phenyl) pyrazolines (3 a-i)(Yar *et al.*,2009)

A mixture of phenyl hydrazine (0.16 gm, 0.0015 mol), chalcones (2a-i) (0.001 mol) and sodium hydroxide (0.001 mol) in (25 ml - 96%) ethanol was refluxed with stirring about (1-2 hrs.) until complete the reaction which was monitored by the formation of ppt.of the pyrazoline products (3 a-i). The ppt. was isolated by suction filtration, washed with ethanol and water to neutralize, dried and purified by recrystalization from xylene-ethanol as suitable double solvent. The physical properties of the prepared pyrazolines (3a-i) were summarized in table (2).

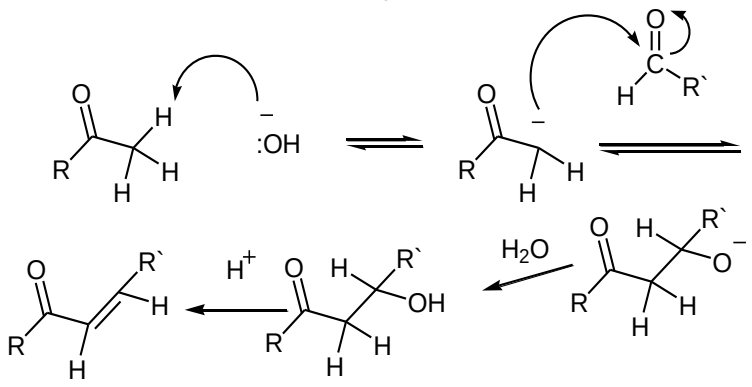
Results and Discussion

The present investigation involves the synthesis of some new pyrazolines from the preparation of starting material 3-(4-chlorobenzyloxy) benzaldehyde (1), on the basis of Williamson synthesis of ethers. Compound (1) subjected to react with a series of substituted acetophenones to give new chalcones (2a-i), the later compounds were treated with phenylhydrazine to form a new derivatves of pyrazolines (3a-i) scheme (1).



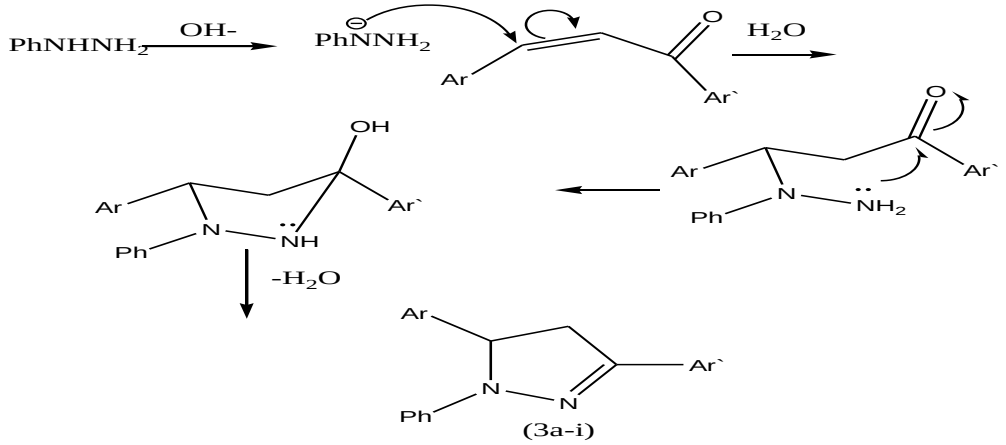
Scheme (1): R: 4-Br, 4-F, 4-Cl, 4-Me, 4-OMe, 4-H, 2-Naph, 4-ph, 4-OCH_2Ph .

Mechanism of chalcone synthesis :



Scheme (2)

Mechanism of pyrazoline synthesis (Michael route):



Scheme (3)

The structures of the synthesized products were confirmed by spectral methods using FT-IR, ^{1}H-nmr, ^{13}C-nmr and ^{13}C-dept 135 spectra.

The IR spectrum of compound (1) shows a strong band at 1679 cm^{-1} attributed to carbonyl group (Bajia *et al*., 2007) and the disappearance of hydroxy group indicates the benzylation of phenolic OH group.

The ^{1}H-nmr spectrum shows a singlet at δ 5.11 for two protons of benzylic CH_2 group(Hawaiz, 2007), a singlet at 9.9 ppm for aldehydic CH group, and other signals for aromatic protons at (7.24-7.48).The ^{13}C-nmr shows eleven singlets for eleven types of carbons in different environments in the molecule. Further support for structure elucidation is come from ^{13}C-Dept-135 spectrum the ^{13}C-Dept spectrum(Field, 2005) (Distortionless Enhancement by Polarization Transfers) is the most commonly used method to determine the multiplicity of ^{13}C-signals. Compound (1), shows a downward singlet at δ -69.42 corresponding to the di-protonated carbon of benzyloxy group and six singlets for six types of mono- protonated

carbons in different chemical shifts and the disappearance of four non-protonated carbons which appeared in normal ^{13}C-nmr is a good evidence for the estimated structure .

The reaction of compound(1) with different substituted acetophenones to form the corresponding chalcones (2a-i) were confirmed and their expected structures were illustrated spectroscopically as follows: The IR spectrum table (3), for all of the synthesized chalcones show the shifting of the absorption band of carbonyl group from 1679 cm^{-1}compound (1) to lower wave numbers 1659 cm^{-1} ; this is a strong evidence for the formation of conjugated enone of chalcones and strong band at 1600 cm^{-1} corresponding C=C double bond of enone and aromatic rings. The ^{1}H-nmr spectra, table(4), figure (1), show the disappearance of methyl signal of compound (1) and showed the Cα-H and Cβ-H protons of chalcone downfield to the extent(Kim *et al*., 2007) of aromatic region δ 7-8.0 with remaining the signals of the rest of the molecule. The ^{13}C-nmr specta table (6), fig.(2) showed the most important signal of C-β carbon atom resonance at~ δ144 appeared downfield of those of the C-α atoms at ~(122 ppm) because of the mesomeric deshielding effect of the carbonyl group (Solankee *et al*.,2009). The Dept spectrum, Table (6), Fig.(2) showed a downward signal at ~70 ppm for benzyl CH_2 group and disappearance of the non-protonated carbons which observed in normal ^{13}C-nmr chart.

Transformation of the synthesized chalcones to pyrazoline derivatives were elucidated spectroscopically, the IR spectra table (3), showed the disappearance of conjugated enones and the ^{1}H-nmr spectra table (5) gave an (ABX) spin system(Levai *et al*.,2007) which appeared three doublet to doublet (dd) signals approximately at approximately 3,4,5 ppm for two geminal and one vicinal protons unequivocally prove a 2-pyrazoline structureSharma *et al*., 2009) .The three important bands in ^{13}C-nmr spectra table (7) for $C_{12, 13, 15}$ at~ 40, 65,and 144 respectively and the disappearance of Cα and Cβ- signals corroborate the expected structure(Ashok *et al*., 2009), further support is also come from the dept spectra table (7) by observing downward signals for CH_2 in the pyrazoline ring and upward signals for CH and CH_3 groups with disappearance of non-protonated signals.

Table (1): Some physical properties for the prepared chalcones (2a-i).

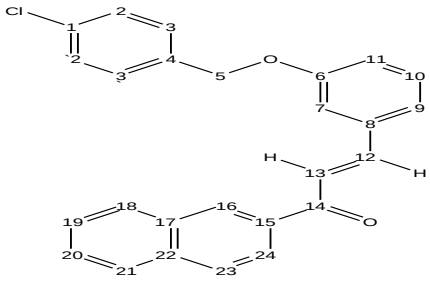
Prod.	R	Molecular formula	M.P. / ^{0}C	% Yield
2a	4-F	$C_{22}H_{16}ClFO_2$	113-114	86
2b	4-Br	$C_{22}H_{16}BrClO_2$	110-111	93
2c	2-Naph	$C_{26}H_{19}ClO_2$	127-128	90
2d	4-C_6H_5	$C_{28}H_{21}ClO_2$	163-164	89
2e	H	$C_{22}H_{17}ClO_2$	115-116	70
2f	4-Cl	$C_{22}H_{16}Cl_2O_2$	130-131	91
2g	4-OCH_3	$C_{29}H_{25}ClN_2O_2$	117-118	87
2h	4-CH_3	$C_{29}H_{25}ClN_2O$	120-121	95
2i	4-O-CH_2-C_6H_5	$C_{29}H_{23}ClO_3$	159-160	93

Table (2): Some physical properties for the prepared pyrazolines (3a-i).

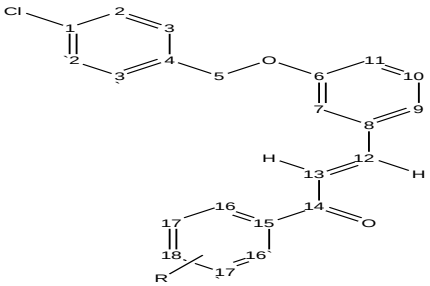
Prod.	R	Molecular formula	M.P. / ^{0}C	% Yield
3a	4-F	$C_{28}H_{22}ClFN_2O$	94-95	72
3b	4-Br	$C_{28}H_{22}BrClN_2O$	147-148	70
3c	2-Naph	$C_{32}H_{25}ClN_2O$	166-167	22
3d	4-C_6H_5	$C_{34}H_{27}ClN_2O$	172-173	31
3e	H	$C_{28}H_{23}ClN_2O$	125-126	41
3f	4-Cl	$C_{28}H_{22}Cl_2N_2O$	122-123	38
3g	4-OCH_3	$C_{29}H_{25}ClN_2O_2$	126-127	59
3h	4-CH_3	$C_{29}H_{25}ClN_2O$	134-135	53
3i	4-O-CH_2-C_6H_5	$C_{35}H_{29}ClN_2O_2$	104-105	61

Table (3): Assignment of characteristic frequencies of(cm^{-1}) IR data for the prepared chalcones (2a-i) and pyrazolines (3a-i) .

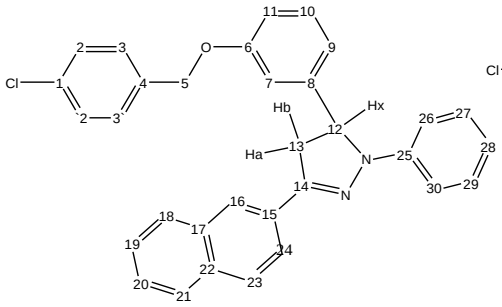
Product	R	Chalcones (2a-i)		Pyrazolines (3a-i)
		C=O(cm^{-1})	C=C(cm^{-1})	C=N(cm^{-1})
A	4-F	1659	1603	1596
B	4-Br	1658	1601	1598
C	2-Naph	1657	1603	1596
D	4-C_6H_5	1657	1605	1598
E	H	1659	1602	1592
F	4-Cl	1659	1603	1598
G	4-OCH_3	1652	1596	1597
H	4-CH_3	1658	1597	1596
I	4-O-CH_2-C_6H_5	1660	1599	1598



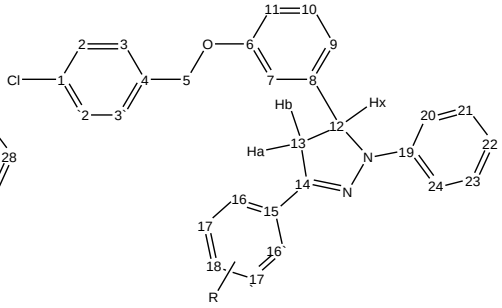
2c



2a-i



3c



3a-i

Table (4): The ^{1}H-NMR data for the prepared chalcones (2b,d,h). (2b, 2c, and 2h): Solvent: DMSO-d^{6}, $CDCl_3$.

Product	δ / ppm	Multiplicity	Intensity	Assignment
2b	5.18	S	2	-O-CH_2:C_5
	7.34	D	1	CH-α:C_{13}
	7.91	D	1	CH-β:C_{12}
	7.3-8.1	M	12	Ar-protons
2c	5.11	S	2	-O-CH_2:C_5
	7.41	D	1	CH-α:C_{13}
	7.83	D	1	CH-β:C_{12}
	7.03-8.55	M	15	Ar-protons
2h	2.46	S	3	-CH_3:C_{19}
	5.09	S	2	-O-CH_2:C_5
	7.24	D	1	CH-α:C_{13}
	7.76	D	1	CH-β:C_{12}
	7.01-7.96	M	15	Ar-protons

Table 5: The ^{1}H-NMR data for the prepared pyrazolines (3b, 3c, and 3h): Solvent: DMSO-d^{6}, $CDCl_3$.

Product	δ / ppm	Multiplicity	Intensity	Assignment
3b	3.11	Dd	1	$H_{a\text{-}13}$
	3.80	Dd	1	$H_{b\text{-}13}$
	4.98	S	2	-O-CH_2:H_5
	5.25	Dd	1	$H_{x\text{-}12}$
	6.82-7.6	M	17	Ar-protons
3c.	3.29	Dd	1	$H_{a\text{-}13}$
	3.96	Dd	1	$H_{b\text{-}13}$
	4.98	S	2	-O-CH_2:H_5
	5.3	Dd	1	$H_{x\text{-}12}$
	6.82-8.18	M	20	Ar-protons
3h	2.41	S	3	-CH_3
	3.14	Dd	1	$H_{a\text{-}13}$
	3.83	Dd	1	$H_{b\text{-}13}$
	4.98	S	2	-O-CH_2:H_5
	5.22	Dd	1	$H_{x\text{-}12}$
	6.8-7.66	M	17	Ar-protons

Table (6):The ^{13}C-nmr and Dept -135 data for some of the synthesized compounds(2b, 2c, and 2h) : Solvent : DMSO-d^6 , $CDCl_3$.

2b ^{13}-C-nmr		**2b Dept- 135**		**2c ^{13}-C-nmr**		**2c Dept- 135**		**2h ^{13}C-nmr**		**2h Dept- 135**	
δ ppm	**Assig.**	**δ ppm**	**Assig.**	**δ ppm**	**Assig.**	**δ ppm**	**Assig**	**δ ppm**	**Assig.**	**δ ppm**	**Assig**
69.01	C_5	69.01	C_5	69.40	C_5	-69.40	C_5	21.69	CH_3	21.69	CH_3
114.86	C_7	114.85	C_7	114.59	C_7	114.59	C_7	69.38	C_5	-69.38	C_5
117.95	C_{11}	117.95	C_{11}	116.98	C_{11}	116.98	C_{11}	114.47	C_7	114.47	C_7
122.48	C_9	122.47	C_9	121.62	C_9	121.63	C_9	116.89	C_{11}	116.89	C_{11}
122.75	C_{13}	122.76	C_{13}	122.54	C_{13}	122.53	C_{13}	121.52	C_9	121.52	C_9
127.85	C_{18}	128.94	$C_{3,3`}$	124.48	C_{24}	124.48	C_{24}	122.55	C_{13}	122.54	C_{13}
128.94	$C_{3,3`}$	130.17	$C_{2,2`}$	126.84	C_{19}	126.84	C_{19}	128.6	$C_{3,3`}$	128.6	$C_{3,3`}$
130.01	$C_{2,2`}$	130.49	$C_{16,16`}$	127.85	C_{21}	127.86	C_{21}	128.81	$C_{2,2`}$	128.81	$C_{2,2`}$
130.50	$C_{16,16`}$	131.07	$C_{17,17`}$	128.62	C_{20}	128.62	C_{20}	128.85	$C_{16,16`}$	128.85	$C_{16,16`}$
131.06	$C_{17,17`}$	132.33	C_{10}	128.83	C_{23}	128.83	C_{23}	129.36	$C_{17,17`}$	129.36	$C_{17,17`}$
132.32	C_{10}	144.88	C_{12}	128.87	$C_{3,3`}$	128.87	$C_{3,3`}$	130.03	C_{10}	130.03	C_{10}
132.97	C_1			129.55	$C_{2,2`}$	129.55	$C_{2,2`}$	133.94	C_1	144.06	C_{12}
136.48	$C_{8,15}$			129.98	$C_{18,10}$	129.98	$C_{18,10}$	135.20	C_{15}		
136.94	C_4			130.09	C_{16}	130.09	C_{16}	135.59	C_8		
144.88	C_{12}			132.58	C_1	144.45	C_{12}	136.54	C_4		
159.03	C_6			133.96	C_{22}			143.72	C_{18}		
188.75	C_{14}			135.10	C_{15}			144.06	C_{12}		
				135.19	C_{17}			158.90	C_6		
				135..5	C_8			189.88	C_{14}		
				136.94	C_4						
				144.88	C_{12}						
				159.03	C_6						
				188.75	C_{14}						

Table (7): The ^{13}C-nmr and Dept -135 data for some of the synthesized compounds (3b, 3c, and 3h): Solvent: DMSO-d^6, $CDCl_3$.

3b ^{13}-C-nmr		**3b Dept- 135**		**3c ^{13}-C-nmr**		**3c Dept- 135**		**3h ^{13}C-nmr**		**3h Dept- 135**	
δ ppm	**Assig.**	**δ ppm**	**Assig.**	**δ ppm**	**Assig.**	**δ ppm**	**Assig**	**δ ppm**	**Assig.**	**δ ppm**	**Assig.**
43.29	C_{13}	-43.29	C_{13}	43.46	C_{13}	-43.46	C_{13}	21.43	CH_3	21.43	CH_3
64.54	C_{12}	64.53	C_{12}	64.53	C_{12}	64.53	C_{12}	43.67	C_{13}	-43.67	C_{13}
69.17	C_5	-69.17	C_5	69.17	C_5	-69.17	C_5	64.43	C_{12}	64.43	C_{12}
112.1	C_{11}	112.15	C_{11}	112.15	C_{11}	112.15	C_{11}	69.15	C_5	-69.15	C_5
113.4	$C_{20,24}$	113.42	$C_{20,24}$	113.45	$C_{30,26}$	113.45	$C_{30,26}$	112.11	C_{11}	112.11	C_{11}
114.0	C_{22}	114.04	C_{22}	114.08	C_{28}	114.08	C_{28}	113.33	$C_{20,24}$	113.33	$C_{20,24}$
118.6	C_7	118.59	C_7	118.67	C_7	118.67	C_7	114.04	C_{22}	114.04	C_{22}
119.4	C_9	119.46	C_9	119.30	C_9	119.30	C_9	118.69	C_7	118.69	C_7
122.5	C_{18}	127.15	$C_{3,3`}$	123.49	C_{24}	123.49	C_{24}	119.04	C_9	119.04	C_9
127.1	$C_{3,3`}$	128.89	$C_{2,2`,16,16`}$	125.11	C_{19}	125.11	C_{19}	125.76	$C_{3,3}$	125.76	$C_{3,3}$
128.8	$C_{2,2`,16,16`}$	130.39	$C_{10,21,21`}$	126.49	C_{20}	126.49	C_{20}	128.71	$C_{16,16`}$	128.71	$C_{16,16`}$
130.3	$C_{10,21,21`}$	131.73	$C_{17,17`}$	127.84	$C_{3,3`}$	127.84	$C_{3,3`}$	128.91	$C_{17,17`}$	128.91	$C_{17,17`}$
131.6	$C_{17,17`}$			128.23	$C_{16,18,21,23}$	128.23	$C_{16,18,21,23}$	129.30	$C_{2,2`,21,23}$	129.30	$C_{2,2`,21,23}$
133.7	$C_{1,15}$			128.89	$C_{2,2`,15}$	128.89	$C_{2,2`,15}$	129.93	C_{15}	129.93	C_{15}
135.2	C_4			130.34	$C_{10,27,29}$	130.34	$C_{10,27,29}$	130.28	C_{10}	130.28	C_{10}
144.2	C_8			133.32	C_1			133.73	C_1		
144.5	C_{19}			133.75	$C_{17,22}$			135.28	C_4		
145.6	C_{14}			135.25	C_4			138.76	C_{18}		
159.2	C_6			144.45	C_8			144.62	C_8		
				144.77	C_{25}			145.07	C_{19}		
				146.86	C_{14}			147.00	C_{14}		
				159.22	C_6			159.19	C_6		

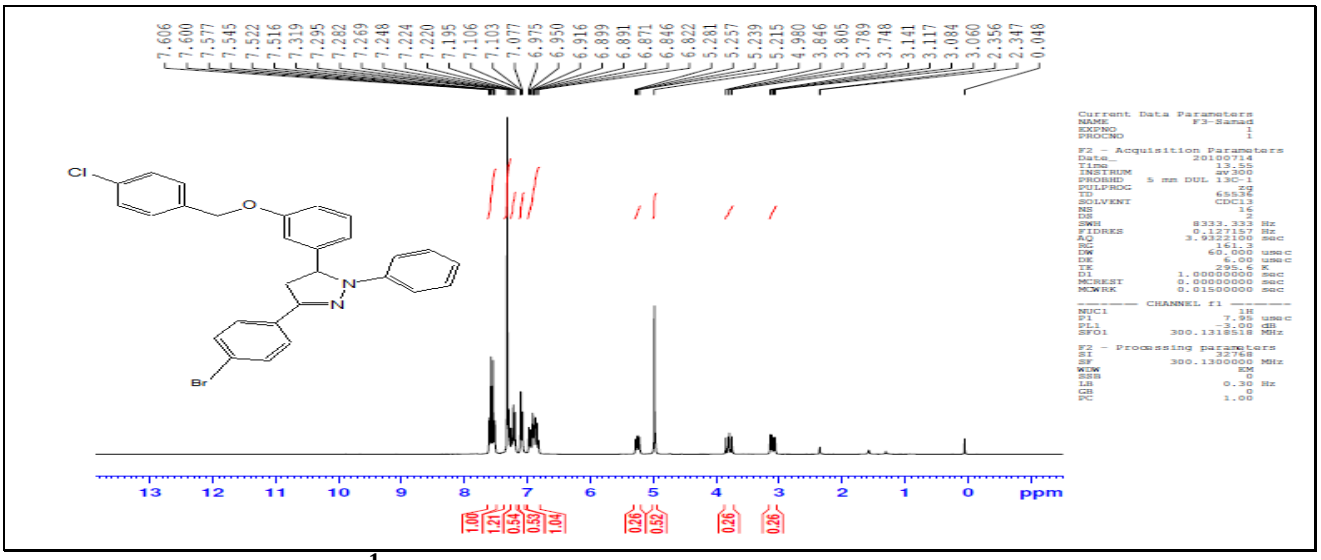


Fig.(1) : ^{1}H-nmr spectrum of compound (3b)

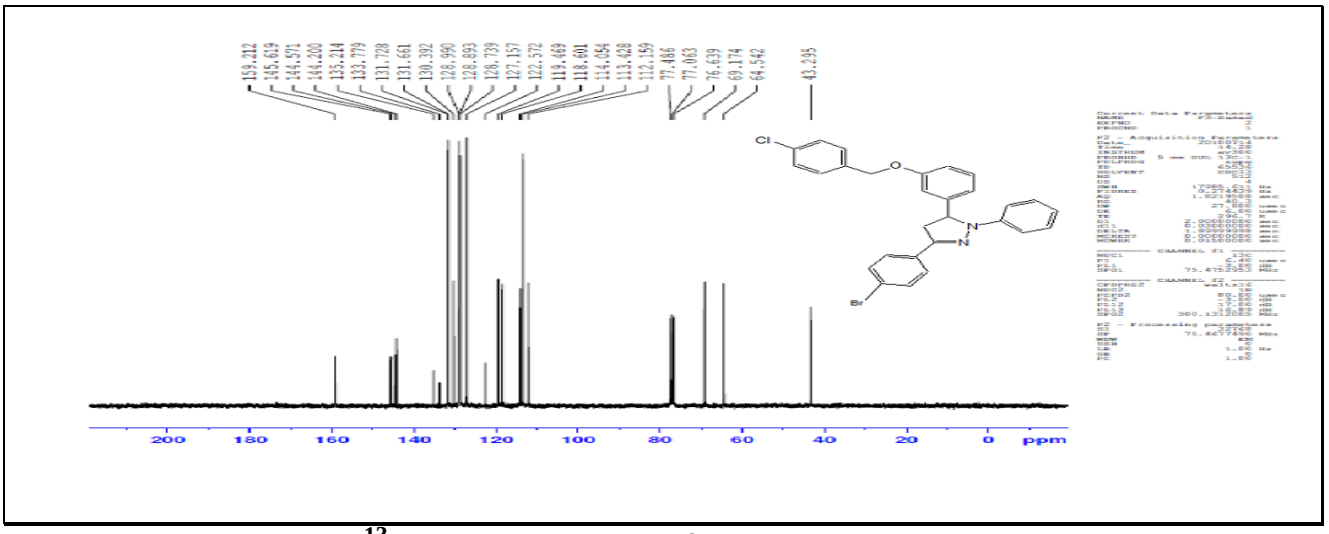


Fig.(2) : ^{13}C-nmr spectrum of compound (3b)

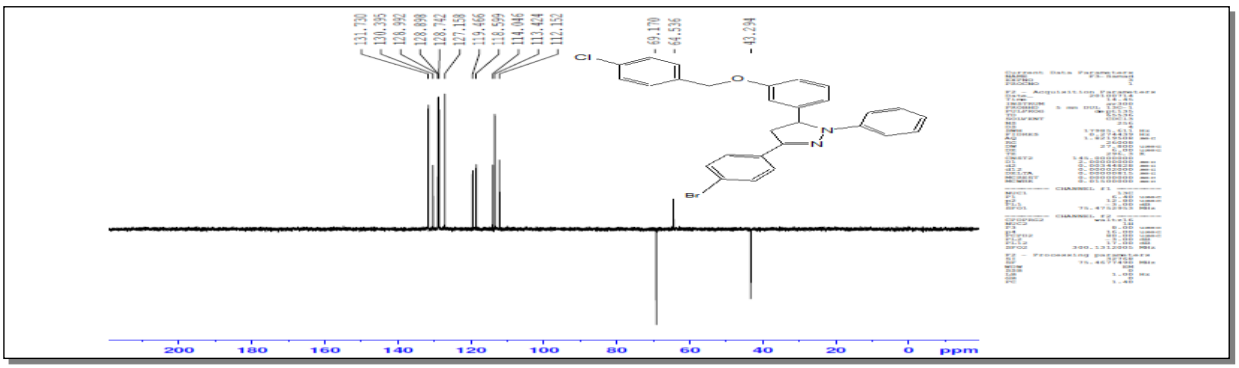


Fig.(3) : Dept-135 spectrum of compound (3b)

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تحضير وتشخيص سلسلة جديدة من الجالكونات و تحويلها الى مشتقات البايرازولين

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الخلاصة

يتضمن هذا البحث ، بالاعتماد على تكاثف كلايسن–شميت تم تحضير سلسلة جديدة من مركبات جالكون الحاوي على مجموعة البنزايلوكسي من تفاعل (3-(4-cholrobenzyloxy)benzaldehyd) و سلسلة من مركبات اسيتوفينون المعوض، ثم بعد ذلك تم مفاعلة الجالكونات مع الهايدرازين بالاعتماد على اضافة مايكل لتعطى سلسلة جديدة من مشتقات البايرازولين. و اخيراً تم تشخيص تراكيب المركبات لناتجة بوساطة الطرق الطيفية مثل:– طيف اشعة تحت الحمراء و طيف الرنين النووي المغناطيسي بانواعها الثلاثة : (^{1}H-nmr, ^{13}C-nmr Dept-135) .