Solvent- Free Synthesis and Spectroscopic Identification of Some Chalcones and Imines Derived From p-Amino acetophenone

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Abstract:

Two series of Chalcones (3a-j) and Imines (4a-j) have been synthesized in high yield via simple and convenient solvent-free process from the same starting material p-amino acetophenone with different substituted benzaldehydes(2a-j) by using the catalysts sodium hydroxide and acetic acid respectively. The structure of the synthesized compounds were elucidated spectroscopically using FT-IR, ^{1}H-NMR, ^{13}C-NMR and ^{13}C-Dept −135 spectra.

Key words: solvent free, chalcones, imines

Introduction:

Chalcones (1,3-diaryl-2-propen-1-one) and schiff bases (substituted benzylidene aniline) belongs to a widely used groups of organic intermediates, possess broad spectrums of biological activity such as antioxidants [1, 2], antileshmanial [3, 4], antifungal [5, 6], and antimicrobial [7, 9] . Both chalcones and Schiff bases are important for synthesis of different active organic compounds such as flavones [10, 11], pyrazoloins [12, 13], β-lactams [14, 15] and metal complexes [16-18].

Generally chalcones and Schiff bases were prepared by condensation of carbonyl compounds (substituted benzaldehydes) as an electrophile with (substituted acetophenone) and amines as a nucleophile on the bases of Claisen- Schmidt condensation[19] and imines [20] synthesis in polar solvents respectively. There was some variation known, such as chalcones and schiff bases preparation in a water suspension medium[21, 22], ultrasonic [23, 24] and microwave irradiation techniques [25, 26], or using different new catalysts[27, 28].

In recent years, environmentally benign synthetic methods have received considerable attention and some solvent free synthesis under microwave irradiation have been developed, consequently, on the bases of these facts and under the framework of green chemistry, this work describes an environmentally benign green synthesis of some chalcones and Schiff bases without the use of solvent and heating from the same compounds by changing only the catalyst sodium hydroxide to acetic acid respectively.

Experimental:

Melting points were determined using Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded on a Bio – Rad Merlin, FT-IR spectrophotometer Model FTS 3000(KBr). The ^{1}H-nmr, ^{13}C-nmr and ^{13}C-Dept 135 were taken on a Bruker ultra shild 300 MH z with TMS as internal reference, at Al-al-Bayt central labs (Jordan).

1- **Solvent –free synthesis of Chalcones: 1-(4-aminophenyl) 3-(substituted phenyl) propenone(3a-j). [29] :**

p-amino acetophenone (0.135 gm, 0.001 mole) , substituted benzaldehydes (0.001 mole) and solid NaOH (0.04gm , 0.001 mole) were combined using a mortar and pestle , the pale yellow mixture was aggregated as tacky solid then to an eutectic melt and finally changed to the powder product about (3-8) minutes .The products were washed with water to neutralize then washed or recrystallized from ethanol or toluene.

2- **Solvent –free synthesis of Schiff bases(Imines) : N-(substituted benzylidene)-4-acetylaniline :(4a-j):**

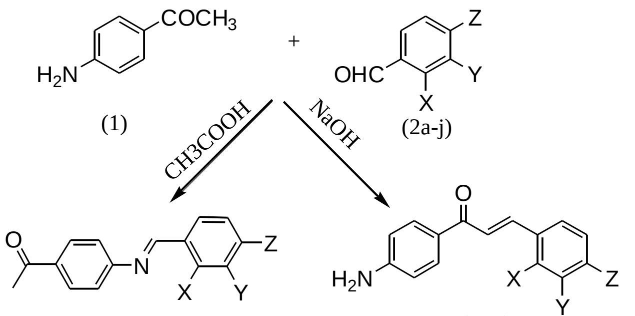
According to the above procedure, using the same starting materials p-amino acetophenone and the same (substituted benzaldehydes) all imines were obtained in high yields, changing only the catalyst (1-2 drops of concentrated acetic acid used instead of sodium hydroxide). The products were purified by recrystallization from ethanol .

Results and Discussion:

The conventional synthesis of chalcones and imines involves the condensation of substituted benzaldehydes with substituted acetophenones in chalcones and substituted amines in imines in polar solvents like ethanol through expelling of water molecule in both reactions, the products must be purified and isolated from the organic solvent.

We have prepared two series of chalcones and imines (Scheme1) without using solvent or heat, by grinding/ mixing the reactants together in the presence of catalyst NaOH in the case of chalcones , and (1-2) drops of acetic acid in the case of imines preparation. The condensation proceeds sufficiently and the products were isolated with out the need of recrystallization by washing with water to remove the catalyst in the preparation of chalcones, while impurities can be removed from imines by washing or recrystallization with ethanol .

The solvent free imine synthesis from, solid-liquid and solid – solid starting materials, were proceeded in quantitative yields, while in the case of chalcones only the solid-solid starting materials needs a drop of water to dissolve the catalyst and mixing the reactants , moreover, the solid-liquid state were proceeded efficiently and high yields were obtained.



(1) (2a-j)

(4a-j) (3a-j)

	a	b	c	d	e	f	g	h	i	j
x	H	H	H	Cl	H	F	H	H	H	H
y	H	H	H	H	H	H	H	NO_2	H	OCH_3
z	CH_3	Br	Cl	H	F	H	NO_2	H	OCH_3	OH

Scheme 1

Considerable interest has been focused on comparison the synthesis of chalcones and imines together and with other procedures in the literature :

First, all reactants and both procedures are the same for synthesis of chalcones and imines, but the difference appeared in the use of the catalyst (sodium hydroxide or acetic acid). Second, bringing down the reaction time from hours to a few minutes without using any (solvents or heat) as compared with classical methods[30-31].

The structures of the synthesized products were established by spectral methods IR, ^{1}H-nmr,^{13}C-nmr and ^{13}C-Dept-135 .The IR spectra for all synthesized chalcones observed the shifting of absorption band of carbonyl group for the two reactants p-amino acetophenone and substituted benzaldehydes from *ca* 1670 cm^{-1} to lower wave number *ca* 1650 cm^{-1} , which is a strong evidence for the formation of conjugated enone of chalcone [32] .Other strong bands appeared at *ca.* 1600 cm^{-1}, corresponding to C=C of the enone and aromatic rings , also the disappearance of aldehydic (C-H) bands and remaining of NH_2 stretching vibration of the amino group is a good evidence for the formation of chalcones.

The ^{1}H-nmr spectra of some chalcones as a representative sample of their series table (3) fig (1) showed that the Cα- protons are consedirably shifted down field to the extent that they appear in aromatic region (7-8) ppm due to the joint deshielding resonance and anistropic effect of the phenyl ring bonded to β-carbon, and the disappearance of the aldehydic proton ca (9-10)ppm is a good evidence for the formation of desired product. The most important features of ^{13}C-nmr spectra of synthesized chalcones table (4) fig (2) is the β-carbon atom resonance at *ca.* 140 ppm which appeared down field of α-carbon atom at *ca*. 120 ppm because of mesomeric deshielding effect of the carbonyl group [33].

The ^{13}C-DEPT[34] (Distortionless Enhancement by Polarization Transfers) is the most commonly used method to determine the multiplicity of ^{13}C-signals. The resulting ^{13}C-DEPT spectrum containing only signals arising from protonated carbons (non-protonated carbons do not give signals in the ^{13}C-DEPT). The signals arising from carbons in CH_3 and CH groups appear oppositely phased from those in CH_2 groups, so signals from CH_3 and CH groups point upwards (+) while signals for CH_2 groups point downwards (-) .

The DEPT spectrum for compound (3g) showed six singlets for six mono protonated carbons and the disappearance of five singlets attributed to five non-protonated carbons which appeared in normal ^{13}C-nmr spectrum..

The IR spectra of imines table (2) showed the disappearance of (NH_2 stretching vibration and aldehydic C-H) of both reactants and the appearance of C=N bands at *ca.* 1625 cm^{-1} furnished a good evidence for the formation of expected structures. The ^{1}H-nmr spectra table (3) fig (4)of some imines as a representative sample of their series were very informative and furnished a good evidence to the expected products by observing a singlet signals at. (8.4)ppm for the imine protons of (H-C=N) and the disappearance of aldehydic protons with the characteristic bands for the other protons [35] . The ^{13}C-nmr spectra table (4) fig (5) showed a singlet at 161 ppm attributed to the imine carbon (C=N) with the other characteristic bands for each carbon atom, and the ^{13}C-Dept 135 spectra table (5) fig (6) gave an important distinguish between CH, and CH_3 and non-protonated carbons in the imines skeletons.

Table (1) : Physical properties and IR v(cm^{-1}) data of the synthesized Chalcones (3a-j) :

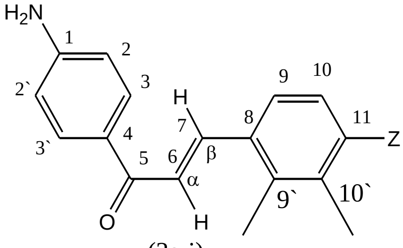
Prod.	x	y	z	Molecular formula	M.P. °C	Yield %	IR v(cm^{-1})		
							NH - str.	C=O str.	C=C str.
3a	H	H	CH_3	$C_{16}H_{15}NO$	177-179	89	3456,3352,3210	1657	1590
3b	H	H	Br	$C_{15}H_{12}BrNO$	188-190	90	3461,3341,3150	1653	1604
3c	H	H	Cl	$C_{15}H_{12}ClNO$	>300	85	3456,3339,3227	1656	1590
3d	Cl	H	H	$C_{15}H_{12}ClNO$	192-194	85	3455,3338,3225	1653	1592
3e	H	H	F	$C_{15}H_{12}FNO$	139-141	85	3460,3336,3213	1651	1579
3f	F	H	H	$C_{15}H_{12}FNO$	220-224	80	3467,3352,3230	1653	1595
3g	H	H	NO_2	$C_{15}H_{12}N_2O_3$	197-199	90	3486,3388,3234	1646	1596
3h	H	NO_2	H	$C_{15}H_{12}N_2O_3$	165-167	85	3480,3375,3232	1645	1595
3 i	H	H	OCH_3	$C_{16}H_{15}NO_2$	280dec.	85	3470,3378,3220	1650	1596
3 j	H	OCH_3	OH	$C_{16}H_{15}NO_3$	>300	90	3395,3331,3224	1654	1583

Table (2) : Physical properties and IR v(cm^{-1}) data of the synthesized Imines (4a-j) :

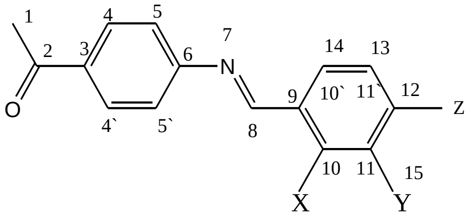
Prod.	x	y	z	Molecular formula	M.P. °C	Yield %	IR v(cm^{-1})		
							C=O str.	C=N str.	C=C str.
4a	H	H	CH_3	$C_{16}H_{15}NO$	135-136	90	1672	1620	1595
4b	H	H	Br	$C_{15}H_{12}BrNO$	145-146	91	1671	1629	1585
4c	H	H	Cl	$C_{15}H_{12}ClNO$	138-139	88	1671	1622	1589
4d	Cl	H	H	$C_{15}H_{12}ClNO$	105-106	89	1679	1622	1600
4e	H	H	F	$C_{15}H_{12}FNO$	113-114	91	1672	1622	1585
4f	F	H	H	$C_{15}H_{12}FNO$	102-103	87	1669	1620	1591
4g	H	H	NO_2	$C_{15}H_{12}N_2O_3$	150-151	89	1672	1620	1589
4h	H	NO_2	H	$C_{15}H_{12}N_2O_3$	108-110	88	1670	1622	1588
4 i	H	H	OCH_3	$C_{16}H_{15}NO_2$	128-129	86	1670	1632	1589
4 j	H	OCH_3	OH	$C_{16}H_{15}NO_3$	168-169	90	1666	1629	1581

Table (3) : The ^1H- NMR data for the prepared Chalcones and Imines Solvent : DMSO-d^6 ,$CDCl_3$.

Prod.	**δ ppm Multiplicity Intensity Assignment**
3 b	4.1 (b, 2H, NH_2) ; 6.64 (d, 2H, $H_{2,2`}$ ) ; 7.64 (d, 2H, $H_{9,9`}$) 7.79 (d, 2H, $H_{10,10`}$) ; 7.82 (d, 1H, $H_{-\alpha}$) ; 7.87 (d, 2H, $H_{3,3`}$) 7.94 (d, 1H, $H_{-\beta}$) .
3 g	3.55 (b, 2H, NH_2) ; 6.62 (d, 2H, $H_{2,2`}$ ) ; 7.65 (d, 2H, $H_{9,9`}$) 7.88 (d, 2H, $H_{3,3`}$) ; 7.9 (d, 1H, $H_{-\alpha}$) ; 7.94 (d, 1H, $H_{-\beta}$) ; 8.2 (d, 2H, $H_{10,10`}$) ;
4 a	2.37 (s, 3H, H_{13}) ; 2.60 (s, 3H, H_1); 7.23 (d, 2H, $H_{11,11`}$); 7.3 (d, 2H, $H_{5,5`}$) ; 7.78 (d, 2H, $H_{10,10`}$); 7.99 (d,2H,$H_{4,4`}$) 8.4(s, 1H, H_8).
4 b	2.59 (s, 3H, H_1) ; 7.24 (d, 2H, $H_{5,5`}$ ); 7.65 (d, 2H, $H_{11,11`}$); 7.74 (d, 2H, $H_{10,10`}$) ; 8.02 (d,2H,$H_{4,4`}$) ;8.41(s, 1H, H_8).
4 c	2.57 (s, 3H, H_1) ; 7.23 (d, 2H, $H_{11,11`}$); 7.48(d, 2H, $H_{5,5`}$); 7.9 (d, 2H, $H_{10,10`}$) ; 8.04 (d,2H,$H_{4,4`}$) ;8.4(s, 1H, H_8).
4 j	2.63 (s, 3H, H_1) ;3.99(3, 3H, H_{15}); 6.65 (d, 1H, H_{11}); 7.02 (d, 2H, $H_{10,14}$) ; 7.24(d, 2H, $H_{5,5`}$ ); 8.05 (d,2H,$H_{4,4`}$) ; 8.35(s, 1H, H_8).



(3a-j)



(4a-j)

Table (4) :The^{13}C-NMR data for the prepared Chalcones and Imines Solvent : DMSO-d^6 , $CDCl_3$,

3b		3g		4a		4b		4c		4j	
δ ppm	**Assig.**	**δ ppm**	**Assig.**	**δ ppm**	**Assig.**	**δ ppm**	**Assig.**	**δ ppm**	**Assig.**	**δ ppm**	**Assig.**
113.2	$C_{2,2'}$	113.3	$C_{2,2'}$	21.75	C_{13}	26.3	C_1	26.59	C_1	26.57	C_1
123.5	C_{11}	124.35	$C_{10,10'}$	26.5	C_1	120.8	$C_{5,5'}$	120.88	$C_{5,5'}$	56.14	C_{15}
123.7	C_α	125.5	C_4	120.9	$C_{5,5'}$	126.6	C_{12}	124.86	C_{12}	108.6	C_{14}
126.5	C_4	127.18	C_α	127.7	$C_{10,10'}$	129.7	$C_{4,4'}$	129.2	$C_{11,11'}$	114.3	C_{11}
130.9	$C_{9,9'}$	129.9	$C_{9,9'}$	128.7	C_9	130.7	$C_{10,10'}$	129.8	$C_{4,4'}$	120.9	$C_{5,5',9}$
131.5	$C_{3,3'}$	131.85	$C_{3,3'}$	129.7	$C_{11,11'}$	132.2	$C_{11,11'}$	130.6	$C_{10,10'}$	125.3	C_{10}
132.5	$C_{10,10'}$	139.0	C_β	129.9	$C_{4,4'}$	134.6	C_9	134.8	$C_{3,9}$	129.5	$C_{4,4'}$
134.9	C_8	142.2	C_8	134.4	C_3	134.8	C_3	155.2	C_6	134.29	C_3
140.6	C_β	148.18	C_{11}	142.7	C_{12}	155.8	C6	160.3	C_8	149.2	C_{13}
153.8	C_1	154.59	C_1	156.3	C_6	160.3	C_8	197.16	C_2	157.5	C_6
192.7	C_5	185.9	C_5	161.6	C_8	197.16	C_2			161.2	C_8
				197.28	C_2					196.5	C_2

Table (5) :The ^{13}C-DEPT- NMR data for the prepared Chalcones and Imines : Solvent DMSO-d^6, $CDCl_3$,

3g		4a		4b		4c		4j	
δ ppm	**Assign.**	**δ ppm**	**Assign.**	**δ ppm**	**Assign.**	**δ ppm**	**Assign.**	**δ ppm**	**Assign.**
113.2	$C_{2,2'}$	21.76	C_{13}	26.5	C_1	26.59	C_1	26.57	C_1
124.35	$C_{10,10'}$	26.5	C_1	120.8	$C_{5,5'}$	120.8	$C_{5,5'}$	56.14	C_{15}
127.18	C_α	120.9	$C_{5,5'}$	129.7	$C_{4,4'}$	129.2	$C_{11,11'}$	108.6	C_{14}

129.9	$C_{9,9`}$	127.7	$C_{10,10`}$	130.7	$C_{10,10`}$	129.7	$C_{4,4`}$	114.3	C_{11}
131.85	$C_{3,3`}$	129.7	$C_{11,11`}$	132.2	$C_{11,11`}$	130.6	$C_{10,10`}$	120.9	$C_{5,5`}$
139.0	C_{β}	130.1	$C_{4,4`}$	160.3	C_{8}	160.3	C_{8}	125.3	C_{10}
		161.7	C_{8}					129.5	$C_{4,4`}$
								161.2	C_{8}

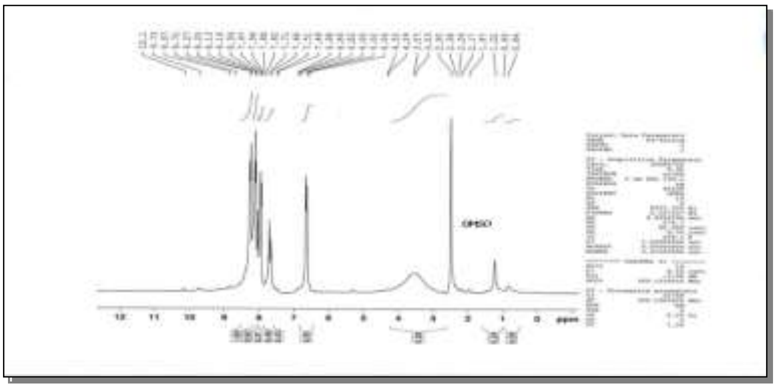


Fig.(1) : ^{1}H-nmr spectrum of compound (3g).

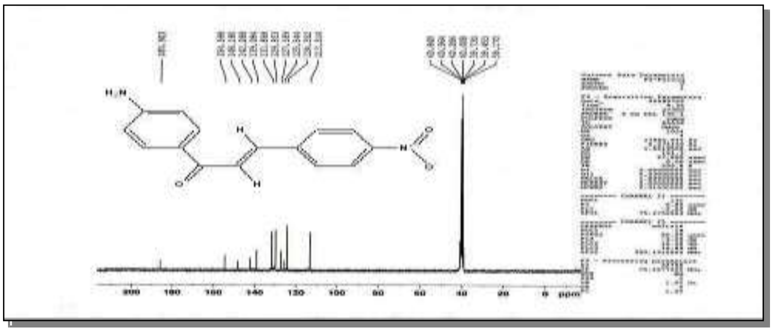


Fig.(2) : ^{13}C-nmr spectrum of compound (3g)

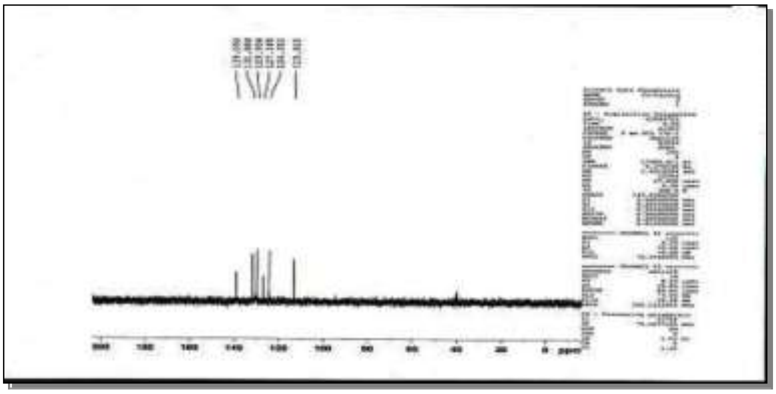


Fig.(3) : ^{13}C-DEPT- spectrum of compound (3g)

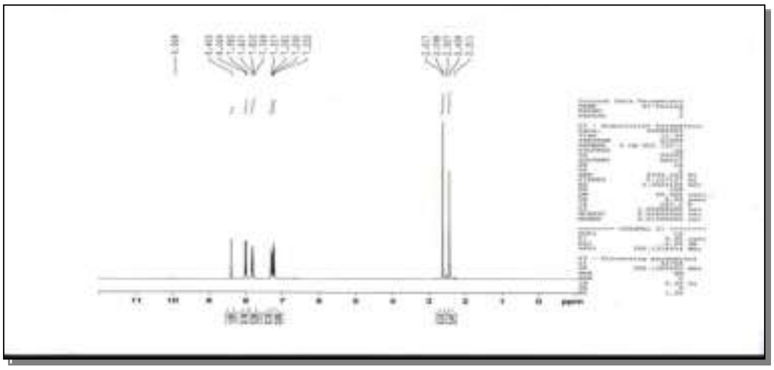


Fig.(4) : ^{1}H-nmr spectrum of compound (4a).

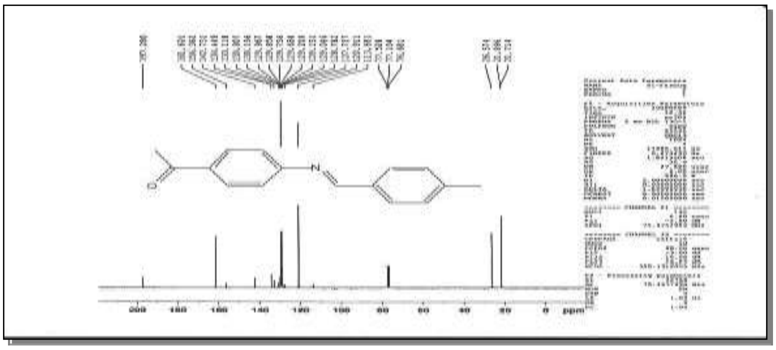


Fig.(5) : ^{13}C-nmr spectrum of compound (4a)

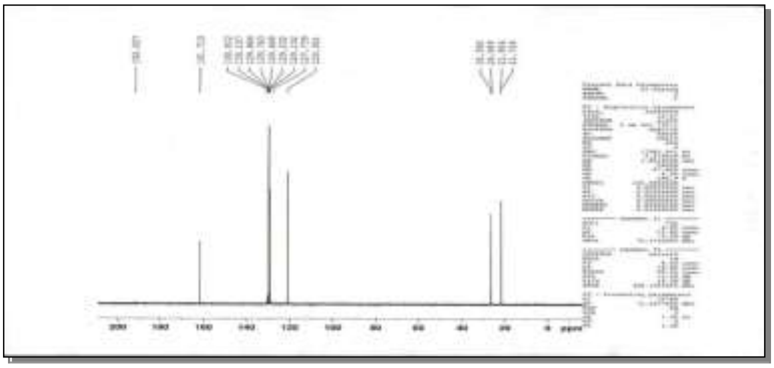


Fig.(6) : ^{13}C-DEPT- spectrum of compound (4a)

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التشيد و التشخيص الطيفي لبعض مركبات الجالكون و الأيمينات المشتقة من بارا–امينو اسيتوفينون بدون استخدام المذيب

فاروق امام حويز ، لانا هادى جاوشلى ، دلير دلشاد غفور

قسم الكيمياء ، كلية التربية العلوم ، جامعة صلاح الدين ، اربيل ، العراق

(تاريخ الاستلام: ٤ / ٨ / ٢٠٠٨ ، تاريخ القبول: ١ / ٣ / ٢٠٠٩)

الملخص

بطريقة مبسطة وملائمة وبدون استخدام المذيب (4a-j) والايمينات (3a-j) تم تحضير سلسلتين من الجالكونات مع معوضات مختلفة للبنزالديهايد باستخدام عاملين بارا–امينو اسيتوفينون من نفس المواد الاولية المستخدمة مساعدين مختلفين هيدروكسيد الصوديوم وحامض الخليك على التوالى. تراكيب المركبات المحضرة تم تشخيصها طيفيا باستخدام اطياف ^{13}C-Dept 135 و ^{13}C-NMR ، ^{1}H-NMR ، FT-IR .