Microwave–assisted Synthesis of Chalcones, Flavanones and 2-pyrazolines: Theoretical and Experimental Study

Abdullah S. Al-Bogami*

Department of Chemistry, Faculty of Science, King Abdulaziz University, North Jeddah, P.O. Box 80203 Jeddah 21589, Saudi Arabia

Received April 02, 2012: Revised May 28, 2012: Accepted June 20, 2012

Abstract: Condensation of 2-acetyl-1-naphthol and 1-acetyl-2-naphthol with benzaldehydes under microwave irradiation gave chalcones or flavanones depending on the type of ketone. Also, 2-pyrazolines were synthesized by the condensation of chalcones with phenyl hydrazine under microwave irradiation in presence of dry acetic acid as a cyclizing agent. The results obtained indicated that, unlike classical heating, microwave irradiation resulted in higher yields, shorter reaction times and cleaner reactions. The structures of the synthesized compounds were elucidated using various spectroscopic methods. Theoretical studies explained the behaviour and reactivity observed for 1-acetyl-2-naphthol with benzaldehydes considering geometries, and electron densities of the formed flavanones.

Keywords: 1-Acetyl-2-naphthol, 2-Acetyl-1-naphthol, 2-Pyrazolines, chalcones, flavanones, microwave irradiation.

INTRODUCTION

Chalcones, either natural or synthetic, are known to exhibit various biological activities [1] such as antioxidant [2], anti-inflammatory [3], antimalarial [4], and antitumor [5]. Also, they are of high interest due to their usage as starting materials in synthesis of a series of heterocyclic compounds [6-9]. 2-hydroxychalcones are considered as precursors in the synthesis and biosynthesis of several flavonoids, such as flavanones, flavones, isoflavones and aurones [10-15]. The members of the flavanoid [16] family are attracting increased attention due to their anticancer [17], antinflammatory [18], antimalarial [19] and anti-AIDS [20] pharmacological activities. These findings explain the significant interest of chemists, biochemists and pharmacologists in this particular group of compounds.

Pyrazolines are well known and important nitrogen-containing five-membered heterocyclic compounds and various methods have been worked out for their synthesis. [21-24]. Several pyrazoline derivatives have been found to possess considerable biological activities, which stimulated research activity in this field. Their prominent effects are such as antimicrobial [25], central nervous system [26], and immunosuppressive [27] activities. 2-Pyrazolines seem to be the most frequently studied pyrazoline type compounds. After the pioneering work of Fischer and Knövenagel in the late nineteenth century [28], and in a continuation of our research, in the synthesis of a wide range of heterocyclic compoubds, for biological screening programme in our laboratory [29-31], the current work describes a microwave accelerated reaction of α,β-unsaturated aldehydes and ketones with hydrazines for the rapid assembly of 2-pyrazolines [32-34].

*Address correspondence to this author at the Department of Chemistry, Faculty of Science, King Abdulaziz University, North Jeddah, P.O BOX 80203 Jeddah 21589, Saudi Arabia; Tel: +966554433416; Fax: +966 26400376; E-mail: chem_org@hotmail.com

RESULTS AND DISCUSSION

A series of chalcones 3 was prepared from the reaction of 2-acetyl-1-naphthol 1 with benzaldehydes 2 under microwave irradiation (Scheme **1**, Table **1**).

The formation of the chalcones **3a-d** was confirmed on the basis of their IR and ^{1}H-NMR data. They show a characteristic IR absorption peak at 1700-1650 cm^{-1} indicating the presence of a conjugated carbonyl group (>C=O). The main features of NMR data of chalcones **3a-d** are the resonances of: (i) the hydroxyl groups at about δ = 14.5 ppm. The high frequency resonances of these protons are due to the intramolecular hydrogen bond formed with the carbonyl group; (ii) the vinylic protons appearing as doublets at $\delta_{H-\alpha}$ 7-8 ppm and $\delta_{H-\beta}$ 7.5-8 ppm. (iii) the vinylic carbons which appear at $\delta_{C-\alpha}$123-132 ppm and $\delta_{C-\beta}$ 137-144 ppm. The CHN analysis and MS spectra of these compounds are in agreement with the proposed structures (Table **2**).

The chalcones **3a-d** were then reacted with phenyl hydrazine to give 2-pyrazoline compounds **4a-d**. This reaction probably takes place through mediation of an appropriate *α, β*-unsaturated hydrazone, which immediately cyclizes to give a 2-pyrazoline ring in the presence of a suitable cyclizing agent like dry acetic acid under microwave irradiation (Scheme **2**, Table **3**). The products formed **4a-d** was often accompanied by small traces (1%) of the hydrzaid derivative (Scheme **2**). These latest was easily eliminated by washing the crystallized major product with diethyl ether.

Structures of all new 2-pyrazolines have been elucidated by microanalyses, IR and NMR spectroscopic measure-

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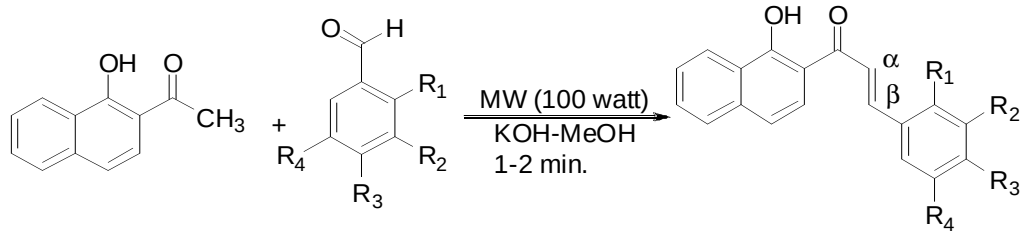


1 **2** **3**

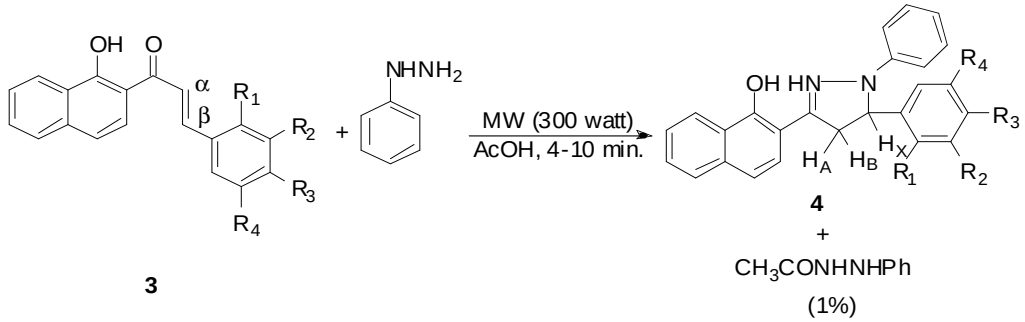
Scheme 1. Microwave assisted synthesis of chalcone **3a-d**.

Table 1. Chalcones 3 Derivatives

R_1	R_2	R_3	R_4	Product	Yield (%)
H	H	H	H	**3a**	94
H	H	Cl	H	**3b**	90
H	OMe	OMe	OMe	**3c**	91
Cl	H	Cl	H	**3d**	87

Table 2. ^{1}H and ^{13}C Chemical Shifts (δ, Ppm, in $CDCl_3$) of Compounds (3a-d)

Compound	H-α	H-β	OH	C-OH	C=O
3a	7.67	7.86	14.86	164.51	193.31
3b	7.94	8.53	14.71	164.62	193.02
3c	7.80	7.88	14.91	164.46	193.04
3d	7.79	8.28	14.70	164.73	192.70



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Scheme 2. Microwave assisted synthesis of 2-pyrazolines 4a-d.

Table 3. 2-pyrazolines 4 Derivatives

R_1	R_2	R_3	R_4	Product	Yield (%)
H	H	H	H	**4a**	83
H	H	Cl	H	**4b**	91
H	OMe	OMe	OMe	**4c**	80
Cl	H	Cl	H	**4d**	85

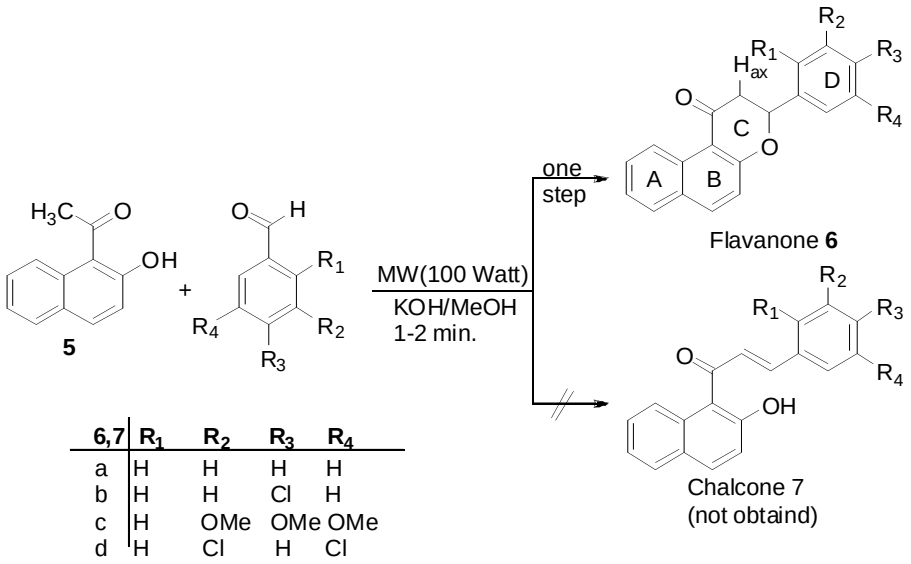
ments. Elemental analyses unambiguously proved the elemental composition of all new compounds. The IR spectra of compounds **4a-d** gave characteristic band at 3650-3500 cm^{-1} (OH), 1590-1580 (C=N). In the ^{1}H NMR spectra of 2-pyrazolines **4a-d** the three hydrogen atoms attached to the C-4 and C-5 carbon atoms of the heterocyclic ring gave an ABX spin system. Measured chemical shift and coupling constant values unequivocally prove the 2-pyrazoline structure (Table **4**).

Table 4. ^{1}H NMR Spectral Data of 4a-d in $CDCl_3$.

Compound	H_A	H_B	H_X
4a	3.36(dd) (*J*=16.84,7.36Hz)	4.05(dd) (*J*=16.84,11.72Hz)	5.26(dd) (*J*=12.48,8.8Hz)
4b	3.25(dd) (*J*=16.84,7.36Hz)	3.92(dd) (*J*=16.84,12.48Hz)	5.10(dd) (*J*=12.44,8.08Hz)
4c	3.34(dd) (*J*=16.85,7.36Hz)	4.03(dd) (*J*=16.88,11.72Hz)	5.13(dd) (*J*=11.72,8.04Hz)
4d	3.26(dd) (*J*=16.84,7.36Hz)	4.17(dd) (*J*=16.88,11.72Hz)	5.58(dd) (*J*=11.72,8.04Hz)

Table 5. ^{13}C NMR Spectral Data of 4a-d in $CDCl_3$

Compound	C-4	C-5	C-OH
4a	44.42	63.55	154.29
4b	44.25	62.82	154.28
4c	44.60	60.69	154.03
4d	42.69	59.94	154.03



6,7	R_1	R_2	R_3	R_4
a	H	H	H	H
b	H	H	Cl	H
c	H	OMe	OMe	OMe
d	H	Cl	H	Cl

Scheme 3. Microwave assisted synthesis of flavanones **6a-d**.

Table 6. Flavanones 6 Derivatives

R_1	R_2	R_3	R_4	Product	Yield (%)
H	H	H	H	**6a**	94
H	H	Cl	H	**6b**	90
H	OMe	OMe	OMe	**6c**	89
Cl	H	Cl	H	**6d**	92

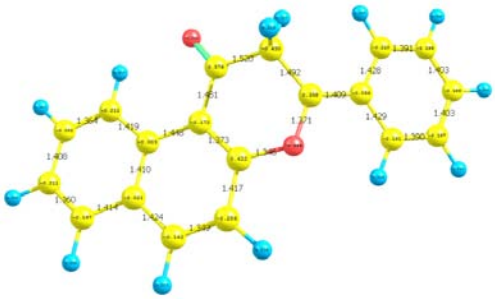
^{13}C NMR chemical shift values of carbon atoms C-3 (146-150 ppm), C-4 (43-44 ppm) and C-5 (62-64 ppm) corroborate the 2-pyrazoline structure deduced from the ^{1}H-NMR spectroscopic data (Table **5**).

The main method for the synthesis of flavanones involves two steps. The first step is Claisen–Schmidt condensation of aromatic aldehydes and ketones yielding chalcone. Chalcone undergoes intramolecular cyclization in the second step to yield flavanone. In this work, we found out that flavanones can be synthesized in good yields from 1-acetyl-2-naphthol **(5)** and benzaldehydes **(2)** using KOH as catalyst in one step without formation of chalcone **7** (Scheme **3**, Table **6**).

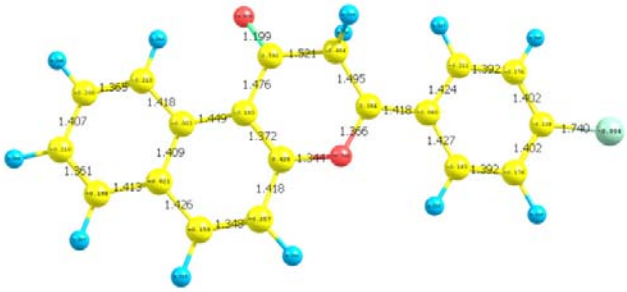
Compounds 6a-d (Table **6**) show in the IR spectra absorbances for the carbonyl group at about 1690 cm-1. The 1H

Table 7. ^{1}H and ^{13}C Chemical Shifts (δ, Ppm, in $CDCl_3$) of Compounds (6a-d)

Compound	H-2	H_{ax}	H_{eq}	C-2	C-3	C=O
6a	5.35	2.98	2.90	163.70	163.53	192.74
6b	5.58	3.20	2.97	167.28	163.53	192.65
6c	5.48	3.23	2.93	164.42	163.64	193.02
6d	5.92	3.09	2.94	163.70	163.53	193.85

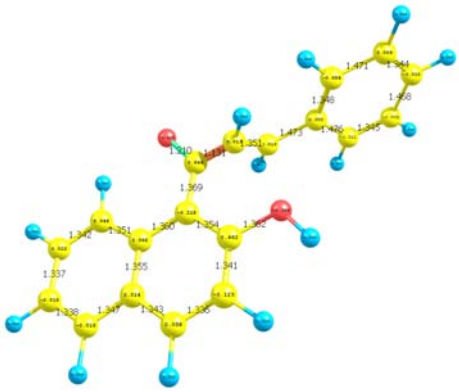


Dipole moment of **6a** (Debye)= 2.5491

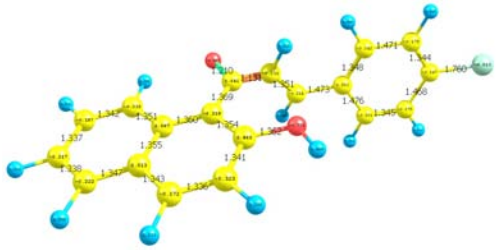


Dipole moment of **6b** (Debye)= 2.6585

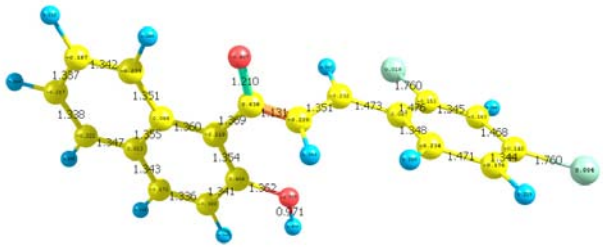
Dipole moment of **6d** (Debye)= 3.8272



Dipole moment of **7a** (Debye)= 5.8479



Dipole moment of **7b** (Debye)= 6.6341



Dipole moment of **7d** (Debye) = 6.4144

Fig. (1). Geometrical parameters, charge distribution and dipole moment for proposed structures (**6a, 6b, 6d, 7a, 7b and 7d**) using HF calculations.

NMR spectrum showed a flavanone structure with the signals at about δ = 5.57 (1H, dd, *J* = 13.92, 2.92 HZ, H-2) and 3.16 (1H, dd, *J* = 16.88, 2.96 HZ, H_{ax}), 2.9 (1H, dd, *J* = 16.12, 2.92 HZ, H_{eq}), which are typical for the C ring. The 13C NMR and MS spectra of these compounds are in agreement with the proposed structures (Table **7**).

To further understand our current experimental results in scheme **3**, we carried out Hartree-Fock (HF) calculations to explore the different pathways of the chemical reaction in Scheme **3**. The structure optimizations were performed with the HF/6-31G* using the GAUSSIAN 03 program system [35]. Vibrational frequency analyses were carried out for the optimized structures in order to assess the nature of stationary points. The characteristic of local minima was verified by have no imaginary frequency. The relative energies, dipole moments, charge distribution and the structural parameters are given in Fig. (**1**).

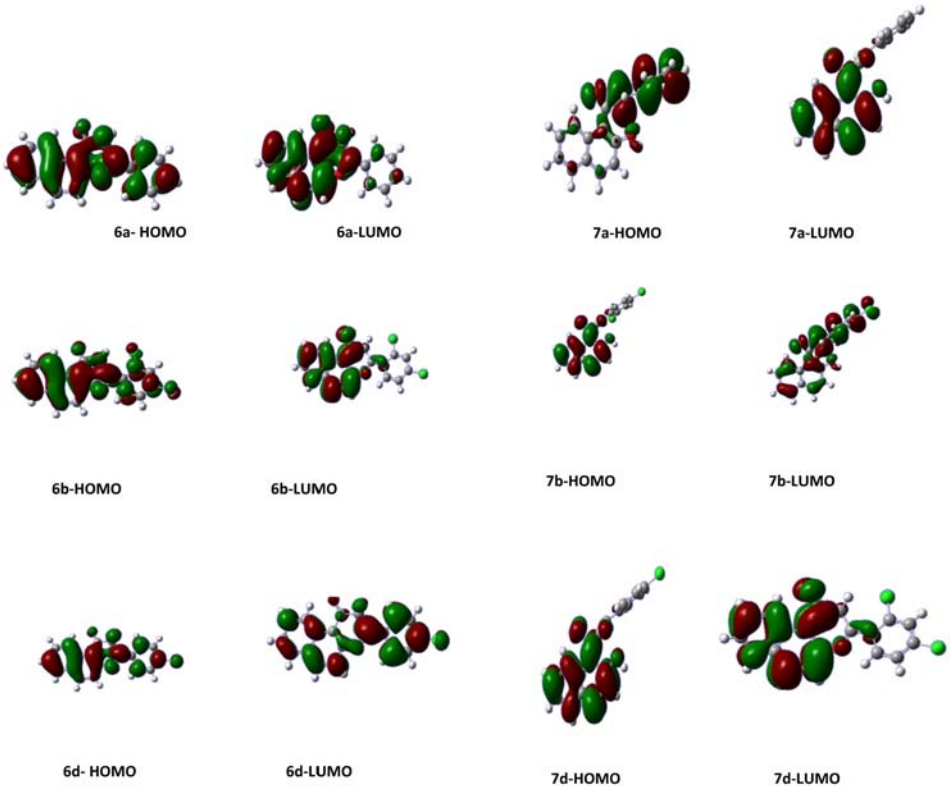


Fig. (2). Frontier Molecular orbitals for the studied structures using HF/6-31G* level.

According to the results given in Fig. (**1**), the structure of product **7** (not formed product) is more stable than proposed structure **6** (already formed product). But the extra stability of product **6** which pushes reaction to form it is mainly due to the formation of the ring and assisted by electron delocalization (Fig. **2**).

CONCLUSION

A very useful and rapid method *via* microwave assisted synthesis of chalcone, 2-pyrazoline and flavanones is described. Furthermore, the combined use of experimental design with theoretical calculations, including evaluation of behavior and reactivity of 1-acetyl-2-naphthol with benzaldehydes to form flavanones provides with a powerful tool to design the synthesis of more derivatives using different substituents, which could help to produce environmentally friendly bioactive compounds.

The difference in behavior between compound **1** and compound **5** in our opinion may be due to 2-OH in compound **5** considered a better nucleophile than 1-OH in compound **1**.

EXPERIMENTAL

Melting points were determined on Gallenkamp-melting point apparatus. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer as KBr pellets and expressed as υ in cm^{-1}. NMR spectra were recorded on JEOL ECP 400 (400 MHz) in $CDCl_3$ and expressed as δ in ppm. Mass spectra were recorded on Shimadzu QP-5050A GC/MS system. Elemental analyses (C, H, N) were performed on Carlo Erba 1106 EA instrument their results were found to be in good agreement (±0.3%) with the calculated values". For the microwave irradiation we used a 800 W STAR SYSTEM-2 monomode reactor (CEM Corporation). TLC was performed on (TLC plates silica gel 60F245 pre-coated 20×20 cm layer thickness 0.25 mm).

General procedure for the preparation of chalcones (3a-d) In a typical procedure, a mixture of 2-acetyl-1-naphthol (2.69 mmol) and benzaldehydes (2.69 mmol) in 2 eq KOH/MeOH was charged in a MW test tube (10 mL) containing a magnetic stirring bar and a rubber cap and 2mL of methanol. The test tube was placed in the microwave cavity (CEM, Discover). The tube was subjected to MW a 70°C (power 100 W) for 1-2 min. After completion of the reaction, the tube was removed, cooled to room temperature, and the reaction mixture was poured into crushed ice water (30 ml). Then conc. HCl (1 ml) was added and the reaction mixture was left to stay at 2-3^{o}C overnight. The separated solid was collected by filtration and recrystallized from methanol.

1-(1-Hydroxy-naphthalen-2-yl)-3-phenyl-propenone (3a)

This compound was prepared from 2-acetyl-1-naphthol and benzaldehyde. Yield = 94 %, green needles, mp 123-125^{o}C; IR: 1590 (C=C), 1700 (C=O), 3100 (OH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-8.04 (11H, m), 7.67 (1H-α, d, $J_{\alpha,\beta}$ = 15.4 Hz), 7.86 (1H-β, d, $J_{\alpha,\beta}$ = 15.4 Hz), 14.86 (1H, s). ^{13}C NMR: δ 113.55, 118.32, 120.53, 123.99, 124.60, 125.57, 126.03, 127.49, 128.77, 129.13, 130.30, 130.39, 134.84, 137.47, 145.16, 164.51, 193.31, MS: m/z (%) 274 (M^{+}, 19), 197, 170, 103, 89, 77, 65, 51; Anal. calcd. (%) for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found (%): C, 83.10; H, 5.20.

3-(4-Chloro-phenyl)-1-(1-hydroxy-naphthalen-2-yl)-propenone (3b)

This compound was prepared from 2-acetyl-1-naphthol and 4-chlorobenzaldehyde. Yield = 90 %, red needles, mp 170-173°C; IR: 1602 (C=C), 1670 (C=O), 3150 (OH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.85 (10H, m), 7.94 (1H-α, d, $J_{\alpha,\beta}$ = 15.4 Hz), 8.53 (1H- β, d, $J_{\alpha,\beta}$ = 15.4 Hz), 14.71(1H, s). ^{13}C NMR: δ 113.48, 118.41, 121.02, 123.88, 124.63, 125.56, 126.11, 127.52, 129.43, 129.89, 130.42, 133.35, 136.85, 137.52, 143.62, 164.62, 193.02, MS: m/z (%) 310 (M+2, 22), 308 (M^+, 55), 170, 103, 89, 77, 65, 51. ; Anal. calcd. (%) for $C_{19}H_{13}ClO_2$: C, 73.91; H, 42.44. Found (%): C, 73.20; H, 42.09.

1-(1-Hydroxy-naphthalen-2-yl)-3-(3,4,5-trimethoxy-phenyl)-propenone (3c)

This compound was prepared from 2-acetyl-1-naphthol and 3,4,5-trimethoxybenzaldehyde. Yield = 91 %, red powder , mp 115-116°C; IR: 1609 (C=C), 1668 (C=O), 3100 (OH); ^{1}H NMR (400 MHz, $CDCl_3$): 3.92 (3H, s), 3.93 (6H, s), 6.87(2H,s), 7.27 (1H ,d , J =8.8H_Z) 7.51-7.61 (3H, m), 7.80 (1H- α, d, $J_{\alpha,\beta}$ = 15.4 Hz), 7.88 (1H- β, d, $J_{\alpha,\beta}$ = 15.4 Hz), 8.48 (1H,d,J=8.08H_Z), 14.91 (1H, s).^{13}C NMR: 56.32, 61.14, 105.95, 113.50, 118.25, 119.56, 123.80, 124.54, 125.54, 126.01, 127.48, 130.28, 137.41, 140.74, 145.32, 153.56, 164.46, 193.04; MS: m/z (%)364 (M^+, 100), 194, 179,115, 103, 89, 77, 65, 51. ; Anal. calcd. (%) for $C_{22}H_{20}O_5$: C, 72.51; H, 5.53. Found (%): C, 72.29; H, 5.77.

3-(2,4-Dichloro-phenyl)-1-(1-hydroxy-naphthalen-2-yl)-propenone (3d)

This compound was prepared from 2-acetyl-1-naphthol and 2,4-dichlorobenzaldehyde Yield = 87 %, red powder, mp 167-169°C; IR: 1619 (C=C), 1655 (C=O), 3111 (OH); ^{1}H NMR (400 MHz, $CDCl_3$): 6.87 (2H,s),7.27 (1H ,d , J = 8.8H_Z) ,7.27-7.76 (7H, m), 7.79 (1H- α, d, $J_{\alpha,\beta}$ = 15.4 Hz), 8.28 (1H-β, d, $J_{\alpha,\beta}$ = 15.4 Hz), 8.50 (1H, d, J = 8.08H_Z), 14.70 (1H,s).;^{13}C NMR: 113.40, 118.49, 123.43, 123.80, 124.66, 125.50, 126.14, 127.51, 127.68, 128.62, 130.32, 130.52, 131.75, 136.36, 137.40, 139.50, 164.73, 192.70; MS: m/z (%) 344 (M+2, 14), 342 (M^+, 20), 307, 197, 170, 103, 89, 77, 65, 51. ; Anal. calcd. (%) for $C_{19}H_{12}Cl_2O_2$: C, 66.49; H, 3.52. Found (%): C, 66.80; H, 3.66.

General Procedure for the Preparation of 2-pyrazolines (4a-d)

In a typical procedure, the phenylhydrazine reagent (3 mmol) is then added dropwise to a stirring solution of the chalcones **3a-d** (1 mmol) in glacial AcOH (5 ml). The mixtures subjected to microwave heating for several min. using a (CEM, Discover) microwave oven (300 watt) to afford 2-pyrazolines, which washed with ether and recrystallized from absolute ethanol then washed with ether to give pure compounds **4a-d** with a 77-91% yield.

2-(1,5-Diphenyl-4,5-dihydro-1H-pyrazol-3-yl)-naphthalen-1-ol (4a)

This compound was prepared from **3a** and phenyl hydrazine Yield = 83 %, green powder, mp 179-180°C; IR: 1687 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$): 3.36 (1H, dd, J = 16.84, 7.36 H_Z, H_A), 4.05 (1H, dd, J = 16.84, 11.72 H_Z, H_B), 5.26 (1H, dd, J = 12.48, 8.8H_Z, H_X), 6.84-8.47 (16H, m), 11.74 (1H, s).;^{13}C NMR: 44.42, 63.55, 109.50, 113.41, 119.07, 119.90, 123.20, 123.75, 125.71, 126.02, 126.06, 127.45, 127.48, 127.93, 129.21, 129.37, 134.52, 142.08, 144.26, 150.37, 154.29; MS: m/z (%) 364 (M^+, 65), 170, 103,91, 89, 77, 65,51 ; Anal. calcd. (%) for $C_{25}H_{20}N_2O$ C, 82.39; H, 5.53; N, 7.69. Found (%): C, 82.22; H, 5.12; N, 7.16.

2-[5-(4-Chloro-phenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl]-naphthalen-1-ol (4b)

This compound was prepared from **3b** and phenyl hydrazine Yield = 91 %, green powder , mp 175-176°C; IR: 1685 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$): 3.25 (1H, dd, J = 16.84, 7.36 H_Z, H_A), 3.92 (1H, dd, J = 16.88, 12.48 H_Z, H_B), 5.10 (1H, dd, J = 12.44, 8.08 H_Z, H_X),6.83-8.47 (15H, m), 11.71 (1H, s).; ^{13}C NMR: 44.25, 62.82, 109.34, 113.44, 119.18, 120.14, 123.21, 123.72, 125.79, 127.47, 127.56, 129.30, 129.57, 133.70, 134.56, 140.57, 144.04, 150.39, 154.28; MS: m/z (%) 400 (M+2, 36),398 (M^+, 100) 170, 103,91, 89, 77, 65,51 ; Anal. calcd. (%) for $C_{25}H_{19}ClN_2O$ C, 75.28; H, 4.80; N,7.02. Found (%): C, 75.43; H, 4.92; N,7.10.

2-[1-Phenyl-5-(3,4,5-trimethoxy-phenyl)-4,5-dihydro-1H-pyrazol-3-yl]-naphthalen-1-ol (4c)

This compound was prepared from **3c** and phenyl hydrazine

Yield = 77 %, green powder , mp 166-168°C; IR: 1692 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$): 3.34 (1H, dd, J = 16.85, 7.36 H_Z, H_A), 3.82 (3H, s), 3.88 (6H, s) 4.03 (1H, dd, J = 16.88, 11.72 H_Z, H_B), 5.13 (1H, dd, J = 11.72, 8.04H_Z, H_X), 6.58-8.45 (13H, m), 11.80 (1H, s).; ^{13}C NMR: 44.60, 56.27, 60.69, 64.52, 102.48, 109.41, 113.58, 119.14, 120.20, 123.17, 123.77, 124.79, 125.79, 127.53, 129.24, 134.66, 137.33, 137.70, 144.72, 150.72, 154.03; MS: m/z (%) 454 (M^+, 100) 170, 103,91, 89, 77, 65,51 ; Anal. calcd. (%) for $C_{28}H_{26}N_2O_4$ C, 73.99; H, 5.77; N,6.16. Found (%): C, 73.15; H, 5.65; N,6.11.

2-[5-(2,4-Dichloro-phenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl]-naphthalen-1-ol (4d)

This compound was prepared from **3d** and phenyl hydrazine Yield = 85 %, yellow powder, mp 188-189°C; IR: 1695 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$): 3.26 (1H, dd, J = 16.84,7.36 H_Z, H_A), 4.17 (1H, dd, J = 16.88, 11.72 H_Z, H_B), 5.58 (1H, dd, J = 11.72, 8.04 H_Z, H_X),6.90-8.47 (14H, m),11.69 (1H, s).;^{13}C NMR: 42.69, 59.94, 109.48, 113.16, 119.22, 120.27, 123.24, 123.72, 125.82, 127.54, 127.65, 128.20, 128.49, 129.45, 129.98, 132.60, 143.72, 150.84, 154.03; MS: m/z (%) 454 (M^+, 100) 170, 103,91, 89, 77, 65,51 ; Anal. calcd. (%) for $C_{25}H_{18}Cl_2N_2O$ C, 69.29; H, 4.19; N, 6.46. Found (%): C, 69.44; H, 4.15; N,6.33.

General Procedure for the Preparation of Flavanones (6a-d)

These compounds were prepared from 1-acetyl-2-naphthol and benzaldehydes using conditions similar to those described in general procedure for synthesis of chalcones **3**.

3-Phenyl-2,3-dihydro-benzo[f]chromen-1-one (6a)

This compound was prepared from 1-acetyl-2-naphthol **5** and benzaldehyde**.** Yield = 95 %, brown powder, mp 106-108 ^{o}C; IR: 1698 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$): 5.35 (1H, dd, *J* = 13.92, 2.92 H_Z,H-2) and 2.89 (1H, dd, *J* = 16.88, 2.92 H_Z, H_{ax}), 2.98 (1H, dd, *J* = 16.12, 2.92 H_Z, H_{eq}); ^{13}C NMR: 45.50, 77.35, 112.33, 118.83, 124.82, 125.64, 126.14, 128.40, 128.74, 129.11, 129.53, 131.27, 137.51, 138.37, 163.53, 192.74; MS: m/z (%) 274 (M^+, 100), 197,161,134, 105, 77, 65,51 ; Anal. calcd. (%) for $C_{19}H_{14}O_2$ C, 83.19; H, 5.14. Found (%): C, 83.28; H, 5.01.

3-(4-Chloro-phenyl)-2,3-dihydro-benzo[f]chromen-1-one (6b)

This compound was prepared from 1-acetyl-2-naphthol **5** and 4-chlorobenzaldehyde.Yield = 86 %, brown powder , mp 140-143^{o}C; IR: 1705 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$): 5.58 (1H, dd, *J* = 13.00,3.00 H_Z, H-2) and 3.2 (1H, dd, *J* = 17.00, 3.92 H_Z, H_{ax}), 2.97 (1H, dd, *J* = 16.80, 2.92 H_Z, H_{eq}); ^{13}C NMR: 45.73, 77.45, 112.67, 118.81, 125.14, 125.97, 127.63, 128.52 ,129.14, 129.40, 129.90, 131.47, 134.71, 137.11, 137.82, 163.53, 192.65; MS: m/z (%) 310 (M+2, 54) , 308 (M^+, 77) ,273,195,161,134, 105, 77, 65,51 ; Anal. calcd. (%) for $C_{19}H_{13}ClO_2$ C, 73.91; H, 4.24. Found (%): C, 73.68; H, 4.54.

3-(3,4,5-Trimethoxy-phenyl)-2,3-dihydro-benzo[f] chromen-1-one (6c)

This compound was prepared from 1-acetyl-2-naphthol **5** and 3,4,5-trimethoxybenzaldehyde.Yield = 81 %, yellow powder , mp 162-165^{o}C; IR: 1698 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$): 5.48 (1H, dd, *J* = 13.20, 3.00 H_Z, H-2) and 3.23(1H, dd, *J* = 17.00, 3.70 H_Z, H_{ax}), 2.93 (1H, dd, *J* = 16.50, 3.70 H_Z, H_{eq}); ^{13}C NMR: 45.91, 56.29, 60.96, 77.60, 103.36, 112.60, 118.90, 125.06, 125.92, 128.52, 129.34, 129.81, 131.48, 134.17, 137.69, 138.26, 153.62, 163.64, 193.02.; MS: m/z (%) 364 (M^+, 65) , 273, 195, 161, 134, 105, 77, 65,51 ; Anal. calcd. (%) for $C_{22}H_{20}O_5$ C, 72.51; H, 5.53. Found (%): C, 72.53; H, 5.67.

3-(2,4-Dichloro-phenyl)-2,3-dihydro-benzo[f] chromen-1-one(6d)

This compound was prepared from 1-acetyl-2-naphthol **5** and 2,4-dichlorobenzaldehyde**.** Yield = 79 %, yellow powder , mp 99-101 ^{o}C; IR: 1710 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$): 5.92 (1H,dd, *J*=13.20,2.92 H_Z,H-2) and 3.09 (1H, dd, *J* = 17.00,3.70 H_Z, H_{ax}), 2.94 (1H, dd, *J* = 16.80, 3.00 H_Z, H_{eq});^{13}C NMR: 44.51, 112.74, 115.74, 118.66, 119.54, 124.23, 125.06, 125.22, 126.02, 127.73, 128.12, 129.54, 130.30, 137.36, 163.53, 193.85; MS:m/z (%) 344 (M+2, 45),342 (M^+,65) ,273,195,161,134, 105, , 77, 65,51 ; Anal. calcd. (%) for $C_{19}H_{12}Cl_2O_2$ C, 66.49; H, 3.52. Found (%): C, 66.43; H, 3.90.

Computational Procedure

All calculations were carried out with HF/6-31G* methods, as implemented in the Gaussian 03 package, [35] This methodology is known to be appropriate for the theoretical study of the electronic and geometric properties to explore the different pathways of the chemical reaction. [36]

ACKNOWLEDGEMENTS

The author is highly thankful to Dr. Hamad Z. Alkhathlan, Professor of Chemistry Department, King Saud University for valuable suggestions and guidance.

CONFLICT OF INTEREST

The author(s) confirm that this article content has no conflicts of interest.

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