

NOVEL PHOTOSYNTHESIS OF 5,8A-DICHLORO-2-(4-METHOXYPHENYL)-8AH-CHROMENE FROM ITS CHALCONE ISOMER AND FT-IR, ¹H AND ¹³C NMR SPECTROSCOPIC INVESTIGATION

ABDULLAH A. YOUSIF and GHAZWAN F. FADHIL

*De.pt of Chemistry, College of Science, University of Duhok, Kurdistan Region–Iraq

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ABSTRACT

In the presence of alcoholic alkali, the base-catalyzed aldol condensation of equimolar quantities of substituted acetophenones and aldehydes to give good yields of condensation product. This reaction is known as the Claisen-Schmidt condensation. The *Trans*-3-(2,6-dichlorophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (*trans* 2,6-methoxy chalcone) was synthesised by Claisen Schmidt reaction, then it exposed to the Xenon lamp to prepare the 5,8a-dichloro-2-(4-methoxyphenyl)-8aH-chromene (2,6-methoxy chromene). A number of techniques were used to characterise the mentioned two products such as, thin layer chromatography, FT-IR, ¹H and ¹³C nuclear magnetic resonance, liquid chromatography/quadrupole time-of-flight mass spectrometry and elemental analysis (CHNO).

KEYWORDS: Chalcone, Chromene, FT-IR, NMR, LC/Q-TOF/MS, CHNO.

1. INTRODUCTION

1,3-diphenyl-2-propene-1-one is the basic chalcone structure, which consists of two aromatic rings and an α,β -unsaturated carbonyl

system (Xue et al., 2012 a) (Figure 1). The α,β -unsaturated carbonyl system is located between the two aromatic rings, forming an enone (Elzupir et al., 2018).

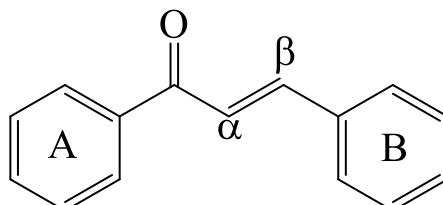


Fig. (1): Basic structure of chalcone

In plants, flavonoids and isoflavonoids are chalcones derivatives, and chemicals can be used to prepare chalcones (Ahmadi et al., 2019). An enormous range of biological activities have been discovered for chalcones and their derivatives (Xue et al., 2012 b); such as, anticancer, antioxidative (Chen et al., 2017), antiviral (Zhou et al., 2018) and anti-inflammatory activities (Wen et al., 2018). The importance of halogens during drug design has been confirmed, due to its contributions to the target-recognition process (Chidan Kumar et al., 2015). In addition to these vital medical applications, chalcones possess useful spectral and optical properties, depending on the group connected to the aromatic ring, and can be used in optoelectronic, metal sensing, and nonlinear

optical (NLO) devices (Xue et al., 2011) (Renuka et al., 2019).

Chalcones exist in different conformations, due to the flexibility of chalcone molecules; moreover, their characteristics depend on the α,β -unsaturated ketone system and the substituents on the two aromatic rings (Opletalová et al., 2000). The presence of a single bond between the vinyl and carbonyl groups allow chalcone molecules to rotate freely, which consequently produces two possible conformations, *s-cis* and *s-trans* (Figure 2). Additionally, the vinyl group itself can exist in either *cis* or *trans* geometry (Kucerova-Chlupacova et al., 2018) (Figure 2). Although the *s-cis* conformation generally displays enhanced stability compared with *s-trans*

conformation, this is not always true for organic compounds. For instance, 1,3-butadiene (Espinoza-Hicks et al., 2016) and acrolein (Puzzarini et al., 2014) are both more stable in

the *s-trans* conformation than in the *s-cis* conformation, due to the full planarity and reduced steric hindrance of the *s-trans* conformer.

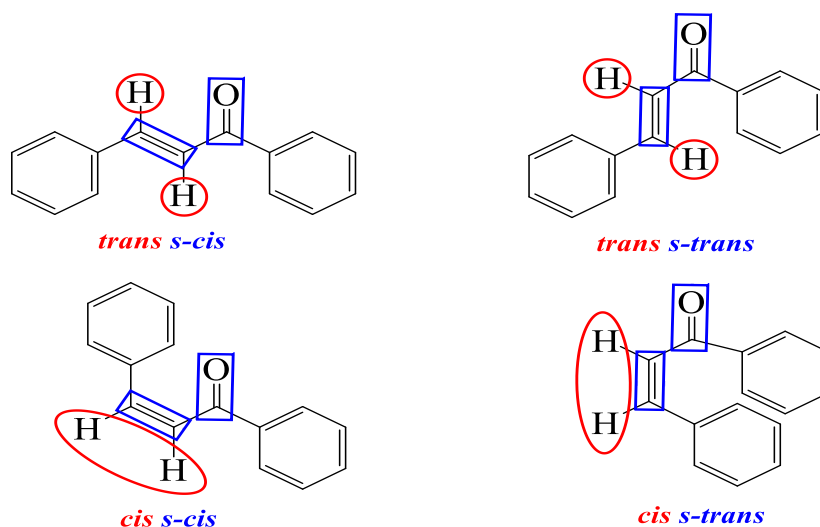


Fig. (2): Cis and trans geometry and s-cis and s-trans conformation of chalcone.

The aim of this study is to synthesise *Trans*-3-(2,6-dichlorophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (*trans* 2,6-methoxy chalcone) by Claisen Schmidt reaction, then using Xenon lamp to prepare the 5,8-dichloro-2-(4-methoxyphenyl)-8a*H*-chromene (2,6-methoxy chromene). These two products were characterised by using different techniques such as, thin layer chromatography, FT-IR, ^1H and ^{13}C nuclear magnetic resonance, liquid chromatography/quadrupole time-of-flight mass spectrometry and elemental analysis (CHNO).

2. EXPERIMENTAL

Material and Methods

2,6-Dichlorobenzaldehyde was purchased from Sigma Aldrich, 4-Methoxyacetophenone was purchased from Uni-Chem, Chloroform, cyclohexane, Ethyl acetate, Absolute ethanol and Toluene were purchased from Scharlau, Deuterium oxide, Deuteriochloroform, Dimethyl Sulfoxide- d_6 and Hydrochloric acid were purchased from Merck Darmstadt. PerkinElmer Spectrum Two FT-IR Spectrometer ($4000\text{--}400\text{cm}^{-1}$) was used for vibration measurements with (4cm^{-1}) resolution. Universal attenuated total reflectance (UATR) accessory was used for solid samples and PerkinElmer Spectrum 10TM software was used for data collection. The reported FT-IR spectra were performed in the Department of Chemistry laboratory, Faculty of Science and Arts at the Inonu University,

Turkey. Bruker (400MHz) using TopSpin 3.2 software used for NMR spectra measurements. The deteriorated chloroform (CDCl_3) solvent was used to obtain ^1H -NMR and ^{13}C -NMR spectra of *trans* 2,6-methoxy chalcone. The deteriorated water (D_2O) solvent with one drop of 1M HCl were used to obtain ^1H -NMR of 2,6-methoxy chromene and the deteriorated dimethylsulfoxide ($\text{DMSO-}d_6$) solvent was used to obtain ^{13}C -NMR of 2,6-methoxy chromene. Because the 2,6-methoxy chromene is not stable, the acidic solution is used to prevent the conversion of 2,6-methoxy chromene to *trans* 2,6-methoxy chalcone, likewise as flavylum salt compounds which have been reported by Roque *et.al* (Roque et al., 2002). The recorded ^1H -NMR spectra were performed in the Department of Chemistry Laboratory at the University of Western Cape town, South Africa. MS analysis was performed using an Agilent 6550 iFunnel high resolution Accurate-Mass Liquid Chromatography/Quadrupole Time-Of-Flight/Mass Spectrometry (LC/Q-TOF/MS) system, equipped with an Agilent Dual Jet Stream electrospray ionization (Dual AJS ESI). The scan range was from m/z 50 to 2000 and acquisition rate was 1.5 spectra/s. Elemental analysis (CHNO) was recorded by Perkin Elmer EA 2400 Series II. The recorded ^{13}C -NMR, (LC/Q-TOF/MS) and (CHNO) spectra were performed in the Advanced Instrumental Analysis Laboratory at the Dicle University,

Turkey. Thin Layer Chromatography (TLC) was made on Macherey-Nagel, 805901, Polygram Sil G/Uv 254, Pack of 25. 100W Auto Car HID Xenon Headlight Lamp was used as a source of light with (380 nm-750 nm) wavelengths. Electro thermal Mel-temp M206780/02 was used for measuring the melting point.

Trans-3-(2,6-dichlorophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (*trans* 2,6-methoxy chalcone)

A quantity of (0.0133mol, 2.325g) of 2,6-dichlorobenzaldehyde and (0.0132mol, 1.981g) of 4-methoxyacetophenone was dissolved in 20ml of absolute ethanol in a flat bottom flask with stirring, then 5ml of 10% NaOH was added

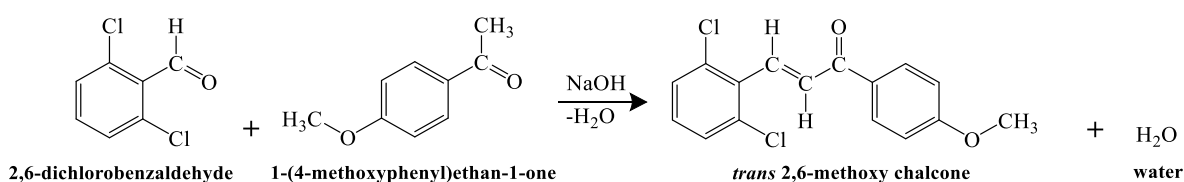


Fig. (3): Preparation reaction of *trans* 2,6-methoxy chalcone.

5,8a-dichloro-2-(4-methoxyphenyl)-8aH-chromene (2,6-methoxy chromene)

A quantity of (1.5g) of *trans* 2,6-methoxy chalcone was dissolved in a mixture of 200ml of cyclohexane and 35ml of chloroform in a 300ml beaker. The beaker was immersed in an ice bath with stirring and the temperature was adjusted between (18-20 °C), using chloroform to dissolve the *trans* 2,6-methoxy chalcone because of the high solubility of *trans* 2,6-methoxy chalcone in chloroform, while the *trans* 2,6-methoxy chalcone is insoluble in cyclohexane unless it is heated. Then the solution was irradiated with Xenon Headlight Lamp for 1 hours, during which the solution color was changed from pale

drop by drop to the mixture with stirring. Stirring was carried on at a room temperature for 10 hours, a thick precipitate formed. The precipitate was filtered off and washed well with distilled water to get rid of the excess base, then a small amount of cold ethanol was added to remove the unreacted reactants. Recrystallization was accomplished by hot ethanol (~70 °C), the thin layer chromatography (TLC) technique was used to check the purity of the product ($R_f = 0.46$) using toluene and ethyl acetate as eluents (3:1). The yield of yellow precipitate and the melting point were (3.914g, 90.9%) and (101-103 °C, uncorrected), respectively.

yellow to dark orange and a precipitate was formed. This is due to the non-solubility of 2,6-methoxy chromene in cyclohexane. The precipitate was filtrated immediately under xenon light and washed very well with cyclohexane then dried on air. Moreover, the same filtration procedure was repeated on the mother liquor several times to increase the yield. The purity of the product was checked by TLC ($R_f = 0$) using toluene and ethyl acetate as eluents (3:1) with one drop of 1M HCl. The yield was (1.3g, 86.66%) and the melting point was over (250 °C) not detected by instrument. This procedure is adopted for the first time.

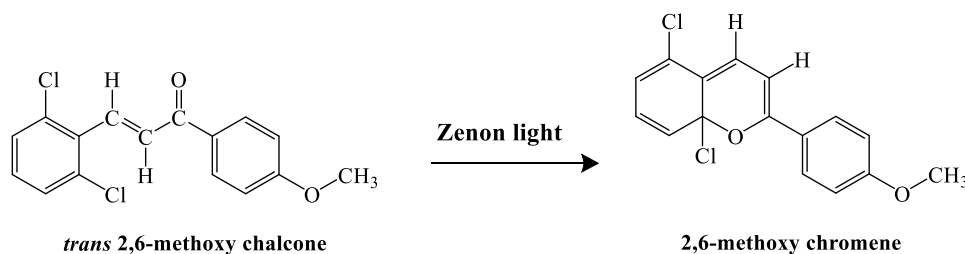


Fig. (4) Preparation reaction of 2,6-methoxy chromene.

3. RESULTS AND DISCUSSION

FT-IR Spectrum Elucidation

The experimental FT-IR spectra of *trans* 2,6-methoxy chalcone and 2,6-methoxy chromene are illustrated in Figure (5) and (6).

C-H Vibration

There are two types of C-H stretching in *trans* 2,6-methoxy chalcone and 2,6-methoxy chromene, one of them belongs to methoxy group (sp^3) and the other to aromatic and vinylic

group (sp^2). The expected asymmetric (sp^3) C-H stretching vibration in methoxy compounds is approximately 2980 cm^{-1} , and the symmetric vibration is around 2870 cm^{-1} (Gussoni et al., 1990).

The asymmetric (sp^3) C-H stretching for *trans* 2,6-methoxy chalcone was observed at 2975 cm^{-1} and 2943 cm^{-1} and for 2,6-methoxy chromene was observed at 2960 . The symmetric (sp^3) C-H stretching for *trans* 2,6-methoxy chalcone and 2,6-methoxy chromene were observed at 2862 cm^{-1} and 2846 cm^{-1} , respectively.

The (sp^2) C-H stretching vibration of aromatic and vinylic are in the region of ($3150\text{--}3050$) cm^{-1} and ($3100\text{--}3000$) cm^{-1} , respectively. The out of plane bending (sp^2) C-H vibration of aromatic and vinylic are in the range of ($900\text{--}690$) cm^{-1} and ($1000\text{--}650$) cm^{-1} respectively (Pavia et al., 2014) (Silverstein et al., 2015). In *trans* 2,6-methoxy chalcone, the experimental vibrational wavenumbers of aromatic C-H stretching and out of plane bending were 3088 cm^{-1} and 829 cm^{-1} , respectively. Moreover, the vinylic C-H stretching observed at 3017 cm^{-1} and out of plane were 985 cm^{-1} . In 2,6-methoxy chromene, the aromatic C-H stretching observed at 3072 cm^{-1} and out of plane bending were at 887 and 843 cm^{-1} , respectively.

C=C Aromatic and Vinylic Vibration

The vinylic group vibrations are extremely sensitive to the extent of charge transfer between both the donor and the acceptor groups; thus, spectroscopists are particularly interested in such stretching modes (Joseph et al., 2013). The C=C stretching vibrations of ethylenic bridge usually fall in the region $1660\text{--}1600\text{ cm}^{-1}$. Usually conjugation with carbonyl or benzene ring move the C=C stretching vibrations to the lower end of expected range of absorption range. The C=C stretching vibrations of phenyl ring occur in the range $1600\text{--}1450\text{ cm}^{-1}$ (Pavia et al., 2014) (Silverstein et al., 2015).

The stretching band C=C vinylic and aromatic of *trans* 2,6-methoxy chalcone observed at 1611 and 1588 cm^{-1} , respectively. The stretching band C=C aromatic of 2,6-methoxy chromene could be observed at $1597, 1581$ and 1534 cm^{-1} .

C=O Vibration

Infrared spectroscopy has most extensively studied the stretching of C=O. This double bond group is strongly polar, giving rise to an intense band of absorption by FT-IR. The double bond between carbon and oxygen is formed through

$\pi\text{-}\pi$ bonding between carbon and oxygen. The bonding electrons are not equally distributed between the two atoms, due to the different electronegativities of carbon and oxygen atoms. In FT-IR spectrum a strong band of C=O stretching frequency expected in the $1715\text{--}1660\text{ cm}^{-1}$ region (Socrates, 2001). The $625\text{--}815$ and $680\text{--}510$ region belong to in-plane and out-of-plane C=O deformation, respectively (Silverstein et al., 2015) (Colthup et al., 1990).

In this study the C=O vibrational stretching of *trans* 2,6-methoxy chalcone was observed at 1667 cm^{-1} , whereas no C=O vibrational stretching signal was detected in 2,6-methoxy chromene, this is an excellent indication that our *trans* 2,6-methoxy chalcone is completely converted to 2,6-methoxy chromene. The in-plane and out-of-plane C=O deformations of *trans* 2,6-methoxy chalcone were observed at 787 cm^{-1} and 586 cm^{-1} , respectively.

C-O-C Methoxy Group Vibration

The stretching vibration of asymmetric C-O-C of the methoxy group attached to the aromatic ring expected in the range $1310\text{--}1110\text{ cm}^{-1}$ and for the symmetric is between $1050\text{--}1010\text{ cm}^{-1}$ (Smith, 1999).

The asymmetric C-O-C stretching observed at $1259, 1224$ and 1168 cm^{-1} and $1286, 1183$ and 1135 cm^{-1} for *trans* 2,6-methoxy chalcone and 2,6-methoxy chromene, respectively (Sheena et al., 2015). The symmetric C-O-C stretching for *trans* 2,6-methoxy chalcone and 2,6-methoxy chromene were at 1017 cm^{-1} and 1010 cm^{-1} , respectively.

C-Cl Vibration

The wave number of C-X (X= Cl, Br and I) vibration is assigned by (Mooney., 1964) in the range $1129\text{--}480\text{ cm}^{-1}$. (Sundaraganesan et al., 2008) reported C-Cl stretching at 704 cm^{-1} (IR), (Sheena et al., 2015) reported the C-Cl stretching mode for ((2E)-1-(2,4-Dichlorophenyl)-3-(3,4,5-trimethoxyphenyl) prop-2-en-1-one) at 680 cm^{-1} .

For the studied compounds the bands for C-Cl stretching were observed at 769 cm^{-1} for *trans* 2,6-methoxy chalcone and at 791 and 654 cm^{-1} for 2,6-methoxy chromene.

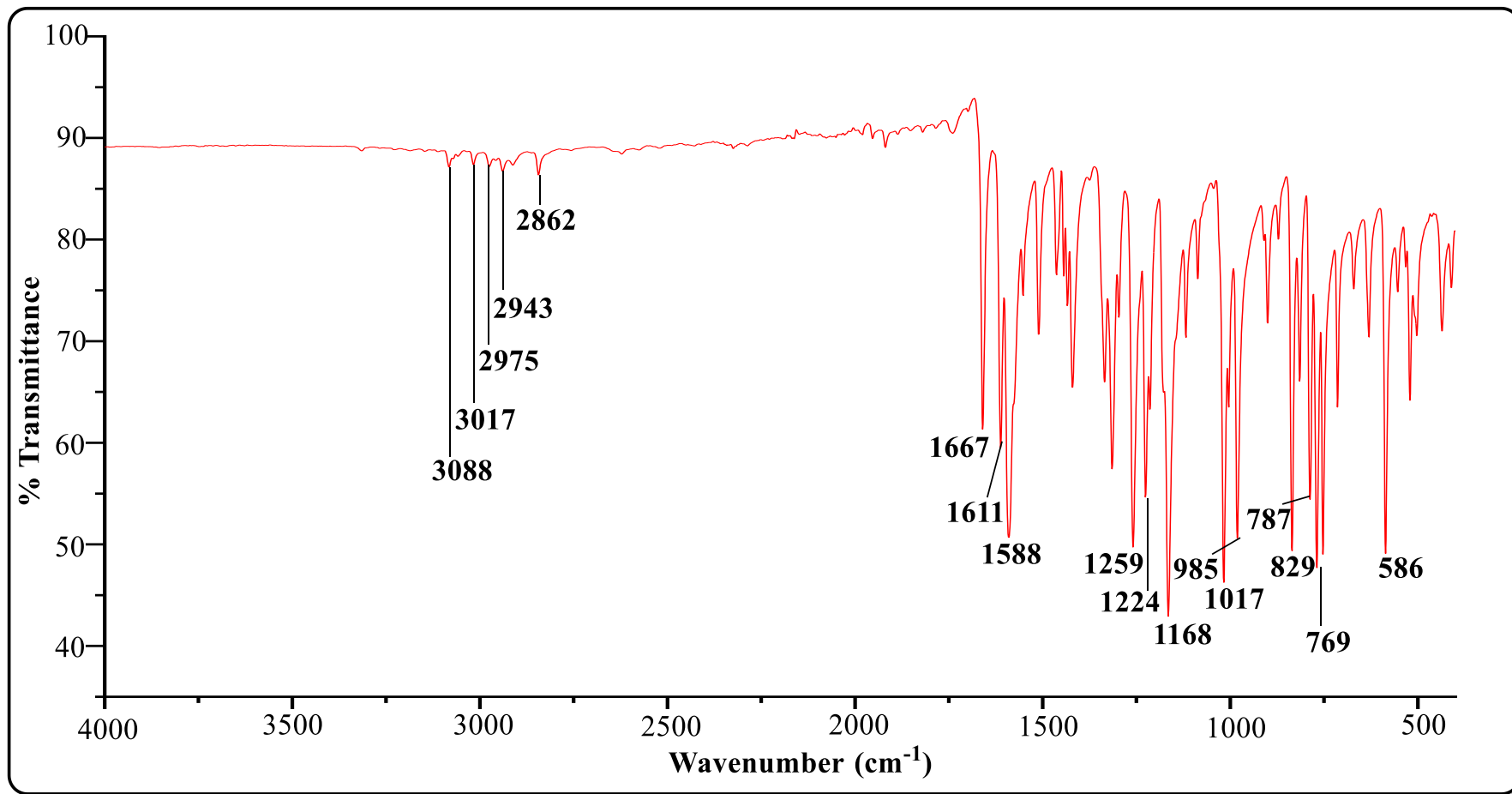


Fig. (5): FT-IR spectrum of *trans* 2,6-methoxy chalcone

abdullah.yousif@uod.ac

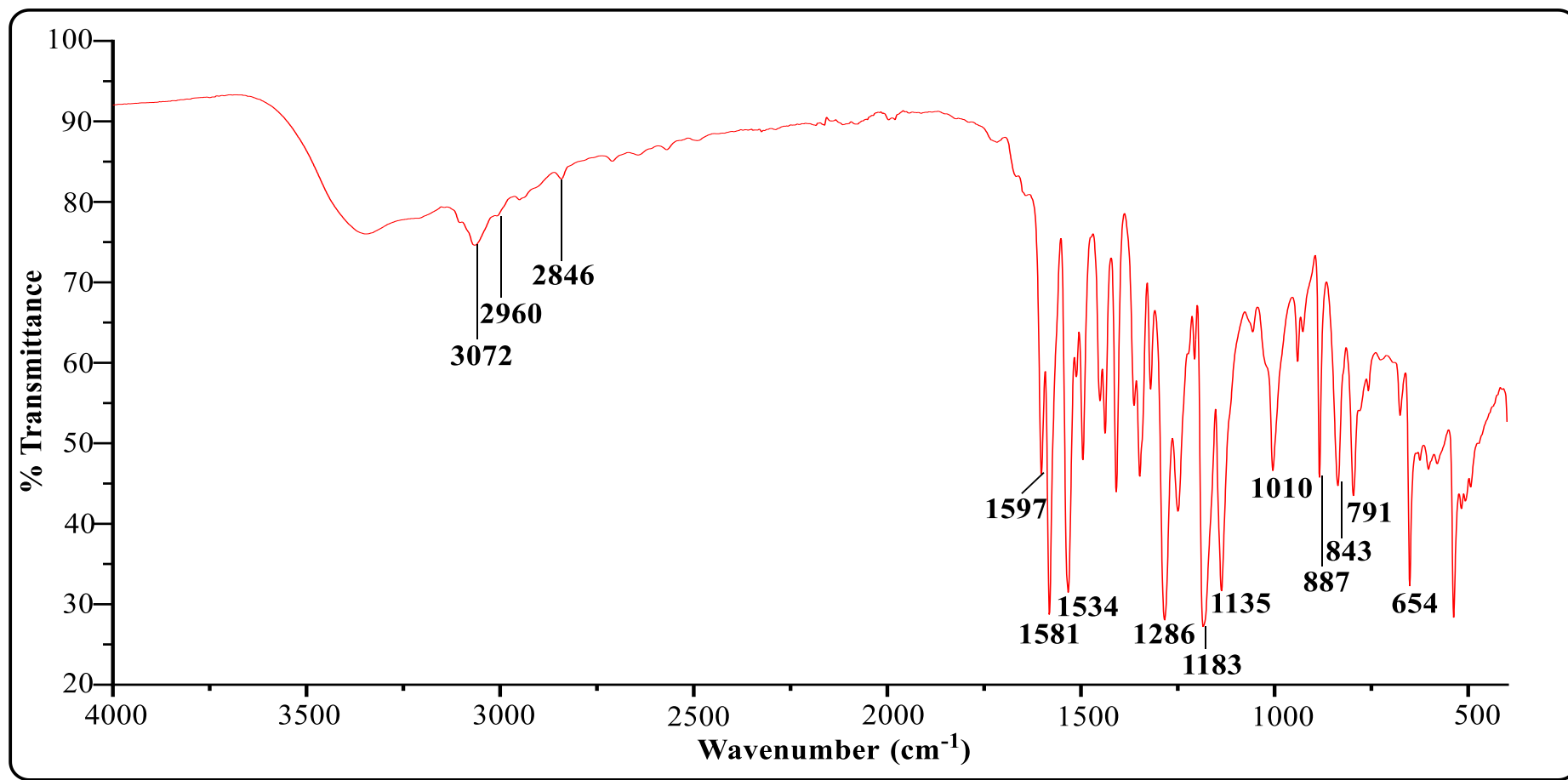


Fig. (6): FT-IR spectrum of 2,6-methoxy chromene

NMR Analysis

The proton chemical shift of aromatic ring is at 6.5-8.0 ppm region in most situations and the proton attached to the methoxy group is in the range 3.2-3.8 ppm. The chemical shift of vinyl hydrogens is in the range 4.5-6.5 ppm, in the case of α - β unsaturated carbonyl group the vinyl hydrogens is de-shielded more due to the anisotropic effect. The ^{13}C chemical shift of α - β unsaturated carbonyl group and aromatic ring are in the 185-220 ppm and 110-175 region, respectively. The chemical shift of vinyl carbon is in the range of 100-150 ppm (Silverstein et al., 2015) (Pavia et al., 2014) (Bruice, 2016).

The H-NMR and ^{13}C -NMR spectra of *trans* 2,6-methoxy chalcone and 2,6-methoxy chromene are illustrated in Figure (8 and 9) and (10 and 11), respectively. Table 1 shows the H-NMR chemical shift, J coupling constants and integration of *trans* 2,6-methoxy chalcone and 2,6-methoxy chromene. Moreover, Solvents chemical shifts in ^1H -NMR and ^{13}C -NMR are shown in Table 3.

The protons of anisole ring belong to AA'XX' splitting pattern; that is, a characteristic of *para* di-substituted benzene ring splitting pattern which gives two mirror image multiplets that look as distorted doublets. In *trans* 2,6-methoxy chalcone and 2,6-methoxy chromene, the chemical shifts of H6-H7 and C11-C12 are more de-shielded than that of H8-H9 and C13-C14, as shown in Tables (1 and 2). This is due to the anisotropic effect of the carbonyl group on H6-H7 and C11-C12. Also, the electron-donating by resonance effect of the methoxy group increases the density of electron on *ortho* and *para* position while it has no effect on *meta* position.

The proton signals of the vinylic proton H4-H5 belong to AB spin system splitting pattern. These two proton signals appeared in the downfield area to the protons of the chlorinated aromatic ring and they appeared as two doublets. The carbonyl group anisotropy is responsible for this downfield effect (Kumar et al., 2014). In *trans* 2,6-methoxy chalcone, the J coupling constant for H4-H5 is 16.07; however, the J coupling constant for H4 and H5 in 2,6-methoxy chromene is observed to be 9.43 and 9.20,

respectively. The two mentioned J coupling constants belong to the *trans* and *cis* configuration (Pavia et al., 2014) (Silverstein et al., 2015), respectively (Table 1). This is a good indication that the *trans* 2,6-methoxy chalcone was converted to 2,6-methoxy chromene.

The chemical shifts of C8 and C7 of ^{13}C -NMR in *trans* 2,6-methoxy chalcone and 2,6-methoxy chromene behave in a similar trend as H5-H4 because of the same reason mentioned above.

In the *trans* 2,6-methoxy chalcone, the ^{13}C -NMR of carbonyl group C9 (188.45 ppm) is the most downfield signal in the ^{13}C spectrum due to the carbonyl anisotropic effect. The C9 (163.37 ppm) in 2,6-methoxy chromene is shielded compared to its value in *trans* 2,6-methoxy chalcone. However, the C9 of 2,6-methoxy chromene is considered as deshielded compared to other signals, except C15, of ^{13}C spectrum of 2,6-methoxy chromene. This observation confirms the synthesis of 2,6-methoxy chromene for the following justification: The C9 of *trans* 2,6-methoxy chalcone is carbonyl and in 2,6-methoxy chromene has moved to shielding position; however, still considered deshielded due to being bonded to etheral oxygen similar to C15 of 2,6-methoxy chromene. The C15 being more deshielded than C9 due to being aromatic carbon so it is under the benzene ring current effect.

The splitting pattern of the protons (H1, H2 and H3) of dichlorobenzene ring in *trans* 2,6-methoxy chalcone belong to AX₂ system (Figure 7). A doublet is observed for the two equivalent H1 and H2 protons and a triplet is observed for H3. The H1-H2 were more down field than H3 due to the closeness to the chlorine atoms. In the 2,6-methoxy chromene the H1 and H2 protons act in similar manner despite the ring has lost its symmetry due to the cyclization and the formation of pyrane ring so the H1 and H2 protons are considered semi-equivalent since they produced on H3 a distorted triplet with one proton integration. The H3 acts in the same manner as in *trans* 2,6-methoxy chalcone. The H3 produced a distorted doublet on H1 and H2 protons of two protons integration (Figure 10).

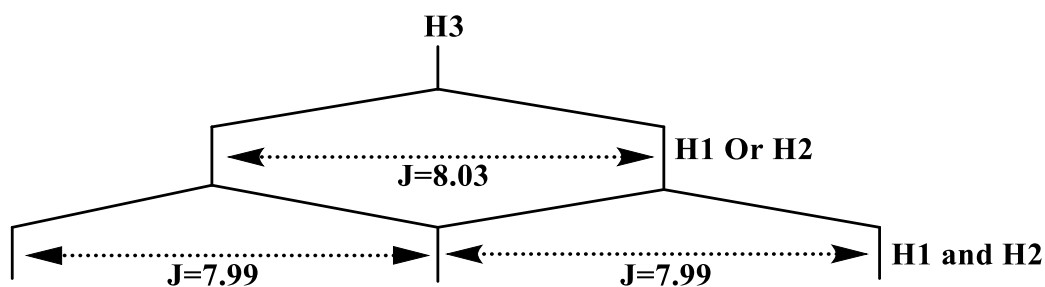


Fig. (7): Tree diagram of dichlorobenzene ring in *trans* 2,6-methoxy chalcone.

In the *trans* 2,6-methoxy chalcone, the C4 and C5 were more deshielded than the C2, C3 and C1 because of the electronegative chlorine atoms attached to C4 and C5.

In the 2,6-methoxy chromene C5 became (sp^3) which shifted the C5 signal to (97.15 ppm) such that it became close to the aliphatic C16 (55.52 ppm) of the methoxy group. This is another evidence for the synthesis of 2,6-methoxy chromene. C4 in 2,6-methoxy chromene is more deshielded than all the carbons of chlorinated ring C1, C2 and C3. Also chemical shift of C4 in *trans* 2,6-methoxy chalcone is (135 ppm) while for the same carbon in 2,6-methoxy chromene it becomes (153.08 ppm), this signal does not exist in the *trans* 2,6-methoxy chalcone spectrum which lends more evidence to the synthesis of 2,6-methoxy chromene.

The chemical shift of C10 in *trans* 2,6-methoxy chalcone is (130.60 ppm) which is down field compared to the same chemical shift of the same carbon (119.15 ppm), C10, in the 2,6-methoxy chromene. This is another evidence of the synthesis of 2,6-methoxy chromene, since its C10 is no longer bonded to the carbonyl as in the *trans* 2,6-methoxy chalcone i.e. no carbonyl anisotropic effect on C10 in 2,6-methoxy chromene.

The C16 (aliphatic sp^3 carbon) of the methoxy group of anisole ring in *trans* 2,6-methoxy chalcone and 2,6-methoxy chromene were found in the highly shielded position compared to other carbons.

The 2,6-methoxy chromene is not stable and during it contacts with solvent it starts to give the *trans* 2,6-methoxy chalcone. The concentration of *trans* 2,6-methoxy chalcone increases gradually as the time of contact of 2,6-methoxy chromene with the solvent increases. The ^{13}C spectrum requires long time of processing to ensure enough signal intensity is obtained. Thus the ^{13}C spectrum of 2,6-methoxy

chromene was noticed to be a mixture of 2,6-methoxy chromene and *trans* 2,6-methoxy chalcone, as shown in (Figure 12). Also, in the same Figure at the top the ^{13}C spectrum of *trans* 2,6-methoxy chalcone is presented. The ^{13}C spectrum of 2,6-methoxy chromene is obtained by deducting the ^{13}C spectrum of *trans* 2,6-methoxy chalcone from the mixture spectrum.

Table (1): The chemical shift, J coupling constant and integration of *trans* 2,6-methoxy chalcone and 2,6-methoxy chromene by ¹H-NMR

| Proton type | Chemical Shift (ppm) | | Coupling Constant (J) (Hz) | | Integration | |
|-------------|-----------------------------------|----------------------|-----------------------------------|----------------------|-----------------------------------|----------------------|
| | <i>Trans</i> 2,6-methoxy chalcone | 2,6-methoxy chromene | <i>Trans</i> 2,6-methoxy chalcone | 2,6-methoxy chromene | <i>Trans</i> 2,6-methoxy chalcone | 2,6-methoxy chromene |
| H1 | 7.37 | 7.92 | 7.99 | 4.38 | 2 | 2 |
| H2 | | | | | | |
| H3 | 7.19 | 7.75 | 8.03 | 4.36 | 1 | 1 |
| H4 | 7.83 | 9.17 | 16.07 | 9.20 | 1 | 1 |
| H5 | 7.66 | 8.38 | 16.07 | 9.43 | 1 | 1 |
| H6 | 8.03 | 8.33 | 8.25 | 8.98 | 2 | 2 |
| H7 | | | | | | |
| H8 | 6.98 | 7.06 | 8.25 | 9.15 | 2 | 2 |
| H9 | | | | | | |
| H10 | 3.88 | 3.81 | - | - | 3 | 3 |

Table (2): The chemical shift of *trans* 2,6-methoxy chalcone and 2,6-methoxy chromene by ¹³C-NMR.

| Carbon Type | Chemical Shift (ppm) | |
|-------------|-----------------------------------|----------------------|
| | <i>Trans</i> 2,6-methoxy chalcone | 2,6-methoxy chromene |
| C1 | 129.73 | 118.66 |
| C2 | 130.39 | 115.08 |
| C3 | | 118.02 |
| C4 | 137 | 153.08 |
| C5 | | 97.15 |
| C6 | 132.79 | 115.88 |
| C7 | 135.14 | 121.84 |
| C8 | 128.84 | 107.06 |
| C9 | 188.45 | 163.37 |
| C10 | 130.60 | 119.15 |
| C11 | 131.10 | 119.82 |
| C12 | | |
| C13 | 113.96 | 114.18 |
| C14 | | |
| C15 | 163.80 | 176.36 |
| C16 | 55.42 | 55.52 |

Table (3): Solvents chemical shift in ¹H-NMR and ¹³C-NMR.

| Solvent | Chemical Shift (ppm) | | Chemical Shift (ppm) | |
|-------------------|-----------------------------------|---------------------|----------------------|---------------------|
| | <i>Trans</i> 2,6-methoxy chalcone | | 2,6-methoxy chromene | |
| | ¹ H-NMR | ¹³ C-NMR | ¹ H-NMR | ¹³ C-NMR |
| CDCl ₃ | 7.26 | 77.29 | - | - |
| D ₂ O | - | - | 4.77 | - |
| DMSO-D6 | - | - | - | 39.69 |

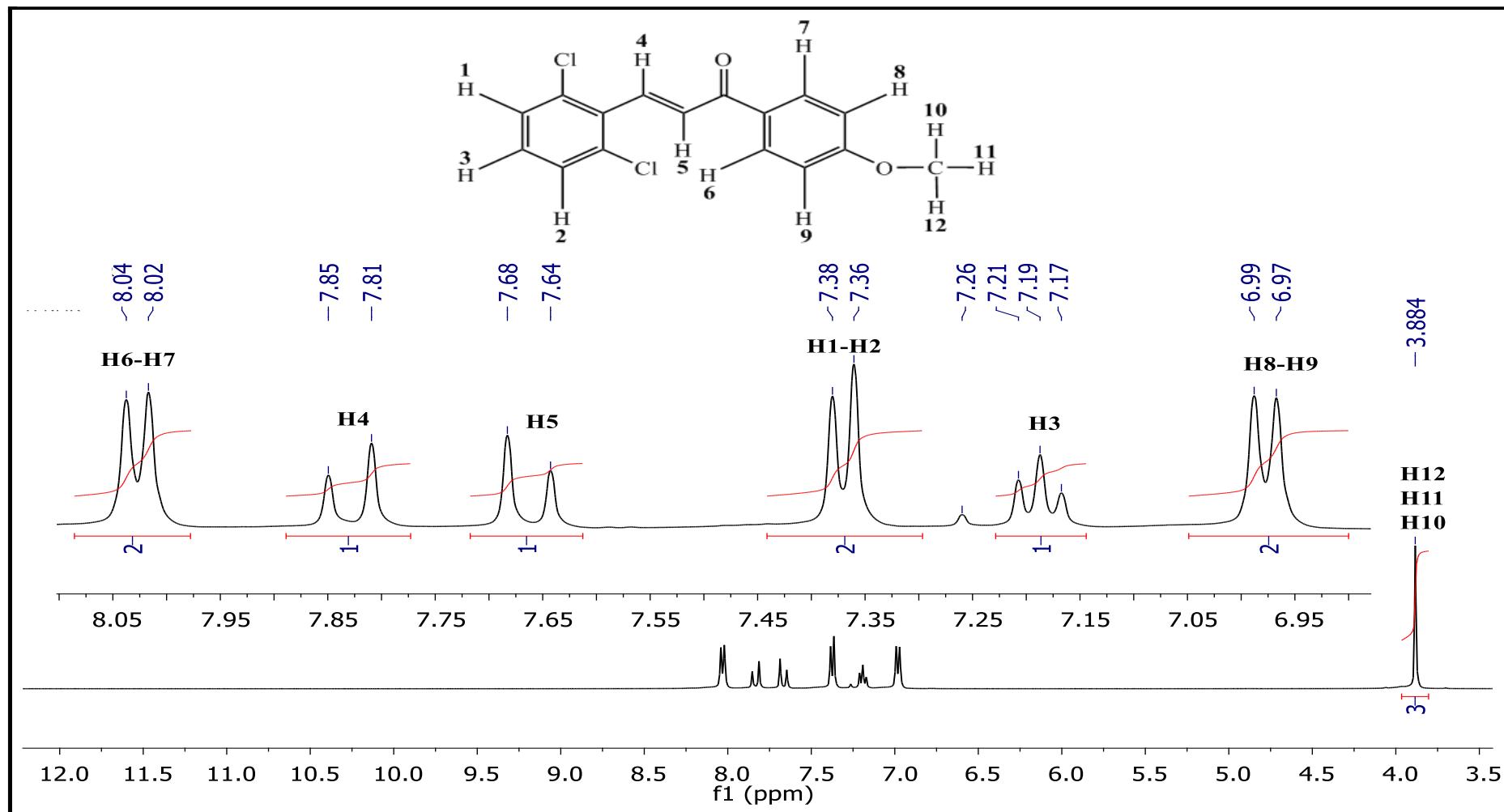


Fig. (8): ¹H-NMR spectrum of *trans* 2,6-methoxy chalcone in CDCl₃.

abdullah.yousif@uod.ac

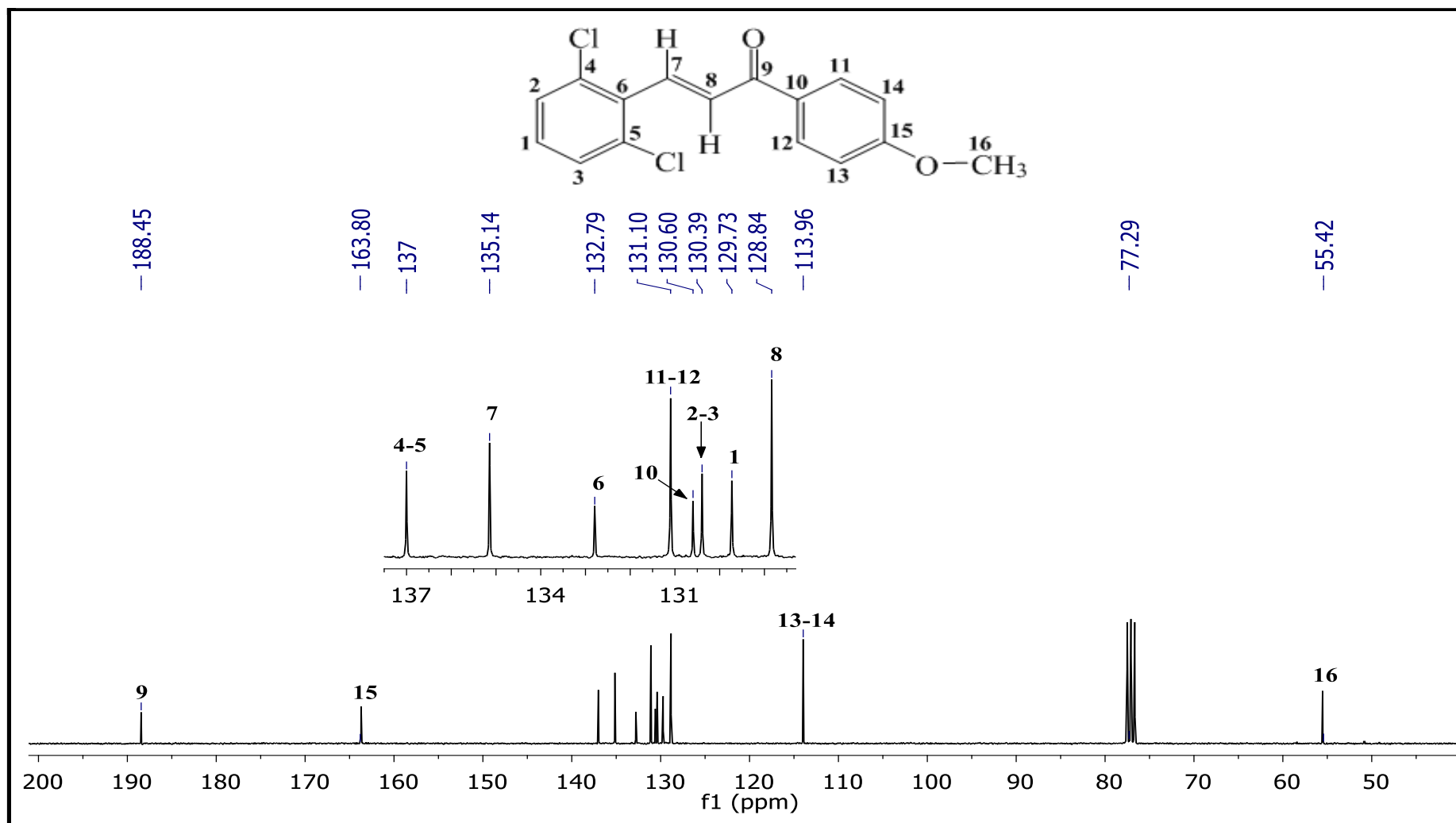


Fig. (9): ¹³C-NMR spectrum of *trans* 2,6-methoxy chalcone in CDCl₃.

abdullah.yousif@uod.ac

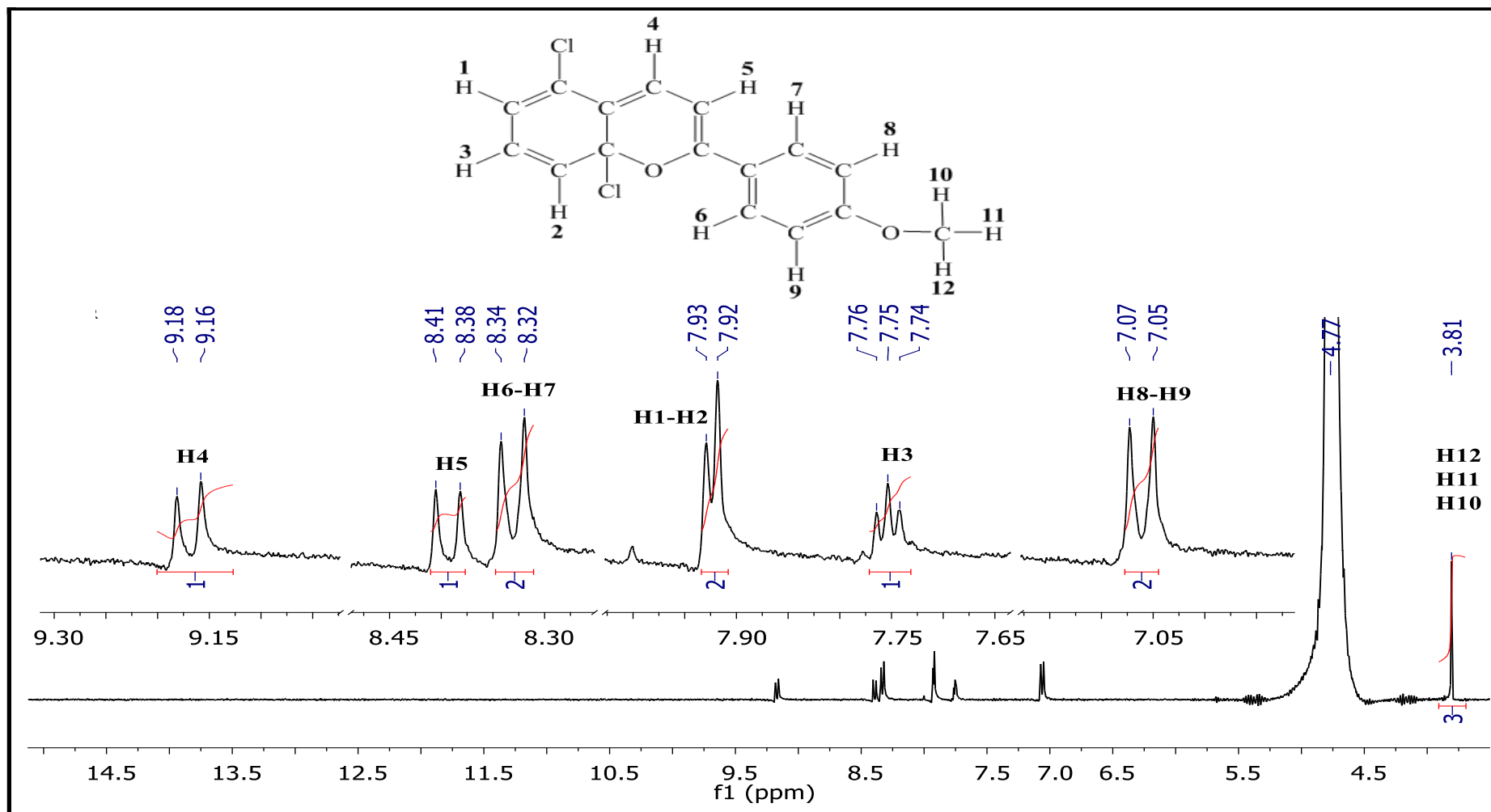


Fig. (10): ¹H-NMR spectrum of 2,6-methoxy chromene in D₂O.

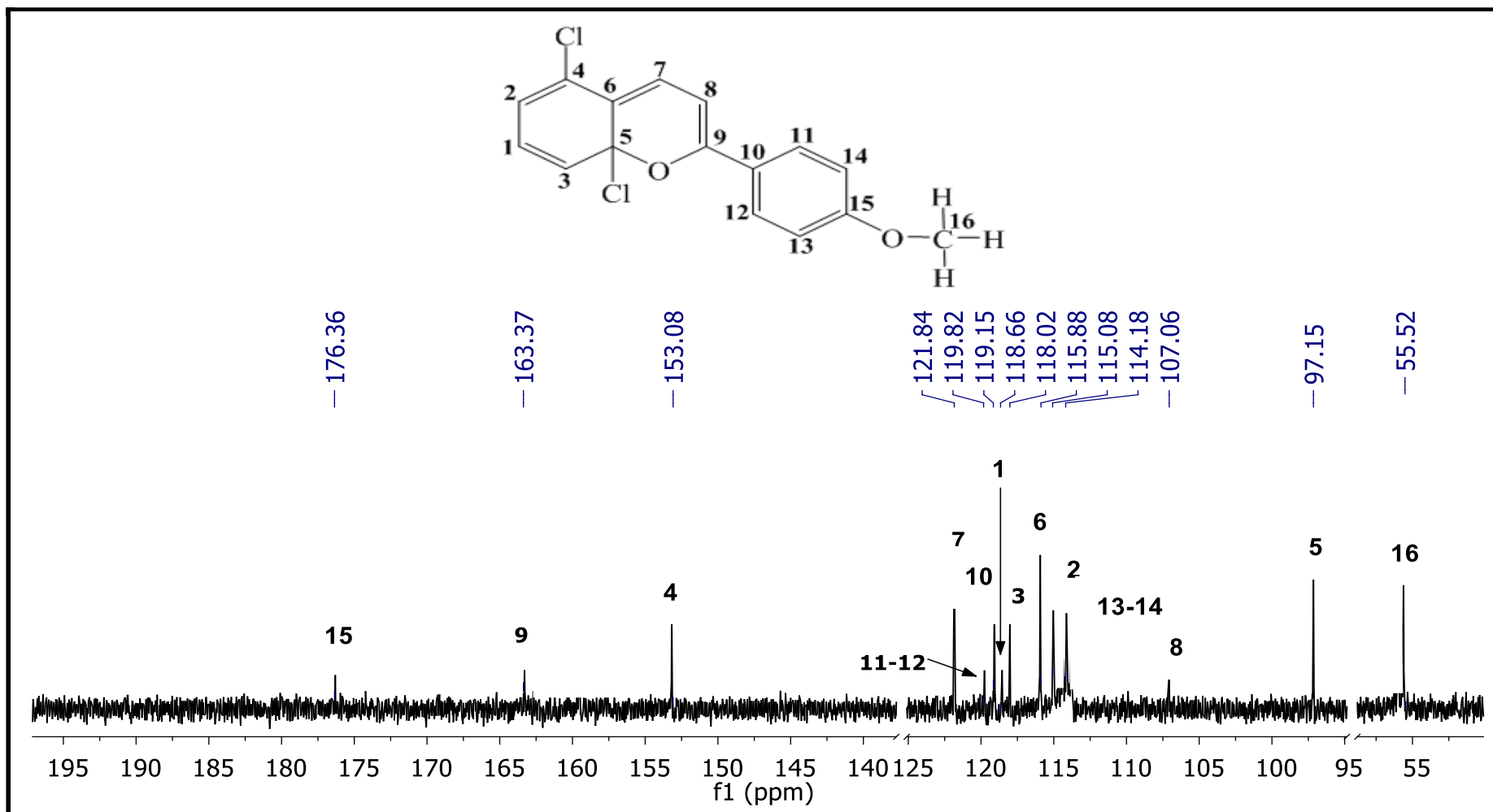


Fig. (11): ^{13}C -NMR spectrum of 2,6-methoxy chromene in DMSO- D_6 .

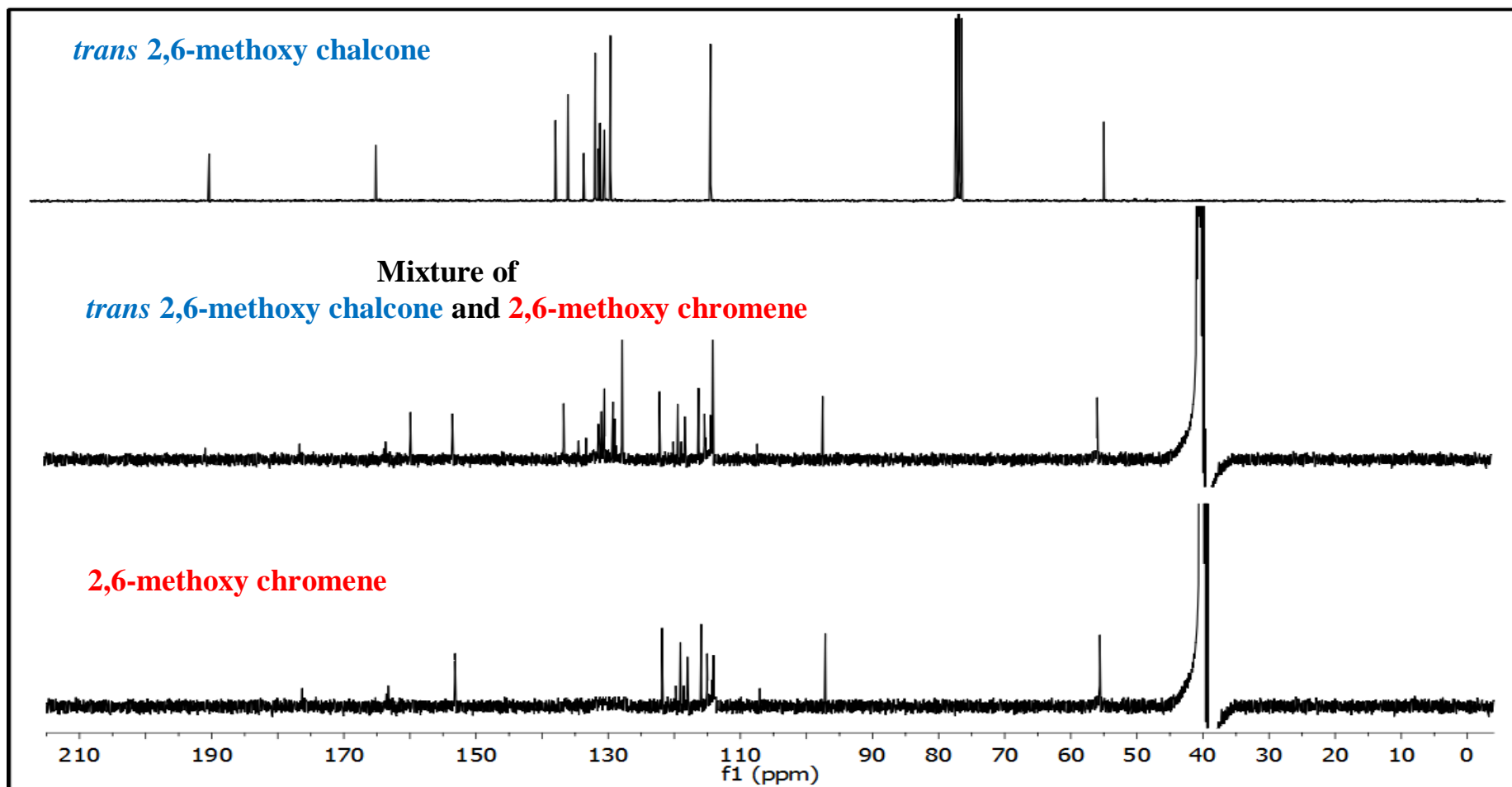


Fig. (12): ^{13}C -NMR spectra of *Trans* 2,6-methoxy chalcone, mixture of *trans* 2,6-methoxy chalcone and 2,6-methoxy chromene and 2,6-methoxy chromene

Liquid Chromatography/Quadrupole Time-Of-Flight/ Mass Spectrometry (LC/Q-TOF/MS)

The molecular ion of 2,6-methoxy chromene was determined by LC/Q-TOF-MS which is equal to 306.9915 at the retention time 8.046

min, the calculated exact mass of 2,6-methoxy chromene is 306.0214.

Elemental Analysis (CHNO)

The experimental and calculated elemental analysis (CHNO) results of 2,6-methoxy chromene are shown in Table 4.

Table (40): Experimental and calculated CHNO analysis of 2,6-methoxy chromene

| Element Name | Experimental Weight (%) | Calculated Weight (%) |
|--------------|-------------------------|-----------------------|
| Carbon | 62.40 | 62.56 |
| Oxygen | 10.49 | 10.42 |
| Hydrogen | 3.90 | 3.94 |
| | Total = 76.79 | Total = 76.92 |
| Chlorine | 100 - 76.79 = 23.21 | 23.08 |

4. CONCLUSION

The synthesis and purification of *trans*-2,6-methoxy chalcone was easy and with an excellent yield. Moreover, the photosynthesis of 2,6-chromene took 1 hour for (0.0048 mol) of the precursor chalcone, and pure with very good yield. An excellent indication for the conversion of *trans* 2,6-methoxy chalcone to 2,6-methoxy chromene is given by FT-IR in which the C=O vibrational stretching disappeared in the 2,6-methoxy chromene FT-IR spectrum. ¹H-NMR showed two different J coupling constants for H4-H5 in *trans* 2,6-methoxy chalcone and 2,6-methoxy chromene. This is a good evidence for the conversion of *trans* geometry in *trans*-2,6-methoxy chalcone to *cis* geometry in 2,6-methoxy chromene. The ¹³C-NMR of carbonyl carbon (C9) appeared at the most downfield signal in the ¹³C spectrum. Whereas the C9 in 2,6-methoxy chromene is shielded compared to its value in *trans*-2,6-methoxy chalcone. This is due to the conversion of carbonyl group in *trans*-2,6-methoxy chalcone to etheral oxygen consequently losing the carbonyl anisotropic effect. The last evidence for the conversion of *trans*-2,6-methoxy chalcone to 2,6-chromene is detected in C10. The C10 in 2,6-chromene is no longer bonded to the carbonyl group, it produces a signal on more shielded region than *trans*-2,6-methoxy chalcone.

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