



SYNTHESIS OF SOME NOVEL CHALCONES AND THEIR FACILE ONE-POT CONVERSION TO 2-AMINO BENZENE-1, 3-DICARBONITRILES USING MALONONITRILE

K.L. Ameta *, Nitu S. Rathore and Biresh Kumar

abstract: A facile synthesis of some novel chalcones (**3a-3k**) by the condensation of variously substituted aromatic aldehydes and 2,4-dihydroxyacetophenone and their subsequent rapid one pot transformations to 2-aminobenzene-1,3-dicarbonitriles (**5a-5k**) with malononitrile and morpholine has been described. It is a comparative study of synthesizing these novel compounds by conventional as well as non-conventional microwave irradiation in a commercially modified microwave oven and also confirms the possible intervention of specific (non-thermal) microwave effect. The present investigation also focused on the remarkable reaction rate enhancement by the use of various inorganic solid supports in non-conventional microwave irradiation which minimizes the hazards of solution phase reactions. The non-conventional protocol offers several advantages such as simple procedure, fast reaction rate, mild reaction condition and improved yields as compared to conventional methods. The structures of newly synthesized compounds have been established on the basis of elemental analysis, ¹H NMR, Mass and IR spectral data.

key words: Aromatic aldehyde; acetophenone; chalcones; malononitrile; 2-aminobenzene-1, 3-dicarbonitrile; Microwave irradiation; Montmorillonite K10 & KSF.

received: February 23, 2011

accepted: March 22, 2011

1. Introduction

The chalcones (1, 3-diaryl-2-propenones) and their derivatives are important intermediates in organic synthesis [1-3]. They serve as starting material for the synthesis of variety of heterocyclic compounds which are of physiological importance. Due to the presence of enone functionality in chalcone moiety confers biological activity upon it, like anti-inflammatory [4], antifungal [5], antioxidant [6], antimalarial [7], antituberculosis [8], analgesic [9], anti HIV [10] and antitumor [11] activities. In recent years, microwave assisted solid support-solvent free organic synthesis have attracted attention as they offer several advantages such as simple procedure, fast reaction rate, mild reaction condition,

* Department of Chemistry, Faculty of Arts Science and Commerce, MITS University, Lakshmangarh - 332311, Rajasthan, India. *corresponding author e-mail:* klameta77@yahoo.co.in

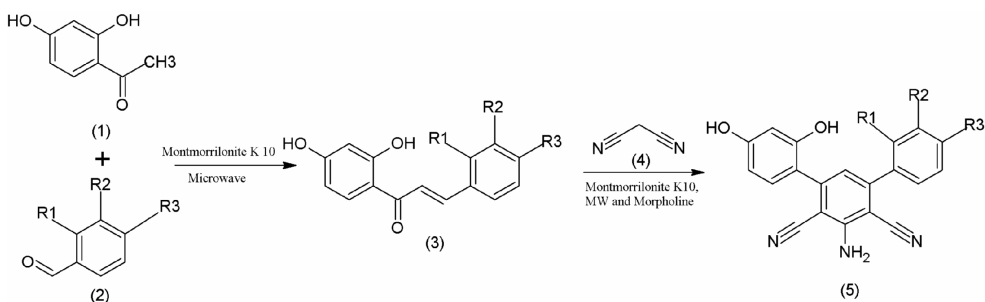
eco-friendly and improved yields as compared to conventional methods. Further the reaction in dry media conditions especially appealing as they provide an opportunity to work with open vessels, thus avoiding the risk of high pressure development and offer the possibility of carrying out reactions that can be scaled up by the industries.

The m-terphenyl moiety is an important structural unit, useful intermediate and act as building blocks for constructing optical active cyclophans [12-13], cyclic ketones [14-17], dendrimers [18] and liquid crystals [19]. Though several approaches have been developed for the synthesis of 2-aminobenzene-1, 3-dicarbonitriles. The majority of them are multistep with poor yield. In continuation of our earlier endeavor [20-22] on MORE (Microwave induced organic reaction enhancement) chemistry for the synthesis of bioactive compounds using solid phase conditions, we herein describes the synthesis of some novel chalcones and their 2-aminobenzene-1,3-dicarbonitrile derivatives by conventional and microwave irradiation coupled with solid support and under neat conditions.

Prompted by the varied biological activities of chalcones and their derivatives and increasing applications of microwave irradiation in organic synthesis [23], it was thought of interest to synthesis variously substituted chalcones and their transformation products 2-aminobenzene-1,3-dicarbonitrile derivatives in multimode commercial microwave oven.

2. Experimental

Condensation of variously substituted aromatic aldehydes (**1**) and 2,4-dihydroxyacetophenone (**2**) furnished the corresponding chalcones (**3a-k**) which on treatment with malononitrile (**4**) in presence of catalytic amount of morpholine afforded the desired products (**5a-5k**) Scheme-1.



Scheme 1: Synthesis of chalcones Chalcones 3_{a-k} and their 2-aminobenzene-1,3-dicarbonitriles 5_{a-k}

The characterization data of the synthesized compounds have been tabulated in Table 1.

Table 1 Characterization data of Compounds 3a-3k and 5a-5k

Compd.	R ₁	R ₂	R ₃	m.p.	Mol. Formula
3a	H	H	H	130-131° C	C ₁₅ H ₁₂ O ₃
3b	Cl	H	H	132-134° C	C ₁₅ H ₁₁ O ₃ Cl
3c	H	Cl	H	123-125° C	C ₁₅ H ₁₁ O ₃ Cl
3d	H	H	Cl	135-137° C	C ₁₅ H ₁₁ O ₃ Cl

Compd.	R ₁	R ₂	R ₃	m.p.	Mol. Formula
3e		Furyl		133-135° C	C ₁₃ H ₁₀ O ₄
3f	H	OCH ₃	OH	99-100° C	C ₁₆ H ₁₄ O ₅
3g	H	CH ₃	H	136-138° C	C ₁₆ H ₁₄ O ₃
3h	H	H	CH ₃	126-128° C	C ₁₆ H ₁₄ O ₃
3i	H	H	F	128-130° C	C ₁₅ H ₁₁ O ₂ F
3j	OH	H	H	130-131° C	C ₁₅ H ₁₂ O ₄
3k	H	H	OH	90-92° C	C ₁₅ H ₁₂ O ₄
5a	H	H	H	195-197° C	C ₂₀ H ₁₃ O ₂ N ₃
5b	Cl	H	H	225-227° C	C ₂₀ H ₁₃ O ₂ N ₃ Cl
5c	H	Cl	H	211-213° C	C ₂₀ H ₁₂ O ₂ N ₃ Cl
5d	H	H	Cl	206-208° C	C ₂₀ H ₁₂ O ₂ N ₃ Cl
5e		FuryL		230-232° C	C ₁₈ H ₁₁ O ₃ N ₃
5f	H	OCH ₃	H	199-200° C	C ₂₁ H ₁₅ O ₄ N ₃
5g	H	CH ₃	H	220-222° C	C ₂₁ H ₁₅ O ₂ N ₃
5h	H	H	CH ₃	250-252° C	C ₂₁ H ₁₅ O ₂ N ₃
5i	H	H	F	208-210° C	C ₂₀ H ₁₂ O ₂ N ₃ F
5j	OH	H	H	244-246° C	C ₂₀ H ₁₃ O ₃ N ₃
5k	H	H	OH	207-209° C	C ₂₀ H ₁₃ O ₃ N ₃

All melting points (m.ps.) were determined in open capillaries on Veego (VMP – PM) melting point apparatus and are uncorrected. Multimode commercial microwave oven with ten power levels was employed for the synthesis of these compounds. The purity of the compounds was routinely checked by thin layer chromatography (TLC) with Silica Gel-G (Merck). The instruments used for spectroscopic data are; IR-FTTR spectrophotometer Bruker Alpha-Zn-Se, ¹HNMR (CDCl₃) on 500 MHz FT-NMR spectrometer Bruker AV III and elemental analysis was carried out on a Carlo Erba 1108 analyzer and were within the ± 0.5% of the theoretical values. Column chromatography was performed on silica gel (Merck, 60-120 mesh).

General procedure for the preparation of chalcones (3a-3k):

a. Solution phase conventional method:

A mixture of 2, 4-dihydroxy acetophenone (0.01 mol) and aryl aldehydes (0.01 mol) was stirred in ethanol (30 mL) and then an aqueous solution of KOH (40%, 15 mL) was added to it. The reaction mixture was kept overnight at room temperature and then it was poured in to crushed ice and acidified with HCl. The solid separated was filtered and recrystallized from ethanol to afforded analytical samples of **3**.

b. Solid phase microwave method:

To a solution of 2, 4-dihydroxyacetophenone (0.01 mol) and substituted aromatic aldehyde (0.01mol) in DMF (5mL) taken in 100 mL borosil flask, was added montmorillonite K 10 clay (4g). The mixture was uniformly mixed with glass rod and air dried to remove the solvent. Adsorbed material was irradiated inside a microwave oven for specified time Table-3 at medium power level (600 W). After the completion of the reaction (monitored by TLC), the reaction mixture was cooled at room temperature and the product was extracted with ethanol (2 x 20 mL). Removal of the solvent and subsequent recrystallisation with ethanol resulted analytical samples of **3**. IR, ¹H NMR and mass spectral data of synthesized compound are mentioned below:

Synthesis of (2E)-1-(2, 4-dihydroxyphenyl)-3-phenylprop-2-en-1-one (3a): It was obtained from the reaction of compound (**2**) with Benzaldehyde. IR (KBr cm⁻¹): 3450 (OH), 3055 (Ar CH), 1732 (C=O), 1637 (CH=CH); ¹HNMR (CDCl₃-d, δ, ppm): 7.88-7.81 (1H, d, =CH-Ar), 7.72-7.30 (8H, m, Ar-H), 6.81 (1H, d, -CO-CH=), 4.9 (1H, s, C-4'-OH); MS, [M⁺], (m/z): 239 (100%); Anal. Calcd for C₁₅H₁₂O₃ (240): C, 75.10; H, 5.00. Found: C, 74.06; H, 4.98.

(2E)-3-(2-chlorophenyl)-1-(2, 4-dihydroxyphenyl) prop-2-en-1-one (3b): It was obtained from the reaction of compound (**2**) with 2-Chlorobenzaldehyde. IR (KBr cm⁻¹): 3466 (OH), 3055 (Ar CH), 1723 (C=O), 1641 (CH=CH), 852 (Ar- Cl); ¹HNMR (CDCl₃-d, δ, ppm): 7.80-6.98 (1H, d, =CH-Ar), 7.72-7.30 (7H, m, Ar-H), 7.34 (1H, d, -CO-CH=), 5.40 (1H, s, C-4'-OH); MS, [M⁺], (m/z): 273.45 (100%); Anal. Calcd for C₁₅H₁₁O₃Cl (274.45): C, 65.58; H, 4.00. Found: C, 65.54; H, 4.02.

(2E)-3-(3-chlorophenyl)-1-(2, 4-dihydroxyphenyl) prop-2-en-1-one (3c): It was obtained from the reaction of compound (**2**) with 3-Chlorobenzaldehyde. IR (KBr cm⁻¹): 3466 (OH), 3055 (Ar CH), 1756 (C=O), 1639 (CH=CH), 830 (Ar-Cl); ¹HNMR (CDCl₃-d, δ, ppm): 7.80-6.98 (1H, d, =CH-Ar), 7.72-7.30 (7H, m, Ar-H), 7.34 (1H, d, -CO-CH=), 5.40 (1H, s, C-4'-OH); MS, [M⁺], (m/z): 273.45 (100%); Anal. Calcd for C₁₅H₁₁O₃Cl (274.45): C, 65.57; H, 4.00. Found: C, 65.54; H, 4.04.

(2E)-3-(4-chlorophenyl)-1-(2, 4-dihydroxyphenyl) prop-2-en-1-one (3d): It was obtained from the reaction of compound (**2**) with 4-Chlorobenzaldehyde. IR (KBr cm⁻¹): 3462 (OH), 3055 (Ar CH), 1721 (C=O), 1640 (CH=CH), 871 (Ar-Cl); ¹HNMR (CDCl₃-d, δ, ppm): 7.82-7.80 (1H, d, =CH-Ar), 7.72-7.30 (7H, m, Ar-H), 7.32 (1H, d, -CO-CH=), 5.34 (1H, s, C-4'-OH); MS, [M⁺], (m/z): 273.45 (100%); Anal. Calcd for C₁₅H₁₁O₃Cl (274.45): C, 65.56; H, 4.00. Found: C, 65.60; H, 4.01.

(2E)-1-(2, 4-dihydroxyphenyl)-3-(furan-2-yl) prop-2-en-1-one (3e): It was obtained from the reaction of compound (**2**) with 2-Furaldehyde. IR (KBr cm⁻¹): 3450 (OH), 3050 (Ar CH), 1721 (C=O), 1636 (CH=CH), 1385 (C-O); ¹HNMR (CDCl₃-d, δ, ppm): 7.88-7.81 (1H, d, =CH-Ar), 7.86-7.59 (7H, m, Ar-H), 7.04 (1H, d, -CO-CH=), 5.32 (1H, s, C-4'-OH); MS, [M⁺], (m/z): 229.00 (100%); Anal. Calcd for C₁₃H₁₀O₄: (230.0): C, 67.82; H, 4.34. Found: C, 67.80; H, 4.36.

(2E)-3-(4-hydroxy-3-methoxyphenyl)-1-(2, 4-dihydroxyphenyl) prop-2-en-1-one (3f): It was obtained from the reaction of compound (**2**) with 4-Hydroxy-3-methoxybenzaldehyde. IR (KBr cm⁻¹): 3452 (OH), 3050 (Ar CH), 1721 (C=O), 1640 (CH=CH), 1385 (C-O), 1174

(OCH₃); ¹HNMR (CDCl₃-*d*, δ, ppm): 7.88-7.81 (1H, d, =CH-Ar), 7.72-7.30 (6H, m, Ar-H), 7.34 (1H, d, -CO-CH=), 5.90 (1H, s, C-4'-OH), 6.40 (2H, s, Ar-H), 3.83 (3H, s, OCH₃); MS, [M⁺], (m/z): 285.00 (100%); Anal. Calcd for C₁₆H₁₄O₅ (286.00): C, 67.13; H, 4.89. Found: C, 67.16; H, 4.91.

(2E)-1-(2, 4-dihydroxyphenyl)-3-(3-methylphenyl) prop-2-en-1-one (3g): It was obtained from the reaction of compound (2) with 3-Methylbenzaldehyde. IR (KBr cm⁻¹): 3450 (OH), 3055 (Ar CH), 1720 (C=O), 1642 (CH=CH), 1385 (C-O); ¹HNMR (CDCl₃-*d*, δ, ppm): 8.67-8.81 (1H, d, =CH-Ar), 7.72-7.30 (6H, m, Ar-H), 7.34 (1H, d, -CO-CH=), 5.40 (1H, s, C-4'-OH), 6.40(2H, s, Ar-H), 2.42(3H, s, Ar-CH₃); MS, [M⁺], (m/z): 253.00 (100%); Anal. Calcd for C₁₆H₁₄O₃ (254.00): C, 75.90; H, 5.51. Found: C, 75.86; H, 5.50.

(2E)-1-(2, 4-dihydroxyphenyl)-3-(4-methylphenyl) prop-2-en-1-one (3h): It was obtained from the reaction of compound (2) with 4-Methylbenzaldehyde. IR (KBr cm⁻¹): 3480 (OH), 3055 (Ar CH), 1720 (C=O), 1642 (CH=CH), 1385 (C-O); ¹HNMR (CDCl₃-*d*, δ, ppm): 7.88-7.81 (1H, d, =CH-Ar), 7.70-7.30 (6H, m, Ar-H), 7.34 (1H, d, -CO-CH=), 5.40 (1H, s, C-4'-OH), 6.40(2H, s, Ar-H), 2.41(3H, s, Ar-CH₃); MS, [M⁺], (m/z): 253.00 (100%); Anal. Calcd for C₁₆H₁₄O₃ (254.00): C, 75.90; H, 5.51. Found: C, 75.93; H, 5.49.

(2E)-1-(2, 4-dihydroxyphenyl)-3-(4-fluorophenyl) prop-2-en-1-one (3i): It was obtained from the reaction of compound (2) with 4-Fluorobenzaldehyde. IR (KBr cm⁻¹): 3450 (OH), 3055 (Ar CH), 1721 (C=O), 1636 (CH=CH), 1390 (C-O), 815 (Ar-F); ¹HNMR (CDCl₃-*d*, δ, ppm): 7.88-7.81 (1H, d, =CH-Ar), 7.70-7.30 (6H, m, Ar-H), 7.34 (1H, d, -CO-CH=), 5.40 (1H, s, C-4'-OH), 6.40 (2H, s, Ar-H); MS, [M⁺], (m/z): 241.00 (100%); Anal. Calcd for C₁₅H₁₁O₂F (242.00): C, 74.38; H, 4.52. Found: C, 74.40; H, 4.55.

(2E)-1-(2, 4-dihydroxyphenyl)-3-(2-hydroxyphenyl) prop-2-en-1-one (3j): It was obtained from the reaction of compound (2) with 2-Hydroxybenzaldehyde. IR (KBr cm⁻¹): 3450 (OH), 3055 (Ar CH), 1721 (C=O), 1636 (CH=CH), 1385 (C-O); ¹HNMR (CDCl₃-*d*, δ, ppm): 7.88-7.81 (1H, d, =CH-Ar), 7.72-7.30 (7H, m, Ar-H), 7.34 (1H, d, -CO-CH=), 5.43 (1H, s, C-4'-OH), 6.35(2H, s, Ar-H); MS, [M⁺], (m/z): 255.00 (100%); Anal. Calcd for C₁₅H₁₂O₄ (256.00): C, 70.31; H, 4.68. Found: C, 70.34; H, 4.64.

(2E)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one (3k): It was obtained from the reaction of compound (2) with 2-Hydroxybenzaldehyde. IR (KBr cm⁻¹): 3450 (OH), 3055 (Ar CH), 1721 (C=O), 1636 (CH=CH), 1385 (C-O); ¹HNMR (CDCl₃-*d*, δ, ppm): 7.79-7.80 (1H, d, =CH-Ar), 7.72-7.30 (7H, m, Ar-H), 7.34 (1H, d, -CO-CH=), 5.03 (1H, s, C-4'-OH), 6.35 (2H, s, Ar-H); MS, [M⁺], (m/z): 255.00 (100%); Anal. Calcd for C₁₅H₁₂O₄ (256.00): C, 70.31; H, 4.68. Found: C, 70.33; H, 4.66; O.

General procedure for the preparation of 2-aminobenzene-1, 3-dicarbonitriles (5a-5k):

a. Solution phase conventional method:

A mixture of chalcone (0.01mol), malononitrile (0.02 mol) and heterocyclic secondary amine (morpholine; 0.01 mol) dissolved in ethanol (15 mL) and was refluxed for 9-10 hrs in a round bottom flask. On completion of reaction (monitored by TLC) the reaction

mixture was concentrated. The solid obtained was filtered, washed with methanol and recrystallized from the appropriate solvent yielded the desired products **5**.

b. Solid phase microwave method:

A mixture of chalcone, malononitrile and heterocyclic secondary amine (morpholine) in 1:2:1 ratio dissolved in DMF (5mL) was taken in a beaker and absorbed over montmorillonite K 10 (4 gm). The reaction mixture was air dried and kept in an alumina-bath and irradiated in microwave oven for specified time (Table-III). On completion of reaction (monitored by TLC) at an interval of every 30 seconds, the products was extracted in to ethanol (3 X 15mL). Recovering the products under reduced pressure yielded the products (**5a-k**) which were purified by recrystallization. IR, ¹H NMR and mass spectral data of synthesized compound are mentioned below:

5'-amino -2, 4 - dihydroxy-1, 1': 3', 1'' - terphenyl-4', 6'-dicarbonitrile (5a): It was obtained from reacting (**3a**) with (**4**) and morpholine. IR (KBr cm⁻¹): 3300 (OH), 3450 (NH₂), 3042 (Ar CH), 2201 (C=N); ¹HNMR (CDCl₃-*d*, δ, ppm): 7.06-7.53 (8H, m, Ar-H), 6.8 (1H, s, Ar-H), 5.83 (2H, br s, - NH₂), 5.01 (2H, d, OH); MS, [M⁺], (m/z): 326.00 (100%); Anal. Calcd for C₂₀H₁₃N₃O₂ (327.00): C, 73.39; H, 4.00; N, 12.84. Found: C, 73.32; H, 3.92; N, 12.80.

5'-amino -2''-chloro-2, 4 - dihydroxy-1, 1': 3', 1'' - terphenyl-4', 6'-dicarbonitrile (5b): It was obtained from reacting (**3b**) with (**4**) and morpholine. IR (KBr cm⁻¹): 3300 (OH), 3450 (NH₂), 3036 (Ar CH), 2201 (C=N), 771 (Ar-Cl); ¹HNMR (CDCl₃-*d*, δ, ppm): 7.06-7.78 (7H, m, ArH), 7.58 (1H, s, ArH), 5.43 (2H, br s, - NH₂), 5.25 (1H, s, OH), 5.01 (1H, s, OH); MS, [M⁺], (m/z): 360.45 (100%); Anal. Calcd for C₂₀H₁₂N₃O₂Cl (361.45): C, 66.34; H, 3.31; N, 11.61. Found: C, 66.40; H, 3.33; N, 11.62.

5'-amino -3''-chloro-2, 4 - dihydroxy-1, 1': 3', 1'' - terphenyl-4', 6'-dicarbonitrile (5c): It was obtained from reacting (**3c**) with (**4**) and morpholine. IR (KBr cm⁻¹): 3300 (OH), 3450 (NH₂), 3093 (Ar CH), 2201 (C=N), 771, 750 (Ar-Cl); ¹HNMR (CDCl₃-*d*, δ, ppm): 7.06-7.78 (7H, m, ArH), 6.8 (1H, s, ArH), 5.40 (2H, br s, - NH₂), 5.12 (1H, s, OH), 4.96 (1H, s, OH); MS, [M⁺], (m/z): 360.45 (100%); Anal. Calcd for C₂₀H₁₂N₃O₂Cl (361.45): C, 66.34; H, 3.31; N, 11.61. Found: C, 66.41; H, 3.34; N, 11.65.

5'-amino -4''-chloro-2, 4 - dihydroxy-1, 1': 3', 1'' - terphenyl-4', 6'-dicarbonitrile (5d): It was obtained from reacting (**3d**) with (**4**) and morpholine. IR (KBr cm⁻¹): 3350 (OH), 3450 (NH₂), 3093 (Ar CH), 2201 (C=N), 765 (Ar-Cl); ¹HNMR (CDCl₃-*d*, δ, ppm): 7.39-7.78 (7H, m, Ar-H), 6.42 (1H, s, Ar-H), 5.40 (2H, br s, - NH₂), 5.01 (1H, s, OH), 4.97(1H, s, OH); MS, [M⁺], (m/z): 360.45 (100%); Anal. Calcd for C₂₀H₁₂N₃O₂Cl (361.45): C, 66.42; H, 3.34; N, 11.61. Found: C, 66.39; H, 3.32; N, 11.64.

3-amino -5-(furan-2-yl)-2', 4' - dihydroxybiphenyl-2, 4-dicarbonitrile (5e): It was obtained from reacting (**3e**) with (**4**) and morpholine. IR (KBr cm⁻¹): 3350 (OH), 3450 (NH₂), 3069 (Ar CH), 2201 (C=N), 1120 (C-O); ¹HNMR (CDCl₃-*d*, δ, ppm): 7.40-7.78 (5H, m, Ar-H), 7.0-7.98 (3H, m, furan), 5.40 (2H, br s, - NH₂); MS, [M⁺], (m/z): 316.00 (100%); Anal. Calcd for C₁₈H₁₁N₃O₃ (317.00): C, 68.14; H, 3.47; N, 13.25. Found: C, 68.16; H, 3.45; N, 13.28.

5'-amino-2, 4, 4'' trihydroxy-3''-methoxy-1, 1':3', 1''-terphenyl-4', 6'-dicarbonitrile (5f): It was obtained from reacting (3f) with (4) and morpholine. IR (KBr cm^{-1}): 3300 (OH), 3450 (NH_2), 3069 (Ar CH), 2201 (C=N), 1068 (C-O); $^1\text{H-NMR}$ (CDCl_3 -*d*, δ , ppm): 7.03-7.63 (8H, m, Ar-H), 5.77 (2H, br s, - NH_2), 5.01 (1H, s, OH), 4.95 (1H, s, OH), 3.83 (3H, s, OCH₃); MS, [M^+], (m/z): 372.00 (100%); Anal. Calcd for $\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}_4$ (373.00): C, 67.56; H, 4.05; N, 11.25. Found: C, 67.55; H, 4.02; N, 11.26.

5'-amino-2, 4- dihydroxy-3''-methyl-1, 1':3', 1''-terphenyl-4', 6'-dicarbonitrile (5g): It was obtained from reacting (3g) with (4) and morpholine. IR (KBr cm^{-1}): 3300 (OH), 3450 (NH_2), 3036 (Ar CH), 2201 (C=N), 2945 (aliphatic CH); $^1\text{H-NMR}$ (CDCl_3 -*d*, δ , ppm): 7.63-7.03 (7H, m, Ar-H), 6.8 (1H, s, Ar-H), 5.77 (2H, br s, - NH_2), 5.11 (1H, s, OH), 4.96 (1H, s, OH), 2.50 (3H, s, CH₃); MS, [M^+], (m/z): 340.00 (100%); Anal. Calcd for $\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}_2$ (341.00): C, 73.90; H, 4.42; N, 12.33. Found: C, 74.00; H, 4.39; N, 12.31.

5'-amino-2, 4- dihydroxy-4''-methyl-1, 1':3', 1''-terphenyl-4', 6'-dicarbonitrile (5h): It was obtained from reacting (3h) with (4) and morpholine. IR (KBr cm^{-1}): 3350 (OH), 3460 (NH_2), 3036 (Ar CH), 2201 (C=N), 2950 (aliphatic CH); $^1\text{H-NMR}$ (CDCl_3 -*d*, δ , ppm): 7.69-7.49 (7H, m, ArH), 6.42 (1H, s, ArH), 5.77 (2H, br s, - NH_2), 5.09 (1H, s, OH), 4.96 (1H, s, OH), 2.34 (3H, s, CH₃); MS, [M^+], (m/z): 340.00 (100%); Anal. Calcd for $\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}_2$ (341.00): C, 73.90; H, 4.42; N, 12.33. Found: C, 73.96; H, 4.43; N, 12.35.

5'-amino- 4''-fluoro-2, 4- dihydroxy-1, 1':3', 1''-terphenyl-4', 6'-dicarbonitrile (5i): It was obtained from reacting (3i) with (4) and morpholine. IR (KBr cm^{-1}): 3350 (OH), 3450 (NH_2), 3069 (Ar CH), 2201 (C=N), 1342 (Ar-F); $^1\text{H-NMR}$ (CDCl_3 -*d*, δ , ppm): 7.40-7.60 (7H, m, Ar-H), 6.8 (1H, s, Ar-H), 6.33 (1H, dd, Ar H- F), 5.78 (2H, br s, - NH_2), 5.01 (1H, s, OH); MS, [M^+], (m/z): 344.00 (100%); Anal. Calcd for $\text{C}_{20}\text{H}_{12}\text{N}_3\text{O}_2\text{F}$ (345.00): C, 69.56; H, 3.50; N, 12.19. Found: C, 69.58; H, 3.52; N, 12.22.

5'-amino- 2, 2'', 4-trihydroxy-1, 1': 3', 1''-terphenyl-4', 6'-dicarbonitrile (5j): It was obtained from reacting (3j) with (4) and morpholine. IR (KBr cm^{-1}): 3350 (OH), 3450 (NH_2), 3069 (Ar CH), 2201 (C=N); $^1\text{H-NMR}$ (CDCl_3 -*d*, δ , ppm): 7.82-7.43 (7H, m, Ar-H), 5.78 (2H, br s, - NH_2), 5.40 (1H, s, OH), 5.01 (2H, d, OH); MS, [M^+], (m/z): 342.00 (100%); Anal. Calcd for $\text{C}_{20}\text{H}_{13}\text{N}_3\text{O}_3$ (343.00): C, 70.00; H, 3.79; N, 12.24. Found: C, 70.05; H, 3.81; N, 12.26.

5'-amino- 2, 4, 4''-trihydroxy-1, 1':3', 1''-terphenyl-4', 6'-dicarbonitrile (5k): It was obtained from reacting (3k) with (4) and morpholine. IR (KBr cm^{-1}): 3350 (OH), 3450 (NH_2), 3069 (Ar CH), 2225 (C=N), 3450 (OH). $^1\text{H-NMR}$ (CDCl_3 -*d*, δ , ppm): 7.50-7.73 (7H, m, Ar-H), 5.78 (2H, br s, - NH_2), 5.20 (1H, s, OH), 5.01 (2H, d, OH), 4.95 (1H, s, OH); MS, [M^+], (m/z): 342.00 (100%); Anal. Calc. for $\text{C}_{20}\text{H}_{13}\text{N}_3\text{O}_3$ (343.00): C, 70.00; H, 3.79; N, 12.24. Found: C, 70.07; H, 3.78; N, 12.24.

3. Results and Discussion

In view of the immense utility of the eco-friendly synthetic approach, we also carried out the improved synthesis of chalcones (3a-3k) under microwave irradiation. A vessel containing neat mixture of aromatic aldehyde (1) and 2,4-dihydroxyacetophenone (2) was placed in an alumina bath (*In alumina bath temperature of the reaction mixture reaches*

101°C whereas in neat condition i.e. without alumina bath temperature reaches 63°C) and irradiated for 5-8 minutes to give (**3 and 5**) in quantitative yield. In this context suitability of different solid supports were examined that included acidic / basic / neutral alumina, silica, montmorillonite K 10 and KSF and reported in Table-2.

Table 2 Comparative study for the synthesis of 3 and 5 by using different solid supports.

Exp. No.	Medium	MW Power / Watts	Time / Min	Temp. /°C	Yield / %
1	Silica- Gel	640	13	108	70
2	Neat + DMF	640	12	102	60
3	Basic Alumina	640	15	101	71
4	Montmorillonite K 10	640	8	109	80
5	Montmorillonite KSF	640	9	100	75

The reaction has also been supported under neat condition (without solid support, catalyst and solvent); however no reaction occurs under neat conditions, which could be made successful by adding a few drops of DMF. The role of DMF can be explained as an energy transfer agent and homogenizer to increase the reaction temperature [24-27]. From the results obtained in Table-2, it is clear that montmorillonite K 10 is the most adaptable and simplest catalyst for synthesizing (**3 and 5**). Since comparatively a higher yield was achieved in shorter reaction time by this method (Table-3) as also observed earlier in clay supported reactions. The identities of the synthesized compounds were confirmed by various methods.

Table 3 Comparison of reaction time and yields of compounds 3 and 5 under classical and microwave methods.

Compd.	Reaction Time		Yields / %		Compd.	Reaction Time		Yields / %	
	MW / Min.	Classical / hrs.	MW	Classical		MW / Min.	Classical / hrs.	MW	Classical
3a	5	15	87	57	5a	5	9	79	45
3b	7	17	89	59	5b	6	8	77	43
3c	7	16	93	55	5c	5	9	80	50
3d	6	15	89	60	5d	7	11	81	47
3e	8	16	89	62	5e	6	8	77	48
3f	7	17	85	61	5f	7	9	70	52
3g	6	15	87	70	5g	6	10	71	55
3h	7	17	88	71	5h	5	11	74	49
3i	6	16	90	66	5i	6	10	78	45
3j	8	15	91	67	5j	7	9	80	47
3k	7	15	90	67	5k	6	10	82	46

Finally, in order to check the possible intervention of specific (non-thermal) microwave effect [28-31]. The best results obtained under microwave irradiation were extrapolated to conventional heating. In the present work the reaction mixture was kept on a preheated oil bath, under the same reaction conditions (time, temperature, pressure and vessel), It was

observed that the reaction did not occur even on extended reaction time, thus suggesting that the effect of microwave is not purely thermal [32-35].

4. Conclusion

A rapid, high yield, simple, practical, economic, readily available system, and convenient procedure for the synthesis of chalcones and their facile one-pot conversion to 2-aminobenzene-1, 3-dicarbonitriles has been developed.

Acknowledgement. The authors are thankful to **Prof. B. L. Verma**, Retd. Professor of Chemistry, M. L. S. University Udaipur and **Dr. Shakti Bajjal**, Dean, FASC, MITS University for their constant encouragement during this work. Authors are also thankful to the Head, Sophisticated Analytical Instrument Facility, **Indian Institute of Technology, Madras** and **Lab India, Mumbai** for spectral analysis.

REFERENCES

1. Straub, T. S. (1995) *Tetrahedron Lett.* **36**, 663.
2. Sandler, S., Karo, W. (1972) In *Organic Functional Group Preparations*. 3, 372.
3. Bergman, E. D., Ginsibm, L., Pappo, R. (1959) *Org. React.* **10**, 179.
4. Ballesteros, J. F., Sanz, M.J., Ubeda, A., Miranda, M. A., Iborra, S., Paya, M., Alcaraz, M. (1995) *J. Med. Chem.* **38**, 2794.
5. Go, M. L., Wu, X., Liu, X.L. (2005) *Curr. Med. Chem.* **12**, 483.
6. Mukerjee, V. K., Prased, A. K., Raj, A. G., Brakhe, M. E., Olsen, C. E., Jain, S. C., Parmer, V. P. (2001) *Bioorg. Med. Chem.* **9**, 337.
7. Liu, U. M., Wilairat, P., Croft, S. L., Tan, A. L., Go, M. (2003) *Bioorg. Med. Chem.* **11**, 2729.
8. Sivakumar, P. M., Geetha Babu, S. K., Mukesh, D. (2007) *Chem. Pharm. Bull.* **55**, 44.
9. Viana, G. S., Bandeira, M. A., Mantos, F. J. (2003) *Phytomedicine*. **10**, 189.
10. Tiwari, N., Dwivedi, B., Nizamuddin, K. F., Nakanshi, Y., Lee, K. H. (2000) *Bioorg. Med. Chem.* **10**, 699.
11. Ducki, S., Forrest, R., Hadfield, J. A., Kendall, A., Lawrence, N. J., Mc-Gown, A.T., Rennison, D. (1998) *Bioorg. Med. Chem.* **8**, 1051.
12. Hart, H., Rajkumar, P. (1995) *Tetrahedron*. **51**, 1313.
13. Viond, T. K., Rajkumar, P., Hart, H. (1995) *Tetrahedron*. **51**, 2267.
14. Kei, G., Gaku, Y. (2001) *Tetrahedron Lett.* **42**, 4875.
15. Grewal, R. S., Hart, H., Viond, T. K. (1992) *J. Org. Chem.* **57**, 2721.
16. Rajkumar, P., Kannan, A. (1993) *Tetrahedron Lett.* **34**, 4407.
17. Viond, T.K., Hart, H. (1990) *J. Org. Chem.* **55**, 881.
18. Rajkumar, P., Srisailas, M. (1997) *Tetrahedron Lett.* **38**, 5323.
19. Rajkumar, P., Srisailas, M. (2001) *Tetrahedron*. **57**, 9749.
20. Ameta, K. L., Verma, B. L. (2002) *J. Indian Chem. Soc.* **79**, 840.
21. Gahlot, U. S.; Rao, S. S.; Dulawat, S. S.; Ameta, K. L.; Verma, B. L. (2003) *Afinidad*. **60**(508), 558.
22. Ameta, K. L., Kumar, Biresh., Rathore, Nitu. S. (2011) *e-Journal of Chem.* **8**(3) In press.
23. Rao, S. S., Gahlot, U. S., Dulawat, S. S., Vyas, R., Ameta, K. L., Verma, B. L. (2003) *Afinidad*. **60**(505), 271.

24. Marquez, K. C., Plutin, A., Rodriguez, Y., Perez, E., Loupy, A. (2000) *Synth. Commun.* **30**, 1067.
25. Saurez, M., Loupy, A., Salfran, E., Moran, L., Ronaldo, E. (1999) *Heterocycles* **51**, 21.
26. Perez, R., Perez, E., Saurez, M., Loupy, A., Jimeno, M, L., Ochoa, C. (1997) *Org. Prep. Proced. Int.* **29**, 71.
27. Saurez, M., Loupy, A., Perez, A., Moran, L., Gerona, G., Morales, A., Autie, M. (1996) *Heterocycl. Commun.* **2**, 275.
28. Gydye, R. N., Wei, J, B. (1998) *Can. J. Chem.*, **76**, 525.
29. Langa, F., De La Cruz, P., De La Hoz, A., Diaz-Ortiz, A., Diaz-Barra, E. (1997) *Contemp. Org. Syn.* **4**, 373.
30. Preux, L., Loupy, A. (2001) *Tetrahedron* **57**, 9199.
31. Gabriel, C., Gabriel, S., Grant, E. H., Halsted, B. S., Mingos, D. N. P. (1998) *Chem. Soc. Rev.* **7**, 231.
32. Syassi, B., Bougrin, K., Soufiaoui, M. (1997) *Tetrahedron Lett.* **38**, 8855.
33. Perez, E, R., Marrero, A. L., Perez, R., Autie, M. A. (1995) *Tetrahedron Lett.* **36**, 1779.
34. Varma, R. S., Varma, M., Chatterjee, A. K. (1993) *J. Chem. Soc., Perkin Trans I* 3207.
35. Ben Alloum, A., Labiad, B., Villemin, D. (1989) *J. Chem. Soc., Chem. Commun.* 607.