Hindawi Publishing Corporation
Organic Chemistry International
Volume 2014, Article ID 851924, 8 pages
http://dx.doi.org/10.1155/2014/851924

Research Article

Microwave-Assisted Three-Component "Catalyst and Solvent-Free" Green Protocol: A Highly Efficient and Clean One-Pot Synthesis of Tetrahydrobenzo[*b*]pyrans

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Received 26 July 2014; Revised 2 September 2014; Accepted 2 September 2014; Published 17 September 2014

Academic Editor: Ashraf Aly Shehata

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A green and highly efficient method has been developed for the one-pot synthesis of tetrahydrobenzo[*b*]pyrans via a three-component condensation of aldehydes, 1,3-cyclic diketones, and malononitrile under MW irradiation without using any catalyst and solvent. This transformation presumably occurs by a sequential Knoevenagel condensation, Michael addition, and intramolecular cyclization. Operational simplicity, solvent and catalyst-free conditions, the compatibility with various functional groups, nonchromatographic purification technique, and high yields are the notable advantages of this procedure.

1. Introduction

Development of environmentally benign and clean synthetic procedures has become the goal of organic synthesis in recent times [1–5]. The multicomponent reactions (MCRs) are one of the most powerful and efficient tools in organic synthesis for the invention of biologically important scaffolds in the viewpoint of green chemistry [6–9]. One-pot multicomponent reactions (MCRs) have attracted considerable attention from the viewpoint of ideal synthesis by virtue of their efficiency, facile implementation, and generally high yield of the products [10–13]. Indeed, the concept of environmental factor (E-factor) and atom economy have gradually become included into conventional organic synthesis in both industry and academia. Solvents are the main reason for an insufficient E-factor, especially in synthesis of fine chemicals and pharmaceutical industries [14, 15]. As a result, it has become imperative both in academia and industry to design catalyst- and solvent-free MCRs, as these processes are rendered green with reduction of waste, time, manpower, and cost [16–21].

Recently MW-assisted chemistry has become a useful technique for a variety of applications in organic synthesis and transformations [22–25]. Microwave (MW)-promoted MCRs have been attracting research interest from chemists because these reactions exhibit some particular or unexpected reactivities and also because of their significant usefulness in green chemistry [5, 26]. In continuation of our research, we have reported few MW-promoted multicomponent coupling reactions in various chemical transformations for the synthesis of useful heterocyclic compounds [27–32]. Very recently, we have reported an efficient synthesis of pyrano[3,2-*c*]coumarin derivatives via copper(II) triflate catalyzed tandem reaction of 4-hydroxycoumarin with α,β-unsaturated carbonyl compounds under solvent-free conditions [33]. 4*H*-Benzo[*b*]pyrans are ubiquitous to a variety of biologically active molecules and have been shown to a wide range of pharmacological activities and biological properties, for example, spasmolytic, diuretic, anticoagulant, anticancer, and anti-anaphylactic activities [34–36]. In the last decade numerous methods have been developed for the synthesis of 4*H*-benzo[*b*]pyrans [37–67] by using a broad variety of toxic nitrogen-containing bases [37–47], electrolytic multicomponent transformation [48], hazardous and volatile organic solvents [49, 50], different types of metal catalysts particularly, MgO [50, 51], nano-MgO in [bmIm]BF_4 [54], SiO_2NPs [55], ZnO NPs [56, 57], biocatalyst [58], and mesoporous material [60]. Few solvent-free and microwave assisted methodologies have also been reported

for the preparation of this moiety with limited substrates scope [61–63]. Very recently meglumine [64], urea [65], $ZnFe_2O_4$ [66], and Fe_3O_4NPs [67] have been used for the synthesis of these compounds. Regardless of their efficiency and reliability, most of these methodologies are not satisfactory in view of green chemistry by means of using large amount of volatile solvents, toxic and uneasily available catalyst, longer reaction times, and lower yields. To avoid these limitations, there is a need for a simple, efficient, and cost-effective "green protocol" for the synthesis of 4*H*-benzo[*b*]pyran derivatives under environmentally friendly conditions.

2. Materials and Methods

Reactions carried out under scientific microwave reactor (Biotage, Initiator EXP EU 355301). Melting points were determined on a glass disk with an electric hot plate and are uncorrected. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were run in DMSO-d_6 and $CDCl_3$ solutions. IR spectra were taken as KBr plates in a Shimazdu 8400S FTIR. Commercially available substrates were freshly distilled before the reaction. Solvents, reagents, and chemicals were purchased from Aldrich, Fluka, Merck, SRL, Spectrochem and Process Chemicals.

*2.1. General Procedure for Tetrahydrobenzo[b]pyran (**4**).* A equimolar mixture of aldehyde (1 mmol), malononitrile (1 mmol) and 1,3-cyclic diketone (1 mmol) was taken in a microwave vessel. The reaction mixture was irradiated under scientific microwave (Biotage, Initiator EXP EU 355301) at 80°C for a certain period of time to complete the reaction. The reaction mixture was then washed with ethanol (10 mL) to afford the crude product as solid, which was recrystallized from EtOH to get the analytically pure product.

*2.1.1. 2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4aa**).* White solid (88%), m.p.: 230-231°C ([53] 230°C); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.23–7.19 (m, 2H, H-Ar), 7.12–7.06 (m, 3H, H-Ar), 6.93 (brs, 2H, NH_2), 4.10 (s, 1H, H-4), 2.45-2.44 (m, 2H, CH_2), 2.18 (d, J = 16.4 Hz, 1H, H-6′), 2.02 (d, J = 16 Hz, 1H, H-6), 0.96 (s, 3H, CH_3), 0.88 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 195.8, 162.6, 158.5, 144.8, 128.4, 127.2, 126.6, 119.8, 112.8, 58.3, 50.0, 35.6, 31.8, 28.4, 26.8 ppm; IR (KBr): 3435, 3318, 2913, 2198, 1672 cm^{-1}.

*2.1.2. 2-Amino-7,7-dimethyl-5-oxo-4-p-tolyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4ba**).* White solid (88%), m.p.: 216-217°C ([53] 218°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12–7.07 (m, 4H, H-Ar), 4.56 (brs, 2H, NH_2), 4.35 (s, 1H, H-4), 2.43 (s, 2H, CH_2), 2.25 (s, 3H, CH_3), 2.21 (d, J = 5.6 Hz, 2H, CH_2), 1.10 (s, 3H, CH_3), 1.03 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.8, 161.3, 157.3, 140.2, 136.6, 129.2, 127.3, 118.7, 114.1, 50.6, 40.6, 35.1, 32.1, 28.8, 27.7, 21.0 ppm; IR (KBr): 3413, 3324, 2956, 2191, 1664 cm^{-1}.

*2.1.3. 2-Amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4ca**).* White solid (84%), m.p.: 208-209°C ([53] 206°C); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.27 (d, J = 8.4 Hz, 2H, H-Ar), 7.19 (d, J = 8.4 Hz, 2H, H-Ar), 4.59 (br, 2H, NH_2), 4.40 (s, 1H, H-4), 2.46 (s, 2H, CH_2), 2.23 (d, J = 7.6 Hz, 2H, CH_2), 1.13 (s, 3H, CH_3), 1.04 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 195.6, 162.6, 158.5, 143.7, 131.1, 129.1, 128.2, 119.5, 112.3, 57.7, 49.9, 35.1, 31.7, 28.3, 26.8 ppm; IR (KBr): 3390, 3321, 3253, 3211, 2962, 2190, 1739, 1681, 1654, 1604, 1213, 1039, 844 cm^{-1}.

*2.1.4. 2-Amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4da**).* Yellow solid (82%), m.p.: 178–180°C ([47] 180–182°C); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.10 (d, J = 8.8 Hz, 2H, H-Ar), 7.37 (d, J = 8.8 Hz, 2H, H-Ar), 7.12 (brs, 2H, NH_2), 4.29 (s, 1H, H-4), 2.47–2.44 (m, 2H, CH_2), 2.20 (d, J = 16 Hz, 1H, H-6′), 2.04 (d, J = 16 Hz, 1H, H-6), 0.97 (s, 3H, CH_3), 0.89 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 195.8, 158.6, 152.3, 146.3, 128.7, 125.6, 123.7, 119.4, 111.7, 57.0, 49.9, 35.7, 31.9, 28.3, 27.0 ppm; IR (KBr): 3436, 3324, 2196, 1668 cm^{-1}.

*2.1.5. 2-Amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4ea**).* Yellow solid (83%), m.p.: 201–203°C ([53] 203°C); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.05 (d, J = 8.8 Hz, 2H, H-Ar), 6.95 (br, 2H, NH_2), 6.84 (d, J = 8.8 Hz, 2H, H-Ar), 4.12 (s, 1H, H-4), 3.71 (s, 3H, OCH_3), 2.50-2.49 (m, 2H, CH_2), 2.22-2.21 (m, 2H, CH_2), 1.03 (s, 3H, CH_3), 0.94 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 195.6, 162.1, 158.4, 157.9, 136.8, 128.2, 119.8, 113.6, 113.0, 58.5, 55.0, 50.1, 34.7, 31.7, 28.4, 26.7 ppm; IR (KBr): 3376, 3316, 2955, 2194, 1683, 1140, 1035, 842 cm^{-1}.

*2.1.6. (E)-2-Amino-7,7-dimethyl-5-oxo-4-styryl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4fa**).* White solid (74%), m.p.: 187-188°C ([47] 183–185°C); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.30 (d, J = 7.2 Hz, 2H, H-Ar), 7.21 (t, J = 7.6 Hz, 2H, H-Ar), 7.16–7.14 (m, 1H, H-Ar), 7.01 (brs, 2H, NH_2), 6.30 (d, J = 16 Hz, 1H, CH), 6.03–5.98 (m, 1H, CH), 3.75 (d, J = 7.2 Hz, 1H, H-4), 2.36-2.35 (m, 2H, CH_2), 2.17 (d, J = 13.2 Hz, 2H, CH_2), 0.96 (s, 3H, CH_3), 0.93 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 196.3, 162.8, 159.6, 136.8, 131.5, 129.6, 129.0, 127.8, 126.6, 120.3, 112.2, 55.5, 50.5, 33.2, 32.2, 28.6, 27.3 ppm; IR (KBr): 3436, 3321, 2933, 2193, 1673 cm^{-1}.

*2.1.7. 2-Amino-4-(3-hydroxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4ga**).* White solid (76%), m.p.: 228-229°C ([53] 225°C); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.29 (s, 1H, OH), 7.01–6.92 (m, 3H, H-Ar), 6.51–6.47 (m, 3H, H-Ar, NH_2), 3.99 (s, 1H, H-4), 2.44-2.43 (m, 2H, CH_2), 2.19 (d, J = 16 Hz, 1H, H-6′), 2.03 (d, J = 16 Hz, 1H, H-6), 0.96 (s, 3H, CH_3), 0.89 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 196.1, 162.8, 158.9, 157.7, 146.5, 129.6, 120.2, 118.1, 114.4, 113.9, 113.2, 58.7, 50.3, 35.8, 32.2, 28.8, 27.1 ppm; IR (KBr): 3431, 3335, 2915, 1668 cm^{-1}.

*2.1.8. 2-Amino-4-(4-hydroxy-3-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4ha**).* White solid (82%), m.p.: 242–244°C ([47] 240–242°C); ^{1}H

NMR (400 MHz, DMSO-d_6): δ = 8.86 (s, 1H, OH), 6.92 (s, 2H, NH_2), 6.68–6.64 (m, 2H, Ar-H), 6.53–6.50 (m, 1H, Ar-H), 4.07 (s, 1H, H-4), 3.71 (s, 3H, OCH_3), 2.51–2.48 (m, 2H, CH_2), 2.25 (d, J = 16 Hz, 1H, H-6′), 2.10 (d, J = 16 Hz, 1H, H-6), 1.03 (s, 3H, CH_3), 0.97 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 195.8, 162.2, 158.4, 147.3, 145.2, 135.8, 119.9, 119.4, 115.3, 113.0, 111.4, 58.8, 55.6, 50.0, 35.0, 31.8, 28.5, 26.6 ppm; IR (KBr): 3416, 3341, 2923, 2192, 1662 cm^{-1}.

*2.1.9. 2-Amino-4-(benzo[d][1,3]dioxol-5-yl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4ia**).* White solid (88%), m.p.: 224-225°C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.97 (brs, 2H, NH_2), 6.81 (d, J = 8 Hz, 1H, H-Ar), 6.62–6.59 (m, 2H, H-Ar), 5.97 (s, 2H, CH_2), 4.10 (s, 1H, H-4), 2.50 (s, 2H, CH_2), 2.24 (d, J = 16 Hz, 1H, H-6′), 2.12 (d, J = 16 Hz, 1H, H-6), 1.03 (s, 3H, CH_3), 0.96 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 195.8, 162.4, 158.4, 147.2, 145.9, 138.9, 120.3, 112.7, 108.0, 107.5, 100.9, 58.5, 50.0, 35.2, 31.8, 28.3, 26.9 ppm; IR (KBr): 3435, 3318, 2923, 2198, 1670 cm^{-1}; Anal. Calcd. for $C_{19}H_{18}N_2O_4$: C, 67.44; H, 5.36; N, 8.28%; Found: C, 67.36; H, 5.31; N, 8.22%.

*2.1.10. 2-Amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4ja**).* White solid (85%), m.p.: 210–212°C ([53] 215°C); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.48 (d, J = 8.4 Hz, 2H, H-Ar), 7.10 (d, J = 8.4 Hz, 2H, H-Ar), 7.06 (brs, 2H, NH_2), 4.18 (s, 1H, H-4), 2.51-2.50 (m, 2H, CH_2), 2.25 (d, J = 16 Hz, 1H, H-6′), 2.10 (d, J = 16 Hz, 1H, H-6), 1.03 (s, 3H, CH_3), 0.94 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 196.1, 163.0, 158.8, 144.5, 131.6, 129.9, 120.0 (2C), 112.6, 58.0, 50.3, 35.6, 32.2, 28.7, 27.2 ppm.

*2.1.11. 2-Amino-4-(furan-2-yl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4ka**).* White solid (72%), m.p.: 224–226°C ([47] 220–222°C); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.41-7.40 (m, 1H, CH), 7.01 (brs, 2H, NH_2), 6.26-6.25 (m, 1H, CH), 5.99-5.98 (m, 1H, CH), 4.25 (s, 1H, H-4), 2.48–2.39 (m, 2H, CH_2), 2.22 (d, J = 16 Hz, 1H, H-6′), 2.10 (d, J = 16 Hz, 1H, H-6), 0.97 (s, 3H, CH_3), 0.91 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 195.6, 163.4, 159.4, 155.8, 141.8, 119.6, 110.5, 110.4, 105.1, 55.4, 49.9, 31.9, 29.0, 28.5, 26.6 ppm; IR (KBr): 3441, 3314, 2923, 2182, 1665 cm^{-1}.

*2.1.12. Typical Procedure for the Synthesis of 2-Amino-4-cyclohexyl-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4la**).* A mixture of cyclohexanecarbaldehyde (1 mmol), malononitrile (1 mmol), and dimedone (1 mmol) was taken in a microwave vessel. The reaction mixture was irradiated under scientific microwave (Biotage, Initiator EXP EU 355301) at 80°C for 7 min to complete the reaction. The reaction mixture was then washed with ethanol (10 mL) to afford the crude product as solid, which was recrystallized from EtOH to get the analytically pure product as white solid (88%). M.p.: 203-204°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.65 (br, 2H, NH_2), 3.31 (s, 1H, H-4), 2.38-2.37 (m, 2H, CH_2), 2.29-2.28 (m, 2H, CH_2), 1.75–1.63 (m, 4H, CH_2), 1.49–1.41 (m, 2H, CH_2), 1.34–1.31 (m, 1H, CH_2), 1.11–1.09 (m, 9H, CH_2 and CH_3), 0.95–0.92 (m, 1H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.5, 163.2, 159.9, 120.3, 114.1, 58.5, 50.8, 43.7, 40.6, 34.7, 32.0, 30.4, 29.2, 27.7, 27.3, 26.5, 26.2, 26.1 ppm. IR (KBr): 3409, 3326, 2923, 2192, 1662, 1373, 1255, 1213, 1033, 945 cm^{-1}; Anal. Calcd. for $C_{18}H_{24}N_2O_2$: C, 71.97; H, 8.05; N, 9.33%; Found: C, 71.91; H, 8.02; N, 9.27%.

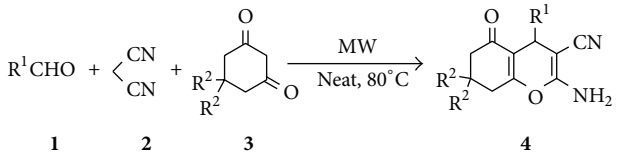
*2.1.13. 2-Amino-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4ab**).* White solid (85%), m.p.: 234–236°C ([48] 238–240°C); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.30–7.26 (m, 2H, H-Ar), 7.20–7.14 (m, 3H, H-Ar), 6.99 (s, 2H, NH_2), 4.18 (s, 1H, H-4), 2.65–2.59 (m, 2H, CH_2), 2.35–2.22 (m, 2H, CH_2), 1.99–1.90 (m, 2H, CH_2) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 196.3, 164.9, 158.8, 145.1, 128.7, 127.5, 126.9, 120.2, 114.1, 58.6, 36.7, 35.8, 26.8, 20.2 ppm; IR (KBr): 3446, 3324, 2903, 2184, 1665 cm^{-1}.

*2.1.14. 2-Amino-5-oxo-4-p-tolyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4bb**).* White solid (86%), m.p.: 227-228°C ([48] 223–225°C); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.09–7.02 (m, 4H, H-Ar), 6.96 (brs, 2H, NH_2), 4.14 (s, 1H, H-4), 2.62–2.59 (m, 2H, CH_2), 2.27–2.24 (m, 5H, CH_2 and CH_3), 1.94–1.84 (m, 2H, CH_2) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 196.3, 164.7, 158.8, 142.2, 136.0, 129.2, 127.4, 120.2, 114.3, 58.7, 36.7, 35.4, 26.8, 20.9, 20.2 ppm; IR (KBr): 3437, 3345, 2924, 1678 cm^{-1}.

*2.1.15. 2-Amino-4-(4-chlorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4cb**).* White solid (88%), m.p.: 230–232°C ([48] 226–228°C); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.35–7.32 (m, 2H, H-Ar), 7.19–7.16 (m, 2H, H-Ar), 7.05 (brs, 2H, NH_2), 4.20 (s, 1H, H-4), 2.62–2.58 (m, 2H, CH_2), 2.31–2.24 (m, 2H, CH_2), 1.97–1.87 (m, 2H, CH_2) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 196.3, 165.0, 158.8, 144.1, 131.5, 129.5, 128.6, 120.0, 113.7, 58.1, 36.6, 35.4, 26.8, 20.1 ppm; IR (KBr): 3451, 3314, 2913, 2197, 1682 cm^{-1}.

*2.1.16. 2-Amino-5-oxo-4-p-tolyl-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (**4bc**).* White solid (86%), m.p.: 253–255°C ([47] 257–259°C); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.91–7.88 (m, 2H, H-Ar), 7.60–7.56 (m, 2H, H-Ar), 7.44–7.31 (m, 4H, H-Ar), 7.02 (s, 2H, NH_2), 4.40 (s, 1H, CH), 2.23 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.9, 158.0, 153.3, 152.3, 140.4, 131.9, 129.1, 128.7, 126.6, 123.8, 118.1, 116.0, 113.0, 104.2, 58.2, 36.6, 35.7, 20.7 ppm; IR (KBr): 3451, 3310, 2935, 1685 cm^{-1}.

*2.1.17. 2-Amino-4-(4-chloro-phenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile (**4cc**).* White solid (85%), m.p.: 262–264°C ([47] 265–267°C); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.87–7.85 (m, 2H, H-Ar), 7.58–7.53 (m, 2H, NH_2), 7.32–7.28 (m, 4H, H-Ar), 7.13 (d, J = 8.4 Hz, 2H, H-Ar), 4.48 (s, 1H, CH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.6, 158.0, 152.4, 142.4, 140.3, 131.6, 129.7, 128.7, 127.9, 124.1, 123.5, 118.8, 115.8, 103.6, 57.6, 36.5, 35.8 ppm; IR (KBr): 3456, 3306, 2934, 2191, 1686 cm^{-1}.



R^1 = aryl, alkyl, heteroaryl, cinnamyl

R^2 = H, Me

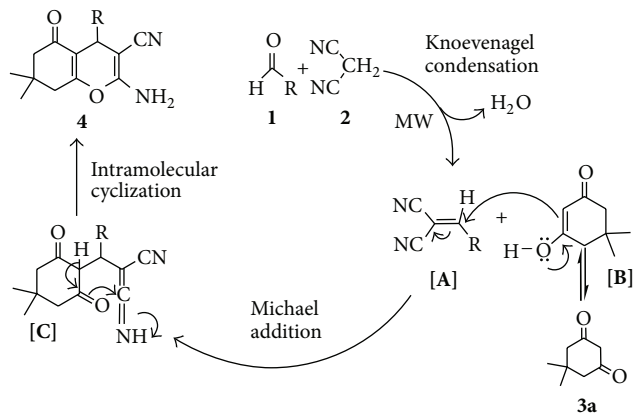
Scheme 1: Synthesis of 4*H*-benzo[*b*]pyran derivatives under MW irradiation.

3. Results and Discussion

As a part of our ongoing research to provide greener methodologies under solvent and catalyst-free conditions [27, 29, 68–71] we have found that the three-component condensation of aldehyde, 1,3-cyclic diketone, and malononitrile under MW irradiation without using any catalyst and solvent produced 4*H*-benzo[*b*]pyran derivatives in high yields within short reaction times (Scheme 1). Indeed, to the best of our knowledge, this is the first report of synthesis of 4*H*-benzo[*b*]pyran under catalyst and solvent-free conditions.

Initially, we commenced our study taking benzaldehyde, malononitrile, and dimedone as the model substrates at 80°C (conventional heating) under catalyst and solvent-free conditions for 3 hours; however, a mixture of products was obtained. By increasing the temperature and time, the progress of the reaction was not satisfactory. We, then, turned our attention towards MW irradiation instead of conventional heating. Gratifyingly, the desired product was obtained in 88% in a microwave reactor (Biotage, Initiator EXP EU 355301) after 7 min at 80°C. By increasing the time and temperature the yield decreased. This may be due to the decomposition of the product at higher temperature. Finally, reaction conditions were optimized using benzaldehyde (1 mmol), malononitrile (1 mmol), and dimedone (1 mmol) at 80°C under microwave irradiation for 7 min. A wide range of structurally varied aldehydes and 1,3-cyclic diketones were subjected under optimized reaction conditions to provide the corresponding 4*H*-benzo[*b*]pyran derivatives as summarized in Scheme 3.

It can be seen that electron-rich and electron-deficient aldehydes reacted efficiently to afford the desired products with good yields. The chloro- and bromo-substituted benzaldehydes gave the corresponding **4ca**, **4ja,** and **4cb** in 84%, 85%, and 88% yields, respectively. Aldehyde containing electron donating –OMe groups on the aromatic ring were well-tolerated (**4ea** and **4ha**). 3-Hydroxybenzaldehyde afforded the corresponding product (**4ga**) with good yield. In addition, aldehyde containing two electron donating functional groups (–OH and –OMe) reacted very well (**4ha**). Heteroaryl aldehydes such as furfural also participated in the multicomponent reaction to produce the desired product in moderate yield without affecting the heterocyclic moiety (**4ka**). We are delighted to find that the α,β-unsaturated aldehyde, such as cinnamaldehyde, was tolerated under our present reaction conditions (**4fa**). Acid-sensitive substrate, such as piperonal, produced the desired condensation product **4ia** in excellent yield. Notable advantage of this method is its efficiency for the synthesis of 4*H*-benzo[*b*]pyrans derivative from aliphatic aldehyde with high yields (**4la**). In addition, 4-hydroxycoumarin also afforded the corresponding products (**4bc** and **4cc**). In general the reactions are clean and reaction procedure is very simple. To provide the analytically pure 4*H*-benzo[*b*]pyran derivatives, only ethanol was employed for recrystallization. Moreover, we have developed greener reaction conditions bearing lower E-factor [14, 15, 72] of 0.21 and 0.25 in the cases of synthesizing **4aa** and **4ba**, respectively.



Scheme 2: Plausible reaction mechanism.

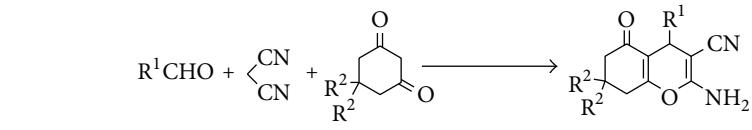
The plausible mechanism for the reaction is exposed in Scheme 2. Based on the literature [61], we assume that Knoevenagel condensation, Michael addition, and intramolecular cyclization are involved subsequently in the synthesis of 4*H*-benzo[*b*]pyran derivatives. In the first step, the aldehyde undergoes a Knoevenagel condensation reaction with malononitrile to afford cyano olefin [**A**] [61, 73], which endures a Michael addition reaction with the tautomeric enolic form of dimedone [**B**] to give the intermediate [**C**]. The intermediate **C** on intramolecular cyclization produces the final product **4**.

4. Conclusions

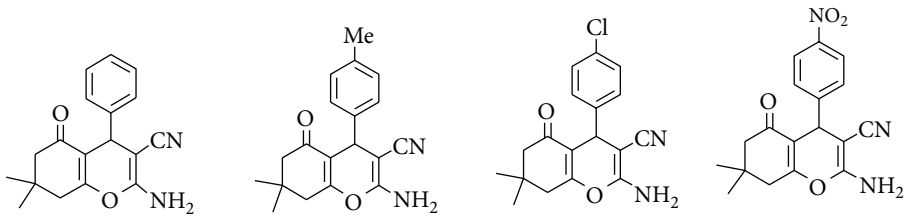
In summary, we have developed an environmentally benign one-pot strategy for the synthesis of 4*H*-benzo[*b*]pyran derivatives in high yields under microwave irradiation using a mixture of aldehydes, malononitrile, and 1,3-cyclic diketones. Operational simplicity, solvent and catalyst-free conditions, compatibility with various functional groups, and nonchromatographic purification technique are notable advantages of this procedure. Lower E-factor values make this protocol better and a more practical alternative to the existing methodologies. The combination of solvent and catalyst-free conditions under microwave irradiation makes this procedure truly environmentally benign.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.



1 **2** **3** **4**

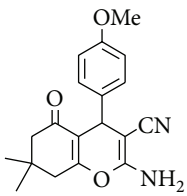


4aa, 88%

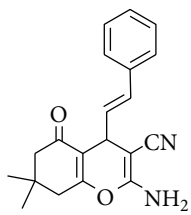
4ba, 85%

4ca, 84%

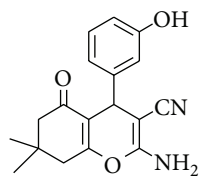
4da, 82%



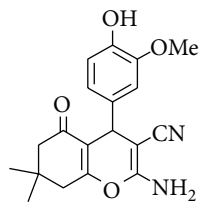
4ea, 83%



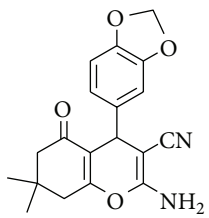
4fa, 74%



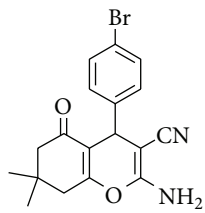
4ga, 76%



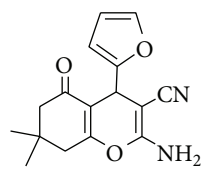
4ha, 82%



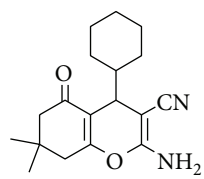
4ia, 88%



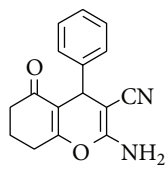
4ja, 85%



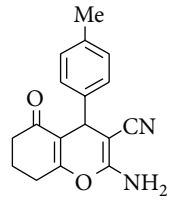
4ka, 72%



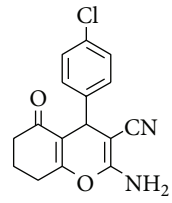
4la, 88%



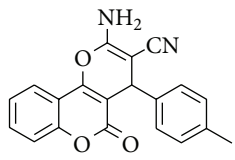
4ab, 85%



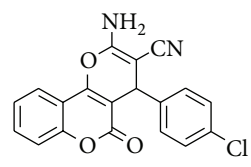
4bb, 86%



4cb, 88%



4bc, 86%[b]



4cc, 85%[b]

Scheme 3: Synthesis of various 4*H*-benzo[*b*]pyran derivatives. *Reaction conditions*: 1 mmol of **1**, 1 mmol of **2**, and 1 mmol of **3** under microwave irradiation at 80°C for 7 min. All are isolated yields. [b]1 mmol of aldehyde, 1 mmol of **2**, and 1 mmol of 4-hydroxycoumarin under microwave irradiation at 80°C for 7 min.

Acknowledgments

Alakananda Hajra is pleased to acknowledge the financial support from CSIR, Government of India (Grant no. 02(0168)/13/EMR-II). The authors are thankful to DST-FIST and UGC-SAP. Sougata Santra thanks UGC, New Delhi, India, for his fellowship.

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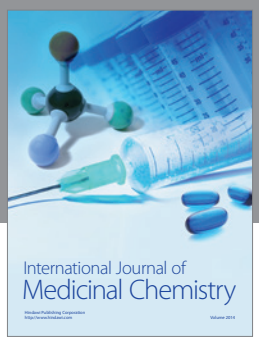

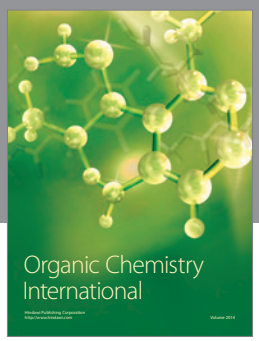

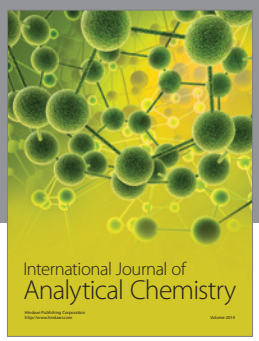

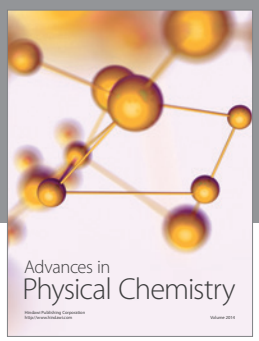

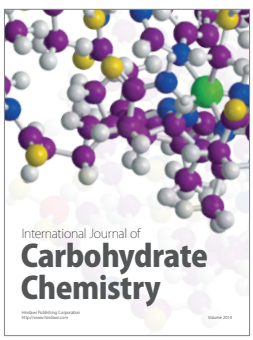

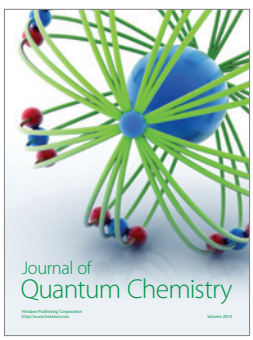

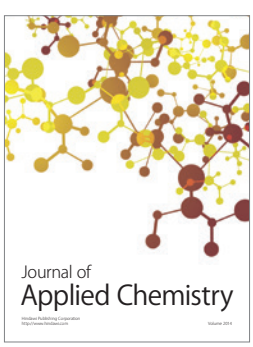

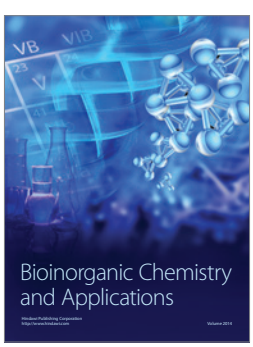

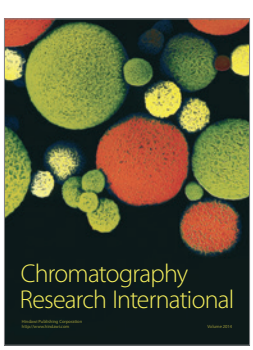

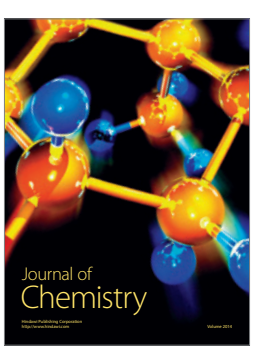

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