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Synthesis of pyran derivatives under ultrasound irradiation using Ni nanoparticles as reusable catalysts in aqueous medium

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ABSTRACT

Ni nanoparticles (NPs)-catalysed synthesis of pyran derivatives was achieved by one-pot three-component reactions of aryl aldehydes/ketone, malononitrile and C–H activated compounds in aqueous medium under ultrasound irradiation. The present approach offer several advantages, such as shorter reaction time, higher yields, and environmental friendliness.

1. Introduction

Metal nanoparticles (NPs) are important due to their remarkable properties and potential application in a variety of areas, such as catalysis, sensors, electronics, and optics [1]. The last decade has witnessed tremendous growth in the field of nanoscience and nanotechnology. The easy accessibility to nanoparticles has prompted investigations on their application in catalysis. Several reports showed a remarkable level of their performance as catalysts in terms of selectivity, reactivity, and improved yields of product [2]. Metal nanoparticles, such as nickel, palladium, gold, platinum, etc. have properties that may well markedly differ from those of their bulk metals [3]. Recently, it has been proved that Ni(0) nanoparticles as catalysts offer great opportunities for a wide range of applications in organic synthesis [4], such as Suzuki–Miyaura cross-coupling [5], hydrogenation [6], oxidative addition [7], Stille coupling [8], Knoevenagel condensation [9], Hantzsch condensation [10], etc. However, more attention has been paid to nickel catalysts because nickel is comparatively cheap and more environmentally friendly. Green chemical reactions have become a prominent issue in recent decades. Reactions in aqueous media are considerably more safe, non-toxic, environmentally friendly, and inexpensive. Organic reaction in water has attracted a great deal of interest in both academic and industrial research because of environmental concerns [11].

Pyran derivatives are of considerable interest in industry as well as in academia owing to their promising biological and medicinal activity, such as analgesic, anti-tumour, anti-cancer, anti-inflammatory properties and also serve as potential inhibitors of human Chk1 kinase (Fig. 1) [12]. Furthermore, they are also found in applications as pharmaceutical ingredient and biological agrochemicals [13].

Considerable effort has been made towards the synthesis of pyran annulated heterocyclic derivatives due to their wide applications. Recently, a few methods have been reported by using various catalysts [14–19]. Although most of these processes offer distinct advantages, at the

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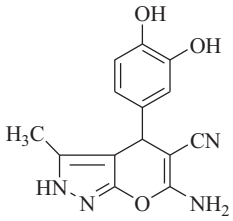

Fig. 1. An inhibitor of human Chk 1 Kinase.

same time they suffer from certain drawbacks, such as longer reaction time, unsatisfactory yields, high costs, harsh reaction conditions, use of stoichiometric amounts as well as of environmentally toxic catalysts, and also lack of recyclability [20].

Ultrasound irradiation has been established as an efficient technique in synthetic organic chemistry. The ultrasonic irradiation with its advantages, i.e. convenient operation, mild reaction conditions, short reaction time and high efficiency, has become particularly popular in recent times [21]. In order to enlarge the application of ultrasound irradiation to the synthesis of heterocyclic compounds, we wish to report a general, efficient and eco-friendly procedure for the synthesis of pyran derivatives.

2. Experimental

2.1. Materials and methods

The melting points were determined in open capillaries and uncorrected. IR spectra were recorded with a PerkinElmer Spectrum BX FT-IR apparatus (υ_{max} in cm^{-1}) on KBr disks. ^1H NMR and ^{13}C NMR (400 MHz and 100 MHz, respectively) spectra were recorded on a Bruker Avance II-400 spectrometer in $CDCl_3$ and DMSO- d6 (chemical shifts in δ with TMS as the internal standard). Mass spectra were recorded on Waters ZQ-2695. Transmission electron microscope (TEM) spectra were recorded with a JEOL JSM 100CX device. Scanning electron microscope (SEM) measurements were recorded with a JEOL JSM-6360. XRD spectra were recorded with a Bruker D8 XRD instrument SWAX. CHN were recorded using a PerkinElmer 2400, Series II, CHN-OS analyser. Silica gel G (E-mark, India) was used for TLC. Hexane refers to the fraction boiling between 60 °C and 80 °C. The ultrasonication reaction was carried out in JAC 1500 (made in Korea).

2.2. X-ray crystallography

The X-ray diffraction data were collected at 296 K using the Mo Kα radiation (λ = 0.71073 Å) using a Bruker Nonius SMART APEX II CCD diffractometer equipped with a graphite monochromator. SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software. All non-H atoms were refined using the anisotropic approximation (CCDC 836545).

2.3. General procedure for the synthesis of pyran derivatives

A mixture of carbonyl compounds **1** (1 mmol), malononitrile **2** (1 mmol) and activated C–H compounds **3**–**5** (1 mmol) was poured into a round-bottom flask; nickel nanoparticles (10 mol%), water (2 mL) or water–ethanol mixture (1:1) (2 mL) [in the case of 4-hydroxy coumarin **5**] were added to it and irradiated in ultrasound for a duration as mentioned in Table 1. After completion (TLC), the reaction mixture was cooled, filtered and the solvent was removed under reduced pressure. The residue was extracted with ethyl acetate (3 × 10 mL) and the combined organic extract was washed with water (3 × 10 mL), brine (10 mL), and dried over anhydrous Na_2SO_4. After removing the solvent, the crude product was purified by column chromatography over silica gel (60–120 mesh) using hexane–ethyl acetate as an eluent to afford the pure products.

2.4. Physical and spectroscopic data for the selected compound

2.4.1. 4-Methyl benzaldehyde (6b)

IR (KBr): 3475, 3326, 2196, 1656 cm^{-1}. ^1H NMR ($CDCl_3$ + DMSO-d_6, 400 MHz): δ = 1.78 (s, 3H), 2.25 (s, 3H), 4.50 (s, 1H), 6.22 (s, 2H), 7.35 (t, J = 7.8 Hz, 5H), 7.65 (d, J = 8.4 Hz, 4H). ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 100 MHz): δ = 12.4, 20.6, 36.6, 60.1, 98.1, 119.7, 120.2, 125.8, 127.3, 128.7, 128.8, 136.2, 137.3, 139.5, 143.6, 145.6, 158.9. ESI–MS m/z 343 $[M + H]^+$. Anal calcd for $C_{21}H_{18}N_4O$: C, 73.67; H, 5.30; N, 16.36. Found: C, 73.75; H, 5.36; N, 16.48 (Table 1, entry 2).

2.4.2. 2-Chloro benzaldehyde (7k)

IR (KBr): 3317, 2380, 2183, 1659, 1593 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.31(d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.8 Hz, 1H), 7.17 (t, J = 7.2 Hz, 1H), 5.19 (s, 1H), 4.46 (s, 2H), 2.50–2.39 (m, 2H), 2.18–2.07 (m, 2H), 1.05 (s, 3H), 0.99 (s, 3H). ESI–MS m/z 345 $[M + H]^+$. Anal calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.64; H, 5.91; N, 7.96 (Table 1, entry 20).

2.4.3. 4-Nitro benzaldehyde (8c)

IR (KBr): 3476, 2196, 1719, 1613 cm^{-1}. ^1H NMR ($CDCl_3$ + DMSO-d_6, 400 MHz): δ = 8.07–7.23 (m, 8H), 4.60 (s, 1H), 3.11 (brs, 2H). ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 100 MHz): δ = 164.9, 163.3, 159.1, 157.3, 154.7, 151.7, 137.8, 133.7, 129.5, 128.5, 127.7, 123.6, 121.4, 117.7, 107.9, 62.5, 41.9. ESI–MS m/z 362 $[M + H]^+$. Anal calcd for: $C_{19}H_{11}N_3O_5$: C, 63.16; H, 3.07; N, 11.63. Found: C, 62.87; H, 2.93; N, 11.54 (Table 1, entry 24).

3. Result and discussion

As part of our continued activities in this area [22], we are reporting for the first time a simple and efficient method for the synthesis of pyran derivatives by a one-pot multi-component reaction, involving C–H activated compounds, (**3**–**5**), malononitrile (**2**), aryl aldehydes, using novel and reusable Ni nanoparticles in water under