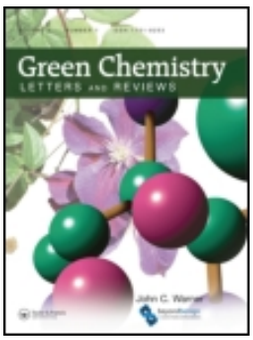

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RESEARCH ARTICLE

Ultrasonic-mediated catalyst-free rapid protocol for the multicomponent synthesis of dihydroquinoline derivatives in aqueous media

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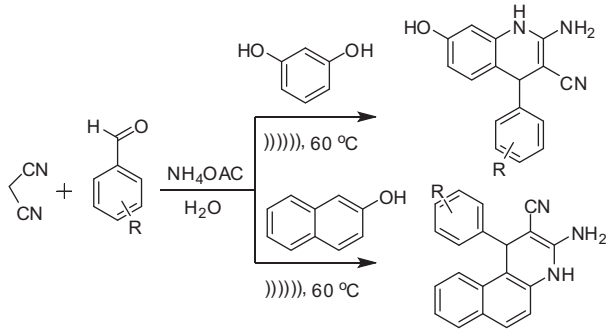
Catalyst-free multicomponent protocol for the condensation of malononitrile, 2-naphthol/resorcinol, aldehydes, and ammonium acetate in aqueous medium under ultrasound irradiation at 60°C afforded a wide range of valuable dihydroquinolines in high yields (90–97%) with short reaction times (60–90 min). This approach offers vital improvements for the synthesis of target compounds with regard to yield of products, simplicity in operation, utilization of water as solvent, and green aspects by avoiding the catalysts or solvents.



Keywords: ultrasound; multicomponent reaction (MCR); dihydroquinoline derivatives; water as a solvent; catalyst-free; green chemistry

Introduction

Quinoline is one of the heterocyclic scaffolds mostly found in many natural products and pharmaceutically active substances and commonly used as a building block in organic synthesis and material science (*1–4*) . Organic compounds containing quinoline scaffold have been studied extensively because of their significant applications as bioactive molecules (*5–11*). 1,4-Dihydroquinoline derivatives have also attracted attention because those comprise a large family of medicinally significant compounds and are used in production of antihypertension, antidiabetic, and many other drugs (*12–14*). Due to their widespread biological activity, a number of synthetic strategies have been developed for the preparation of substituted quinolines (*15–21*). However, the scarce availability of starting materials, harsh reaction conditions, and the tedious workup procedures are the main drawbacks of many of these methods. To overcome such difficulties, much competent and convenient synthetic methodology is still desirable.

The development of green and efficient methodologies for chemically and biologically important products from low-cost starting materials has been at focal point in modern organic chemistry (*22–26*). In this context, multicomponent domino reactions are attractive tools to achieve this goal (*27–32*). It is pertinent to note that multicomponent reactions (MCRs) have advantages such as high bond forming efficiency, convergence, operational simplicity, and reduction in waste generation and hence conform to the principles of green chemistry. Sonication of MCR

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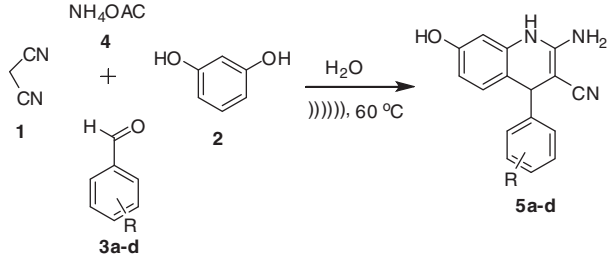
systems accelerates the reaction by confirming a better contact and increasing the reaction rate (*33*, *34*). Shorter reaction time is the main benefit of ultrasound-assisted reactions. Simple experimental procedure, high yields, improved selectivity, and clean reaction of many ultrasound-induced organic transformations offer additional convenience in the field of synthetic organic chemistry. With respect to green chemistry, the possibility of designing catalyst-free ultrasonic MCRs using water as a sole solvent is ideally the best choice owing to an easier workup procedure and the inherent environmental and economic advantages of such process.

From an environmental point of view, ultrasonic MCRs have several advantages such as utilization of water as a solvent, creation of C–C and C–N bonds in one sequence, and water as a sole waste. We initiated our studies with the catalyst-free four-component reaction involving malononitrile (1 mmol), 2-naphthol/ resorcinol (1 mmol), aldehydes (1 mmol), and ammonium acetate (2.5 mmol) under ultrasonic irradiation, which afforded a range of valuable dihydroquinolines.

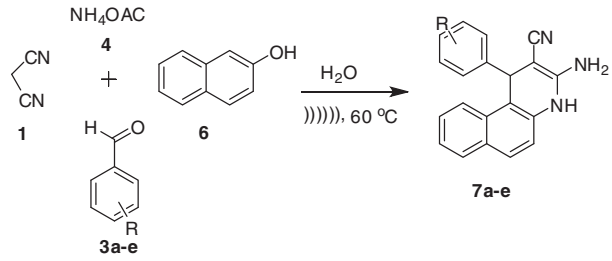
Results and discussion

To examine the ultrasonic effect on the four-component tandem reaction under mild and catalyst-free conditions, we explored the reaction of benzaldehyde, malononitrile, 2-naphthol/resorcinol, and ammonium acetate as the model (Schemes 1 and 2). Initially, the model reaction under stirring conditions at room temperature without ultrasonic radiation was investigated. This attempt failed and the materials remained unreacted (Table 1, entries 1 and 2). Hence this reaction mixture was subjected to heating, whereupon the reaction completed in 5 h affording **5a** in 55% yield (Table 1, entry 3) in ethanol under silent condition.

In view of the advantages associated with the use of ultrasound irradiation in performing reactions (*33*), the reaction was investigated under ultrasound irradiation at 60°C in EtOH. This reaction was completed in 3 h affording a good yield (Table 1, entry 3) relative



Scheme 1. Four-component reaction for the synthesis of dihydroquinolines (**5a–d**).



Scheme 2. Four-component reaction for the synthesis of dihydroquinolines (**7a–e**).

to the thermal reaction. The reaction mechanism may cautiously be visualized to occur via a tandem system of the reactions represented in the reaction scheme in Mechanism 1.

To further improve the reaction conditions, the reaction was investigated in aqueous medium and the desired product **5a** was obtained with 96% yield (Table 1, entry 4) at 60°C. All the other reactions thus carried similar conditions and the reaction products were cleanly isolated by simple filtration. The solid products were easily recrystallized from ethanol and were obtained in high yields during the short reaction times. A distinct characteristic of the current procedure is the formation of single products without any by-product. In order to make the reaction green and simple, it is essential to use eco-friendly procedures. Catalyst-free condition with water as solvent is the most ideal combination for MCRs. This simple, environmentally benign, and convenient methodology extends the scope toward a wide spectrum of novel compounds possessing an important structural subunit of a variety of biologically active molecules.

Furthermore, various aromatic aldehydes were subjected to reaction under the optimized conditions in order to widen the scope of this multicomponent ultrasound irradiation reaction procedure with water as a solvent. The obtained results are summarized in Table 2. The structures of all the synthesized target compounds were fully characterized and corroborated by FTIR, ^{1}H NMR, ^{13}CNMR, and ^{15}N GHSQC (Supplementary material).

These reactions probably fall into the class of heterogeneous sonochemical reactions (*35*), occurring in heterogeneous medium, where cavitation phenomena generates the reaction intermediates such as ionic intermediates to accelerate and facilitate the reaction. The phenomenon responsible for the beneficial effects of ultrasound on chemical reactions is cavitation. An ultrasonic wave is a pressure wave with alternate compressions and rarefactions which is able to break the intermolecular forces maintaining the cohesion of the liquid and produces a cavity in the rarefaction section of the wave. Possibly, the occurrence

Table 1. Optimization of reaction conditions of the four-component reactions.

				Conventional		Sonication	
Entry	Product no.	Solvent	Temp (°C)	Time (h)	Yield[a] (%)	Time (h)	Yield[a] (%)
1	**5a**	EtOH	rt	10.0	b	5.0	b
2	**5a**	H_2O	rt	10.0	b	5.0	b
3	**5a**	EtOH	60	5.0	55	3.0	75
4	**5a**	H_2O	60	4.0	80	1.0	96

Note: rt, room temperature: 25 ± 2°C; b, products were not found.
[a]Isolated yields.

of cavitation for nuclei in water is faster relative to other solvents.

Materials and methods

Apparatus and analysis

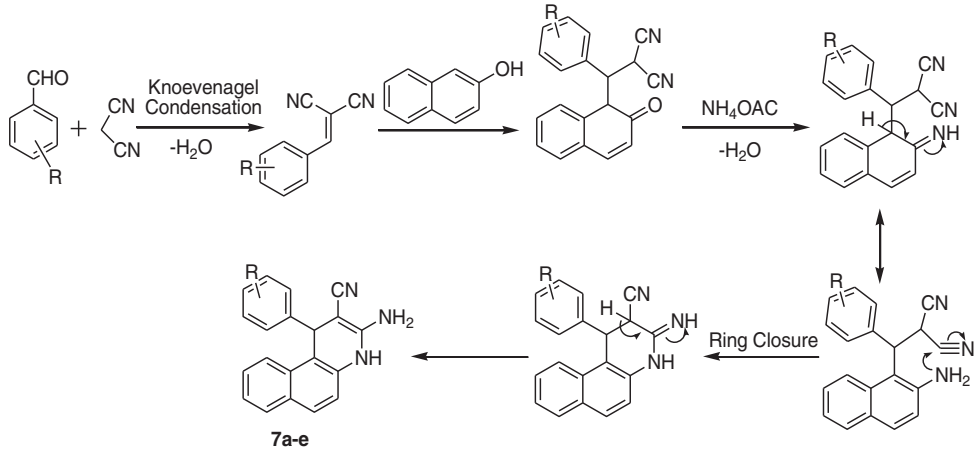
All chemicals used were reagent grade and were used as received without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25°C at 400 MHz and 100 MHz (Bruker Avance) instrument respectively, using TMS as internal standard. Chemical shifts are given in parts per million (ppm). The FT-IR spectroscopy of samples was carried out on a Perkin Elmer Perkin Elmer Precisely 100 FT-IR spectrometer in the 400–4000 cm^{-1} region. ESI–MS spectra were determined on a LCQ ion trap mass spectrometer (Thermo Fisher, San Jose, CA, USA), equipped with an ESI source. The ultrasonic-assisted reactions are carried out in a "Spectralab model UMC 20 Ultrsonic cleaner" with a frequency of 40 kHz and a nominal power 250 W. Melting points were recorded on a hot stage melting point apparatus Ernst Leitz Wetzlar, Germany and were uncorrected. All the reactions and the purity of products were monitored using thin layer chromatography (TLC) on aluminum-backed plates coated with Merck Kieselgel 60 F254 silica gel, visualizing the spots under ultraviolet light and iodine chamber.

General procedure for the synthesis of dihydroquinolines in aqueous medium under silent conditions (5a–dl7a–e).

To a solution of freshly distilled benzaldehyde (1.0 mmol), malononitrile (1.0 mmol), 2-naphthol/ resorcinol (1.0 mmol), water (10 mL) was added followed by ammonium acetate (2.5 mmol). The reaction mixture was stirred at 60°C for 4 h. After the starting material was completely consumed, the solid deposit was collected by the filtration and was washed with water and dried. The crude product was recrystallized from ethanol to offer pure product.

General procedure for the synthesis of dihydroquinolines in aqueous medium under ultrasound irradiation (5a–dl 7a–e).

A 100-mL conical flask was charged with freshly distilled benzaldehyde (1.0 mmol), malononitrile (1.0 mmol), 2-naphthol/resorcinol (1.0 mmol), and water (10 mL), followed by ammonium acetate (2.5



Mechanism 1. Probable reaction mechanism for the formation of dihydroquinolines (**7a–e**).

Table 2. Multi-component reaction for the synthesis of dihydroquinolines (**5a–f/7a–f**) under both ultrasonic irradiation and silent method.

			Conventional		Sonication	
Entry	Product no.	R	Time (h)	Yield[a] (%)	Time (h)	Yield[a] (%)
1	**5a**	H	4.0	80.0	1.0	96.0
2	**5b**	4-Br	3.5	74.0	1.5	94.0
3	**5c**	4-OH	4.5	70.0	1.0	90.0
4	**5d**	4-Cl	3.0	76.0	1.0	92.0
5	**7a**	H	3.0	82.0	1.0	97.0
6	**7b**	4-Br	4.0	80.0	1.0	95.0
7	**7c**	2-Cl	4.0	70.0	1.5	90.0
8	**7d**	4-Cl	3.5	78.0	1.0	94.0
9	**7e**	4-OH	4.0	74.0	1.5	90.0

[a]Isolated yields.

mmol). The reaction flask was put in the ultrasonic bath at 60°C, where the surface of reactants is slightly lower than the level of the bath water level, and irradiated for the period of time as summarized in Table 2. The reaction temperature of ultrasonic bath was controlled manually by addition or removal of small amounts water. After completion of the reaction, solid deposit was collected by the filtration and was washed with water and dried. The crude product was recrystallized from ethanol to offer pure product.

Compound **5a**: White solid: mp 218 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 4.61 (1H, s), 6.41 (1H, s), 6.46 (1H, d, J = 8.3 Hz), 6.78 (1H, d, J = 8.4 Hz), 6.84 (2H, s, $-NH_2$), 7.15–7.31 (5H, m), 7.50 (1H, s, –NH), 9.70 (1H, s, –OH); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 39.9, 56.2, 102.1, 112.3, 113.7, 120.6, 126.5, 127.3, 128.5, 129.8, 146.3, 148.8, 157.0, 160.2; IR (KBr, cm^{-1}): 3495, 3426, 3329, 2192; Mass spectra, m/z = 286 (M + Na, 100%); Anal. calc ($C_{16}H_{13}N_3O$): C 72.99, H 4.98, N 15.96%. Found: C 72.88, H 4.95, N 15.94%.

Compound **5b**: White solid: mp 240 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 4.64 (1H, s), 6.40 (1H, s), 6.47 (1H, d, J = 8.4 Hz), 6.76 (1H, d, J = 8.4 Hz), 6.89 (2H, s, $-NH_2$), 7.11 (2H, d, J = 8.3 Hz), 7.48 (2H, d, J = 8.3 Hz), 7.58 (1H, s, –NH), 9.74 (1H, s, –OH); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 39.3, 55.7, 102.1, 112.4, 113.0, 119.7, 120.4, 129.6, 129.8, 131.4, 145.6, 148.7, 157.1, 160.2; IR (KBr, cm^{-1}): 3470, 3337, 3233, 2189; Mass spectra, m/z = 343 (M + 1, 100%); Anal. calc ($C_{16}H_{12}BrN_3O$): C 56.16, H 3.53, N 12.28%. Found: C 56.21, H 3.62, N 12.23%.

Compound **5c**: Off-white solid: mp 289°C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 4.48 (1H, s), 6.37 (1H, s), 6.45 (1H, d, J = 8.4 Hz), 6.65–6.77 (5H, m, Ar-H & $-NH_2$), 6.93 (2H, d, J = 8.3 Hz), 7.56 (1H, s, –NH), 9.27 (1H, s, –OH), 9.65 (1H, s, –OH); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 38.0, 56.7, 102.0, 112.2, 114.2, 115.1, 120.7, 128.3, 129.8, 136.7, 148.7, 155.9, 156.8, 160.0; IR (KBr, cm^{-1}): 3478, 3348, 3193, 2191; Mass spectra, m/z = 280 (M + 1, 100%); Anal. calc ($C_{16}H_{13}N_3O_2$): C 68.81, H 4.69, N 15.05%. Found: C 68.86, H 4.61, N 15.12%.

Compound **5d**: White solid: mp 257°C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 4.63 (1H, s), 6.41 (1H, s), 6.48 (1H, d, J = 8.4 Hz), 6.75 (1H, d, J = 8.4 Hz), 6.89 (2H, s, $-NH_2$), 7.12 (2H, d, J = 8.3 Hz), 7.50 (2H, d, J = 8.3 Hz), 7.59 (1H, s, –NH), 9.74 (1H, s, –OH); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 39.4, 55.9, 102.1, 112.3, 113.2, 119.9, 120.6, 129.5, 130.1, 131.7, 145.6, 148.8, 157.0, 160.2; IR (KBr, cm^{-1}): 3478, 3341, 3218, 2193; Mass spectra, m/z = 298 (M + 1, 100%); Anal. calc ($C_{16}H_{12}ClN_3O$): C 64.54, H 4.06, N 14.11%. Found: C 64.51, H 4.15, N 14.16%.

Compound **7a**: White solid: mp 208°C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 5.28 (1H, s), 6.95 (2H, s, $-NH_2$), 7.12–7.27 (5H, m), 7.40–7.50 (3H, m), 7.51 (1H, s, –NH), 7.82–7.94 (3H, m); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 38.0, 57.8, 115.6, 116.7, 120.4, 123.5, 124.8, 126.5, 126.9, 127.0, 128.4, 128.6, 129.4, 130.1, 130.7, 145.6, 146.7, 159.6; IR (KBr, cm^{-1}): 3428, 3335, 2182; Mass spectra, m/z = 320 (M + Na, 100%); Anal. calc ($C_{20}H_{15}N_3$): C 80.78, H 5.08, N 14.13%. Found: C 80.85, H 5.15, N 14.15%.

Compound **7b:** White solid: mp 195°C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 5.35 (1H, s), 6.96 (2H, s, $-NH_2$), 7.14–7.28 (4H, m), 7.41–7.50 (3H, m), 7.53 (1H, s, –NH), 7.80–7.94 (3H, m); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 37.1, 57.3, 115.5, 116.8, 120.6, 123.2, 124.4, 126.0, 127.2, 127.6, 128.4, 128.6, 129.5, 130.2, 130.6, 145.4, 146.8, 159.6; IR (KBr, cm^{-1}): 3419, 3326, 2179; Mass spectra, m/z = 377 (M + 1, 100%); Anal. calc ($C_{20}H_{14}BrN_3$): C 63.84, H 3.75, N 11.17%. Found: C 63.76, H 3.79, N 11.10%.

Compound **7c**: Off-white solid: mp 210°C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 5.70 (1H, s), 6.97

(1H, t, J = 8.8 Hz), 7.03 (2H, s, $-NH_2$), 7.15–7.96 (10H, m, Ar−H & −NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 35.0, 56.1, 114.7, 116.7, 119.8, 122.6, 125.0, 127.4, 128.1, 128.4, 128.6, 129.5, 129.8, 130.02, 130.05, 130.7, 131.0, 142.5, 147.1, 159.8; IR (KBr, cm^{-1}): 3459, 3348, 2178; Mass spectra, m/z = 332 (M + 1, 100%); Anal. calc ($C_{20}H_{14}ClN_3$): C 72.40, H 4.25, N 12.66%. Found: C 72.45, H 4.32, N 12.62%.

Compound **7d**: White solid: mp 221°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 5.34 (1H, s), 6.95 (2H, s, $-NH_2$), 7.13–7.29 (4H, m), 7.41–7.51 (3H, m), 7.54 (1H, s, −NH), 7.80–7.94 (3H, m); ^{13}C NMR (100 MHz, DMSO-d_6): δ 37.3, 57.0, 115.2, 116.8, 120.5, 123.4, 124.5, 126.1, 127.3, 127.8, 128.4, 128.7, 129.8, 130.1, 130.7, 145.4, 146.9, 159.6; IR (KBr, cm^{-1}): 3425, 3338, 2187; Mass spectra, m/z = 332 (M + 1, 100%); Anal. calc ($C_{20}H_{14}ClN_3$): C 72.40, H 4.25, N 12.66%. Found: C 72.34, H 4.21, N 12.64%.

Compound **7e**: White solid: mp 217°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 5.30 (1H, s), 6.96 (2H, s, $-NH_2$), 7.14–7.29 (4H, m), 7.38–7.49 (3H, m), 7.52 (1H, s, −NH), 7.81–7.95 (3H, m), 9.65 (1H, s, −OH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 37.2, 57.1, 115.0, 116.7, 120.4, 123.1, 124.2, 126.2, 127.4, 127.7, 128.6, 128.8, 129.4, 130.4, 130.8, 145.3, 146.7, 159.6; IR (KBr, cm^{-1}): 3442, 3321, 3290, 2188; Mass spectra, m/z = 336 (M + Na, 100%); Anal. calc ($C_{20}H_{15}N_3O$): C 76.66, H 4.82, N 13.41%. Found: C 76.61, H 4.85, N 13.36%.

Conclusions

In conclusion, a highly efficient method is developed for the synthesis of dihydroquinolines in water under ultrasonic irradiation and catalyst-free conditions. This method is bestowed with several advantages, such as cost effectiveness, high conversions, simplicity in operation and water as a solvent, and thus meaningfully and positively contributes to the practice of green chemistry.

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Supplemental material

All Supplemental material is available alongside this article on www.tandfonline.com – go to http://dx.doi.org/10.1080/17518253.2014.902505

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