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Titanium Dioxide Nanoparticles Catalyzed Synthesis of Hantzsch Esters and Polyhydroquinoline Derivatives

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Abstract: 1,4-Dihydropyridine and polyhydroquinoline derivatives have been prepared efficiently in a one-pot synthesis via Hantzsch condensation using nanosized titanium dioxide as a heterogeneous catalyst. The present methodology offers several advantages such as excellent yields, short reaction times (30–120 min), environmentally benign, and mild reaction conditions. The catalyst can be readily separated from the reaction products and recovered in excellent purity for direct reuse.

Key words: titanium dioxide nanoparticles; Hantzsch reaction; 1,4-dihydropyridine; polyhydroquinoline

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Heterocyclic chemistry is an inexhaustible resource of novel compounds [1]. Heterocycles play a major part in biochemical processes and are also side groups of the most typical and essential constituents of living cells. Other important practical applications of these compounds can also be cited, for instance, their use as additives and modifiers in a wide variety of industries including cosmetics, reprography, information storage, plastics, solvents, antioxidants, and vulcanization accelerators. Among N-containing heterocycles, 1,4-dihydropyridines (1,4-DHPs) attracted immense attention because of their wide pharmaceutical activity range acting, for example, as vasodilator, bronchodilator, antiatherosclerotic, antitumour, antidiabetic, geroprotective, and hepatoprotective agents [2–4]. These examples clearly demonstrate the remarkable potential of 1,4-DHP derivatives as a source of valuable drugs. Preparation of 1,4-DHP was first reported by Hantzsch in 1882 via the reaction of aldehydes with ethyl acetoacetate and ammonia in acetic acid or by refluxing in alcohols [5]. Recently, a number of modified methods have been developed [6]. Other procedures comprise the utilization of microwaves [7–9], ionic liquids [10], high temperatures [11–18], TMSCl-NaI [19], $InCl_3$ [20], I_2 [21], SiO_2/$NaHSO_4$ [22], SiO_2/$HClO_4$ [23], CAN [24], Na- and Cs-Norit carbons [25], fermenting Baker's yeast [26], organocatalysts [27], metal triflates [28], Co NPs [29], and fluorinated solvents [30].

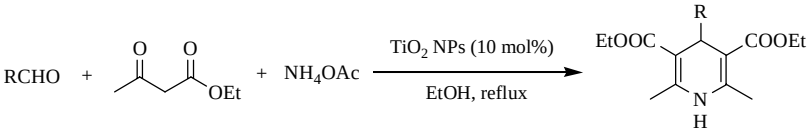
Although many of these methods are effective it is still necessary to continue the search for a better catalyst for the synthesis of 1,4-DHP and polyhydroquinolines in terms of operational simplicity, reusability, economic viability, and greater selectivity.

Heterogeneous catalysts are advantageous over conventional homogeneous catalysts as they can be easily recovered from the reaction mixture by simple filtration and can be reused after activation, thereby making the process economically viable. Khadikar et al. [7] reported that nanocrystalline titanium (IV) oxide efficiently catalyzes the conjugate 1,4-addition of indoles to α,β-unsaturated ketones and 1,2-addition of Me_3SiCN to carbonyl compounds. They demonstrated the efficiency of nano titanium dioxide and attributed it to the enhanced acidic sites and surface area.

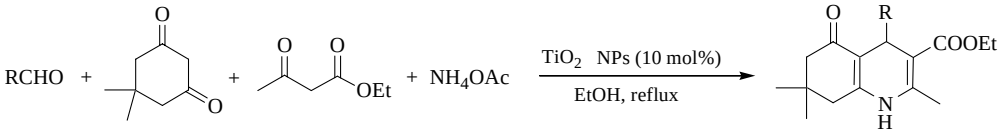
In continuation of our effort towards the development of efficient synthetic procedures for multicomponent reactions [30–33], we turned our attention towards the synthesis of 1,4-DHPs and polyhydroquinolines. We report herein a practical synthesis of these compounds using a catalytic amount of titanium dioxide nanoparticles (Schemes 1 and 2).

1 Experimental

Starting materials used in the reactions were procured from Aldrich or Merck Chemical Co. Scanning electron microscopy (SEM) images were taken with a CAM-



Scheme 1. One-pot synthesis of 1,4-DHPs. NPs–nanoparticles.



Scheme 2. One-pot synthesis of polyhydroquinoline derivatives.

Scan-MV2300 instrument (England). Atomic force microscopy (AFM) images were recorded by a Nanoserf easyScan 2 flex AFM instrument. Surface area and pore size analysis (BET) were carried out with Belsorp-mini instrument. X-ray powder diffraction (XRD) patterns of the PIs were recorded with an X-ray diffractometer (XRD, GBC MMA Instrument) with Be-filtered Cu K_α radiation. Melting points (mp) were determined on a Thermo Scientific IA9200 instrument and are uncorrected.

1.1 Synthesis of 1,4-DHPs

A mixture of aldehyde (1 mmol), ethyl acetoacetate (2 mmol), ammonium acetate (2 mmol), and titanium dioxide nanoparticles (10 mol%) was stirred in ethanol (2 ml) at 80 °C. The progress of the reaction was checked by TLC. After completion, the reaction mixture was filtered off to separate the catalyst. The solvent was evaporated under reduced pressure to yield the crude product, which was then purified by recrystallization from hot ethanol and water to afford pure 1,4-DHPs.

1.2 Synthesis of polyhydroquinoline derivatives

A mixture of aldehyde (1 mmol), ethyl acetoacetate (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (1 mmol), ammonium acetate (2 mmol), and titanium dioxide nanoparticles (10 mol%) was stirred in ethanol (2 ml) at 80 °C. The progress of the reaction was checked by TLC. After completion, the reaction mixture was filtered off to separate the catalyst. The ethanol was evaporated under reduced pressure to yield the crude product, which was then purified by recrystallization from hot ethanol and water to afford pure polyhydroquinolines.

All the products were characterized through mp, ^{1}H and ^{13}C NMR, and by comparison with authentic samples reported in the literature.

2,6-Dimethyl-4-phenyl-1,4-dihydro-pyridine-3,5-dicarboxylic acid diethyl ester (Table 1, entry 1). mp: 157–157 °C; IR (KBr, cm^{-1}) 3342, 1689, 1651, 1491, 1218, 1127, 704. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (t, J = 7.2 Hz, 6H), 2.34 (s, 6H), 4.06–4.16 (m, 4H), 5.00 (s, 1H), 5.79 (brs, 1H, NH), 7.12–7.16 (m, 1H), 7.2–7.31 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.25, 19.55, 39.63, 59.73, 104.13, 126.10, 127.83, 128.00, 143.92, 147.78, 167.68.

2,6-Dimethyl-4-(4-nitro-phenyl)-1,4-dihydro-pyridine-3,5-dicarboxylic acid diethyl ester (Table 1, entry 6). mp: 128–130 °C; IR (KBr, cm^{-1}) 3326, 1694, 1646, 1523, 1346, 1218, 1116, 704. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, J = 7.2 Hz, 6H), 2.37 (s, 6H), 4.06–4.13 (m, 4H), 5.10 (s, 1H), 5.80 (brs, 1H, NH), 7.46 (d, J = 8.7 Hz, 2H), 8.09 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.27, 19.67, 40.14, 60.01, 103.21, 123.30, 128.91, 144.63, 146.34, 155.10, 167.06.

2,6-Dimethyl-4-(4-methoxy-phenyl)-1,4-dihydro-pyridine-3,5-dicarboxylic acid diethyl ester (Table 1, entry 7). mp: 160–162 °C; IR (KBr, cm^{-1}) 3342, 2983, 1694, 1491. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (t, J = 7.2 Hz, 6H) , 2.33 (s, 6H), 3.76 (s, 3H), 4.04–4.16 (m, 4H), 4.94 (s, 1H), 5.70 (brs, 1H, NH), 6.76 (d, J = 8.6 Hz, 2H),7.20 (d, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.30, 19.60, 38.74, 55.14, 59.71, 104.40, 113.18, 128.97, 140.34, 143.58, 157.87, 167.71.

2,6-Dimethyl-4-(4-cyano-phenyl)-1,4-dihydro-pyridine-3,5-dicarboxylic acid diethyl ester (Table 1, entry 10). mp: 141–142 °C; IR (KBr, cm^{-1}) 3331, 2983, 2234, 1694, 1485, 1047. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (t, J = 7.2 Hz, 6H) , 2.35 (s, 6H), 4.03–4.15 (m, 4H), 5.04 (s, 1H), 5.80 (brs, 1H, NH), 7.40 (d, J = 8.2 Hz, 2H),7.50 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.25, 19.56, 40.25, 59.95, 103.20, 109.70, 119.31, 128.90, 131.82, 144.63, 153.09, 167.16.

2,7,7-Trimethyl-5-oxo-4-phenyl-1,4,4a,5,6,7,8,8a-octahydro-quinoline-3-carboxylic acid ethyl ester (Table 2, entry 1). mp: 201–203 °C; IR (KBr, cm^{-1}) 3275, 3080, 2963, 1700, 1610. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (s, 3H), 1.08 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H), 2.14–2.34 (m, 4H), 2.36 (s, 3H), 4.07 (q, J = 7.1 Hz, 2H), 5.06 (s, 1H), 6.61

(brs, 1H, NH), 7.09–7.33 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.21, 19.34, 27.14, 29.44, 32.70, 36.60, 40.90, 50.73, 59.08, 106.05, 112.08, 126.03, 127.90, 128.01, 143.60, 147.06, 148.50, 167.50, 195.66.

4-(4-Chloro-phenyl)-2,7,7-trimethyl-5-oxo-1,4,4a,5,6,7,8, 8aoctahydro-quinoline-3-carboxylic acid ethyl ester (Table 2, entry 4). mp: 244–245 °C; IR (KBr, cm^{-1}) 3275, 3196, 3080, 2963, 1711, 1645, 1605. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (s, 3H), 1.08 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H), 2.14–2.36 (m, 4H), 2.38 (s, 3H), 4.07 (q, J = 7.2 Hz, 2H), 5.04 (s, 1H), 6.12 (brs, 1H, NH), 7.16–7.18; ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.21, 19.46, 27.11, 29.43, 32.72, 36.21, 41.10, 50.66, 59.92, 105.76, 111.90, 128.00, 129.45, 131.6, 143.61, 145.56, 148.12, 167.22, 195.50.

4-(4-Methoxy-phenyl)-2,7,7-trimethyl-5-oxo-1,4,4a,5,6,7, 8,8aoctahydro-quinoline-3-carboxylic acid ethyl ester (Table 2, entry 8). mp: 254–255 °C; IR (KBr, cm^{-1}) 3286, 3212, 3080, 2963, 1695, 1615, 1498. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (s, 3H),0.98 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H), 2.15–2.36 (m, 4H), 2.40 (s, 3H), 3.75 (s, 3H), 4.05 (q, J = 7.2, 2H), 5.01 (s, 1H), 5.94 (brs, 1H, NH), 6.70 (d, J = 8 Hz, 2H), 7.20 (d, J = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.24, 19.50, 27.20, 29.43, 32.75, 35.67, 41.16, 50.66, 55.13, 59.83, 106.45, 112.45, 113.24, 128.90, 139.53, 142.90, 147.80, 157.51, 167.5, 195.52.

4-(4-Methyl-phenyl)-2,7,7-trimethyl-5-oxo-1,4,4a,5,6,7,8, 8aoctahydro-quinoline-3-carboxylic acid ethyl ester (Table 2, entry 12). mp: 261–262 °C; IR (KBr, cm^{-1}) 3275, 3207, 3085, 2963, 1700, 1610, 1494. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (s, 3H), 1.08 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H), 2.14–2.36 (m, 10H), 4.05–4.10 (m, 2H), 5.02 (s, 1H), 6.20 (brs, 1H, NH), 7.01 (d, J = 7.8 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.22, 19.40, 21.05, 27.23, 29.42, 32.72, 36.08, 41.10, 50.73, 59.83, 106.25, 112.30, 127.90, 128.61, 135.40, 143.40, 144.15, 148.15, 167.53, 195.64.

2 Results and discussion

Nano sized titanium dioxide was prepared by a sol-gel method using titanium tetrachloride and ethanol as reported in the literature [34]. The results indicated that the surface area is 51.859 m^2/g for the prepared titanium dioxide. This corresponds to 18.94 nm in size based on a calculation assuming a spherical shape for the catalyst particles.

The XRD pattern showed the characteristic peak located at 25.34°. Figure 1 shows the XRD peaks associated with the (101), (004), (200), (105), (211), and (204) reflections for anatase which is in agreement with the reported data [35]. Based on the Scherrer formula the crystallite diameters are calculated to be 10 nm from the half-height width of 2° of the peak at 25.34° for this sample.

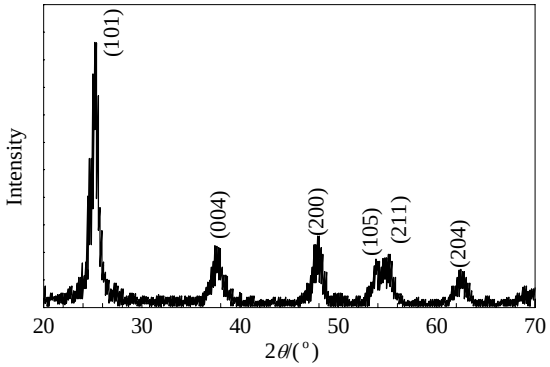


Fig. 1. XRD pattern from pure TiO_2.

The difference in particle size resulting from the specific surface area measurement and the XRD diffraction pattern is due to the difference in the assumption of the particle shape i.e. a spherical shape is assumed for the BET analysis while the XRD analysis is based on the anatase phase. The SEM image of the morphology shows that the particles are approximately 29 nm in size, and they agglomerate (Fig. 2).

The AFM image of the pure nano titanium dioxide shows that the particles are approximately 28 nm in size (Fig. 3). These combined results demonstrate the formation of single-phase anatase [34].

Initially, we examined the treatment of benzaldehyde and ammonium acetate with two equivalent amounts of ethyl

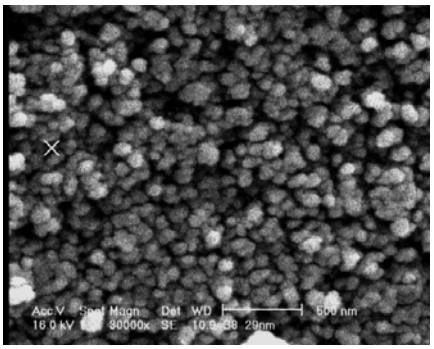


Fig. 2. SEM image of the synthesised TiO_2.

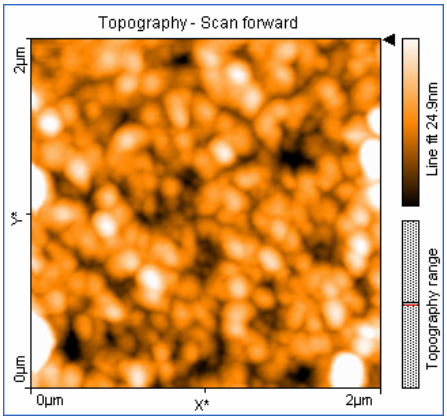


Fig. 3. AFM image of pure TiO_2.

acetoacetate as a model reaction in EtOH using different catalysts in order to determine the efficiency of the titanium dioxide nanoparticles in this reaction.

Various catalysts were tested and representative results are listed in Table 1. It turned out that titanium dioxide nanoparticles gave better results than titanium dioxide and the other catalysts listed in Table 1 in terms of yield and reaction rate.

As shown in Table 1, we first assayed Amberlyst-15, sulfamic acid, phenylphosphonic acid, phenylphosphinic acid, β-CD-OSO_2H, and silica sulfuric acid as catalysts, but the yields obtained were only moderate, even with high catalyst loadings (Table 1, entries 1–7). The best result was obtained with titanium dioxide nanoparticles in ethanol with 92% isolated yield (Table 1, entry 8). The high efficiency of the TiO_2 nanoparticles may be due to their high surface area compared with the other catalysts.

Table 1 Comparison of catalytic activity of titanium dioxide nanoparticles with some other catalysts

Entry	Catalyst	Time (h)	Yield[a] (%)
1	sulfamic acid	6	30
2	Amberlyst-15 (10%, *w*/*w*)	10	30
3	β-CD-OSO_2H	12	50
4	$C_6H_5PO(OH)_2$	8	45
5	$C_6H_5PO_2H_2$	8	45
6	H_2SO_4/SiO_2 (10%, *w*/*w*)	8	50
7	TiO_2	6	75
8	titanium dioxide nanoparticles	1.75	92
9	none	12	30

[a]Yield refers to isolated products.

An increase in the amount of the catalyst from 10 mol% to 20 mol% did not improve the yield to a greater extent and lowering the catalyst loading from 10 mol% to 5 mol% and decreasing the temperature from 80 to 40 °C reduced the yield and increased the reaction time.

To demonstrate the efficiency of the catalyst a blank reaction was carried out in the absence of catalyst under refluxing EtOH. After 12 h stirring, classical work-up and recrystallization from ethanol, only 30% of the product was isolated (Table 1, entry 9).

We then continued to optimize the model reaction mentioned above by determining the efficiency of several classical solvents which were chosen as the medium for comparison (Table 2). In each case, the substrates were mixed together with 10 mol% of titanium dioxide nanoparticles and agitated with 2 ml solvent.

It was found that, CH_2Cl_2, CH_3CN, toluene, H_2O, and the solventless system were unfavorable for the formation of the product (Table 2, entries 1–6)

The effect of temperature was also studied by carrying out the model reaction at different temperatures (Table 2, entries 8–10). It was observed that the product was obtained in excellent yield if the reaction was carried out in EtOH at reflux temperature (Table 2, entry 8).

Table 2 The efficiency of several classical solvents

Entry	Solvent	Temperature (°C)	Time (h)	Yield[a] (%)
1	—	25	6	60
2	—	80	6	68
3	CH_2Cl_2	reflux	6	35
4	CH_3CN	reflux	6	45
5	toluene	reflux	6	50
6	H_2O	reflux	6	30
7	H_2O + EtOH	reflux	6	42
8	EtOH	reflux	1.75	92
9	EtOH	40	6	78
10	EtOH	25	4	45

[a]Yield refers to isolated products.

We evaluated the efficacy and applicability of our protocol for the three component condensation using a variety of structurally distinct aldehydes. Various aliphatic, aromatic, and heterocyclic aldehydes underwent smooth cyclocondensation in good to excellent yields and the results are depicted in Table 3. As shown in this Table, aromatic aldehydes bearing electron-deficient or electron-rich substituents on the aromatic ring as well as aliphatic aldehydes afforded the desired 1,4-DHP in excellent yields (Table 3, entries 1–15).

After successfully synthesizing a series of Hantzsch esters in excellent yields, we turned our attention towards the four component reaction of cyclic 1,3-diketone, aldehyde, acetoacetic ester, and ammonium acetate to prepare the

Table 3 Titanium dioxide nanoparticle-catalyzed synthesis of 1,4-DHPs via Hantzsch reaction

Entry	R	Time (h)	Yield[a] (%)	mp (°C)	
				Found	Reported
1	C_6H_5	1.75	92	157–158	158–160 [36]
2	4-Br-C_6H_4	1.75	89	160–163	162–164 [37]
3	4-Cl-C_6H_4	2	90	145–147	147–148 [36]
4	3-Cl-C_6H_4	2	86	140–142	141–143 [38]
5	2-Cl-C_6H_4	2	80	82–84	83–85 [39]
6	4-O_2N-C_6H_4	2	87	128–130	129–131 [36]
7	4-MeO-C_6H_4	3	81	160–162	161–163 [36]
8	4-HO-C_6H_4	2	93	225–226	227–228 [40]
9	4-CH_3-C_6H_4	1.75	90	135–138	135–137 [7]
10	4-CN-C_6H_4	2	90	141–142	—
11	C_6H_5-CH=CH	2	86	146–148	141–143 [39]
12	C_7H_5O	2	92	280–283	—
13	2-furyl	3.75	50	159–162	160–161 [36]
14	2-thienyl	4	90	170–172	171–173 [36]
15	$C_6H_{12}O$	1.5	95	—	[29]

[a]Yield refers to isolated products.

Table 4 Titanium dioxide nanoparticle-catalyzed synthesis of polyhydroquinoline derivatives via Hantzsch reaction

Entry	R	Time (min)	Yield[a] (%)	mp (°C) Found	mp (°C) Reported
1	C_6H_5	30	96	201–203	202–204 [28]
2	4-Br-C_6H_4	30	94	252–253	253–255 [28]
3	3-Br-C_6H_4	30	90	235	235–236 [28]
4	4-Cl-C_6H_4	30	92	244–245	244–246 [41]
5	2-Cl-C_6H_4	45	90	208–210	209–211 [42]
6	3-Cl-C_6H_4	45	90	231–234	234–235 [24]
7	4-$(CH_3)_2N$-C_6H_4	40	80	230–231	229–231 [28]
8	4-MeO-C_6H_4	30	93	254–255	257–259 [28]
9	4-F-C_6H_4	30	90	182–184	184–186 [28]
10	4-O_2N-C_6H_4	25	88	241–243	245–246 [42]
11	2-O_2N-C_6H_4	30	82	210–215	208–211 [43]
12	4-CH_3-C_6H_4	40	92	261–262	260–261 [28]
13	4-HO-C_6H_4	30	86	232–233	232–234 [28]
14	C_6H_5-CH=CH	40	90	204–207	204–206 [41]
15	2-Thienyl	30	89	241–243	241–244 [42]
16	3-Thienyl	30	91	250–253	248–250 [28]
17	2-Furyl	30	90	245–248	246–248 [28]
18	3-Pyridyl	40	89	65–66	66–67 [28]
19	C_4H_8O	40	84	145–146	147–148 [28]

[a]Yield refers to isolated products.

polyhydroquinoline derivatives under similar reaction conditions.

In this regard, aliphatic, aromatic, heterocyclic, and conjugated aldehydes reacted smoothly under similar conditions to give the corresponding polyhydroquinolines in high yields as summarized in Table 4.

It can be seen that the variations in the yields were small and both electron-rich and electron-deficient aldehydes as well as heterocyclic ones worked well, giving good to excellent yields of the substituted polyhydroquinoline derivatives (Table 4, entries 1–19).

In view of environmental friendly methodologies, the advantages of the used catalyst will clearly be higher if the catalyst can be recovered and reused. So, to explore the recyclability of the catalyst, the titanium dioxide nanoparticles were recovered from the reaction mixture in the model reaction by a simple work up and used in six successive runs without significant loss of their catalytic activity (Table 5).

Table 5 Recyclability of the catalyst in the model reaction

Entry	Cycle	Yield[a] (%)
1	1	92
2	2	90
3	3	87
4	4	87
5	5	85
6	6	87

[a]Yield refers to isolated products.

3 Conclusions

We have developed a simple and efficient method for the synthesis of 1,4-DHPs and polyhydroquinolines using titanium dioxide nanoparticles as catalyst in EtOH. This method offers several advantages including high yield, short reaction time, simple work-up procedure with the avoidance of discharging harmful organic solvents, ease of separation and recyclability of the catalyst.

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