

# Three-component one-pot synthesis of unsymmetrical 1,4-dihydropyridine derivatives in aqueous media

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A series of methyl ethyl 2,6-dimethyl-4-substituted-1,4-dihydropyridine-3,5-dicarboxylates were synthesised by the three-component reaction of aldehydes, ethyl acetoacetate and methyl  $\beta$ -aminocrotonate in the presence of triethylbenzylammonium chloride (TEBAC) in aqueous medium. This method has the advantage of good yields.

**Keywords:** unsymmetrical Hantzsch 1,4-dihydropyridines, multi-component reactions, aqueous media

The need to reduce the amount of toxic waste and by-products arising from chemical processes requires increasing emphasis on the use of environmentally compatible materials in the design of new synthetic methods.<sup>1–3</sup> One of the most promising approaches uses water as a reaction medium.<sup>4–6</sup> Breslow and Rideout,<sup>7,8</sup> who showed that hydrophobic effects could strongly enhance the rates of several organic reactions, rediscovered the use of water as a solvent in organic reactions in the 1980s. In recent years there has been increasing recognition that water is an attractive medium for many organic reactions.<sup>9–14</sup> The aqueous medium is not expensive, dangerous or environmentally unfriendly in comparison with organic solvents. Generally, the low solubility<sup>15</sup> of most reagents in water is not an obstacle to the reactivity, which, on the contrary, is reduced by the use of co-solvents.

1,4-Dihydropyridines (1,4-DHPs) are well-known because of their pharmacological profile as calcium channel modulators.<sup>16</sup> Among various cardiovascular 1,4-DHP calcium channel antagonists,<sup>17,18</sup> Darodipine, Nifedipine and Flordipine are compounds containing symmetrical structure in their ester functionality at 3- and 5-position;<sup>19,20</sup> other drugs such as Amlodipine, Nimodipine, Nicardipine, Nilvadipine, Falodipine, Isradipine, Reodipine, Nitrendipine, Lacidipine, Bernidipine, Benidipine, Furaldipine, Manidipine, Sangandipine, and Toludipine are unsymmetrical, with different groups in the 3- and 5-positions of the ring.<sup>21–23</sup>

The usual method for the synthesis of 1,4-DHPs is that of Hantzsch.<sup>24</sup> This reaction involves a one-pot condensation of an aldehyde with ethyl acetoacetate, and ammonia either in acetic or by refluxing in alcohol for a longer time. However, the yields of 1,4-DHPs obtained by the Hantzsch method are generally low. Even though a number of modified methods<sup>25–31</sup> under improved conditions have been reported, some of them suffer from drawbacks such as unsatisfactory yields, high temperature, long reaction times, use of organic solvents, and environmental unfriendliness. Recently, the preparation of 1,4-DHPs in water has been reported. Salehi and Guo<sup>32</sup> reported the synthesis of substituted symmetrical 1,4-DHPs in water using phase-transfer catalyst under microwave

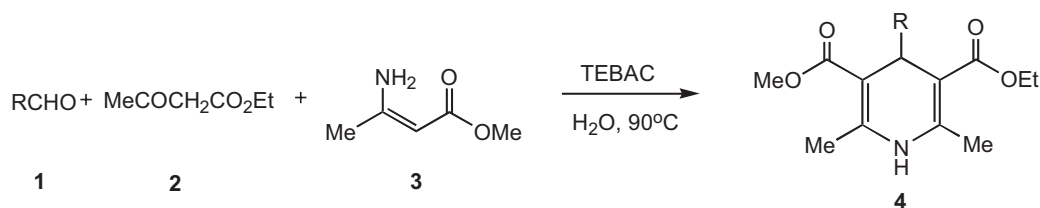
**Table 1** The synthesis of unsymmetrical 1,4-DHPs in aqueous media

Compd	R	Time/h	Yield/%
<b>4a</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	15	71
<b>4b</b>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	15	80
<b>4c</b>	4-FC <sub>6</sub> H <sub>4</sub>	17	70
<b>4d</b>	4-ClC <sub>6</sub> H <sub>4</sub>	16	86
<b>4e</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	14	76
<b>4f</b>	4-BrC <sub>6</sub> H <sub>4</sub>	16	76
<b>4g</b>	3,4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	17	71
<b>4h</b>	3,4-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	13	76
<b>4i</b>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	20	56
<b>4j</b>	c-C <sub>6</sub> H <sub>11</sub>	24	43

irradiation. Wang *et al.*<sup>33,34</sup> reported the one-pot synthesis and aromatisation of symmetrical 1,4-DHPs in water. Memarian *et al.*<sup>35</sup> reported the preparation of some new unsymmetrical substituted 1,4-DHPs, which have ethoxycarbonyl and acetyl groups on 3- and 5-positions. Khadilkar *et al.*<sup>36</sup> reported the synthesis of Hantzsch esters by condensing alkyl  $\beta$ -aminocrotonate, aldehyde and alkyl acetoacetate in aqueous sodium butylmonoglycolsulfate as a safe reaction medium in an unmodified domestic microwave oven, but only one unsymmetrical 1,4-DHP was prepared in 64% yield. Thus, the development of an efficient and versatile method for the preparation of other unsymmetrical 1,4-DHPs is an active research area and there is scope for further improvement toward milder reaction conditions and improved yields. In the course of our search for green methods of construction of the 1,4-DHP nucleus, we have reported the synthesis of symmetrical 1,4-DHPs by one-pot three-component reaction of aldehyde, ethyl or methyl acetoacetate, and ammonium acetate catalysed by TEBAC in aqueous media.<sup>37</sup> Here we report the synthesis of unsymmetrical 1,4-DHPs in aqueous media.

## Results and discussion

When an aldehyde (**1**), ethyl acetoacetate (**2**) and methyl  $\beta$ -aminocrotonate (**3**) were stirred for 13–24 h at 90 °C in aqueous



**Scheme 1** Preparation of unsymmetrical dihydropyridines.

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suspension in the presence of triethylbenzylammonium chloride (TEBAC), the unsymmetrical 1,4-DHPs – methyl ethyl 4-substituted 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylates (**4**) were obtained in excellent yields (Scheme 1). The results are summarised in Table 1.

Table 1 shows the results using a series of aromatic aldehydes and aliphatic aldehydes that undergo the reaction to give excellent yields (70–86%) of the products. This procedure does not require the use of any organic solvent. In fact the target compounds (**4**) were isolated in a practically pure form by simple Buchner filtration of the final aqueous mixture.

All the products were characterised by IR and  $^1\text{H}$  NMR analysis. The IR spectra of compound **4** show the NH stretching in the region 3360–3325  $\text{cm}^{-1}$ , the CO groups at around 1700  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectra of compound **4** show the NH proton absorption as a broad singlet in the region  $\delta$  8.74–9.01 ppm. The lone proton on C-4 gives a singlet at 4.79–4.97 ppm.

In conclusion, we have developed a facile and efficient procedure for the synthesis of methyl ethyl 2,6-dimethyl-4-substituted-1,4-dihydropyridine-3,5-dicarboxylates from aldehyde, ethyl acetoacetate and methyl  $\beta$ -aminocrotonate in water in the presence of TEBAC. Compared to the classical synthetic method, this method has the advantages of excellent yields, inexpensive operation and environmental friendliness.

## Experimental

Melting points were determined on a XT-5 apparatus. IR spectra were recorded on a Tensor 27 spectrometer; samples in KBr.  $^1\text{H}$  NMR spectra were determined on a Bruker DPX 400 MHz spectrometer in DMSO- $d_6$  solution. Chemical shifts are expressed in ppm downfield from internal TMS. Microanalyses were carried out on Perkin-Elmer 2400 II instruments.

All the products described in this paper are racemic.

### Synthesis of methyl ethyl 4-substituted-2,6-dimethyl-1,4-(*R,S*)-dihydropyridine-3,5-dicarboxylates (**4**): general procedure

A mixture of aldehyde **1** (2 mmol), ethyl acetoacetate (**2**) (2 mmol), methyl  $\beta$ -aminocrotonate (**3**) (2 mmol) and TEBAC (0.15 g) in water (10 ml) was stirred for 13–17 h at 90°C, then cooled to room temperature. The solid material formed was collected by filtration, washed with water and recrystallised from ethanol to give pure **4**.

**Ethyl methyl 4-(4-methylphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4a)**: M.p. 128–129°C. IR:  $\nu_{\text{max}}$  3355, 2990, 2947, 1699, 1652, 1489, 1432, 1377, 1337, 1301, 1215, 1125, 1090, 1052, 1019, 786, 748  $\text{cm}^{-1}$ . NMR (DMSO- $d_6$ ):  $\delta_{\text{H}}$  1.13 (3H, t,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 2.20 (3H, s,  $\text{CH}_3$ ), 2.24 (6H, s,  $2 \times \text{CH}_3$ ), 3.53 (3H, s,  $\text{CH}_3\text{O}$ ), 3.99 (2H, q,  $J = 7.2$  Hz,  $\text{CH}_2\text{O}$ ), 4.81 (1H, s, CH), 6.90–7.11 (4H, m, ArH), 8.79 (1H, s, NH). Anal. calcd for  $\text{C}_{19}\text{H}_{23}\text{NO}_4$ : C, 69.28; H, 7.04; N, 4.25; found C, 69.52; H, 6.93; N, 4.07%.

**Ethyl methyl 2,6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4b)**: M.p. 151–153°C (lit.<sup>23</sup> m.p. 151–152°C). IR:  $\nu_{\text{max}}$  3325, 2990, 2950, 1704, 1651, 1595, 1520, 1484, 1437, 1382, 1346, 1306, 1260, 1215, 1121, 1090, 1018, 866, 827, 754, 704  $\text{cm}^{-1}$ . NMR (DMSO- $d_6$ ):  $\delta_{\text{H}}$  1.13 (3H, t,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 2.27 (6H, s,  $2 \times \text{CH}_3$ ), 3.54 (3H, s,  $\text{CH}_3\text{O}$ ), 3.99 (2H, q,  $J = 7.2$  Hz,  $\text{CH}_2\text{O}$ ), 4.97 (1H, s, CH), 7.42 (2H, d,  $J = 8.4$  Hz, ArH), 8.10 (2H, d,  $J = 8.4$  Hz, ArH), 9.01 (1H, s, NH). Anal. calcd for  $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_6$ : C 59.99, H 5.59, N 7.77; found C 60.17, H 5.36, N 7.85%.

**Ethyl methyl 4-(4-fluorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4c)**: M.p. 122–124°C. IR:  $\nu_{\text{max}}$  3349, 3070, 2988, 1695, 1653, 1610, 1496, 1378, 1305, 1214, 1125, 1089, 1048, 1018, 849, 753, 680  $\text{cm}^{-1}$ . NMR (DMSO- $d_6$ ):  $\delta$  1.12 (3H, t,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 2.25 (6H, s,  $2 \times \text{CH}_3$ ), 3.53 (3H, s,  $\text{CH}_3\text{O}$ ), 3.98 (2H, q,  $J = 7.2$  Hz,  $\text{CH}_2\text{O}$ ), 4.84 (1H, s, CH), 6.99–7.05 (2H, m, ArH), 7.13–7.17 (2H, m, ArH), 8.84 (1H, s, NH). Anal. calcd for  $\text{C}_{18}\text{H}_{20}\text{FNO}_4$ : C 64.85, H 6.05, N 4.20; found C 65.02, H 5.86, N 3.95%.

**Ethyl methyl 4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4d)**: M.p. 138–139°C. IR:  $\nu_{\text{max}}$  3354, 2991, 2955, 1692, 1648, 1489, 1373, 1300, 1213, 1090, 1053, 1017, 843, 785, 741, 690  $\text{cm}^{-1}$ . NMR (DMSO- $d_6$ ):  $\delta_{\text{H}}$  1.12 (3H, t,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 2.25 (6H, s,  $2 \times \text{CH}_3$ ), 3.53 (3H, s,  $\text{CH}_3\text{O}$ ), 3.99 (2H, q,  $J = 7.2$  Hz,  $\text{CH}_2\text{O}$ ), 4.84 (1H, s, CH), 7.13 (2H, d,  $J = 8.4$  Hz, ArH), 7.27 (2H, d,  $J = 8.4$  Hz, ArH), 8.89 (1H, s, NH). Anal. calcd for  $\text{C}_{18}\text{H}_{20}\text{ClNO}_4$ : C 61.80, H 5.76, N 4.00; found C 61.98, H 5.63, N 3.95%.

**Ethyl methyl 4-(4-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4e)**: M.p. 145–146°C (lit.<sup>23</sup> m.p. 112–113°C). The molecular formula in the literature was stated as  $\text{C}_{19}\text{H}_{23}\text{NO}_5 \cdot 0.21\text{EtOAc}$ . IR:  $\nu_{\text{max}}$  3344, 2991, 2955, 1693, 1651, 1611, 1500, 1377, 1302, 1263, 1212, 1123, 1089, 1024, 901, 835, 749, 683  $\text{cm}^{-1}$ . NMR (DMSO- $d_6$ ):  $\delta_{\text{H}}$  1.13 (3H, t,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 2.24 (6H, s,  $2 \times \text{CH}_3$ ), 3.53 (3H, s,  $\text{CH}_3\text{O}$ ), 3.67 (3H, s,  $\text{CH}_3\text{O}$ ), 3.97 (2H, q,  $J = 7.2$  Hz,  $\text{CH}_2\text{O}$ ), 4.79 (1H, s, CH), 6.76 (2H, d,  $J = 8.4$  Hz, ArH), 7.03 (2H, d,  $J = 8.4$  Hz, ArH), 8.75 (1H, s, NH). Anal. calcd for  $\text{C}_{19}\text{H}_{23}\text{NO}_5$ : C 66.07, H 6.71, N 4.06; found C 66.25, H 6.53, N 3.96%.

**Ethyl methyl 4-(4-bromophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4f)**: M.p. 153–155°C. IR:  $\nu_{\text{max}}$  3361, 2991, 2955, 1699, 1656, 1489, 1373, 1300, 1213, 1104, 1017, 828, 770, 741, 669  $\text{cm}^{-1}$ . NMR (DMSO- $d_6$ ):  $\delta_{\text{H}}$  1.12 (3H, t,  $J = 6.8$  Hz,  $\text{CH}_3$ ), 2.25 (6H, s,  $2 \times \text{CH}_3$ ), 3.53 (3H, s,  $\text{CH}_3\text{O}$ ), 4.01 (2H, q,  $J = 6.8$  Hz,  $\text{CH}_2\text{O}$ ), 4.83 (1H, s, CH), 7.08 (2H, d,  $J = 8.8$  Hz, ArH), 7.38 (2H, d,  $J = 8.8$  Hz, ArH), 8.85 (1H, s, NH). Anal. calcd for  $\text{C}_{18}\text{H}_{20}\text{BrNO}_4$ : C 54.84, H 5.11, N 3.55; found C 55.06, H 4.97, N 3.47%.

**Ethyl methyl 2,6-dimethyl-4-(3,4-dimethylphenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4g)**: M.p. 112–113°C. IR:  $\nu_{\text{max}}$  3361, 2990, 2945, 1698, 1660, 1485, 1373, 1336, 1215, 1162, 1055, 1017, 886, 800, 785, 755, 726, 663  $\text{cm}^{-1}$ . NMR (DMSO- $d_6$ ):  $\delta_{\text{H}}$  1.14 (3H, t,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 2.11 (3H, s,  $\text{CH}_3$ ), 2.13 (3H, s,  $\text{CH}_3$ ), 2.24 (6H, s,  $2 \times \text{CH}_3$ ), 3.52 (3H, s,  $\text{CH}_3\text{O}$ ), 3.98 (2H, q,  $J = 7.2$  Hz,  $\text{CH}_2\text{O}$ ), 4.79 (1H, s, CH), 6.80–6.98 (3H, m, ArH), 8.74 (1H, s, NH). Anal. calcd for  $\text{C}_{20}\text{H}_{25}\text{NO}_4$ : C 69.95, H 7.34, N 4.08; found C 70.16, H 7.19, N 3.94%.

**Ethyl methyl 4-(3,4-dimethoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4h)**: M.p. 135–137°C. IR:  $\nu_{\text{max}}$  3343, 2989, 2946, 1692, 1650, 1591, 1518, 1483, 1375, 1336, 1302, 1260, 1215, 1129, 1089, 1020, 853, 767, 690  $\text{cm}^{-1}$ . NMR (DMSO- $d_6$ ):  $\delta_{\text{H}}$  1.15 (3H, t,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 2.25 (6H, s,  $2 \times \text{CH}_3$ ), 3.55 (3H, s,  $\text{CH}_3\text{O}$ ), 3.68 (6H, s,  $2 \times \text{CH}_3\text{O}$ ), 4.00 (2H, q,  $J = 7.2$  Hz,  $\text{CH}_2\text{O}$ ), 4.81 (1H, s, CH), 6.59–6.65 (1H, m, ArH), 6.74 (1H, s, ArH), 6.80 (1H, d,  $J = 7.2$  Hz, ArH), 8.80 (1H, s, NH). Anal. calcd for  $\text{C}_{20}\text{H}_{25}\text{NO}_6$ : C 63.99, H 6.71, N 3.73; found C 64.08, H 6.73, N 3.56%.

**Ethyl methyl 2,6-dimethyl-4-propyl-1,4-dihydropyridine-3,5-dicarboxylate (4i)**: M.p. 98–100°C (lit.<sup>23</sup> m.p. 95–96°C). IR:  $\nu_{\text{max}}$  3350, 2950, 1699, 1647, 1495, 1436, 1378, 1324, 1302, 1216, 1140, 1083, 1010, 792, 729  $\text{cm}^{-1}$ . NMR (DMSO- $d_6$ ):  $\delta_{\text{H}}$  0.78 (3H, t,  $J = 6.4$  Hz,  $\text{CH}_3$ ), 1.14–1.22 (7H, m,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.20 (6H, s,  $2 \times \text{CH}_3$ ), 3.60 (3H, s,  $\text{CH}_3\text{O}$ ), 3.77 (1H, t,  $J = 4.6$  Hz, CH), 4.06 (2H, q,  $J = 6.4$  Hz,  $\text{CH}_2\text{O}$ ), 8.67 (1H, s, NH). Anal. calcd for  $\text{C}_{15}\text{H}_{23}\text{NO}_4$ : C 64.03, H 8.24, N 4.98; found C 64.37, H 8.06, N 5.13%.

**Ethyl methyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4j)**: M.p. 102–104°C. IR:  $\nu_{\text{max}}$  3339, 2928, 1694, 1652, 1491, 1383, 1370, 1325, 1298, 1218, 1173, 1096, 1053, 1015, 784, 773, 739  $\text{cm}^{-1}$ . NMR (DMSO- $d_6$ ):  $\delta_{\text{H}}$  0.72–0.85 (2H, m,  $\text{CH}_2$ ), 0.98–1.06 (2H, m,  $\text{CH}_2$ ), 1.19 (3H, t,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 1.31–1.59 (7H, m,  $3 \times \text{CH}_2$ , CH), 2.21 (6H, s,  $2 \times \text{CH}_3$ ), 3.34 (3H, s,  $\text{CH}_3\text{O}$ ), 3.74 (1H, d,  $J = 5.6$  Hz, CH), 4.01–4.10 (2H, m,  $\text{CH}_2\text{O}$ ), 8.68 (1H, s, NH). Anal. calcd for  $\text{C}_{18}\text{H}_{27}\text{NO}_4$ : C 67.26, H 8.47, N 4.36; found C 67.54, H 8.11, N 4.55%.

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