Res Chem Intermed
DOI 10.1007/s11164-012-0762-z

One-pot synthesis of benzoquinoline and coumarin derivatives using Meldrum's acid in three-component reactions

Xue-Mei Wang · He-Lin Ye · Zheng-Jun Qaun · Xi-Cun Wang

Received: 3 June 2012 / Accepted: 6 August 2012

Abstract A series of 1-aryl-1,2-dihydrobenzo[*f*]quinolin-3(4*H*)-one derivatives and 4-aryl-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin derivatives have been synthesized by one-pot multicomponent reaction of Meldrum's acid with benzaldehyde, naphthalene-2-amine, or cyclohexanedione in PEG-400. The method has the advantages of mild reaction conditions, good yields, and easy processing, and is environmentally benign.

Keywords One-pot synthesis · Meldrum's acid · Multicomponent reaction · Synthesis · Benzo[*f*]quinoline derivatives · Hexahydrocoumarin derivatives

Introduction

Compared with conventional methods of organic synthesis, multicomponent reactions (MCR) have the advantages of high-selectivity, good yields, milder reaction conditions, and simple work-up procedures, among others. The probability that three or more molecules collide in the right direction and at the appropriate energy is very low, and most known multicomponent one-pot reactions can be regarded more precisely as domino or tandem reactions. Thus, a vast number of diverse compounds can be obtained in a parallel synthesis [1–4].

X.-M. Wang (✉)
School of Mechanical and Electronic Engineering, Lanzhou University of Technology, Qilihe Langongping Road 287, Lanzhou 730050, Gansu, China
e-mail: teacherwang0105@163.com

H.-L. Ye · Z.-J. Qaun · X.-C. Wang
Key Laboratory of Eco-Environment-Related Polymer Materials Ministry of Education, China, Gansu Key Laboratory of Polymer Materials, College of Chemistry and Chemical Engineering, Northwest Normal University, Anning East Road 967, Lanzhou 730070, Gansu, China

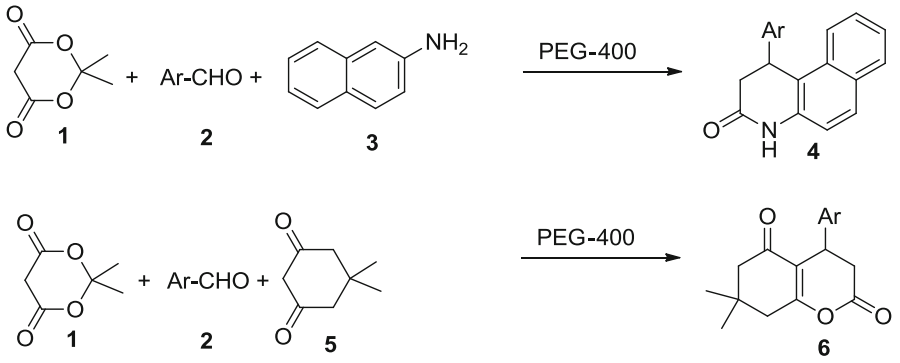
Published online: 28 August 2012

Meldrum's acid is a very active substrate frequently used in MCRs [5]. Most MCRs based on utilization of Meldrum's acid involve fundamental reactions, for example domino Knoevenagel–hetero-Diels–Alder reactions [6], domino Wittig–Knoevenagel–pseudo-Diels–Alder reactions [7], modified Hantzsch synthesis [8], Yonemitsu reaction (domino Knoevenagel–Michael) [9, 10], domino (Knoevenagel)–cycloaddition–solvolysis-I-MCR (isonitrile-MCR) [11], and Biginelli-like reactions [12]. In most of these reactions Meldrum's acid first condenses with carbonyl moieties, ultimately leading to a substituted propionic acid extension of the molecules. Domino Knoevenagel–isonitrile-cycloaddition is a unique subclass, because the major product retains two carboxyl groups of the masked malonic acid moiety. Some MCRs cannot be clearly classified, for example, when Meldrum's acid reacts with unsaturated carbonyl compounds in a Knoevenagel condensation and ring closure is followed by condensation. In other cases Meldrum's acid acts as a Michael donor with its highly acidic methylene moiety in an aldol-type reaction.

PEG-400 is inexpensive, thermally stable, non-volatile, non-toxic, and easily degradable. It has emerged as a green solvent for organic reactions and has been attracting much attention [13–16].

Benzoquinoline derivatives have excellent biological and medical activity, for example antibacterial [17], anti-hypertension [18], antimalarial [19], and antivirus [20]. Hexahydrocoumarins are a series of natural products with physiological activity; they have been widely investigated as laser dyes, and for anticancer and antivirus activity [21–23]. There has, therefore, been much interest in the synthesis of benzoquinoline and hexahydrocoumarin derivatives in recent years. There have been several reports [24–27] of the synthesis of 1-aryl-1,2-dihydrobenzo[*f*]quinolin-3(4*H*)-one derivatives. One method was two-component reaction of a Schiff base and Meldrum's acid; another was two-component reaction of naphthalene-2-amine and an α,β-unsaturated Meldrum's acid. Zhang et al. [28] recently reported the synthesis of heterocyclic acetanilide 1-aryl-1,2-dihydrobenzo[*f*]quinolin-3(4*H*)-one derivatives by three-component one-pot reaction of benzaldehyde, naphthalene-2-amine, and Meldrum's acid at reflux temperature catalyzed by triethylbenzylammonium chloride in water. Although water is inexpensive, simple to use, and environmentally benign, most organic compounds are hydrophobic, a disadvantage which has limited the scope of reactions in water. Analogously, there have been reports of the synthesis of 4-aryl-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin derivatives [29–31] in organic solvent or in water, by use of a catalyst, or microwave-induced in ethanol. The former methods have the problem of pollution; in the latter inconvenient work-up could be a problem. Recently, Li et al. [32] and Du et al. [33] reported the synthesis of 4-aryl-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin derivatives in water and an ionic liquid, respectively, but ionic liquids are relatively expensive and there is uncertainly about their toxicity. There is, therefore, no environmentally benign method with mild reaction conditions, good yields, easy processing for synthesis of 1-aryl-1,2-dihydrobenzo[*f*]quinolin-3(4*H*)-one derivatives and 4-aryl-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin derivatives.

In this communication, we report a simple and effective method for synthesis of a series of quinoline derivatives and hexahydrocoumarin derivatives by one-pot MCR of Meldrum's acid (**1**) with benzaldehyde (**2**), naphthalene-2-amine (**3**) or



Scheme 1 One-pot synthesis of benzoquinoline derivatives and coumarin derivatives

5,5-dimethyl-1,3-cyclohexanedione (**5**) in PEG-400. 1-Aryl-1,2-dihydrobenzo[*f*]quinolin-3(4*H*)-one derivatives (**4**) or 4-aryl-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin derivatives (**6**) were obtained in high yields (Scheme 1).

Results and discussion

We tried the synthesis of **4b** with the reactive substrates 4-chlorobenzaldehyde, naphthalene-2-amine, and Meldrum's acid under different reaction conditions. The results are presented in Table 1. The yield of 1-(4-chlorophenyl)-1,2-dihydrobenzo[*f*]quinolin-3(4*H*)-one (**4b**) was affected by the time and temperature of the reaction. The yield was better under reflux than at lower temperature for a short time. We deduced that the desired 1-(4-chlorophenyl)-1,2-dihydrobenzo[*f*]quinolin-3(4*H*)-one (**4b**) can be obtained in 84 % yield in PEG-400 under reflux for 14 h. In addition, the yield increases gradually with increasing temperature of the reaction; the maximum yield was obtained at 100 °C.

To investigate the feasibility of the reaction, we chose benzaldehyde with different substitutents to react with naphthalene-2-amine and Meldrum's acid (Table 2). The results showed that all reactions resulted in good yields irrespective of whether benzaldehyde or benzaldehyde with substituents in the *ortho*, *meta*, or *para* positions was used, or whether the substituents were electron-withdrawing (for

Table 1 Yields of **4b** in PEG-400 under different reaction conditions

Entry	*t*/°C	Time/h	Yield/ %[a]
1	r.t.	40	73
2	40	35	79
3	60	30	81
4	80	20	83
5	100	12	81
6	100	14	84
7	100	16	84

Reaction conditions: **1** (2.0 mmol), **2** (2.0 mmol), **3** (2.0 mmol), PEG 400 (2 g)

[a] Isolated yields

Table 2 Synthesis of 1-arylbenzo[*f*]quinoline derivatives **4a** in PEG-400

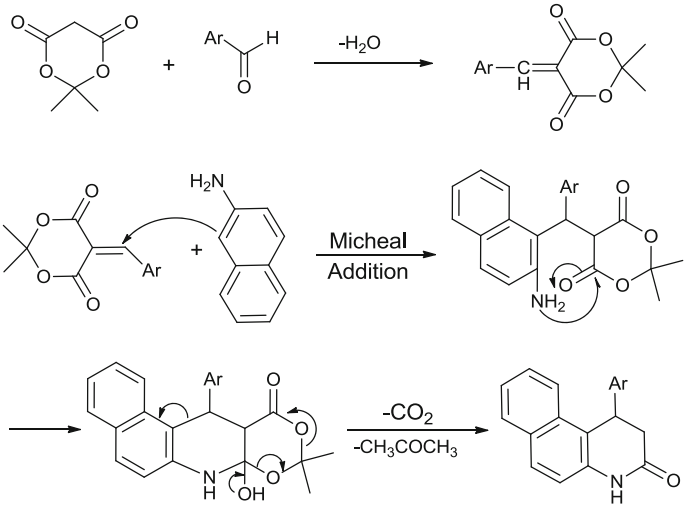
Entry	Ar	Time/h	Product	Yield/ %[a]	Mp (Lit)/ °C
1	C_6H_5	20	**4a**	80	259–261/(256–261) [28]
2	4-ClC_6H_4	16	**4b**	84	242–244/(242–243) [27]
3	2,4-$Cl_2C_6H_3$	14	**4c**	81	268–270/(259–261) [28]
4	4-BrC_6H_4	16	**4d**	80	244–245/(244–247) [28]
5	4-FC_6H_4	14	**4e**	85	255-257/(255-258) [28]
6	4-$CH_3OC_6H_4$	18	**4f**	82	240–242/(241–243) [28]
7	2-$NO_2C_6H_4$	15	**4g**	83	245–247
8	3-$NO_2C_6H_4$	15	**4h**	86	269–270
9	4-$NO_2C_6H_4$	14	**4i**	82	256–257

Reaction conditions: **1** (2.0 mmol), **2** (2.0 mmol), **3** (2.0 mmol), PEG-400 (2 g),100 °C, under reflux

[a] Isolated yields

example halide) or electron-donating (for example alkoxy group) groups. The electronic effect of substituents on the benzaldehyde had little effect on the yields of the reactions. This indicates the selectivity of the experimental conditions is excellent. Also, we did not obtain the bis substituted products.

On the basis of product structure, Wang et al. [27] believe that formation of compound **4** can be explained by the possible mechanism presented in Scheme 2. They found that 1-aryl-1,2-dihydrobenzo[*f*]quinolin-3(4*H*)-one derivatives were readily obtained when arylidene Meldrum's acids was treated with naphthalene-2-amine in PEG-400. This suggested that Michael addition occurs place in the mechanism mentioned above.



Scheme 2 Mechanism of the Michael addition reaction

Table 3 Yields of **6a** in PEG-400 under different reaction conditions

Entry	*t*/°C	Time/h	Yield/ %[a]
1	50	6	45
2	60	6	72
3	70	4	65
4	70	5	70
5	70	6	81
6	70	7	81
7	80	6	81

Reaction conditions: **1** (2.0 mmol), **2** (2.0 mmol), **4** (2.0 mmol), PEG-400 (2 g)

[a] Isolated yields

Table 4 Synthesis of hexahydrocoumarin derivatives **6a** in PEG-400

Entry	Ar	Time/h	Product	Yield/ %[a]	Mp(Lit)/°C
1	4-ClC_6H_4	6	**6a**	81	160–162/(162–163) [32]
2	4-$CH_3C_6H_4$	6	**6b**	75	107–109/(106–108)[32]
3	4-$NO_2C_6H_4$	6	**6c**	83	132–134/(133–135) [32]
4	3-CH_3O-4-OHC_6H_3	6	**6d**	72	178–180/(181–183) [32]
5	4-$CH_3OC_6H_4$	6	**6e**	70	129–131/(128–130) [33]
6	4-$(CH3)_2NC_6H_4$	6	**6f**	68	182–184/(179–181) [33]

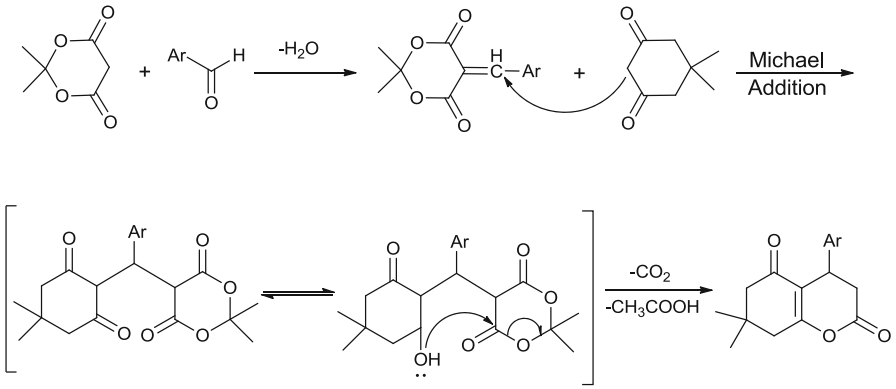
Reaction conditions: **1** (2.0 mmol), **2** (2.0 mmol), **3** (2.0 mmol), PEG-400 (2 g), 70 °C, 6 h

[a] Isolated yields

Similarly, we tried synthesis of **6a** with the reactive substrates 4-chlorobenzaldehyde, Meldrum's acid, and 5,5-dimethyl-1,3-cyclohexanedione under different reaction conditions. The results shown in Table 3 indicate that the yield of 4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin (**6a**) was affected by the time and temperature of reaction. We concluded that **6a** can be obtained in 81 % yield in PEG-400 at 70 °C for 14 h.

To demonstrate the efficiency and the applicability of this method, we performed the reaction with a variety of substituted benzaldehydes in PEG-400 at 70 °C (Table 4). As shown in Table 4, a series of 4-aryl-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin derivatives **6** bearing electron-withdrawing groups (for example halide) or electron-donating groups (for example hydroxy and alkoxy) were synthesized by reaction of Meldrum's acid with **2** and **5** to give the corresponding products **6** in good yields under the same reaction conditions. Therefore, we concluded that the electronic nature of the substituents has no significant effect on this reaction.

On the basis of the structure of the products, Margaretha [29] believed the reaction route to compound **6** may be the mechanism presented in Scheme 3. Meldrum's acid and benzaldehyde react to form the arylidene Meldrum acid. The arylidene Meldrum acid and 5,5-dimethyl-1,3-cyclohexanedione produce an intermediate by Michael addition, and the intermediate then isomerizes to form a ring, eliminating acetone and carbon dioxide, to give compound **6**.



Scheme 3 The synthetic mechanism for compound **6**

In this procedure, PEG-400 not only acts as a phase-transfer catalyst but also as a clean solvent by significantly enhancing intramolecular cyclization. Moreover, PEG-400 is a recyclable reagent. In the reaction of **4a**, we recycled the PEG-400 three times and the reaction proceeded cleanly with good yields (85, 83, and 82 %), although a little weight loss of PEG-400 was observed from cycle to cycle because of mechanical loss. Further studies to develop the new clean environmentally benign reagent for synthesis of biologically active compounds are in progress.

In summary, this work describes an efficient and environmentally friendly approach for one-pot multicomponent synthesis of 1-aryl-1,2-dihydrobenzo[*f*]quinolin-3(*4H*)-one derivatives and 4-aryl-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin derivatives, by use of Meldrum's acid in PEG-400. The method has very attractive features, for example excellent yields, simple reaction conditions, and easy work up; it is also environmentally benign. Moreover, participation of Meldrum's acid makes this process highly efficient.

Experimental

All reagents were obtained commercially and used without further purification. Meldrum's acid **3** was synthesized in accordance with literature methods [34]. Melting points were measured on an XT-4 Electrothermal micromelting-point apparatus, and are uncorrected. IR spectra were recorded using KBr pellets on a Digilab Merlin FT-IR spectrophotometer. NMR spectra were recorded at 400 (^{1}H) and 100 (^{13}C) MHz, respectively, on a Varian Mercury plus-400 instrument using DMSO as solvent and TMS as internal standard.

General synthetic procedure for compounds (**4a**–**i**)

A mixture of benzaldehyde **1** (2 mmol), naphthalene-2-amine (2 mmol), and Meldrum's acid 3 (2 mmol) in PEG-400 (2 g) was stirred for 14–20 h under reflux. The progress of the reaction was monitored by TLC. After completion of the

reaction, the reaction mixture was filtered and the precipitate washed with water. The crude products were purified by recrystallization from ethanol (95 %) to give products **4a–i**.

*1-Phenyl-1,2-dihydrobenzo[f]quinolin-3(4H)-one (**4a**)*

Yield 79 %, m.p. 259–261 °C. ^{1}H NMR (400 MHz, DMSO-*d*6) δ: 2.62 (d, J = 16.0 Hz, 1H, CH_2), 3.17 (dd, J = 16.0, 7.6 Hz, 1H, CH_2), 5.02 (d, J = 7.6 Hz, 1H, CH), 7.06–7.94 (m, 11H, ArH), 10.42 (s, 1H, NH). IR (KBr) *v*: 3194, 3064, 2937, 1684, 1625, 1603, 1522, 1493, 1473, 1452, 1426, 1388, 1334, 1243, 1197, 1182, 1166, 1075, 1031, 965, 906, 863, 820, 760, 747, 722, 698 cm^{-1}.

*1-(4-Chlorophenyl)-1,2-dihydrobenzo[f]quinolin-3(4H)-one (**4b**)*

Yield 83 %, m.p. 242–244 °C.^{1}H NMR (400 MHz, DMSO-*d*6) δ: 2.50 (d, J = 16.8. Hz, 1H, CH_2), 3.18 (dd, J = 16.8 Hz, 8.0 Hz, 1H, CH_2), 5.03 (d, J = 4.4 Hz, 1H, CH), 7.10 (d, J = 8.4 Hz, 2H, ArH), 7.26–7.35 (m, 4H, ArH), 7.41 (t, J = 7.6 Hz, 1H, ArH), 7.80 (t, J = 7.6 Hz, 1H, ArH), 7.85–7.88 (m, 2H, ArH), 10.44 (s, 1H, NH). IR (KBr) *v*: 3194, 3078, 3042, 2941, 2907, 1677, 1625, 1490, 1382, 1323, 1242, 1092, 1013, 955, 901, 831, 733, 685, 645, 594, 521, 476, 426 cm^{-1}.

*1-(2,4-Dichlorophenyl)-1,2-dihydrobenzo[f]quinolin-3(4H)-one (**4c**)*

Yield 81 %, m.p. 268–270 °C. ^{1}H NMR (400 MHz, DMSO-*d*6) δ: 2.56(d, J = 16.4 Hz, 1H, CH_2) 3.24 (dd, J = 16.4, 7.6 Hz, 1H, CH_2), 5.28 (d, J = 7.6 Hz, 1H, CH), 6.50–7.92 (m, 9H, ArH), 10.50 (s, 1H, NH). IR (KBr) *v*: 3164, 3075, 3046, 2948, 2927, 1683, 1627, 1603, 1587, 1557, 1525, 1468, 1427, 1383, 1344, 1323, 1249, 1200, 1160, 1142, 1100, 1049, 961, 905, 887, 861, 824, 799, 780, 746, 722 cm^{-1}.

*1-(4-Bromophenyl)-1,2-dihydrobenzo[f]quinolin-3(4H)-one (**4d**)*

Yield 80 %, m.p. 244–245 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.62 (d, J = 16.0 Hz, 1H, CH_2), 3.16 (dd, J = 16.0, 7.2 Hz, 1H, CH_2), 5.02 (d, J = 7.2 Hz, 1H, CH), 7.08 (d, J = 8.0 Hz, 2H, ArH), 7.25–7.36(m, 4H, ArH), 7.45 (t, 1H, ArH), 7.80 (d, J = 8.8 Hz, 1H, ArH), 7.82–7.88 (m, 2H, ArH), 10.40 (s, 1H, NH). IR (KBr) *v*: 3196, 3078, 3044, 2965, 2909, 1677, 1625, 1606, 1587, 1524, 1488, 1473, 1425, 1383, 1327, 1290, 1259, 1244, 1182, 1170, 1073, 1011, 958, 832, 816, 799, 782, 736 cm^{-1}.

*1-(4-Fluorophenyl)-1,2-dihydrobenzo[f]quinolin-3(4H)-one (**4e**)*

Yield 85 %, m.p. 255–257 °C. ^{1}H NMR (400 MHz, DMSO-*d*6) δ: 2.64(d, J = 16.0 Hz, 1H, CH_2), 3.14 (dd, J = 16.0, 7.6 Hz, 1H, CH_2), 5.02 (d, J = 7.6 Hz, 1H, CH), 7.02–7.86 (m, 10H, ArH), 10.40 (s, 1H, NH). IR (KBr) *v*: 3199, 3069, 2993,

2907, 1677, 1626, 1603, 1522, 1505, 1472, 1427, 1387, 1343, 1322, 1276, 1241, 1194, 1155, 1103, 1029, 970, 833, 818, 797, 783, 750, 736 cm^{-1}.

*1-(4-Methoxyphenyl)-1,2-dihydrobenzo[f]quinolin-3(4H)-one (**4f**)*

Yield 82 %, m.p. 240–242 °C. ^{1}H NMR (400 MHz, DMSO-*d*6) δ: 2.62 (d, J = 16.4 Hz, 1H, CH_2), 3.12 (dd, J = 16.4, 7.2 Hz, 1H, CH_2), 3.68 (s, 3H, CH_3), 4.94 (d, J = 7.2 Hz, 1H, CH), 6.82 (d, J = 8.8 Hz, 2H, ArH), 7.02 (d, J = 8.8 Hz, 2H, ArH), 7.26 (d, J = 8.8 Hz, 2H, ArH), 7.30–7.36 (m, 1H, ArH), 7.42–7.47 (m, 1H, ArH), 7.82 (d, J = 8.8 Hz, 1H, ArH), 7.84 (d, J = 8.8 Hz, 2H, ArH), 10.34 (s, 1H, NH). IR (KBr) *v*: 3205, 3089, 2991, 2955, 2902, 2833, 1687, 1625, 1604, 1581, 1508, 1463, 1417, 1388, 1346, 1317, 1251, 1177, 1158, 1111, 1032, 830, 818, 796, 780, 744 cm^{-1}.

*1-(2-Nitrophenyl)-1,2-dihydrobenzo[f]quinolin-3(4H)-one (**4g**)*

Yield 83 %, m.p. 245–247 °C. ^{1}H NMR (400 MHz, DMSO-*d*6) δ: 2.59 (d, J = 16.8 Hz, 1H, CH_2), 3.37 (dd, J = 16.4, 8.0 Hz, 1H, CH_2), 5.44 (d, J = 5.2 Hz, 1H, CH), 6.79 (d, J = 4.0 Hz, 1H, ArH), 7.34–7.57 (m, 6H, ArH), 7.88–8.05 (m, 3H, ArH), 10.6 (s, 1H, NH). IR (KBr) *v*: 3217, 3078, 2941, 2141, 1954, 1820, 1679, 1626, 1602, 1518, 1475, 1387, 1347, 1238, 1111, 1026, 965, 854,818, 750, 701, 633, 510, 432 cm^{-1}.

*1-(3-Nitrophenyl)-1,2-dihydrobenzo[f]quinolin-3(4H)-one (**4h**)*

Yield 86 %, m.p. 245-247 °C. ^{1}H NMR (400 MHz, DMSO-*d*6) δ: 2.64 (d, J = 16.4 Hz, 1H, CH_2), 3.24 (dd, J = 16.0, 7.2 Hz, 1H, CH_2), 5.28 (d, J = 4.40 Hz, 1H, CH), 7.31–7.58 (m, 5H, ArH), 7.85–8.06 (m, 5H, ArH), 10.53 (s, 1H, NH). IR (KBr) *v*: 3195, 3088, 2930, 1689, 1627, 1529, 1473, 1383, 1348, 1242, 1198, 1094, 1032, 976, 914, 864, 822, 798,777, 745, 695, 612, 584, 509, 426 cm^{-1}.

*1-(4-Nitrophenyl)-1,2-dihydrobenzo[f]quinolin-3(4H)-one (**4i**)*

Yield 82 %, m.p. 256–257 °C. ^{1}H NMR (400 MHz, DMSO-*d*6) δ: 2.6 (d, J = 16.4 Hz, 1H, CH_2), 3.38 (dd, J = 16.4, 7.6 Hz, 1H, CH_2), 5.46 (d, J = 5.2 Hz, 1H, CH), 6.82 (d, J = 8.4 Hz, 2H, ArH), 7.12–7.31 (m, 4H, ArH), 7.36 (t, J = 7.6 Hz, 1H, ArH), 7.76 (d, J = 7.6 Hz, 1H, ArH), 7.92–8.09 (m, 2H, ArH), 10.62 (s, 1H, NH). IR (KBr) *v*: 3203, 3067, 2941, 1680, 1626, 1524, 1474, 1391, 1348, 1317, 1237, 1161,973, 850, 818, 788, 748, 567, 432 cm^{-1}.

General synthetic procedure for compounds (**6a**–**f**)

A mixture of benzaldehyde **1** (2 mmol), naphthalene-2-amine (2 mmol), and Meldrum's acid 3 (2 mmol) in PEG-400 (2 g) was stirred for 7 h at 70 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, the

reaction mixture was filtered and the precipitate washed with water. The crude products were purified by recrystallization from ethanol (95 %) to give products **6a–f**.

*4-(4-Chlorophenyl)-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin (**6a**)*

Yield 81 %, m.p. 160–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.07 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 2.31 (s, 2H, CH_2), 2.47 (s, 2H,$COCH_2$), 2.83–2.91 (m, 2H, $OCOCH_2$), 4.22–4.24 (m, 1H, CH), 7.01 (d, $J = 8.0$ Hz, 2H, ArH). IR (KBr) *v*: 1776, 1658, cm^{-1}.

*4-(4-Benzyl)-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin (**6b**)*

Yield 75 %, m.p. 107–109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.08 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 2.26 (s, 2H, CH_2), 2.29 (s, 3H, CH_3), 2.50 (s, 2H,$COCH_2$), 2.85–2.93 (m, 2H, $OCOCH_2$), 4.22–4.25 (m, 1H, CH), 7.01 (d, $J = 8.0$ Hz, 2H, ArH), 7.06 (d, $J = 8.0$ Hz, ArH). IR (KBr) *v*: 1789, 1680, cm^{-1}.

*4-(4-Nitrophenyl)-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin (**6c**)*

Yield 83 %, m.p. 132–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.07 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), 2.54 (s, 2H,$COCH_2$), 2.89–3.03 (m, 2H, $OCOCH_2$), 4.37–4.39 (m, 1H, CH), 7.32 (d, $J = 8.0$ Hz, 2H, ArH), 8.14 (d, $J = 8.0$ Hz, 2H, ArH). IR (KBr) *v*: 1789, 1655, cm^{-1}.

*4-(3-Methoxy-4-hydroxyphenyl)-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin (**6d**)*

Yield 72 %, m.p. 178–180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.12 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 2.35 (s, 2H, CH_2), 2.55 (s, 2H,$COCH_2$), 2.92–2.95 (m, 2H, $OCOCH_2$), 3.88 (s, 3H, OCH_3), 4.24–4.26 (m, 1H, CH),6.61–6.85 (m, 3H, ArH), 10.92 (s, 1H, OH). IR (KBr) *v*: 1788, 1650, cm^{-1}.

*4-(4-Methoxyphenyl)-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin (**6e**)*

Yield 70 %, m.p. 129–131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.11 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 2.32 (s, 2H, CH_2), 2.53 (s, 2H,$COCH_2$), 2.90–2.92 (m, 2H, $OCOCH_2$), 3.77 (s, 3H, OCH_3), 4.25–4.27 (m, 1H, CH),6.68–7.06 (m, 4H, ArH), 10.92 (s, 1H, OH). IR (KBr) *v*: 1771, 1650, cm^{-1}.

*4-(4-(Dimethylamino)phenyl)-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin (**6f**)*

Yield 68 %, m.p. 182–184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.91 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 2.10 (s, 2H, CH_2), 2.38 (s, 2H,$COCH_2$), 2.64 (m, 2H, $OCOCH_2$), 2.91 (s, 6H, $2NCH_3$), 4.06-4.34 (m, 1H, CH),6.50–7.15 (m, 4H, ArH), 10.92 (s, 1H, OH). IR (KBr) *v*: 1791, 1703, cm^{-1}.

In conclusion, two types of compound have been synthesized by use of a three-component one-step reaction in the green medium PEG-400. All reagents were obtained commercially and used without further purification. Melting points were determined on an XT-4 electrothermal micromelting point apparatus and are uncorrected. IR spectra were recorded using KBr pellets on a Digilab Merlin FT-IR spectrophotometer. NMR spectra were recorded at 400 (^{1}H) and 100 (^{13}C) MHz, respectively, on a Varian Mercury plus-400 instrument using $CDCl_3$ as solvent and TMS as an internal standard. Elemental analysis was performed on a Carlo-Erba 1106 elemental analysis instrument. Mass spectra were recorded on a Trace DSQ instrument. Results were consistent with literature data.

Compared with the traditional two-step method, this method has the advantages of milder reaction conditions, good yields, and easy processing; the method is also environmentally benign. Reactions promoted by PEG-400 have attracted the attention of organic chemists because of its solvating properties and its ability to act as a phase-transfer catalyst. It also has negligible vapor pressure, is readily recyclable, work up is easy, and it is eco-friendly and economical. Compared with the reaction in organic solvent or in water with a catalyst, PEG-400 is more environmentally friendly. PEG-400 is not only the reaction solvent but also the phase-transfer catalyst, and is even recyclable. It also compares well with use of ionic liquids, which are expensive and their lack of toxicity has not been confirmed. We wish to report a simple but effective synthesis of benzo[*f*]quinolin derivatives and hexahydrocoumarin derivatives using PEG-400 as reaction medium.

References

1. D.H. Yang, Z.C. Chen, S.Y. Chen, Q.G. Zheng, Synthesis **12**, 1891–1894 (2003)
2. B.C. Ranu, S.S. Dey, Tetrahedron Lett. **44**, 2865–2868 (2003)
3. C.D. Lu, Z.Y. Chen, H. Liu, W.H. Wu, A.Q. Mi, M.P. Doyle, J. Org. Chem. **69**, 4856–4859 (2004)
4. B. Beck, A. Dömling, S. Hess, Bioorg. Med. Chem. Lett. **10**, 1701–1705 (2000)
5. J. Gerencsér, G. Dormán, F. Darvas, QSAR Comb. Sci. **25**, 439–448 (2006)
6. L.F. Tietze, A. Modi, Med. Res. Rev. **20**, 304–322 (2000)
7. D.B. Ramachary, C.F. Barbas, Chem. Eur. J. **10**, 5323–5331 (2004)
8. J. Svetlik, I. Goljer, F. Turecek, J. Chem. Soc. Perkin Trans. **1**, 1315–1318 (1990)
9. Y. Oikawa, H. Hirasawa, O. Yonemitsu, Tetrahedron Lett. **20**, 1759–1762 (1978)
10. Y. Oikawa, H. Hirasawa, O. Yonemitsu, Chem. Pharm. Bull. **30**, 7437–7439 (1982)
11. A. Shaabani, I. Yavari, M.B. Teimouri, Tetrahedron **57**, 1375–1378 (2001)
12. A. Shaabani, A. Bazgir, H.R. Bijanzadeh, Mol. Divers. **8**, 141–145 (2004)
13. V.V. Kouznetsov, D.R. Merchan Arenas, A.R. Romero Bohórquez, Tetrahedron Lett. **49**, 3097–3100 (2008)
14. B. Das, M. Krishnaiah, P. Thirupathi, K. Laxminarayana, Tetrahedron Lett. **48**, 4263–4265 (2007)
15. S. Chandrasekhar, N.R. Reddy, S.S. Sultana, Tetrahedron **62**, 338–345 (2006)
16. X.C. Wang, H.P. Gong, Z.J. Quan, L. Li, H.L. Ye, Chin. Chem. Lett. **20**, 44–47 (2009)
17. G. Selvi, S.P. Rajendran, Asian J. Chem. **16**, 1017–1022 (2004)
18. C.H. Lin, WO 9100856. Chem. Abstr. **115**, 92093 (1991)
19. F.S. Mikhailitsyn, N.P. Kozyreva, S.A. Rabinovich, Y.V. Maksakovskaya, I.M. Kulikovskaya, N.R. Dadasheva, M.N. Lebedeva, A.F. Bekhli, N.D. Lychko, N.A. Uvarova, Med. Parazitol. Parazit. Bolezni. **1**, 50–53 (1992)
20. N.S. Kozlov, G.P. Korotyshova, M.N. Shashikhina, Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk **6**, 76–78 (1983)

21. T. Mladen, I. Zrinka, J Heterocycl. Chem. **37**, 137–141 (2000)
22. S. Soroush, M. Yoki, H. Kiyoshi, G.M. Ronald, N. Sansei, D. Mohsen, Bioorg. Med. Chem. **7**, 1933–1940 (1999)
23. M.M. Birau, Z.Y. Wang, Tetrahedron Lett. **41**, 4025–4028 (2000)
24. J. Strods, R. Kampare, I. Lielbriedis, O. Neilands, Khim. Geterotsikl. Soedin. (1977) 977–976
25. J. Strods, V. Ciekure, V. Kampars, I. Lielbriedis, O. Neilands, Khim. Geterotsikl. Soedin. (1978) 1369–1372
26. N.G. Kozlov, L.I. Basalayeva, L.Y. Tychinskaya, Russ. J. Org. Chem. **38**, 1166–1170 (2002)
27. X.S. Wang, M.M. Zhang, Z.S. Zeng, D.Q. Shi, S.J. Tu, X.Y. Wei, Z.M. Zong, Tetrahedron Lett. **46**, 7169–7173 (2005)
28. M.M. Zhang, X.S. Wang, Q. Li, C.S. Yao, S.J. Tu, Chin. J. Org. Chem. **28**, 881–884 (2008). (in Chinese)
29. P. Margaretha, Tetrahedron Lett. **11**, 1449–1452 (1970)
30. W.H. Perkin, J. Chem. Soc. **21**, 53–63 (1868)
31. P. Bose, J. Banerji, Indian J. Chem. **29B**, 422–424 (1990)
32. Y.Z. Li, Y.X. Su, W.X. Xue, X.S. Fan, Y.X. Zhang, G.R. Qu, J. Henan Normal Univ. **34**, 99–101 (2006). (in Chinese)
33. B.X. Du, Y.L. Li, X.S. Wang, D.Q. Shi, S.J. Tu, J. Xuzhou Normal Univ. **26**, 60–62 (2008). (in Chinese)
34. D. Davidson, S.A. Bernhard, J. Am. Chem. Soc. **70**, 3426–3428 (1948)