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PAPER

Sulfuric acid-modified PEG-6000 (PEG-OSO_3H): an efficient, bio-degradable and reusable polymeric catalyst for the solvent-free synthesis of poly-substituted quinolines under microwave irradiation

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Sulfuric acid-modified polyethylene glycol 6000 (PEG-OSO_3H) is applied as an efficient and eco-friendly polymeric catalyst for Friedländer synthesis of poly-substituted quinolines from 2-aminoaryl ketones (or anthranilonitrile) and carbonyl compounds possessing a reactive methylene group under microwave irradiation and solvent-free conditions. The reactions are completed in short times, and the products are obtained in good to excellent yields.

Introduction

Nowadays, green chemistry has attained the status of a major scientific discipline.[1,2] Cleaner and more benign processes in organic synthesis have been developed in parallel with the development of new technologies each year. For many chemical processes, a major adverse effect to environment is the consumption of energy for heating and cooling. Genesis of microwave irradiation as a method of heating was a great revolution in green chemistry. A recent study comparing the energy efficiency of conventional oil-bath synthesis and microwave-assisted synthesis has indicated that for most chemical transformations, a significant energy savings, up to 85-fold, can be expected using microwaves as an energy source on a laboratory scale.[3] Rapid uncontrolled heating of organic solvents under microwave irradiation has made several hazardous situations. Hence, the first attempts at solvent-free microwave chemistry, which eliminated the danger of explosions, were made in 1990s.[4–6]

The utility of polymer-supported catalysts is now well-recognized because of their ease of workup and separation of products and catalysts, from the economical point of view, and in application to industrial processes.[7] Most polymers of this type have high molecular weights and unique solubility profile. Between them, PEGs with $M_w > 2000$ Da are mostly soluble in many polar solvents and insoluble in a few nonpolar solvents. Because of this solubility profile, PEG-based supports combine the advantageous features of homogeneous catalysis such as high reactivity, lack of diffusion phenomena and analytical simplicity, as well as solid phase methods.[8] Moreover, due to their low melting points (<100 °C), these compounds can be used as a solvent for high temperature reactions.[9] Sulfuric acid-modified PEG-6000 (PEG-OSO_3H) is an example of polyethylene glycol-supported catalyst that is functionalized by acidic groups and is a mild, non-volatile and non-corrosive organic acid. This catalyst has been used for the synthesis of 3,4-dihydropyrimidones *via* the Biginelli reaction under microwave and solvent-free conditions,[9] regioselective ring opening of epoxides with thiocyanate anion in water,[10] Beckmann rearrangement and dehydration of oximes.[11]

Quinolines are nitrogen-containing heterocycles with wide range of medicinal properties which have been used as antimalarial, antiasthmatic, antihypertensive, antibacterial and tyrosine kinase inhibiting agents.[12–16] These compounds have been also applied for the preparation of nano- and mesostructures having enhanced electronic and photonic properties.[17] 4-Aminoquinolines are an important group of quinoline derivatives, and have been found to be a potent acetylcholinesterase inhibitors[18] and an even stronger inhibitor of the butyrylcholinesterase family of enzymes.[19] Moreover, these compounds have been shown to possess a much broader pharmacological profile than cholinesterase inhibition: blockage of potassium channels,[20] inhibition of the neuronal monoamine uptake processes,[21] and inhibition of monamine oxidase.[22] Two biological active quinolines are shown in Scheme 1.

A straightforward synthesis of quinolines is Friedländer annulation reaction.[23–28] In this method, quinoline derivatives have been prepared by condensation of 2-aminoaryl ketones with carbonyl compounds possessing a reactive methylene group followed by cyclodehydration.[23–28] This reaction has been generally carried out either by refluxing an aqueous or alcoholic solution of reactants in the presence of a base at high temperature, 150–220 °C.[23] However, under basic or thermal-catalysis conditions, 2-aminobenzophenone does not react with simple ketones such

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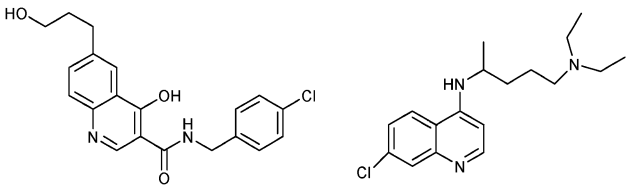


Scheme 1 Two biologically active quinolines.

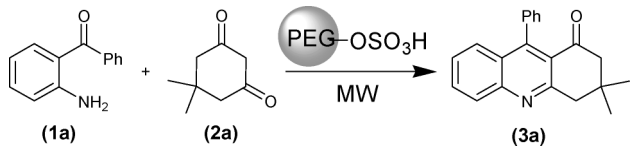
as cyclohexanone and β-ketoesters.[24] In order of improve the generality of Friedländer method, some catalytic systems have been reported.[23–28] The common procedure for the synthesis of 4-aminoquinolines is the acid-catalyzed condensation reaction between 2-aminonitriles (such as anthranilonitrile) with carbonyl compounds possessing a reactive methylene group followed by cyclodehydration.[29] Some of the catalytic systems which have been used include zinc chloride in nitrobenzene at 120 °C,[29a] aluminium trichloride in 1,2-dichloroethane at reflux,[29b] boron trifluoride diethyl etherate in toluene at reflux,[29c] or titanium tetrachloride in methylene chloride.[29d] Most of the reported procedures for the synthesis of poly-substituted quinolines and 4-aminoquinolines suffer from drawbacks such as low yields of the products, long reaction times, the use of hazardous and often expensive catalysts, the use of volatile and hazardous organic solvents, harsh reaction conditions, tedious work-up, and no compliance with the green chemistry protocols. Consequently, development of the efficient, inexpensive and environmentally benign methods for the synthesis of quinolines is in demand.

In this paper, we wish to report a convenient and rapid method for the Friedländer synthesis of poly-substituted quinolines and 4-aminoquinolines *via* the condensation of 2-aminoaryl ketones or anthranilonitrile with carbonyl compounds in the presence of PEG-OSO_3H as an efficient, green, inexpensive, reusable and biodegradable polymeric catalyst under microwave irradiation and solvent-free conditions.

Results and discussions

In order to find the best reaction conditions for the synthesis of quinoline derivatives, the microwave-assisted condensation of 2-aminobenzophenone (**1a**) (1 mmol) with dimedone (**2a**) (1.5 mmol) was examined in the presence of different amounts of PEG-OSO_3H at range of 100–800 W of microwave power and 100–140 °C in the absence of solvent (Scheme 2).

The best results were obtained in the presence of 3 mol% of PEG-OSO_3H at 600 W (130 °C) of microwave irradiation. The reaction was also checked without the catalyst in which the



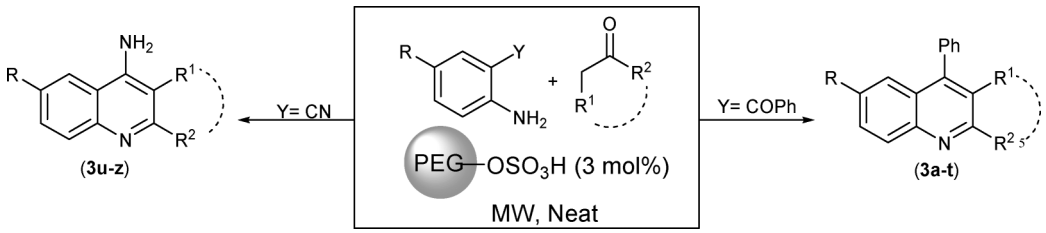
Scheme 2 The condensation of 2-aminobenzophenone (**1a**) with dimedone (**2a**) using PEG-OSO_3H under microwave irradiation.

yield of the product was very low (28% after 20 min). These observations established the crucial rule of PEG-OSO_3H for the expedition of the reaction time and the product yield.

To realize the efficiency and the scope of PEG-OSO_3H for the synthesis of quinolines, 2-aminoarylketones were reacted with various carbonyl compounds including cyclic and acyclic 1,3-diketones, β-ketoesters and cyclic ketones under the optimized reaction conditions (Scheme 3). The results are displayed in Table 1.

As can be seen in Table 1, cyclic and acyclic 1,3-diketones as well as β-ketoesters were efficiently condensed with 2-aminoaryl ketones, and the corresponding quinolines were obtained in good to excellent yields and in short reaction times (Table 1, compounds **3a–g** and **3k–q**). Interestingly, cyclic mono-functionalized ketones were successfully reacted with 2-aminoarylketones to afford the respective tricyclic quinolines in reasonable yields and in short reaction times (Table 1, compounds **3h–j** and **3r–t**). Moreover, the catalyst was applied for the synthesis of a sterically hindered quinoline, by the condensation of 1,3-diphenyl-1,3-propandione with 5-chloro-2-aminobenzophenone (Table 1, compound **3q**). In the next step, the efficiency of PEG-OSO_3H were examined for the synthesis of 4-aminoquinolines *via* the condensation of anthranilonitrile with carbonyl compounds (Scheme 3, compound **3u–z**). As Table 1 indicates, anthranilonitrile was efficiently condensed with dimedone, 1,3-cyclohexanedione or mono-functionalized cyclic ketones in the presence of 3 mol% of PEG-OSO_3H under microwave irradiation (600 W, 130 °C) and solvent-free conditions to provide the products **3u–z** in high yields and in short reaction times.

After completion of each reaction, H_2O was added to the reaction mixture and was shaken for a few minutes to dissolve PEG-OSO_3H. The crude product (insoluble in water) was filtered and recrystallized from hot ethanol for more purification. In order to recover the catalyst, H_2O was evaporated under reduced pressure, and the resulting solid was washed with *t*-butylmethyl ether, and dried. The recovered catalyst was reused ten times in the condensation of 2-aminobenzophenone (**1a**) with dimedone (**2a**), and smooth loss of catalytic activity was observed from the 7th time of reuse (Fig. 1).



Scheme 3 The condensation of 2-aminobenzophenones or 2-aminobenzonitrile with carbonyl compounds using PEG-OSO_3H as catalyst under solvent-free and microwave conditions.

Table 1 Friedländer synthesis of poly-substituted quinolines and 4-aminoquinolines in the presence of PEG-OSO_3H under microwave and solvent-free conditions (Scheme 3)

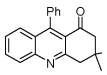
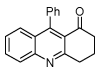
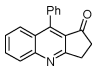
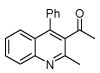
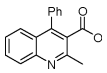
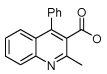
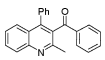
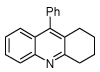
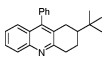
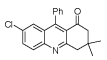
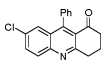
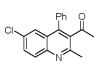
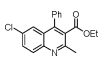
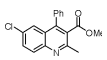
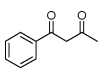
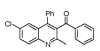
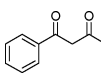
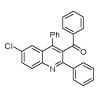
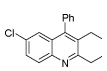
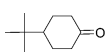
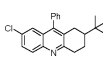
Entry	R	Y	Ketone	Product	Time/min	Yield[a] (%)
3a	H	COPh			4	91
3b	H	COPh			6	93
3c	H	COPh			8	75
3d	H	COPh			4	90
3e	H	COPh			7	83
3f	H	COPh			4	90
3g	H	COPh			5	88
3h	H	COPh			7	84
3i	H	COPh			8	79
3j	H	COPh			12	81
3k	Cl	COPh			3	94
3l	Cl	COPh			4	92
3m	Cl	COPh			5	90
3n	Cl	COPh			6	89
3o	Cl	COPh			6	91
3p	Cl	COPh			4	87
3q	Cl	COPh			10	83
3r	Cl	COPh			6	85
3s	Cl	COPh			9	82

Table 1 *(Contd.)*

Entry	R	Y	Ketone	Product	Time/min	Yield[a] (%)
3t	Cl	COPh			10	80
3u	H	CN			4	91
3v	H	CN			9	94
3w	H	CN			12	91
3x	H	CN			8	93
3y	H	CN			9	90
3z	H	CN			12	91

[a] Yields refer to isolated pure products.

Fig. 1 The catalytic activity of PEG-OSO_3H in ten cycles for the reaction of 2-aminobenzophenone (**1a**) with dimedone (**2a**).

To assess the capability and efficiency of our catalyst with respect to the reported catalysts for Friedländer synthesis of quinoline derivatives, the results of the application of these catalysts for the preparation of some quinolines are tabulated in Table 2. As is clear from Table 2, PEG-OSO_3H was more efficient.

In another study, to recognize the applicability of our method at large scales, we examined some reactions in scales of 100 and 300 mmol. The results are summarized in Table 3. As shown in Table 3, the reactions were successfully performed at large scales without significant loss of the yields.

The microwave-enhanced chemistry in this reaction is based on the efficient heating of materials by "microwave dielectric heating" effects. This phenomenon refers to the ability of PEG-OSO_3H to absorb microwave energy and convert it into heat because of polar skeleton.[30] Traditionally, organic synthesis is carried out by conductive heating with an oil bath. This is a

Table 2 Comparison of the condensation of 2-aminobenzophenone (**1a**) or anthralinonitrile (**4**) with cyclopentanone using the reported catalysts *versus* PEG-OSO_3H

Reagents and conditions	Y	Time/min	Yield (%)	Ref.
NH_2SO_3H (5 mol%), solvent-free, 70 °C	COPh	50	87	27d
Cellulose sulfuric acid, solvent-free, 100 °C	COPh	50	60	27c
Amberlyst-15, EtOH, reflux	COPh	180	92	36
$Zr(DS)_4$ (5 mol%), EtOH–H_2O (1 : 2), reflux	COPh	360	90	28c
$HClO_4$-SiO_2, CH_3CN, 60 °C	COPh	120	90	37
$BF_3{\cdot}(Et_2O)_2$ (200 mol), toluene, reflux	CN	720	41	29c
PEG-OSO_3H (3 mol%), solvent-free, MW	COPh	12	81	Our catalyst
PEG-OSO_3H (3 mol%), solvent-free, MW	CN	12	91	Our catalyst

Table 3 The large scale synthesis of poly-substituted quinolines and 4-aminoquinolines using PEG-OSO_3H under microwave and solvent-free conditions

2-Aminoarylketone (or nitrile) amount/mmol	Product	Time/min	Yield (%)
1	**3a**	4	91
100	**3a**	5	89
300	**3a**	10	84
1	**3j**	12	81
100	**3j**	15	78
300	**3j**	20	71
1	**3p**	4	87
100	**3p**	6	86
300	**3p**	10	82
1	**3w**	12	91
100	**3w**	16	87
300	**3w**	22	76

[a] Yields refer to isolated pure products.

comparatively slow and inefficient method for transferring energy into the system, since it depends on the thermal conductivity of the various materials that must be penetrated, and results in the temperature of the reaction vessel being higher than that of the reaction mixture. In contrast, microwave irradiation produces efficient internal heating (in-core volumetric heating) by direct coupling of microwave energy with the molecules that are present in the reaction mixture. These effects should be termed "specific microwave effects" and the formation of "molecular radiators" or microscopic hotspots,[31] and the elimination of wall effects caused by inverted temperature gradients.[32] Furthermore, at the initial moments of microwave irradiation, PEG-OSO_3H melts and works as solvent as well as catalyst for these reactions. So, these dual activation modes lead to reduce the reaction times and improve the yield of the products.

Conclusions

In conclusion, we have reported a highly efficient and green method for Friedländer synthesis of poly-substituted quinolines and 4-aminoquinolines using PEG-OSO_3H as an inexpensive, biodegradable and reusable catalyst. This method not only offers substantial improvements in the reaction rates and yields, but also avoids the use of hazardous catalysts or solvents. Moreover, the uses of microwave irradiation for direct heating of the reaction mixture and solvent-free conditions have marked our work as a green and economically benign methodology.

Experimental

All chemicals were purchased from Merck or Fluka chemical companies. All reactions were carried out using a laboratory microwave oven (MicroSYNTH, Milestone Company, Italy). The ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) were run on a Bruker Avance DPX-250, FT-NMR spectrometer (δ in ppm). Microanalysis was performed on a Perkin–Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. All known compounds were identified by comparison of their melting points, ^1H NMR and ^{13}C NMR data with those reported in the literature.

Preparation of PEG-OSO_3H

At 0 °C, chlorosulfonic acid (10 mmol) was added to a solution of PEG-6000 (1 mmol) in CH_2Cl_2 (10 mL), and the resulting solution was stirred at room temperature overnight. Then, the solution was concentrated under vacuum, and ether was added to it. The resulting precipitate was filtered and washed with ether three times to afford PEG-OSO_3H as a gummy solid.[9] ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 3.40–3.54 (m, PEG), 4.18 (s, 2H, CH_2OSO_3H), 12.69 (s, 1H, SO_3H).

General procedure for the synthesis of poly-substituted quinolines and 4-aminoquinolines

A well-ground mixture of 2-aminoarylketone or 2-aminobenzonitrile (1 mmol), carbonyl compound (1.5 mmol) and PEG-OSO_3H (0.18 g, 0.03 mmol) in a test tube was irradiated and stirred in a microwave oven at 600 W. The microwave oven was programmed to enhance the internal reaction temperature to 130 °C within 1.5 min, and then continue suitable irradiation (0–600 W) at this temperature, for the appropriate time. The combined times are showed in Tables 1 and 2. Afterward, the reaction mixture was cooled to room temperature, and H_2O (5 mL) was added to it, and shaken for 3 min to dissolve PEG-OSO_3H. The crude product (insoluble in water) was filtered and recrystallized from hot ethanol (3 mL) to afford the pure product. In order to recover the catalyst, H_2O was evaporated under reduced pressure, the resulting solid was washed with *t*-butylmethyl ether (2 mL) and dried. The recovered PEG-OSO_3H was reused for another time without loss of its activity.

General procedure for the synthesis of poly-substituted quinolines and 4-aminoquinolines in large scale

A well-ground mixture of 2-aminoarylketone or 2-aminobenzonitrile (300 mmol), carbonyl compound (330 mmol) and PEG-OSO_3H (54 g, 9 mmol) in a round-bottomed flask connected to a reflux condenser, was irradiated and stirred in a microwave oven at 600 W. The microwave oven was programmed to enhance the internal reaction temperature to 130 °C within 4 min, and then continue suitable irradiation (0–600 W) at this temperature, for the appropriate time. The combined times are showed in Table 3. Afterward, the reaction mixture was cooled to room temperature, H_2O (600 mL) was added to it, and it was shaken for 5 min to dissolve PEG-OSO_3H. The crude product (insoluble in water) was filtered and recrystallized from hot ethanol (400 mL) to afford the pure product. In order to recover the catalyst, H_2O was evaporated under reduced pressure, the resulting solid was washed with *t*-butylmethyl ether (150 mL) and dried. The recovered PEG-OSO_3H was reused for another time without loss of its activity.

Physical and spectral data of the products

3,3-Dimethyl-9-phenyl-3,4-dihydroacridin-1(2*H*)-one (3a). Yield = 91% (0.274 g), m.p. = 193–194 °C (lit.[33] 192 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 1.16 (s, 6H), 2.56 (s, 2H), 3.27 (s, 2H), 7.17 (d, 2H, J = 6.5 Hz), 7.40 (t, 1H, J = 7.5 Hz), 7.47–7.50 (m, 4H), 7.75 (t, 1H, J = 7.0 Hz), 8.06 (d, 1H, J = 8.5 Hz); ^{13}C-NMR (DMSO-d_6, 125 MHz): δ (ppm) 28.3, 32.8, 47.8, 53.8, 126.0, 127.1, 127.7, 127.9, 128.3, 128.6, 128.7, 128.9, 131.3, 132.1, 134.6, 137.8, 148.7, 150.1, 161.6, 197.7. Anal. calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65%. Found: C, 83.64; H, 6.39; N, 4.71%.

9-Phenyl-3,4-dihydroacridin-1(2*H*)-one (3b). Yield = 93% (0.254 g), m.p. = 157–159 °C (lit.[33] 151–153 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 2.62–2.65 (t, 2H, J = 6.5 Hz), 3.22 (t, 2H, J = 6.5 Hz), 3.75–3.78 (m, 2H), 7.25–7.26 (m, 2H), 7.32 (d, 1H, J = 2.2 Hz), 7.51–7.66 (m, 5H), 8.00 (d, 1H, J = 8.7 Hz); ^{13}C NMR (DMSO d_6, 125 MHz): δ (ppm) 21.6, 34.6, 40.9, 127.7, 127.5, 127.5, 128.1, 128.2, 128.7, 129.0, 129.1, 132.5, 138.2, 148.7, 150.8, 163.2, 198.3. Anal. calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12%. Found: C, 83.53; H, 5.49; N, 5.17%.

9-Phenyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinolin-1-one (3c). Yield = 75% (0.194 g), m.p. = 170–173 °C (lit.[34] 171–175 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 2.71 (m, 2H), 3.42 (m, 2H), 7.31 (m, 2H), 7.58 (m, 4H), 7.64 (m, 2H), 8.07 (d, 1H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 28.3, 36.6, 123.4, 126.3, 126.4, 127.7, 128.1, 128.5, 128.8, 129.2, 130.4, 131.8, 132.9, 148.7, 151.0, 170.6, 203.3. Anal. calcd for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; N, 5.40%. Found: C, 83.33; H, 5.09; N, 5.49%.

1-(2-Methyl-4-phenylquinolin-3-yl)ethanone (3d). Yield = 90% (0.235 g), m.p. = 109–110 °C (lit.[28c] 105–106 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 2.04 (s, 3H), 2.74 (s, 3H), 7.39–7.41 (m, 2H), 7.48 (t, 1H, J = 7.5 Hz), 7.55–7.56 (m, 3H), 7.66 (d, 1H, J = 8.3 Hz), 7.76 (t, 1H, J = 7.4 Hz), 8.12 (d, 1H, J = 8.3 Hz). Anal. calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36%. Found: C, 82.70; H, 5.72; N, 5.44%.

Ethyl 2-methyl-4-phenylquinoline-3-carboxylate (3e). Yield = 83% (0.241 g), m.p. = 102–103 °C (lit.[33] 99 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 0.99 (t, 3H, J = 6.6 Hz), 2.83 (s, 3H), 4.08–4.12 (q, 2H, J = 5.3 Hz), 7.40–7.41 (m, 2H), 7.45–7.48 (t, 1H, J = 7.5 Hz), 7.49–7.54 (m, 3H), 7.62 (d, 1H, J = 8.3 Hz), 7.74–7.77 (t, 1H, J = 7.6 Hz), 8.12 (d, 1H, J = 8.4 Hz); ^{13}C NMR (DMSO d_6, 125 MHz): δ (ppm) 13.8, 23.7, 61.4, 124.7, 126.4, 127.3, 128.8, 129.0, 129.5, 130.9, 135.4, 145.9, 147.5, 154.3, 167.9. Anal. calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81%. Found: C, 78.39; H, 5.84; N, 4.90%.

Methyl 2-methyl-4-phenylquinoline-3-carboxylate (3f). Yield = 90% (0.249 g), m.p. = 105–107 °C (lit.[33] 107 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 2.77 (s, 3H), 3.56 (s, 3H), 7.34–7.35 (m, 2H), 7.41 (t, 1H, J = 7.5 Hz), 7.43–7.49 (m, 3H), 7.57 (d, 1H, J = 8.0 Hz), 7.70 (t, 1H, J = 7.2 Hz), 8.07 (d, 1H, J = 8.5 Hz). Anal. calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05%. Found: C, 77.98; H, 5.48; N, 5.02%.

(2-Methyl-4-phenylquinolin-3-yl)(phenyl)methanone (3g). Yield = 88% (0.284 g), m.p. = 135–138 °C (lit.[25] 133–134 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 2.48 (s, 3H), 7.29 (m, 7H), 7.31 (m, 2H), 7.57 (m, 3H), 7.67 (m, 1H), 8.05 (d, 1H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 24.1, 125.0, 126.0, 126.3, 127.7, 128.0, 128.3, 128.7, 129.0, 129.8, 129.9, 132.3, 133.3, 134.4, 136.9, 145.4, 147.6, 154.3, 197.4. Anal. calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33%. Found: C, 85.39; H, 5.33; N, 4.35%.

9-Phenyl-1,2,3,4-tetrahydroacridine (3h). Yield = 84% (0.217 g), m.p. = 143–145 °C (lit.[33] 139 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 1.83–1.85 (m, 2H), 2.00–2.01 (m, 2H), 2.65 (t, 2H, J = 6.2 Hz), 3.25 (t, 2H, J = 6.2 Hz), 7.27 (d, 2H, J = 7.0 Hz), 7.36 (s, 2H), 7.49– 7.52 (m, 1H), 7.55– 7.58 (m, 2H), 7.64– 7.65 (m, 1H), 8.07 (d, 1H, J = 8.2 Hz); ^{13}C NMR (DMSO d_6, 125 MHz): δ (ppm) 22.7, 22.8, 27.9, 34.0, 125.6, 126.0, 126.4, 127.7, 128.3, 128.4, 128.5, 128.6, 128.7, 129.3, 136.8, 146.2, 159.0. Anal. calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40%. Found: C, 87.89; H, 6.63; N, 5.38%.

2-*tert*-Butyl-9-phenyl-1,2,3,4-tetrahydroacridine (3i). Yield = 79% (0.249 g), m.p. = 133–135 °C (lit.[35] 132–133 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 0.90 (s, 9H), 1.47–1.58 (m, 2H), 2.08–2.10 (m, 1H), 2.22–2.27 (m, 1H), 2.63–2.65 (m, 1H), 3.09–3.15 (m 1H), 3.23–3.27 (m, 1H), 7.32–7.37 (m, 3H), 7.43–7.46 (m, 1H), 7.49–7.52 (m, 2H), 7.61–7.65 (m, 2H), 8.06 (d, 1H, J = 8.4 Hz). Anal. calcd for $C_{23}H_{25}N$: C, 87.57; H, 7.99; N, 4.44%. Found: C, 87.67; H, 8.06; N, 4.39%.

9-Phenyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (3j). Yield = 81% (0.198 g), m.p. = 142–143 °C (lit.[35] 140–142 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 2.18–2.24 (m, 2H), 2.95 (t, 2H, J = 7.3 Hz), 3.29 (t, 2H, J = 7.6 Hz), 7.40–7.44 (m, 3H), 7.49–7.52 (m, 1H), 7.55–7.58 (m, 2H), 7.65–7.68 (m, 2H), 8.12 (d, 1H, J = 8.5 Hz). Anal. calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71%. Found: C, 88.10; H, 6.13; N, 5.77%.

7-Chloro-3,3-dimethyl-9-phenyl-3,4-dihydroacridin-1(2*H*)-one (3k). Yield = 94% (0.315 g), m.p. = 211–212 °C, (lit.[33] 211 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 1.15 (s, 6H), 2.56 (m, 2H), 3.25 (s, 2H), 7.14–7.16 (m, 2H), 7.42 (d, 1H, J = 2.5 Hz), 7.50–7.51 (m, 3H), 7.66–7.68 (dd, 1H, J = 2.5, 8.9 Hz), 7.99 (d,

1H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 28.4, 32.3, 48.1, 54.3, 124.0, 126.5, 127.9, 128.4, 130.5, 132.3, 136.7, 147.9, 150.1, 162.0, 196.9. Anal. calcd for $C_{21}H_{18}ClNO$: C, 75.11; H, 5.40; N, 4.17%. Found: C, 75.17; H, 5.38; N, 4.21%.

7-Chloro-9-phenyl-3,4-dihydroacridin-1(*2H*)-one (3l). Yield = 92% (0.283 g), m.p. = 187–188 °C (lit.[33] 185 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 2.23–2.26 (m, 2H), 2.70 (t, 2H, J = 6.6 Hz), 3.35 (t, 2H, J = 6.3 Hz), 7.14–7.16 (m, 2H), 7.41 (d, 1H, J = 2.5 Hz), 7.49–7.51 (m, 3H), 7.67–7.69 (dd, 1H, J = 2.5, 8.9 Hz), 7.99 (d, 1H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 20.8, 34.1, 40.2, 124.1, 126.1, 127.8, 129.9, 132.0, 136.5, 146.6, 149.9, 162.1, 196.8. Anal. calcd for $C_{19}H_{14}ClNO$: C, 74.15; H, 4.58; N, 4.55%. Found: C, 74.17; H, 4.55; N, 4.63%.

1-(6-Chloro-2-methyl-4-phenylquinolin-3-yl)ethanone (3m). Yield = 90% (0.266 g), m.p. = 157–158 °C (lit.[33] 157 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 1.98 (s, 3H), 2.66 (s, 3H), 7.31–7.33 (m, 2H), 7.51–7.52 (m, 3H), 7.55 (d, 1H, J = 2.0 Hz), 7.62–7.64 (dd, 1H, J = 2.0, 8.9 Hz), 7.99 (d, 1H, J = 8.5 Hz); ^{13}C NMR (DMSO-d_6, 125 MHz): δ (ppm) 24.1, 53.2, 125.3, 126.0, 128.5, 129.4, 129.8, 129.8, 131.8, 131.9, 132.3, 135.0, 145.6, 146.4, 155.4, 169.6. Anal. calcd for $C_{18}H_{14}ClNO$: C, 73.10; H, 4.77; N, 4.74%. Found: C, 73.16; H, 4.80; N, 4.86%.

Ethyl 6-chloro-2-methyl-4-phenylquinoline-3-carboxylate (3n). Yield = 89% (0.289 g), m.p. = 99–100 °C (lit.[33] 101 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 0.92 (t, 3H, J = 7.0 Hz), 2.75 (s, 3H), 4.02–4.06 (q, 2H, J = 5.2 Hz), 7.32 (m, 2H), 7.46–7.51 (m, 4H), 7.60–7.62 (m, 1H), 7.97 (d, 1H, J = 9.0 Hz); ^{13}C NMR (DMSO d_6, 125 MHz): δ (ppm) 13.8, 23.7, 61.6, 124.9, 125.7, 129.1, 129.3, 129.4, 129.5, 131.3, 131.4, 131.8, 134.6, 145.1, 145.9, 155.0, 167.5. Anal. calcd for $C_{19}H_{16}ClNO_2$: C, 70.05; H, 4.95; N, 4.30%. Found: C, 70.07; H, 4.92; N, 4.38%.

Methyl 6-chloro-2-methyl-4-phenylquinoline-3-carboxylate (3o). Yield = 91% (0.283 g), m.p. = 136–137 °C (lit.[33] 135 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 2.75 (s, 3H), 3.57 (s, 3H), 7.32–7.34 (m, 2H), 7.49–7.54 (m, 4H), 7.46–7.66 (dd, 1H, J = 2.5, 9.0 Hz), 8.00 (d, 1H, J = 9.0 Hz); ^{13}C NMR (DMSO d_6, 125 MHz): δ (ppm) 24.1, 53.2, 125.3, 126.0, 128.5, 129.4, 129.8, 131.8, 131.9, 132.3, 135.0, 145.6, 146.4, 155.4, 168.6. Anal. calcd for $C_{18}H_{14}ClNO_2$: C, 69.35; H, 4.53; N, 4.49%. Found: C, 69.42; H, 4.59; N, 4.58%.

(6-Chloro-2-methyl-4-phenylquinolin-3-yl)(phenyl)methanone (3p). Yield = 87% (0.311 g), m.p. = 214–216 °C (lit.[25] 209–211 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 2.68 (s, 3H), 7.22 (s, 1H), 7.30–7.35 (m, 5H), 7.50 (t, 1H, J = 7.3 Hz), 7.59–7.62 (m, 3H), 7.71–7.73 (dd, 1H, J = 2.15, 8.9 Hz), 8.11 (d, 1H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 24.4, 125.4, 126.5, 128.9, 129.0, 129.6, 130.3, 131.0, 131.4, 132.9, 133.6, 134.1, 134.5, 137.3, 145.2, 146.6, 155.5, 197.7. Anal. calcd for $C_{23}H_{16}ClNO$: C, 77.20; H, 4.51; N, 3.91%. Found: C, 77.16; H, 4.53; N, 4.03%.

(6-Chloro-2,4-diphenylquinolin-3-yl)(phenyl)methanone (3q). Yield = 83% (0.348 g), m.p. = 170–172 °C, ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.16–7.19 (t, J = 7.7 Hz, 3H), 7.25–7.34 (m, 8H), 7.46 (d, J = 7.0 Hz, 2H), 7.58–7.60 (m, 3H), 7.73 (dd, J = 2.5, 9.0 Hz, 1H), 8.22 (d, J = 8.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 121.2, 125.5, 125.9, 126.3, 126.7, 128.2, 128.6, 129.5, 131.0, 131.5, 132.0, 132.3, 132.4, 133.10, 133.18, 133.6, 134.3, 140.2, 142.9, 152.8, 201.2. Anal. calcd for $C_{28}H_{18}ClNO$: C, 80.09; H, 4.32; N, 3.34%. Found: C, 80.16; H, 4.30; N, 3.32%.

7-Chloro-9-phenyl-1,2,3,4-tetrahydroacridine (3r). Yield = 85% (0.249 g), m.p. = 166–167 °C (lit.[33] 165 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 1.77 (m, 2H), 1.94–1.95 (m, 2H), 2.57–2.59 (m, 2H), 3.15–3.18 (m, 2H), 7.20 (d, 2H, J = 7.0 Hz), 7.26–7.27 (m, 1H), 7.47–7.52 (m, 4H), 7.93 (d, 1H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 23.0, 23.1, 28.4, 34.4, 124.5, 127.6, 129.1, 129.7, 129.8, 130.2, 130.8, 131.4, 136.4, 145.0, 145.7, 160.4. Anal. calcd for $C_{19}H_{16}ClN$: C, 77.68; H, 5.49; N, 4.77%. Found: C, 77.75; H, 5.51; N, 4.85%.

2-*tert*-Butyl-7-chloro-9-phenyl-1,2,3,4-tetrahydroacridine (3s). Yield = 82% (0.286 g), m.p. = 154–155 °C, ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 0.83 (s, 9H), 1.45–1.57 (m, 2H), 2.11–2.13 (m, 1H), 2.26–2.32 (m, 1H), 2.64–2.67 (m, 1H), 3.06–3.13 (m 1H), 3.27–3.31 (m, 1H), 7.20–7.21 (m, 2H), 7.27–7.28 (m, 1H), 7.46–7.53 (m, 4H), 7.93 (d, 1H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 25.1, 30.7, 33.5, 45.2, 125.1, 125.8, 126.7, 126.8, 128.4, 128.9, 129.6, 131.3, 131.7, 132.0, 142.7, 145.8, 146.9, 160.4. Anal. calcd. for $C_{23}H_{24}ClN$: C, 78.95; H, 6.91; N, 4.00%. Found: C, 78.74; H, 6.81; N, 4.13%.

7-Chloro-9-phenyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (3t). Yield = 80% (0.223 g), m.p. = 106–108 °C (lit.[25] 105 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 2.21–2.32 (m, 2H), 2.98 (m, 2H), 2.28 (t, 2H, J = 7.0 Hz), 7.38 (m, 2H), 7.44–7.56 (m, 5H), 8.22 (d, 1H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 23.3, 30.4, 35.0, 124.1, 126.7, 128.3, 128.7, 129.2, 130.3, 131.4, 134.1, 135.6, 141.8, 146.3, 167.5. Anal. calcd. for $C_{18}H_{14}ClN$: C, 77.28; H, 5.04; N, 5.01%. Found: C, 77.21; H, 5.12; N, 5.17%.

9-Amino-3,3-dimethyl-3,4-dihydroacridin-1(*2H*)-one (3u). Yield = 91% (0.218 g), m.p. = 173–175 °C, ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 1.12 (s, 6H), 2.25 (s, 2H), 2.37 (s, 2H), 5.53 (s, 1H), 6.88–7.38 (m, 4H), 8.74 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 28.12, 29.38, 32.51, 43.18, 50.25, 100.54, 125.72, 133.84, 141.38, 159.84, 198.39. Anal. Calcd for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66%. Found: C, 75.07; H, 6.76; N, 11.73%.

9-Amino-3,4-dihydroacridin-1(*2H*)-one (3v). Yield = 94% (0.199 g), m.p. = 208–210 °C (dec.), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 1.91–1.96 (m, 2H), 2.33–2.36 (t, J = 6.0 Hz, 2H), 2.65–2.67 (t, J = 6.0 Hz, 2H), 5.23 (s, 1H), 7.50–7.53 (t, J = 7.0 Hz, 2H), 7.78–7.81 (t, J = 7.5 Hz, 1H), 7.94–7.96 (d, J = 7.5 Hz, 1H), 8.53 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 21.93, 28.71, 34.73, 40.88, 98.98, 110.00, 117.14, 128.29, 128.61, 134.89, 135.46, 141.01, 195.51. Anal. calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20%. Found: C, 74.01; H, 5.65; N, 13.29%.

2,3-Dihydro-1*H*-cyclopenta[*b*]quinolin-9-amine (3w). Yield = 91% (0.167 g), m.p. = 181–183 °C (lit.[29c] 180–182 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 2.17 (m, 2H), 2.79 (t, J = 7.6 Hz, 2H), 3.09 (t, J = 7.5 Hz, 2H), 4.66 (s, 2H), 7.35 (t, J = 8.0 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.77 (d, J = 8.5 Hz, 1H). Anal. calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21%. Found: C, 78.26; H, 6.53; N, 15.26%.

1,2,3,4-Tetrahydroacridin-9-amine (3x). Yield = 93% (0.184 g), m.p. = 177–179 °C (lit.[29c] 178–180 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 1.88–1.93 (m, 4H), 2.51 (t, J = 6.5 Hz, 2H), 3.11 (t, J = 5.5 Hz, 2H), 4.71 (s, 2H), 7.18 (m, 1H), 7.56 (m, 1H), 7.61 (dd, J = 8.5, 1.0 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H). Anal. calcd for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13%. Found: C, 78.77; H, 7.15; N, 14.08%.

7,8,9,10-Tetrahydro-6*H*-cyclohepta[*b*]quinolin-11-amine (3y). Yield = 90% (0.191 g), m.p. = 169–170 °C (lit.[29c] 167–171 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 1.67– 1.90 (m, 6H), 2.71 (m, 2H), 3.22 (m, 2H), 4.63 (s, 2H), 7.43 (m, 1H), 7.65 (m, 1H), 7.71 (dd, J = 8.3, 0.8 Hz, 1H), 7.97 (dd, J = 8.3, 0.60 Hz, 1H). Anal. calcd for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20%. Found: C, 79.27; H, 7.52; N, 13.12%.

6,7,8,9,10,11-Hexahydrocycloocta[*b*]quinolin-12-amine (3z). Yield = 91% (0.205 g), m.p. = 197–199 °C (lit.[29c] 198–200 °C), ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 1.27–1.59 (m, 4H), 1.62–1.96 (m, 4H), 2.89 (m, 2H), 3.07 (m, 2H), 4.82 (s, 2H), 7.44 (m, 1H), 7.67 (m, 1H), 7.76 (dd, J = 8.5, 0.6 Hz, 1H), 7.96 (dd, J = 8.5, 0.6 Hz, 1H). Anal. calcd for $C_{15}H_{18}N_2$: C, 79.61; H, 8.02; N, 12.38%. Found: C, 79.56; H, 8.04; N, 12.41%.

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Notes and references

1 J. H. Clark, D. Macquarrie, *Handbook of Green Chemistry & Technology*; Blackwell Publishers: Oxford, 2002.
2 A. Zare, A. Parhami, A. R. Moosavi-Zare, A. Hasaninejad, A. Khalafi-Nezhad and M. H. Beyzavi, *Can. J. Chem.*, 2009, **87**, 416–421.
3 M. J. Gronnow, R. J. White, J. H. Clark and D. Macquarrie, *Org. Process Res. Dev.*, 2005, **9**, 516–518.
4 C. R. Strauss and R. W. Trainor, *Aust. J. Chem.*, 1995, **48**, 1665–1692.
5 C. R. Strauss, *Aust. J. Chem.*, 1999, **52**, 83–96.
6 B. A. Roberts and C. R. Strauss, *Acc. Chem. Res.*, 2005, **38**, 653–661.
7 D. C. Bailey and S. H. Langer, *Chem. Rev.*, 1981, **81**, 109–148.
8 L. A. Thompson and J. A. Ellman, *Chem. Rev.*, 1996, **96**, 555–600.
9 X. Wang, Z. Quan, F. Wang, M. Wang, Z. Zhang and Z. Li, *Synth. Commun.*, 2006, **36**, 451–456.
10 A. Kiasat and M. F. Mehrjardi, *Catal. Commun.*, 2008, **9**, 1497–1500.
11 X. C. Wang, L. Li, Z. J. Quan, H. P. Gong, H. L. Ye and X. F. Cao, *Chin. Chem. Lett.*, 2009, **20**, 651–655.
12 R. D. Larsen, E. G. Corley, A. O. King, J. D. Carrol, P. Davis, T. R. Verhoeven, P. J. Reider, M. Labelle, J. Y. Gauthier, Y. B. Xiang and R. J. Zamboni, *J. Org. Chem.*, 1996, **61**, 3398–3405.
13 Y. L. Chen, K. C. Fang, J.-Y. Sheu, S. L. Hsu and C. C. Tzeng, *J. Med. Chem.*, 2001, **44**, 2374–2377.
14 G. Roma, M. D. Braccio, G. Grossi, F. Mattioli and M. Ghia, *Eur. J. Med. Chem.*, 2000, **35**, 1021–1035.
15 B. Kalluraya and S. Sreenivasa, *Farmaco*, 1998, **53**, 399–404.
16 D. Doube, M. Blouin, C. Brideau, C. Chan, S. Desmarais, D. Eithier, J. P. Fagueyret, R. W. Friesen, M. Girard, Y. Girard, J. Guay, P. Tagari and R. N. Young, *Bioorg. Med. Chem. Lett.*, 1998, **8**, 1255–1260.
17 A. K. Agarwal and S. A. Jenekhe, *Macromolecules*, 1991, **24**, 6806–6808.
18 (*a*) F. H. Shaw and G. Bentley, *Aust. J. Exp. Biol. Med. Sci.*, 1953, **31**, 573–576; (*b*) E. Heilbronn, *Acta Chem. Scand.*, 1961, **15**, 1386–1390.
19 S. Maayani, H. Weinstein, N. Ben-Zvi, S. Cohen and M. Sokolovsky, *Biochem. Pharmacol.*, 1974, **23**, 1263–1281.
20 A. L. Harvey, E. G. Rowan, *Action of THA, 3,4-diaminopyridine, physostigmine and galanthamine on neuronal K^+ currents at a cholinergic nerve terminal. Current Research in Alzheimer Therapy*; E. Giacobini, R. Becker, ed.; Taylor and Francis: New York, pp. 191–197.
21 (*a*) B. Drukarch, J. E. Leysen and J. C. Stoof, *Life Sci.*, 1988, **42**, 1011–1017; (*b*) J. Sokhwinder, A. Adem, B. Winblad and L. Oreland, *Pharmacol. Toxicol.*, 1992, **71**, 213–215.
22 (*a*) P. N. Kaul, *J. Pharm. Pharmacol.*, 1962, **14**, 243–248; (*b*) J. A. Neilsen, E. E. Mena, I. H. Williams, M. R. Nocerini and D. Liston, *Eur. J. Pharmacol.*, 1989, **173**, 53–64; (*c*) W. McNally, R. Young, H. Brockbrader and T. Chang, *Pharm. Res.*, 1989, **06**, 924–930.
23 S. Glaldiali, G. Chelucci, M. S. Mudadu, M. A. Gastaut and R. P. Thummel, *J. Org. Chem.*, 2001, **66**, 400–405.
24 E. A. Fehnel, *J. Heterocycl. Chem.*, 1967, **4**, 565–570.
25 S. S. Palimkar, S. A. Siddiqui, T. Daniel, R. J. Lahoti and K. V. Srinivasan, *J. Org. Chem.*, 2003, **68**, 9371–9378.
26 S. Ghassamipour and A. R. Sardarian, *Tetrahedron Lett.*, 2009, **50**, 514–519.
27 (*a*) M. Dabiri, M. Baghbanzadeh and E. Arzroomchilar, *Heterocycles*, 2008, **75**, 397–402; (*b*) A. Shaabani, E. Soleimani and Z. Badri, *Synth. Commun.*, 2007, **37**, 629–635; (*c*) A. Shaabani, A. Rahmati and Z. Badri, *Catal. Commun.*, 2008, **9**, 13–16; (*d*) J. S. Yadav, P. P. Rao, D. Sreenu, R. S. Rao, V. N. Kumar, K. Nagaiah and A. R. Prasad, *Tetrahedron Lett.*, 2005, **46**, 7249–7253.
28 (*a*) M. A. Zolfigol, P. Salehi, M. Shiri, T. F. Rastegar and A. Ghaderi, *J. Iran. Chem. Soc.*, 2008, **5**, 490–497; (*b*) M. Shiri and M. A. Zolfigol, *Tetrahedron*, 2009, **65**, 587–598; (*c*) M. A. Zolfigol, P. Salehi, A. Ghaderi, M. Shiri and Z. Tanbakouchian, *J. Mol. Catal. A: Chem.*, 2006, **259**, 253–258.
29 (*a*) L. M. Rodrigues, C. S. Francisco, A. M. F. Oliveira-Campos and A. M. Salaheldin, *Synth. Commun.*, 2008, **38**, 4369–4378; (*b*) P. Camps, X. Formosa, C. Galdeano, T. Go'mez, D. Munoz-Torrero, M. Scarpellini, E. Viayna, A. Badia, M. V. Clos, A. Camins, M. Pallas, M. Bartolini, F. Mancini, V. Andrisano, J. Estelrich, M. Lizondo, A. Bidon-Chanal and F. J. Luque, *J. Med. Chem.*, 2008, **51**, 3588–3598; (*c*) M. T. McKenna, G. R. Proctor, L. C. Young and A. L. Harvey, *J. Med. Chem.*, 1997, **40**, 3516–3523; (*d*) M. C. Desai and P. F. Thadeio, *Tetrahedron Lett.*, 1989, **30**, 5223–5226.
30 C. O. Kappe, *Angew. Chem., Int. Ed.*, 2004, **43**, 6250–6284, and references cited therein.
31 M. Hajek, *Microwaves in Organic Synthesis* (Ed.: A. Loupy), Wiley-VCH, Weinheim, 2002, pp. 345–378.
32 K. Olofsson, S.-Y. Kim, M. Larhed, D. P. Curran and A. Hallberg, *J. Org. Chem.*, 1999, **64**, 4539–4541.
33 R. Ghorbani-Vaghei and S. Akbari-Dadamahaleh, *Tetrahedron Lett.*, 2009, **50**, 1055–1058.
34 S. K. De and R. A. Gibbs, *Tetrahedron Lett.*, 2005, **46**, 1647–1649.
35 D. S. Bose and R. K. Kumar, *Tetrahedron Lett.*, 2006, **47**, 813–816.
36 B. Das, K. Damodar, N. Chowdhury and R. A. Kumar, *J. Mol. Catal. A: Chem.*, 2007, **274**, 148–152.
37 M. Narasimhulu, T. S. Reddy, K. C. Mahesh, P. Prabhakar, Ch. B. Rao and Y. Venkateswarlu, *J. Mol. Catal. A: Chem.*, 2007, **266**, 114–117.

