Reaction of 2-aminobenzamides with indoline-2,3-dione in an ionic liquid in the presence and absence of iodine

Jie Sheng[a], Ke Yang[a], Mei-Mei Zhang[b] and Xiang-Shan Wang[a]*

[a]*School of Chemistry and Chemical Engineering, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Xuzhou Normal University, Xuzhou Jiangsu 221116, P. R. China*

[b]*The Key Laboratory of Biotechnology on Medical Plant of Jiangsu Province, Xuzhou Normal University, Xuzhou Jiangsu 221116, P. R. China*

The reaction of 2-aminobenzamides with indoline-2,3-dione in ionic liquids, selectively gives 1′,3′-dihydrospiro[indolin-2-one-3,2′-quinazolin]-4′-ones in the presence of 5 mol% iodine, while giving 2-(1-acetyl-3-hydroxy-2-oxoindolin-3-ylamino) benzamide derivatives in the absence of iodine. Quinazolinones have great physiological significance and pharmaceutical uses.

Keywords: quinazolinone, 2-aminobenzamide, indoline-2,3-dione, ionic liquids

Quinazolinones are an important class of molecules with physiological significance and pharmaceutical utility.[1–3] In particular, the 4(3*H*)-quinazolinone core, is well-known as a "privileged structure"[4,5] for drug design, which is defined as being present in a class of molecules that are capable of binding to multiple receptors with high affinity.[6,7] The potential therapeutic applications of 4(3*H*)-quinazolinones include anti-inflammatory,[8] antihypertensive,[9] anticancer,[10] antitumour[11] and antibacterial activities.[12]

Although a number of useful synthetic procedures to prepare these compounds have been developed,[13–24] there are still several limitations. For example, most of the procedures involve several steps, give low yields or take place in organic solvents. Thus, a simple, efficient, and green method to synthesise quinazoline would be attractive.

Room temperature ionic liquids (RTILs), especially those based on the 1-*N*-alkyl-3-methyl imidazolium cation, have shown great promise as attractive alternatives to conventional solvents.[25,26]

As a continuation of our research devoted to the development of new methods for the preparation of heterocycles in environmentally benign media,[27,28] we now report the synthesis of 1′,3′-dihydrospiro[indolin-2-one-3,2′-quinazolin]-4′-one derivatives in ionic liquids by a one-pot procedure, involving the reaction of 2-aminobenzamides with indoline-2,3-dione catalysed by iodine.

Results and discussion

Treatment of 2-aminobenzamides **1** with indoline-2,3-dione **2** in the ionic liquid [bmim]Br in the presence of 5 mol% iodine at 80 °C resulted in the corresponding 1′,3′-dihydrospiro [indolin-2-one-3,2′-quinazolin]-4′-one derivatives **3a–j** in high yields (Scheme 1).

Using the conversion of 2-aminobenzamide **1a** (R = H) and indoline-2,3-dione **2** into **3a** as a model, several parameters were explored as shown in Table 1. Compound **3a** was obtained successfully in the presence of various quantities of the catalyst, reaching a maximum of 87% yield with 5 mol% iodine (Table 1, entries 3, 5, and 6). The yield of **3a** was also dependent on temperature (entries 1–4), proceeding smoothly at 80 °C. Different imidazolium ionic liquid were also tested, and [bmim]Br appeared to be the best medium for this transformation (entry 3 *versus* 7–11).

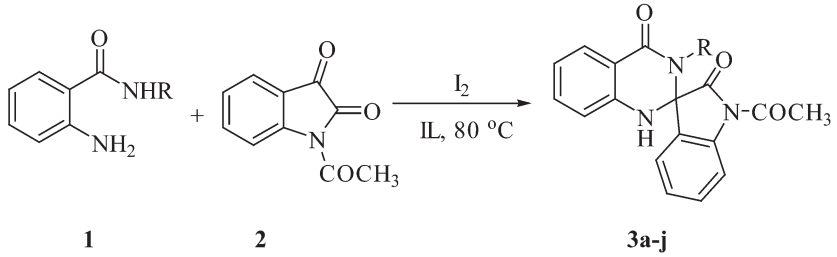
After completion of the reaction as monitored by TLC, products were isolated by simple filtration after the addition of a small amount of water to the cooled reaction mixture. Water in the filtrate was removed by distillation under reduced pressure and the [bmim]Br in the residue could be reused after being heated at 80 °C for 4 h under reduced pressure. Successive reuse of the recycled ionic liquid of [bmim]Br in the model reaction gave high yields of **3a** (85%) even after the fourth cycle.

First of all, these optimised conditions were applied to various kinds of 2-aminobenzamides. They all reacted well to give corresponding spiro[indolin-2-one-3,2′-quinazolin]-4′-one derivatives **3a–j** in good yields (Table 2).

Table 1 Synthetic results of **3a** under different reaction conditions [a]

Entry	Temp./°C	Ionic liquid[b]	I_2 /mol%	Yield/%[c]
1	r.t.	[bmim]Br	5	Trace
2	50	[bmim]Br	5	73
3	80	[bmim]Br	5	87
4	100	[bmim]Br	5	87
5	80	[bmim]Br	10	86
6	80	[bmim]Br	20	86
7	80	[emim]Br	5	82
8	80	[pmim]Br	5	81
9	80	[emim][BF_4]	5	82
10	80	[pmim][BF_4]	5	80
11	80	[bmim][BF_4]	5	84

[a] Reaction condition: 2.0 mL solvent, 2-aminobenzamide (0.136 g, 1.0 mmol), and indoline-2,3-dione (0.189 g, 1.0 mmol).
[b] bmim, 1-butyl-3-methylimidazolium; emim, 1-ethyl-3-methylimidazolium; pmim, 1-propyl-3-methylimidazolium.
[c] Isolated yields.



1 **2** **3a-j**

Scheme 1 Reaction of **1** and **2** at 80 °C catalysed by iodine

* Correspondent. E-mail: xswang1974@yahoo.com

Table 2 Synthetic results of **3** catalysed by iodine[a]

Entry	R	Time/h	Product	Yield/%[b]
1	H	8	**3a**	87
2	$C_6H_5CH_2$	10	**3b**	82
3	$C_6H_5CH_2CH_2$	8	**3c**	90
4	4-$MeOC_6H_4CH_2$	12	**3d**	84
5	4-$MeOC_6H_4(CH_2)_2$	8	**3e**	86
6	Cyclopropyl	9	**3f**	76
7	Naphthalen-2-yl	14	**3g**	72
8	Cyclopentyl	9	**3h**	80
9	4-$MeC_6H_4CH_2$	10	**3i**	90
10	(Furan-2-yl)methyl	10	**3j**	84

[a] Reaction conditions: 2.0 mL [bmim]Br, **1** (1.0 mmol), **2** (0.189 g, 1.0 mmol) and iodine (0.013 g, 0.05 mmol), 80 °C.
[b] Isolated yields.

In order to get more insight into the reaction, we also performed the same reaction in the absence of iodine. Although these reactions proceeded smoothly at 80 °C, they unexpectedly gave 2-(1-acetyl-3-hydroxy-2-oxoindolin-3-ylamino) benzamide derivatives **4a**–**n** (Scheme 2, Table 3). All the products were characterised by IR, ^{1}H and 13C NMR and HRMS, and the analytical data were in good agreement with the proposed structures. The structure of **3h** was additionally confirmed by X-ray diffraction analysis, and its crystal structure is shown in Fig. 1.

Although the detailed mechanism of above reactions is not known, a possible mechanism is shown in Scheme 3. The reaction of **1** and **2** gives **4** in the absence of iodine firstly, and then the iodine works as a milder Lewis acid to help the dehydration reaction to form the Schiff base. Finally, an intra-molecular cyclisation reaction takes place to give **3**.

Table 3 Synthetic results of **4** without iodine[a]

Entry	R	Time/h	Product	Yield/%[b]
1	(*R*)-1-Phenylethyl	6	**4a**	83
2	(*S*)-1-Phenylethyl	6	**4b**	78
3	C_6H_5	8	**4c**	72
4	Cyclohexyl	8	**4d**	86
5	$C_6H_5CH_2CH_2$	6	**4e**	90
6	4-FC_6H_4	10	**4f**	76
7	4-MeC_6H_4	10	**4g**	78
8	H	8	**4h**	89
9	Piperonylethyl	6	**4i**	86
10	*i*-Pr	8	**4j**	78
11	*n*-Bu	6	**4k**	90
12	Et	6	**4l**	85
13	*n*-Pr	6	**4m**	92
14	(Furan-2-yl)methyl	8	**4n**	85

[a] Reaction condition: 2.0 mL [bmim]Br, **1** (1.0 mmol), **2** (0.189 g, 1.0 mmol), 80 °C.
[b] Isolated yields.

Experimental

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a Tensor 27 spectrometer in KBr pellets. ^{1}H NMR spectra were obtained from a solution in DMSO-d_6 with Me_4Si as internal standard using a Bruker-400 spectrometer. HRMS analyses were carried out using a Bruker-micro-TOF-Q-MS analyser.

Synthesis of spiro[indolin-2-one-3,2′-quinazolin]-4′-one derivatives **3***; general procedure*

A dry flask (50 mL) was charged with the 2-aminobenzamide **1** (1.0 mmol), indoline-2,3-dione **2** (0.189 g, 1.0 mmol), iodine (0.013 g, 0.05 mmol), and the ionic liquid [bmim]Br (2.0 mL). The reaction mixture was stirred at 80 °C for 8–14 h, a small amount of water (5 mL) was then added to the mixture, and the resulting yellow solid was filtered off. The water in the filtrate was removed by distillation under reduced pressure, and the ionic liquid in the residue could be reused by being heated at 80 °C for 4 hours under reduced pressure. The crude yellow products were washed with water and purified by recrystallisation from 95% EtOH, the resulting solid was dried at 80 °C for 2 hours under reduced pressure to give **3**.

1-Acetyl-1′H-spiro[indoline-3,2′-quinazoline]-2,4′(3′H)-dione (**3a**): M.p. 281–283 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.55 (s, 3H, CH_3), 6.36 (d, J = 8.0 Hz, 1H, ArH), 6.77 (t, J = 7.6 Hz, 1H, ArH), 7.29 (t, J = 7.6 Hz, 1H, ArH), 7.37 (d, J = 7.6 Hz, 1H, ArH), 7.43 (s, 1H, NH), 7.54 (t, J = 8.0 Hz, 1H, ArH), 7.68 (dd, J = 8.0 Hz, J' = 7.6 Hz, 2H, ArH), 8.16 (d, J = 8.0 Hz, 1H, ArH), 8.38 (s, 1H, NH). IR (KBr): ν 3296, 3122, 3034, 2922, 1776, 1697, 1654, 1608, 1518, 1485, 1412, 1373, 1338, 1305, 1280, 1195, 1166, 1144, 1037, 1017, 797, 786, 763, 754, 710 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{13}N_3O_3$ $[M + Na]^+$ 330.0855; found 330.0869.

1-Acetyl-3′-benzyl-1′H-spiro[indoline-3,2′-quinazoline]-2,4′(3′H)-dione (**3b**): M.p. 245–247 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.13 (s, 3H, CH_3), 3.85 (d, J = 15.2 Hz, 1H, CH), 5.13 (d, J = 15.2 Hz, 1H, CH), 6.65 (d, J = 8.0 Hz, 1H, ArH), 6.72 (d, J = 6.8 Hz, 2H, ArH), 6.82–6.86 (m, 1H, ArH), 7.10–7.19 (m, 3H, ArH), 7.30–7.34 (m, 1H, ArH), 7.35–7.39 (m, 1H, ArH), 7.56 (s, 1H, NH), 7.57–7.61 (m, 1H,

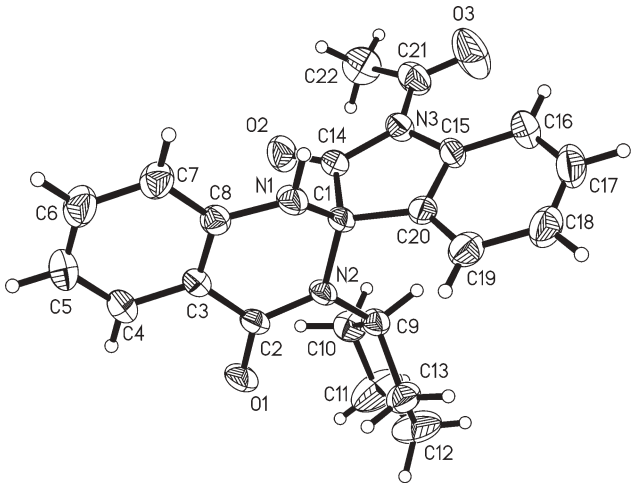
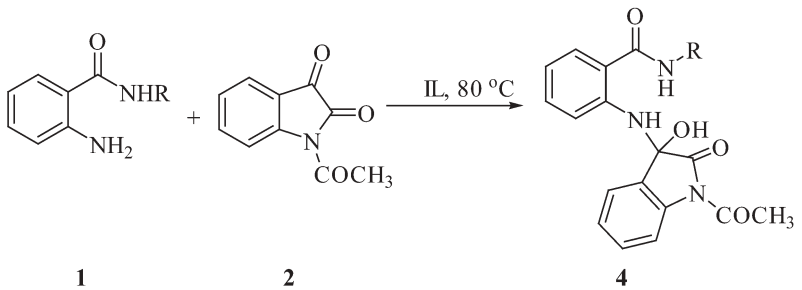
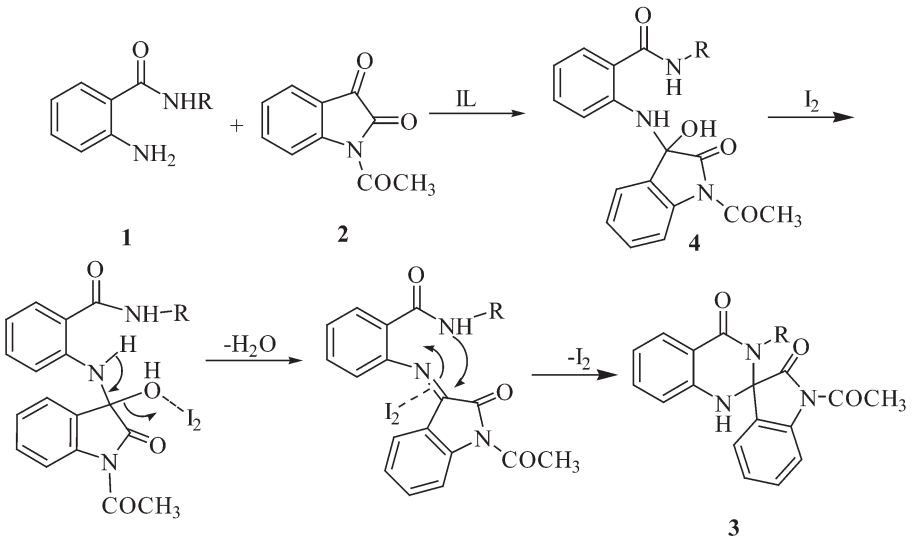


Fig. 1 The crystal structure of the **3h**.



1 **2** **4**

Scheme 2 Reaction of **1** and **2** in the absence of iodine.



Scheme 3 A possible reaction mechanism.

ArH), 7.69 (d, *J* = 7.6 Hz, 1H, ArH), 7.81 (d, *J* = 7.6 Hz, 1H, ArH) , 8.09 (d, *J* = 8.4 Hz, 1H, ArH). IR (KBr): *v* 3213, 3124, 3029, 2954, 1765, 1720, 1622, 1586, 1522, 1491, 1466, 1432, 1384, 1369, 1353, 1331, 1302, 1264, 1239, 1198, 1169, 1157, 1125, 1016, 978, 758, 748, 702 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{24}H_{19}N_3O_3$ $[M + Na]^+$ 420.1324; found 420.1345.

1-Acetyl-3′-phenethyl-1′H-spiro[indoline-3,2′-quinazoline]-2,4′(3′H)-dione (**3c**): M.p. 175–176 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.57 (s, 3H, CH_3), 2.72–2.84 (m, 2H, CH_2), 3.40–3.49 (m, 2H, CH_2), 6.66 (d, *J* = 8.0 Hz, 1H, ArH), 6.78–6.84 (m, 3H, ArH), 7.12–7.19 (m, 3H, ArH), 7.29–7.34 (m, 1H, ArH), 7.43–7.47 (m, 1H, ArH), 7.59 (s, 1H, NH), 7.63–7.67 (m, 1H, ArH), 7.74 (dd, *J* = 7.6 Hz, *J′* = 1.2 Hz, 1H, ArH), 7.79 (d, *J* = 7.2 Hz, 1H, ArH), 8.24 (d, *J* = 8.0 Hz, 1H, ArH). IR (KBr): *v* 3220, 3125, 3069, 3026, 2959, 2940, 1764, 1716, 1623, 1589, 1521, 1490, 1466, 1455, 1434, 1390, 1368, 1351, 1332, 1303, 1266, 1241, 1198, 1168, 1119, 1033, 1015, 761, 744, 697 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{25}H_{21}N_3O_3$ $[M + Na]^+$ 434.1481; found 434.1484.

1-Acetyl-3′-(4-methoxybenzyl)-1′H-spiro[indoline-3,2′-quinazoline]-2,4′(3′H)-dione (**3d**): M.p. 227–229 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.12 (s, 3H, CH_3), 3.65–3.69 (m, 4H, OCH_3+CH), 5.24 (d, *J* = 14.8 Hz, 1H, CH), 6.57–6.59 (m, 2H, ArH), 6.63–6.68 (m, 3H, ArH), 6.83 (t, *J* = 7.6 Hz, 1H, ArH), 7.29–7.33 (m, 1H, ArH), 7.40–7.44 (m, 1H, ArH), 7.53 (s, 1H, NH), 7.59–7.63 (m, 1H, ArH), 7.73 (d, *J* = 7.6 Hz, 1H, ArH), 7.80 (d, *J* = 7.6 Hz, 1H, ArH), 8.11 (d, *J* = 8.0 Hz, 1H, ArH). IR (KBr): *v* 3302, 3011, 2959, 2934, 1763, 1722, 1628, 1612, 1588, 1512, 1485, 1468, 1432, 1377, 1367, 1353, 1334, 1320, 1302, 1290, 1268, 1250, 1199, 1177, 1167, 1111, 1032, 1017, 977, 962, 789, 779, 759, 695 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{25}H_{21}N_3O_4$ $[M + Na]^+$ 450.1430; found 450.1439.

1-Acetyl-3′-(4-methoxyphenethyl)-1′H-spiro[indoline-3,2′-quinazoline]-2,4′(3′H)-dione (**3e**): M.p. 185–187 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.55 (s, 3H, CH_3), 2.64–2.71 (m, 1H, CH), 2.75–2.82 (m, 1H, CH), 3.41–3.69 (m, 5H, OCH_3+CH_2), 6.64–6.70 (m, 3H, ArH), 6.73–6.75 (m, 2H, ArH), 6.80–6.83 (m, 1H, ArH), 7.29–7.33 (m, 1H, ArH), 7.43–7.47 (m, 1H, ArH), 7.58 (s, 1H, NH), 7.62–7.66 (m, 1H, ArH), 7.72–7.74 (m, 1H, ArH), 7.78 (d, *J* = 7.6 Hz, 1H, ArH), 8.25 (d, *J* = 8.4 Hz, 1H, ArH). IR (KBr): *v* 3311, 3066, 3015, 2951, 2933, 2911, 2835, 1769, 1717, 1633, 1514, 1489, 1466, 1400, 1375, 1335, 1300, 1267, 1242, 1199, 1181, 1158, 1124, 1106, 1034, 1016, 968, 827, 779, 758 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{26}H_{23}N_3O_4$ $[M + H]^+$ 442.1767; found 442.1768.

1-Acetyl-3′-cyclopropyl-1′H-spiro[indoline-3,2′-quinazoline]-2,4′(3′H)-dione (**3f**): M.p. 231–232 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 0.30–0.41 (m, 2H, CH_2), 0.46–0.59 (m, 2H, CH_2), 2.16–2.20 (m, 1H, CH), 2.57 (s, 3H, CH_3), 6.33 (d, *J* = 8.0 Hz, 1H, ArH), 6.79 (t, *J* = 7.2 Hz, 1H, ArH), 7.27–7.31 (m, 1H, ArH), 7.38 (t, *J* = 7.6 Hz, 1H, ArH), 7.54 (s, 1H, NH), 7.54–7.58 (m, 1H, ArH), 7.66–7.72 (m, 2H, ArH), 8.22 (d, *J* = 8.0 Hz, 1H, ArH). IR (KBr): *v* 3276, 3124, 3068, 3019, 2955, 1769, 1717, 1644, 1616, 1522, 1489, 1467, 1372, 1350, 1333, 1302, 1265, 1217, 1196, 1164, 1141, 1099, 1028, 1015, 962, 762, 748 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{20}H_{17}N_3O_3$ $[M + Na]^+$ 370.1168; found 370.1174.

SAFETY CAUTION: The preparation of the *N*-(2-naphthyl) -2-aminobenzamide starting material involved 2-naphthylamine. 2-Naphthylamine (β-naphthylamine, naphthalene-2-amine) is a known potent carcinogen. Studies of workers with occupational exposure to it have shown clear evidence of a link between exposure and bladder cancer. In the UK, it appears in Schedule 2 of the Control of Substances Hazardous to Health Regulations (COSHH) 1999 which prohibits its 'manufacture and use for all purposes'.

1-Acetyl-3′-(naphthalen-2-yl)-1′H-spiro[indoline-3,2′-quinazoline]-2,4′(3′H)-dione (**3g**): M.p. 204–205 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.65 (s, 3H, CH_3), 6.78 (d, *J* = 8.0 Hz, 1H, ArH), 6.85–6.89 (m, 1H, ArH),7.17 –7.21 (m, 2H, ArH), 7.24–7.28 (m, 1H, ArH), 7.38–7.42 (m, 1H, ArH), 7.44–7.50 (m, 2H, ArH), 7.56 (s, 1H, NH), 7.74–7.77 (m, 2H, ArH), 7.80–7.86 (m, 5H, ArH). IR (KBr): *v* 3291, 3057, 3013, 2936, 2869, 1771, 1715, 1641, 1507, 1487, 1370, 1334, 1302, 1265, 1236, 1217, 1199, 1168, 1127, 1101, 1062, 1038, 1016, 974, 909, 801, 752 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{27}H_{19}N_3O_3$ $[M + Na]^+$ 456.1324; found 456.1317.

1-Acetyl-3′-cyclopentyl-1′H-spiro[indoline-3,2′-quinazoline]-2,4′(3′H)-dione (**3h**): M.p. 223–225 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 1.18–1.42 (m, 3H, 3CH), 1.50–1.52 (m, 1H, CH), 1.68–1.82 (m, 2H, CH_2), 2.04–2.15 (m, 2H, CH_2), 2.56 (s, 3H, CH_3), 2.92–3.00 (m, 1H, CH), 6.59 (d, *J* = 8.0 Hz, 1H, ArH), 6.75–6.79 (m, 1H, ArH), 7.25–7.29 (m, 1H, ArH), 7.41 (t, *J* = 7.6 Hz, 1H, ArH), 7.49 (s, 1H, NH), 7.56–7.60 (m, 1H, ArH), 7.67 (d, *J* = 8.0 Hz, 2H, ArH), 8.23 (d, *J* = 8.4 Hz, 1H, ArH). IR (KBr): *v* 3360, 3283, 2951, 2869, 1771, 1718, 1695, 1654, 1616, 1512, 1489, 1466, 1449, 1429, 1372, 1347, 1302, 1269, 1235, 1200, 1164, 1116, 1037, 1015, 790, 753, 691 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{22}H_{21}N_3O_3$ $[M + Na]^+$ 376.1661; found 376.1687.

1-Acetyl-3′-(4-methylbenzyl)-1′H-spiro[indoline-3,2′-quinazoline]-2,4′(3′H)-dione (**3i**): M.p. 242–244 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.10 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 3.71 (d, *J* = 15.2 Hz, 1H, CH), 5.21 (d, *J* = 15.2 Hz, 1H, CH), 6.57 (d, *J* = 7.6 Hz, 2H, ArH), 6.64 (d, *J* = 8.0 Hz, 1H, ArH), 6.83 (t, *J* = 7.6 Hz, 1H, ArH), 6.92 (d, *J* = 8.0 Hz, 2H, ArH), 7.29 –7.33 (m, 1H, ArH), 7.38–7.42 (m, 1H, ArH), 7.54 (s, 1H, NH), 7.58–7.62 (m, 1H, ArH), 7.72 (d, *J* = 7.6 Hz, 1H, ArH), 7.80 (d, *J* = 7.6 Hz, 1H, ArH), 8.09 (d, *J* = 8.4 Hz, 1H, ArH). IR (KBr): *v* 3331, 3044, 2945, 1758, 1722, 1631, 1614, 1591, 1511, 1488, 1468, 1435, 1416, 1372, 1351, 1334, 1310, 1299, 1269, 1236, 1196, 1180, 1168, 1114, 1039, 1016, 970, 960, 950, 767, 754, 692 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{25}H_{21}N_3O_3$ $[M + Na]^+$ 434.1481; found 434.1512.

1-Acetyl-3'-(furan-2-ylmethyl)-1'H-spiro[indoline-3,2'-quinazoline]-2,4'(3'H)-dione **(3j)**: M.p. 204–205 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.32 (s, 3H, CH_3), 3.81 (d, J = 15.6 Hz, 1H, CH), 5.16 (d, J = 15.6 Hz, 1H, CH), 5.67 (d, J = 2.8 Hz, 1H, ArH), 6.23–6.24 (m, 1H, ArH), 6.64 (d, J = 8.0 Hz, 1H, ArH), 6.82 (t, J = 7.2 Hz, 1H, ArH), 7.29 –7.33 (m, 1H, ArH), 7.41–7.47 (m, 2H, ArH), 7.58 (s, 1H, NH), 7.59–7.63 (m, 1H, ArH), 7.72 (d, J = 7.6 Hz, 2H, ArH), 8.19 (d, J = 8.0 Hz, 1H, ArH). IR (KBr): ν 3323, 3131, 3056, 2946, 1766, 1722, 1636, 1613, 1593, 1507, 1487, 1468, 1429, 1387, 1368, 1347, 1332, 1299, 1269, 1237, 1202, 1172, 1121, 1011, 979, 968, 755 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{22}H_{17}N_3O_4$ [M + Na]$^+$ 410.1117; found 410.1144.

Synthesis of 2-(1-acetyl-3-hydroxy-2-oxoindolin-3-ylamino) benzamide derivatives **4***; general procedure*

A dry flask (50 mL) was charged with the 2-aminobenzamide **1** (1.0 mmol), indoline-2,3-dione **2** (0.189 g, 1.0 mmol), and the ionic liquid [bmim]Br (2 mL). The reaction mixture was stirred at 80 °C for 6-10 h, and then a small amount of water (5 mL) was added to the mixture, and the generated yellow solid was filtered off. The water in the filtrate was removed by distillation under reduced pressure, and the ionic liquid in the residue could be reused by being evaporated at 80 °C for 4 h under reduced pressure. The crude solid was washed with water and purified by recrystallisation from 95% EtOH to give **4**.

2-((1-Acetyl-3-hydroxy-2-oxoindolin-3-yl)amino)-N-((R)-1-phenylethyl) benzamide **(4a)**: M.p. 201–202 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 1.51 (d, J = 6.8 Hz, 3H, CH_3), 1.93 (s, 3H, CH_3), 5.21–5.28 (m, 1H, CH), 7.23–7.29 (m, 3H, ArH), 7.34–7.39 (m, 3H, ArH), 7.44–7.46 (m, 2H, ArH), 7.56–7.61 (m, 3H, ArH), 7.94 (d, J = 7.6 Hz, 1H, ArH), 8.53 (d, J = 8.4 Hz, 1H, ArH), 9.17 (d, J = 8.0 Hz, 1H, NH), 10.41 (s, 1H, NH), 12.30 (s, 1H, OH). IR (KBr): ν 3337, 3299, 3275, 3238, 3104, 3065, 3032, 2975, 2934, 1709, 1694, 1625, 1580, 1519, 1449, 1370, 1318, 1297, 1258, 1228, 1182, 1164, 1127, 990, 887, 757, 728, 700 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{25}H_{23}N_3O_4$ [M + Na]$^+$ 452.1586; found 452.1599.

2-((1-Acetyl-3-hydroxy-2-oxoindolin-3-yl)amino)-N-((S)-1-phenylethyl) benzamide **(4b)**: M.p. 200–201 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 1.51 (d, J = 6.8 Hz, 3H, CH_3), 1.93 (s, 3H, CH_3), 5.21–5.28 (m, 1H, CH), 7.22–7.29 (m, 3H, ArH), 7.34–7.37 (m, 3H, ArH), 7.45 (d, J = 8.0 Hz, 2H, ArH), 7.56–7.60 (m, 3H, ArH), 7.95 (d, J = 8.0 Hz, 1H, ArH), 8.53 (d, J = 8.0 Hz, 1H, ArH), 9.18 (d, J = 8.0 Hz, 1H, NH), 10.42 (s, 1H, NH), 12.31 (s, 1H, OH). ^{13} C NMR (DMSO-d_6, 100 MHz): δ_C 22.1, 23.3, 48.5, 119.86, 119.88, 121.63, 121.66, 123.4, 123.7, 126.0, 126.7, 128.3, 128.6, 130.0, 132.1, 132.4, 136.0, 137.9, 144.4, 159.6, 167.0, 168.6, 187.3. IR (KBr): ν 3336, 3276, 3238, 3065, 3032, 2975, 2934, 1709, 1694, 1625, 1580, 1519, 1449, 1371, 1319, 1297, 1258, 1228, 1182, 1164, 1127, 990, 887, 757, 700 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{25}H_{23}N_3O_4$ [M + H]$^+$ 430.1767; found 430.1755.

2-((1-Acetyl-3-hydroxy-2-oxoindolin-3-yl)amino)-N-phenylbenzamide **(4c)**: M.p. 237–239 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 1.96 (s, 3H, CH_3), 7.15–7.18 (m, 1H, ArH), 7.24 (t, J = 7.2 Hz, 1H, ArH), 7.31–7.35 (m, 1H, ArH), 7.38–7.43 (m, 3H, ArH), 7.56–7.65 (m, 3H, ArH), 7.76–7.78 (m, 2H, ArH), 7.93 (d, J = 7.6 Hz, 1H, ArH), 8.46 (d, J = 8.0 Hz, 1H, ArH), 10.45 (s, 1H, NH), 10.56 (s, 1H, NH), 11.77 (s, 1H, OH). IR (KBr): ν 3323, 3287, 3106, 3063, 1699, 1668, 1660, 1639, 1623, 1599, 1578, 1511, 1447, 1433, 1362, 1326, 1298, 1254, 1223, 1160, 1121, 1002, 984, 890, 754, 713, 694 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{23}H_{19}N_3O_4$ [M + Na]$^+$ 424.1273; found 424.1275.

2-((1-Acetyl-3-hydroxy-2-oxoindolin-3-yl)amino)-N-cyclohexylbenzamide **(4d)**: M.p. 203–205 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 1.10–1.18 (m, 1H, CH), 1.29–1.40 (m, 4H, 2CH_2), 1.63 (d, J = 11.6 Hz, 1H, CH), 1.75–1.76 (m, 2H, CH_2), 1.85–1.86 (m, 2H, CH_2), 1.95 (s, 3H, CH_3), 3.81–3.83 (m, 1H, CH), 7.21–7.28 (m, 2H, ArH), 7.36–7.39 (m, 1H, ArH), 7.53–7.62 (m, 3H, ArH), 7.80 (d, J = 7.6 Hz, 1H, ArH), 8.51 (d, J = 8.4 Hz, 1H, ArH), 8.59 (d, J = 7.6 Hz, 1H, NH), 10.42 (s, 1H, NH), 12.32 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 24.9, 25.5, 25.6, 33.0, 48.9, 118.4, 120.9, 121.3, 121.5, 122.4, 124.1, 126.6, 132.7, 134.4, 136.5, 138.5, 142.5, 160.9, 167.6, 169.5, 191.4. IR (KBr): ν 3402, 3309, 2932, 2849, 1689, 1634, 1579, 1515, 1448, 1370, 1339, 1297, 1256, 1222, 1162, 1127, 1058, 885, 857, 753, 697 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{23}H_{25}N_3O_4$ [M + Na]$^+$ 430.1743; found 430.1755.

2-((1-Acetyl-3-hydroxy-2-oxoindolin-3-yl)amino)-N-phenethylbenzamide **(4e)**: M.p. 192–193 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 1.95 (s, 3H, CH_3), 2.88–2.92 (m, 2H, CH_2), 3.52–3.57 (m, 2H, CH_2), 7.20–7.34 (m, 7H, ArH), 7.37–7.40 (m, 1H, ArH), 7.55–7.63 (m, 3H, ArH), 7.75 (d, J = 8.0 Hz, 1H, ArH), 8.54 (d, J = 8.4 Hz, 1H, ArH), 8.92 (t, J = 6.4 Hz, 1H, NH), 10.43 (s, 1H, NH), 12.40 (s, 1H, OH). ^{13} C NMR ($CDCl_3$, 100 MHz): δ_C 25.6, 35.4, 41.1, 118.5, 120.9, 121.0, 121.5, 122.4, 124.1, 126.5, 126.8, 128.78, 128.84, 132.8, 134.4, 136.5, 138.47, 138.51, 142.5, 160.9, 168.5, 169.4, 191.3. IR (KBr): ν 3388, 3281, 3107, 3061, 3030, 2948, 1688, 1637, 1579, 1513, 1447, 1368, 1327, 1295, 1256, 1228, 1195, 1180, 1161, 1124, 1107, 1049, 1004, 983, 886, 860, 754, 699 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{25}H_{23}N_3O_4$ [M + Na]$^+$ 452.1586; found 452.1597.

2-((1-Acetyl-3-hydroxy-2-oxoindolin-3-yl)amino)-N-(4-fluorophenyl) benzamide **(4f)**: M.p. 224–225 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 1.96 (s, 3H, CH_3), 7.22–7.27 (m, 3H, ArH), 7.33 (t, J = 7.6 Hz, 1H, ArH), 7.40–7.43 (m, 1H, ArH), 7.56–7.65 (m, 3H, ArH), 7.77–7.80 (m, 2H, ArH), 7.92 (d, J = 7.6 Hz, 1H, ArH), 8.46 (d, J = 8.0 Hz, 1H, ArH), 10.46 (s, 1H, NH), 10.64 (s, 1H, NH), 11.77 (s, 1H, OH). IR (KBr): ν 3308, 3066, 1687, 1644, 1608, 1578, 1521, 1447, 1402, 1371, 1335, 1295, 1261, 1214, 1162, 1125, 1101, 1084, 1058, 1013, 986, 902, 884, 858, 836, 754 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{23}H_{18}FN_3O_4$ [M + Na]$^+$ 442.1179; found 442.1187.

2-((1-Acetyl-3-hydroxy-2-oxoindolin-3-yl)amino)-N-(4-methylphenyl) benzamide **(4g)**: M.p. 248–249 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 1.96 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 7.19–7.26 (m, 3H, ArH), 7.32 (t, J = 7.6 Hz, 1H, ArH), 7.41 (d, J = 8.0 Hz, 1H, ArH), 7.56–7.66 (m, 5H, ArH), 7.92 (d, J = 7.6 Hz, 1H, ArH), 8.47 (d, J = 8.4 Hz, 1H, ArH), 10.45 (s, 1H, NH), 10.51 (s, 1H, NH), 11.83 (s, 1H, OH). IR (KBr): ν 3290, 3107, 3033, 2923, 1698, 1638, 1579, 1510, 1447, 1404, 1365, 1325, 1295, 1255, 1161, 1123, 1053, 1003, 984, 908, 886, 815, 759 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{24}H_{21}N_3O_4$ [M + Na]$^+$ 438.1430; found 438.1445.

2-((1-Acetyl-3-hydroxy-2-oxoindolin-3-yl)amino)benzamide **(4h)**: M.p. 217–218 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 1.95 (s, 3H, CH_3), 7.20–7.27 (m, 2H, ArH), 7.35 (d, J = 8.0 Hz, 1H, ArH), 7.55–7.61 (m, 3H, ArH), 7.80 (s, 1H, NH), 7.86 (d, J = 8.0 Hz, 1H, ArH), 8.34 (s, 1H, NH), 8.57 (d, J = 8.4 Hz, 1H, ArH), 10.42 (s, 1H, NH), 12.69 (s, 1H, OH). ^{13} C NMR (DMSO-d_6, 100 MHz): δ_C 23.2, 119.8, 120.7, 121.7, 123.3, 123.7, 126.9, 128.8, 130.0, 132.3, 132.4, 136.0, 138.4, 159.6, 168.7, 170.3, 187.4. IR (KBr): ν 3412, 3217, 3116, 1694, 1650, 1610, 1580, 1518, 1449, 1398, 1337, 1297, 1258, 1232, 1160, 1126, 886, 757 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{17}H_{15}N_3O_4$ [M + Na]$^+$ 348.0960; found 348.0992.

2-((1-Acetyl-3-hydroxy-2-oxoindolin-3-yl)amino)-N-piperonylethylbenzamide **(4i)**: M.p. 211–213 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 1.95 (s, 3H, CH_3), 2.79–2.83 (m, 2H, CH_2), 3.47–3.52 (m, 2H, CH_2), 5.96 (s, 2H, CH_2), 6.71–6.73 (m, 1H, ArH), 6.82–6.86 (m, 2H, ArH), 7.21–7.28 (m, 2H, ArH), 7.36–7.39 (m, 1H, ArH), 7.54–7.62 (m, 3H, ArH), 7.74 (d, J = 7.6 Hz, 1H, ArH), 8.53 (d, J = 8.4 Hz, 1H, ArH), 8.87 (t, J = 6.4 Hz, 1H, NH), 10.43 (s, 1H, NH), 12.38 (s, 1H, OH). IR (KBr): ν 3352, 3287, 3184, 3115, 3071, 2932, 2901, 1687, 1642, 1583, 1518, 1448, 1372, 1325, 1298, 1251, 1190, 1165, 1128, 1105, 1037, 992, 936, 924, 888, 872, 806, 755 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{26}H_{23}N_3O_6$ [M + Na]$^+$ 496.1485; found 496.1516.

2-((1-Acetyl-3-hydroxy-2-oxoindolin-3-yl)amino)-N-isopropylbenzamide **(4j)**: M.p. 178–180 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 1.20 (d, J = 6.4 Hz, 6H, 2CH_3), 1.94 (s, 3H, CH_3), 4.09–4.22 (m, 1H, CH), 7.21–7.27 (m, 2H, ArH), 7.36 (d, J = 8.0 Hz, 1H, ArH), 7.54–7.62 (m, 3H, ArH), 7.81 (d, J = 8.0 Hz, 1H, ArH), 8.52 (d, J = 8.4 Hz, 1H, ArH), 8.61 (d, J = 7.6 Hz, 1H, NH), 10.44 (s, 1H, NH), 12.36 (s, 1H, OH). ^{13} C NMR ($CDCl_3$, 100 MHz): δ_C 22.7, 25.6, 42.2, 113.2, 118.4, 120.9, 121.2, 122.4, 124.1, 126.6, 132.7, 134.4, 136.5, 138.5, 142.5, 161.0, 163.1, 169.4, 191.4. IR (KBr): ν 3298, 3109, 3069, 2979, 2933, 1769, 1713, 1697, 1635, 1606, 1585, 1518, 1449, 1371, 1340, 1300, 1257, 1229, 1204, 1162, 1147, 1131, 888, 781, 756, 692 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{20}H_{21}N_3O_4$ [M + Na]$^+$ 390.1430; found 390.1447.

2-((1-Acetyl-3-hydroxy-2-oxoindolin-3-yl)amino)-N-(n-butyl) benzamide **(4k)**: M.p. 180–181 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 0.92 (t, J = 7.2 Hz, 3H, CH_3), 1.34–1.41 (m, 2H, CH_2), 1.51–1.59 (m, 2H, CH_2), 1.95 (s, 3H, CH_3), 3.28–3.33 (m, 2H, CH_2), 7.21–7.27 (m, 2H, ArH), 7.36 (d, J = 8.0 Hz, 1H, ArH), 7.54–7.62 (m, 3H, ArH), 7.80 (d, J = 7.6 Hz, 1H, ArH), 8.54 (d, J = 8.0 Hz, 1H, ArH), 8.81 (t, J = 5.2 Hz, 1H, NH), 10.42 (s, 1H, NH), 12.42 (s, 1H, OH). ^{13} C NMR

($CDCl_3$, 100 MHz): δ_C 13.7, 20.2, 25.6, 31.5, 39.9, 118.5, 120.9, 121.2, 121.5, 122.4, 124.1, 126.6, 132.7, 134.3, 136.5, 138.5, 142.5, 161.0, 168.5, 169.4, 191.3. IR (KBr): *v* 3381, 3319, 3083, 3061, 2958, 2934, 2873, 2856, 1686, 1640, 1598, 1580, 1518, 1447, 1371, 1337, 1296, 1261, 1231, 1181, 1162, 1126, 1107, 884, 751 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{21}H_{23}N_3O_4$ $[M + Na]^+$ 404.1586; found 404.1612.

2-((1-Acetyl-3-hydroxy-2-oxoindolin-3-yl)amino)-N-ethylbenzamide (**4l**): M.p. 153–154 °C; ^1H NMR (DMSO-d_6, 400 MHz): δ_H 1.17 (t, J = 7.2 Hz, 3H, CH_3), 1.95 (s, 3H, CH_3), 3.30–3.33 (m, 2H, CH_2), 7.24 (dd, $J = J'$ = 8.0 Hz, 2H, ArH), 7.36 (d, J = 8.4 Hz, 1H, ArH), 7.56 (t, J = 8.0 Hz, 3H, ArH), 7.81 (d, J = 8.0 Hz, 1H, ArH), 8.54 (d, J = 8.4 Hz, 1H, ArH), 8.83 (t, J = 4.8 Hz, 1H, NH), 10.43 (s, 1H, NH), 12.47 (s, 1H, OH). ^{13} C NMR ($CDCl_3$, 100 MHz): δ_C 14.7, 25.6, 35.1, 118.4, 120.9, 121.0, 121.5, 122.4, 124.1, 126.7, 132.8, 134.4, 136.5, 138.5, 142.5, 160.9, 168.4, 169.4, 191.3. IR (KBr): *v* 3392, 3319, 3104, 3061, 2975, 2934, 2877, 1688, 1656, 1635, 1605, 1578, 1516, 1445, 1371, 1330, 1297, 1277, 1227, 1179, 1161, 1122, 987, 885, 752, 699 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{19}H_{19}N_3O_4$ $[M + Na]^+$ 376.1273; found 376.1295.

2-((1-Acetyl-3-hydroxy-2-oxoindolin-3-yl)amino)-N-(n-propyl) benzamide (**4m**): M.p. 160–161 °C; ^1H NMR (DMSO-d_6, 400 MHz): δ_H 0.93 (t, J = 7.6 Hz, 3H, CH_3), 1.53–1.62 (m, 2H, CH_2), 1.95 (s, 3H, CH_3), 3.26 (dd, $J = J'$ = 6.4 Hz, 2H, CH_2), 7.22–7.27 (m, 2H, ArH), 7.36 (d, J = 8.0 Hz, 1H, ArH), 7.54–7.61 (m, 3H, ArH), 7.81 (d, J = 8.0 Hz, 1H, ArH), 8.54 (d, J = 8.4 Hz, 1H, ArH), 8.83 (t, J = 5.2 Hz, 1H, NH), 10.43 (s, 1H, NH), 12.43 (s, 1H, OH). IR (KBr): *v* 3388, 3322, 3105, 3056, 2961, 2932, 2867, 1775, 1689, 1657, 1636, 1606, 1580, 1549, 1446, 1371, 1336, 1298, 1283, 1260, 1228, 1162, 1125, 1107, 884, 751 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{20}H_{21}N_3O_4$ $[M + Na]^+$ 390.1430; found 390.1458.

2-((1-Acetyl-3-hydroxy-2-oxoindolin-3-yl)amino)-N-(furan-2-ylmethyl) benzamide (**4n**): M.p. 188–189 °C; ^1H NMR (DMSO-d_6, 400 MHz): δ_H 1.95 (s, 3H, CH_3), 4.52 (d, J = 5.6 Hz, 2H, CH_2), 6.36 (d, J = 3.2 Hz, 1H, ArH), 6.43 (s, 1H, ArH), 7.22–7.27 (m, 2H, ArH), 7.36 (d, J = 8.0 Hz, 1H, ArH), 7.56–7.62 (m, 4H, ArH), 7.85 (d, J = 7.6 Hz, 1H, ArH), 8.56 (d, J = 8.4 Hz, 1H, ArH), 9.34 (t, J = 5.2 Hz, 1H, NH), 10.43 (s, 1H, NH), 12.43 (s, 1H, OH). IR (KBr): *v* 3344, 3277, 3254, 3168, 3123, 3091, 2995, 1687, 1673, 1643, 1582, 1524, 1452, 1366, 1329, 1310, 1296, 1284, 1259, 1232, 1191, 1164, 1146, 1011, 886, 791, 767, 755 cm^{-1}. HRMS (ESI, *m/z*): Calcd for $C_{22}H_{19}N_3O_5$ $[M + Na]^+$ 428.1222; found 428.1250.

Conclusion

In summary, a mild, facile and environmentally benign method has been developed for the synthesis of 1′,3′-dihydrospiro [indolin-2-one-3,2′-quinazolin]-4′-one and 2-(1-acetyl-3-hydroxy-2-oxoindolin-3-ylamino)benzamide derivatives in high yields in ionic liquids. The advantages of this procedure include mild reaction conditions, high yields, one-pot procedure, operational simplicity and being environmentally benign.

We are grateful to the National Natural Science foundation of China (20802061), the Priority Academic Program Development of the Jiangsu Higher Education Institutions and the Qing Lan Project (08QLT001, 10QLD008) of the Jiangsu Education Committee for financial support.

Crystallographic data for the structure of **3h** reported in this paper has been deposited at the Cambridge Crystallographic Data Centre as supplementary publication with No. CCDC-855710, respectively. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or E-mail: deposit@ccdc.cam.ac.uk).

Received 6 September 2011; accepted 10 February 2012
Paper 1100878 doi: 10.3184/174751912X13303708813998
Published online: 22 March 2012

References

1 D.W. Fry, A.J. Kraker, A. McMichael, L.A. Ambroso, J.M. Nelson, W.R. Leopold, R.W. Connors and A.J. Bridges, *Science*, 1994, **265**, 1093.
2 S.E.D. Laszlo, R.S. Chang, T.B. Cheng, K.A. Faust, W.J. Greenlee, S.D. Kivlighn, V.J. Lotti, S.S. O'Malley, T.W. Schorn, P.K. Siegl, J. Tran and G.J. Zingaro, *Bioorg. Med. Chem. Lett.*, 1995, **5**, 1359.
3 S. Johne, *Pharmazie*, 1981, **36**, 583.
4 D.A. Horton, G.T. Bourne and M.L. Smythe, *Chem. Rev.*, 2003, **103**, 893.
5 J.F. Liu, C.J. Wilson, P. Ye, K. Sprague, K. Sargent, Y. Si, G. Beletsky, D. Yohannes and S.C. Ng, *Bioorg. Med. Chem. Lett.*, 2006, **16**, 686.
6 B.E. Evans, K.E. Rittle, M.G. Bock, R.M. DiPardo, R.M. Freidinger, W.L. Whitter, G.F. Lundell, D.F. Veber, P.S. Anderson, R.S.L. Chang, V.J. Lotti, D.J. Cerino, T.B. Chen, P.J.Kling, K.A. Kunkel, J.P. Springer and J. Hirshfieldt, *J. Med. Chem.*, 1988, **31**, 2235.
7 C.D. Duarte, E.J. Barreiro and C.A.M. Fraga, *Mini.-Rev. Med. Chem.*, 2007, **7**, 1108.
8 V. Alagarsamy, V. Raja Solomon and K. Dhanabal, *Bioorg. Med. Chem.*, 2007, **15**, 235.
9 V. Alagarsamy and U.S. Pathak, *Bioorg. Med. Chem.*, 2007, **15**, 3457.
10 V. Murugan, M. Kulkarni, R.M. Anand, E.P. Kumar, B. Suresh and V.M. Reddy, *Asian J. Chem.*, 2006, **18**, 900.
11 A.A.A. Godfrey, PCT Int. Appl. WO 2005012260 A2 10 Feb 2005, *Chem. Abstr.*, 2005, **142**, 198095.
12 P. Selvam, K. Girija, G. Nagarajan and E. De Clerco, *Indian J. Pharm. Sci.*, 2005, **67**, 484.
13 A. Shaabani, A. Maleki and H. Mofakham, *Synth. Commun.*, 2008, **38**, 3751.
14 M. Rueping, A.P. Antonchick, E. Sugiono and K.A. Grenader, *Angew. Chem. Int. Ed.*, 2009, **48**, 908.
15 H.L. Yale and M. Kalkstein, *J. Med. Chem.*, 1967, **10**, 334.
16 M. Baghbanzadeh, P. Salehi, M. Dabiri and G. Kozehgarya, *Synthesis*, 2006, 344.
17 J.X. Chen, W.K. Su, H.Y. Wu, M.C. Liu and C. Jin, *Green Chem.*, 2007, **9**, 972.
18 D.Q. Shi, J.X. Wang, L.C. Rong, Q.Y. Zhuang, S.J. Tu and H.W. Hu, *J. Chem. Res.*, 2003, 671.
19 J. Bergman, R. Engqvist, C. Stålhandske and H. Wallberg, *Tetrahedron*, 2003, **59**, 1033.
20 A. Shaabani, A. Maleki and H. Mofakham, *Synth. Commun.*, 2008, **38**, 3751.
21 X. Cheng, S. Vellalath, R. Goddard and B. List, *J. Am. Chem. Soc.* 2008, **130**, 15786.
22 M. Dabiri, Ali A. Mohammadi and H. Qaraat, *Monatsch. Chem.*, 2009, **140**, 401.
23 B.V. Subba Reddy, A. Venkateswarlu, C. Madan and A. Vinu, *Tetrahedron, Lett.* 2011, **52**, 1891.
24 G. Lesma, N. Landoni, T. Pilati, A. Sacchetti and A. Silvani, *J. Org. Chem.*, 2009, **74**, 4537.
25 J. Dupont, R.F. De Souza and P.A.Z. Suarez, *Chem. Rev.*, 2002, **102**, 3667.
26 M.A.P. Martins, C.P. Frizzo, D.N. Moreira, N. Zanatta and H.G. Bonacorso, *Chem. Rev.*, 2008, **108**, 2015.
27 X.S. Wang, J.R. Wu, J. Zhou and S.J. Tu, *J. Comb. Chem.*, 2009, **11**, 1011.
28 X.S. Wang, K. Yang, J. Zhou and S.J. Tu, *J. Comb. Chem.*, 2010, **12**, 417.