The cyclisation of 2'-aminochalcones using silica-supported $Yb(OTf)_3$ under solvent-free conditions

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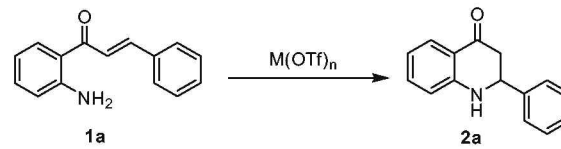
Silica-supported $Yb(OTf)_3$ is utilised as a catalyst for the synthesis of 2-substituted dihydroquinolinones from 2'-amino chalcones in good yields. The catalyst is easily prepared and is active under solvent-free conditions and environmentally friendly conditions.

Keywords: 2'-aminochalcones, $Yb(OTf)_3$, solventless, dihydroquinolinones

2-Substitued dihydroquinolinones display various important pharmacological activities and can also be utilised as valuable precursors for the synthesis of medicinally important compounds.[1-3] The catalysts used previously for their synthesis are homogeneous, hazardous and corrosive acids or bases such as H_3PO_4 or NaOEt. They are well known for their corrosive properties and the troublesome workup procedure as well as for excessive waste production.[4,5] Donnelly and his group reported that 2-substitued dihydroquinolinones can be obtained from the cyclisation of 2'-aminochalcones by using orthophosphoric acid in acetic acid.[6] Perumal *et al.* demonstrated that 2-aminochalcones can be cyclised by using silica gel supported $InCl_3$ as a catalyst under microwave irradiation to give 2-aryl-2,3-dihydroquinolin-4(1*H*)-ones.[7] In general, these procedures are associated with the use of corrosive acid, strong alkali or long reaction times. In addition, many of the existing procedures are of limited synthetic scope due to low yields, the need for large amount of catalyst, microwave activation[8] and specialised solvents. Therefore, designing a novel and efficient procedure for preparation of dihydroquinolinones has achieved synthetic importance.

During the last decade, metal triflates have been widely used as Lewis acids in various organic syntheses.[9-12] In many cases, they are reported to be of low toxicity, high stability, and are easy to handle and recover from water unlike $AlCl_3$, $ZnCl_2$, and $TiCl_4$.[13] In continuation of our studies on the synthesis of these heterocyclic compounds, we report an efficient and simple method for the synthesis of 2-substituted dihydroquinolinones from the cyclisation of the 2'-aminochalcones and its analogues using $Yb(OTf)_3$ as catalyst. In detailed studies of this reaction, we find that $Yb(OTf)_3$ impregnated on silica gel has better catalytic properties than $Yb(OTf)_3$ in solution. The salient features of $Yb(OTf)_3$ absorbed on silica gel are the rapid reaction rates, absence of unwanted products, improved and operational simplicity under conventional heating. However, to the best of our knowledge, there is no report on the use of this catalyst in such cyclisation reactions.



1a **2a**

Scheme 1

Preliminary experiments were carried out using (*E*)-1-(2-aminophenyl)-3-phenylprop-2-en-1-one as a typical reactant. In order to optimise the reaction conditions, various factors including catalysts, solvents, reaction temperature and time were investigated. The results are summarised in Table 1.

As shown in Table 1, we found that among organic solvents, CH_3CN was the preferred solvent for the synthesis of **1a** compared to other solvents under similar reaction conditions (Table 1 entries 1–6). Secondly a higher loading of the catalyst had no significant influence on the reaction yield, while temperature is an important factor, when the temperature was lowered to room temperature, the yield was lower even after long reaction time (Table 1 entries 1–3). Thirdly the use of silica-supported $Yb(OTf)_3$ as catalyst under solvent-free condition gave much better results compared to $Yb(OTf)_3$ in solution (Table 1 entries 1, 8). Among all the metal triflate catalysts we used, $Yb(OTf)_3$ was particularly effective for this cyclisation reaction with a short reaction time and higher yield (Table1 entries 8–12). In the absence of $Yb(OTf)_3$, there was no reaction in solution. On the other hand, 55% yield of **1a** was obtained in the presence of silica gel alone (Table 1 entries 7, 13).

Table 1 The synthesis of 2-phenyl-2,3-dihydroquinolin-4(1*H*)-one under different reaction conditions[a]

Entry	Catalyst	Loading/mol%	Solvent	Temp./°C	Time/h	Yield[b]/%
1	$Yb(OTf)_3$	5	MeCN	Reflux	4	89
2	$Yb(OTf)_3$	10	MeCN	Reflux	4	90
3	$Yb(OTf)_3$	5	MeCN	r. t.	15	20
4	$Yb(OTf)_3$	5	PhMe	Reflux	4	85
5	$Yb(OTf)_3$	5	CH_3NO_2	Reflux	4	86
6	$Yb(OTf)_3$	5	MeOH	Reflux	10	60
7	No catalyst	0	MeCN	Reflux	15	0
8	$Yb(OTf)_3$-Silica	5	No	80	2	95
9	$Y(OTf)_3$-Silica	5	No	80	3	90
10	$Mg(OTf)_2$-Silica	5	No	80	10	56
11	$Cu(OTf)_2$-Silica	5	No	80	10	50
12	$Sr(OTf)_2$-Silica	5	No	80	8	68
13	Silica	0	No	80	15	55

[a]All reactions were run with 1.0 mmol **1a** under different reaction conditions.
[b]Isolated yields based on **1a**.

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With these preliminary results in hand, in order to test the general applicability of silica-supported $Yb(OTf)_3$ as a catalyst for the cyclisation of 2'-aminochalcone and its analogues, a wide range of substrates were treated as described above. The results are summarised in Table 2. In all cases, compounds bearing either electron-donating or electron-withdrawing substituents underwent the reaction well and gave the corresponding products in good yield. It could also be concluded that aromatic substrates bearing electron-donating substituents required a shorter reaction time with high yields (Table 2 entries 1–13). We studied the cyclisation of the heterocyclic or aliphatic substituted 2'-aminochalcone analogue under similar conditions. It was found that the corresponding 2-(thiophen-2-yl)-2,3-dihydroquinolin-4(1*H*)-one **2n** and 2-tert-butyl-2,3-dihydroquinolin-4(1*H*)-one **2o** could also be obtained in high yields (Table 2 entries 14, 15).

Inspection of the data in Table 2 also shows that the use of $Yb(OTf)_3$ impregnated on silica gel as catalyst (Method A) has significantly higher yields compared to using silica gel alone (Method B). Compared with method B, we can see that $Yb(OTf)_3$ impregnated on silica gel as catalyst can significantly improve the yields to 90%. This lack of reactivity may be due to the low acidity of silica gel compared to silica-supported $Yb(OTf)_3$.

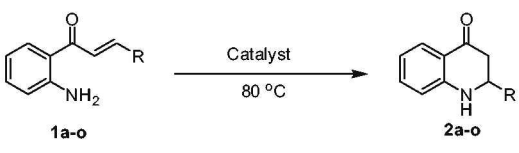
Based on the experimental results, a plausible mechanism can be proposed (Scheme 3). The mechanism of this process includes intramolecular Michael addition of amino group to the α,β-unsaturated ketone followed by subsequent cyclisation under the catalysis of $Yb(OTf)_3$/silica gel.

We also tried to cyclise 2'-hydroxychalcones to their corresponding flavanones using silica-supported $Yb(OTf)_3$ under the same reaction conditions. Disappointingly, no product was observed even after prolonged reaction times of 2 days (Scheme 4) or an increased amount of catalyst. This lack of reactivity may be due to the low nucleophilicity of oxygen in 2'-hydroxychalcones as compared to the amino nitrogen in 2'-aminochalcone.

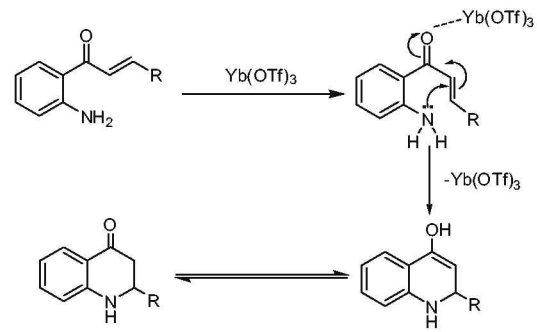
In summary, the present procedure using a silica-supported $Yb(OTf)_3$ catalyst provides an efficient synthesis of 2-substitued dihydroquinolinones by the cyclisation of the corresponding 2'-aminochalcones and its analogues. We believe that this procedure will provide a better and more practical alternative to the existing procedures for the synthesis of 2-substitued dihydroquinolinones.

Experimental

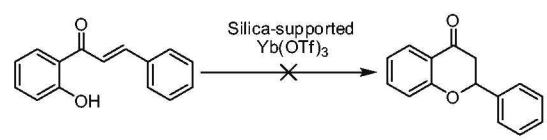
2'-Hydroxy-chalcones and **1a–o** were prepared according to literature.[14-16] $Yb(OTf)_3$ was prepared from Yb_2O_3 and triflic acid. Melting points were measured on a Büchi B-540 capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet Aviatar-370, spectrometer using samples as neat liquids or as KBr discs. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian 400 MHz or Bruker Avance III (500 MHz) instrument using $CDCl_3$ as the solvent, and chemical shifts were expressed in parts per million (ppm) using TMS as an internal standard. Mass spectra were measured with a Trace Finnigan DSQ. High resolution mass spectral (HRMS) analysis was measured on an Agilent 6210 TOF LC/MS using APCI (electrospray ionisation) techniques. All spectral data of the products were identical to authentic samples.



Scheme 2



Scheme 3



Scheme 4

Table 2 The synthesis of 2-substituted dihydroquinolinones under solvent-free conditions

Entry	R	Product	Method A[a] Time/h (Yield/%)[b]	Method B[c] Time/h (Yield%)[b]
1	Ph	**2a**	2 95	15 60
2	3-$MeOC_6H_4$	**2b**	2 90	15 40
3	4-$MeOC_6H_4$	**2c**	2 96	15 42
4	2,4-$(MeO)_2C_6H_3$	**2d**	2 95	15 45
5	3,4-$(OCH_2O)C_6H_3$	**2e**	2 94	15 50
6	4-$N(Me)_2C_6H_4$	**2f**	2 90	24 25
7	3,4-$(Me)_2C_6H_3$	**2g**	2 94	10 70
8	4-$O_2NC_6H_4$	**2h**	3 85	15 30
9	3-$O_2NC_6H_4$	**2i**	3 90	15 35
10	3-BrC_6H_4	**2j**	3 87	15 50
11	4-ClC_6H_4	**2k**	3 82	15 53
12	3-FC_6H_4	**2l**	3 92	24 5
13	2-ClC_6H_4	**2m**	3 75	15 35
14	Thiophen-2-yl	**2n**	2 98	15 56
15	$C(Me)_3$	**2o**	3 90	15 40

[a]Method A: **1a–o** (1.0 mmol) and silica-gel supported $Yb(OTf)_3$ (0.05 mmol) were kept at 80 °C for 2–3 h.
[b]Isolated yields based on **1a–o**.
[c]Method B: **1a–o** (1.0 mmol) and silica gel alone were kept at 80 °C for 10–24 h.

Preparation of 2-substituted dihydroquinolinones in solvent: general procedure

1a (1 mmol) was added to 2 mL of solvent such as MeCN with $Yb(OTf)_3$ (0.05 mmol). The whole mixture was stirred in oil-bath for the appropriate time. On completion, the solvent was evaporated under reduced pressure, and the remainder was extracted with ethyl acetate (2 × 10 mL). The combined organic extracts were washed with water followed by brine and dried over anhydrous Na_2SO_4. Removal of solvent followed by purification on silica gel column with a mixture of ethyl acetate:petroleum ether = 1:10 afforded the corresponding products.

Preparation of 2-substituted dihydroquinolinones under solvent free conditions – general procedure, Method A: **1a–o** (1 mmol) was added to silica gel (200~300 mesh) (0.5 g) impregnated with $Yb(OTf)_3$ (0.05 mmol). The whole mixture was ground for 5 min for uniform mixing and was then kept in a water bath at 80 °C for the appropriate time. On completion, the reaction mixture was directly charged on a small silica gel column and eluted with a mixture of ethyl acetate:petroleum ether = 1:10 to afford the corresponding products in high yields.

Method B: **1a–o** (1 mmol) was added to silica gel (200~300 mesh) (0.5 g). The whole mixture was stirred for 5 min for uniform mixing and was then kept in a water bath at 80 °C for the appropriate time. On completion, the reaction mixture was directly charged on a small silica gel column and eluted with a mixture of ethyl acetate:petroleum ether = 1:10 to afford the corresponding products. The physical and spectra data of the compounds **2a–o** are as follows.

2-Phenyl-2,3-dihydroquinolin-4(1H)-one **(2a)**: Pale yellow solid. M.p. 147–149 °C (Lit.[7] m.p. 149–150 °C). IR (cm^{-1}): 3346 (NH), 1659 (C=O). ^1H NMR δ: 2.72–2.89 (m, 2H, CH_2), 4.57 (br s, 1H, NH), 4.72 (dd, 1H, J_1 = 3.6, J_2 = 13.6 Hz), 6.70–6.80 (m, 2H), 7.31–7.45 (m, 6H), 7.86 (dd, 1H, J_1 = 1.2, J_2 = 7.6 Hz). ^{13}C NMR δ: 46.4, 58.4, 115.9, 118.4, 119.0, 126.6, 127.5, 128.4, 128.9, 135.3, 141.0, 151.5, 193.2. MS (EI): *m/z* (%) = 224 (17), 223 (M^+, 98), 146 (100).

2-(3-methoxyphenyl)-2,3-dihydroquinolin-4(1H)-one **(2b)**: Pale yellow solid. M.p. 129–130 °C (Lit.[2] m.p. 129–131 °C). IR (cm^{-1}): 3339 (NH), 1656 (C=O). ^1H NMR δ: 2.74–2.90 (m, 2H), 3.82(s, 3H, OCH3), 4.56 (br s, 1H, NH), 4.71 (dd, 1H, J_1 = 4.0, J_2 = 13.6 Hz), 6.72 (d, 1H, J = 8.0 Hz), 6.77–6.81 (m, 1H), 6.87–6.90 (m, 1H), 7.01–7.03 (d, 2H, J = 7.2 Hz), 7.29–7.36 (m, 2H), 7.86(dd, 1H, J_1 = 1.6, J_2 = 8.0 Hz). ^{13}C NMR δ: 46.4, 55.3, 55.4, 112.2, 113.7, 115.9, 118.4, 118.8, 119.0, 127.6, 130.0, 135.4, 142.6, 151.5, 160.0, 193.2. MS (ESI): *m/z* = 254 (M^+ + 1).

2-(4-methoxyphenyl)-2,3-dihydroquinolin-4(1H)-one **(2c)**: Pale yellow solid. M.p. 145–147 °C (Lit.[7] m.p. 147 °C). IR (cm^{-1}): 3416 (NH), 1647 (C=O). ^1H NMR δ: 2.73 (dd, 1H, J_1 = 3.6, J_2 = 16.4 Hz), 2.86 (dd, 1H, J_1 = 14.0, J_2 = 16.8 Hz), 3.82 (s, 3H, OCH3), 4.47 (br s, 1H, NH), 4.69 (dd, 1H, J_1 = 3.6, J_2 = 13.6 Hz), 6.69 (d, 1H, J = 8.4 Hz) 6.76–6.80 (m, 1H) 6.90–6.94 (m, 2H), 7.30–7.39 (m, 3H), 7.87 (dd, 1H, J_1 = 1.2, J_2 = 8.0 Hz). ^{13}C NMR δ: 46.5, 55.4, 57.9, 114.3, 115.9, 118.4, 119.0, 127.6, 127.8, 133.1, 135.3, 151.6, 159.7, 193.4. MS (EI): *m/z* (%) = 254 (12), 253 (M^+, 80), 146 (100).

2-(2,4-dimethoxyphenyl)-2,3-dihydroquinolin-4(1H)-one **(2d)**: Pale yellow solid. M.p. 135–137 °C. IR (cm^{-1}): 3334 (NH), 1651 (C=O). ^1H NMR δ: 2.83–2.85 (m, 2H), 3.81(d, 6H, OCH_3, J = 5.6 Hz), 4.62 (br s, 1H, NH), 5.07 (dd, 1H, J_1 = 5.6, J_2 = 10.0 Hz), 6.48–6.50 (m, 2H), 6.67–6.76 (m, 2H), 7.26–7.36 (m, 2H), 7.85 (d, 1H, J = 7.6 Hz). ^{13}C NMR δ: 43.8, 51.0, 55.4, 98.7, 104.3, 116.0, 117.9, 119.0, 121.4, 127.2, 127.5, 135.1, 151.9, 157.8, 160.6, 194.0. MS (EI): *m/z* (%) = 284 (17), 283 (M^+, 100), 146 (58). HRMS (EI): *m/z* calcd for $C_{17}H_{17}NO_3$: 283.1208, found: 283.1201.

2-(benzo[d][1,3]dioxo-5-yl)-2,3-dihydroquinolin-4(1H)-one[17] **(2e)**: Pale yellow solid. M.p. 131–133 °C. IR (cm^{-1}): 3329 (NH), 1651 (C=O). ^1H NMR δ: 2.69–2.85 (m, 2H), 4.52(br s, 1H, NH), 4.65 (dd, 1H, J_1 = 3.6, J_2 = 13.2 Hz), 5.97 (s, 2H), 6.71 (d, 1H, J = 8.4 Hz), 6.76–6.81(m, 2H), 6.88 (dd, 1H, J_1 = 1.2, J_2 = 8.0 Hz), 6.96 (d, 1H, J = 0.8 Hz), 7.31–7.35 (m, 1H), 7.85 (d, 1H, J = 8.0 Hz). ^{13}C NMR δ: 46.6, 58.2, 101.2, 106.9, 108.4, 115.9, 118.4, 119.0, 120.1, 127.5, 134.9, 135.4, 147.6, 148.0, 151.5, 193.3. MS (ESI): *m/z* = 268 (M^+ + 1).

2-(4-(dimethylamino)phenyl)-2,3-dihydroquinolin-4(1H)-one **(2f)**: Pale yellow solid. M.p. 182–184 °C (Lit.[18] m.p. 185–186 °C). IR (cm^{-1}): 3339 (NH), 1651 (C=O). ^1H NMR δ: 2.73 (dd, 1H, J_1 = 3.6, J_2 = 16.4 Hz), 2.89 (dd, 1H, J_1 = 14.6, J_2 = 24.4 Hz), 2.97 (s, 6H, CH3), 4.44 (br s, 1H, NH), 4.65 (dd, 1H, J_1 = 3.6, J_2 = 14.4 Hz), 6.67 (d, 1H, J = 7.6 Hz), 6.75–6.79 (m, 3H), 7.30–7.34 (m, 3H), 7.87 (dd, 1H, J_1 = 1.6, J_2 = 8.0 Hz). ^{13}C NMR δ: 40.6, 46.5, 58.0, 112.7, 115.8, 118.2, 119.0, 127.5, 127.6, 135.2, 151.7, 193.9. MS (ESI): *m/z* = 267 (M^+ + 1).

2-(3,4-dimethylphenyl)-2,3-dihydroquinolin-4(1H)-one **(2g)**: Pale yellow solid. M.p. 87–89 °C. IR (cm^{-1}): 3351 (NH), 1652 (C=O). ^1H NMR δ: 2.27 (d, 6H, CH_3, J = 3.6 Hz), 2.71 (dd, 1H, J_1 = 3.6, J_2 = 16.4 Hz), 2.84 (dd, 1H, J_1 = 14.0, J_2 = 16.0 Hz), 4.53 (br s, 1H, NH), 4.65 (dd, 1H, J_1 = 3.6, J_2 = 13.6 Hz), 6.69 (d, 1H, J = 8.4 Hz), 6.76 (t, 1H, J = 7.2 Hz), 7.13–7.17 (m, 2H), 7.29–7.34 (m, 1H), 7.85 (dd, 1H, J_1 = 1.2, J_2 = 8.0 Hz). ^{13}C NMR δ: 19.4, 19.8, 46.4, 58.1, 115.9, 118.2, 118.9, 123.9, 127.5, 127.8, 130.1, 135.3, 136.8, 137.2, 138.4, 151.6, 193.5. MS (EI): *m/z* (%) = 252 (18), 251 (M^+, 100), 146 (73). HRMS (EI): *m/z* calcd for $C_{17}H_{17}NO$: 251.1310, found: 251.1310.

2-(4-nitrophenyl)-2,3-dihydroquinolin-4(1H)-one **(2h)**: Yellow solid. M.p. 200–202 °C (Lit.[5] m.p. 192–193 °C). IR (cm^{-1}): 3364 (NH), 1678 (C=O). ^1H NMR δ: 2.82–2.85 (m, 2H), 4.62 (br s, NH, 1H), 4.90 (dd, 1H, J_1 = 6.8, J_2 = 10.0 Hz), 6.78 (d, 1H, J = 8.4 Hz), 6.85 (t, 1H, J = 7.2 Hz), 7.37–7.41 (m, 1H), 7.66 (d, 2H, J = 8.8 Hz), 7.87 (d, 1H, J = 8.4 Hz), 8.25 (d, 2H, J = 8.8 Hz). ^{13}C NMR δ: 46.1, 57.9, 116.1, 119.1, 124.3, 127.5, 127.6, 135.7, 147.8, 148.3, 150.9, 191.9. MS (ESI): *m/z* = 267 (M^+-1).

2-(3-nitrophenyl)-2,3-dihydroquinolin-4(1H)-one **(2i)**: Pale yellow solid. M.p. 183–185 °C(Lit.[7] m.p. 185–186 °C). IR (cm^{-1}): 3442 (NH), 1655 (C=O). ^1H NMR δ: 2.84–2.91 (m, 2H), 4.62(br s, 1H, NH), 4.90 (dd, 1H, J_1 = 4.8, J_2 = 12.4 Hz), 6.78 (d, 1H, J = 8.0 Hz), 6.82–6.86 (m, 1H), 7.36–7.41 (m, 1H), 7.59 (t, 1H, J = 7.6 Hz), 7.80 (d, 1H, J = 8.0 Hz),7.86–7.88 (m, 1H), 8.20–8.22 (m, 1H), 8.38 (d, 1H, J = 2.0 Hz). ^{13}C NMR δ: 46.2, 57.7, 116.0, 119.1, 121.6, 123.4, 127.6, 129.4, 130.1, 132.7, 135.6, 143.2, 148.6, 150.9, 192.0. MS (EI): *m/z* (%) = 269 (7), 268 (M^+, 41), 146 (100).

2-(3-bromophenyl)-2,3-dihydroquinolin-4(1H)-one **(2j)**: Pale yellow solid. M.p. 123–125 °C (Lit.[18] m.p. 124–125 °C). IR (cm^{-1}): 3330 (NH), 1660 (C=O). ^1H NMR δ: 2.73–2.87 (m, 2H), 4.53(br s, 1H, NH), 4.71 (dd, 1H, J_1 = 4.4, J_2 = 13.2 Hz), 6.73 (d, 1H, J = 8.0 Hz), 6.81 (t, 1H, J = 6.8 Hz), 7.28–7.33 (m, 1H), 7.35–7.38 (m, 2H), 7.46–7.63 (m, 1H), 7.64 (s, 1H), 7.86 (dd, 1H, J_1 = 1.6, J_2 = 8.0 Hz). ^{13}C NMR δ: 46.3, 58.0, 116.0, 118.8, 119.1, 123.0, 125.3, 127.6, 129.7, 130.6, 131.6, 135.5, 143.4, 151.2, 192.6. MS (EI): *m/z* (%) = 303 (40), 301 (M^+, 44), 146 (100).

2-(4-chlorophenyl)-2,3-dihydroquinolin-4(1H)-one **(2k)**: Pale yellow solid. M.p. 169–171 °C (Lit.[7] m.p. 168 °C). IR (cm^{-1}): 3307 (NH), 1652 (C=O). ^1H NMR δ: 2.72–2.87 (m, 2H), 4.49(br s, 1H, NH), 4.73 (dd, 1H, J_1 = 4.4, J_2 = 13.2 Hz), 6.72 (d, 1H, J = 8.0 Hz), 6.81 (dd, 1H, J_1 = 7.6, J_2 = 8.0 Hz), 7.33–7.41 (m, 5H), 7.87 (d, 1H, J = 7.6 Hz). ^{13}C NMR δ: 46.4, 57.9, 115.9, 118.7, 119.1, 127.6, 128.0, 129.2, 134.2, 135.5, 139.6, 151.3, 192.7. MS (EI): *m/z* (%) = 259 (33), 257 (M^+, 100), 146(100).

2-(3-fluorophenyl)-2,3-dihydroquinolin-4(1H)-one **(2l)**: Pale yellow solid. M.p. 140–142 °C. IR (cm^{-1}): 3341 (NH), 1662 (C=O). ^1H NMR δ: 2.73–2.86 (m, 2H), 4.60 (br s, 1H, NH), 4.74 (dd, 1H, J_1 = 4.4, J_2 = 12.8 Hz), 6.74 (d, 1H, J = 8.4 Hz), 6.80 (t, 1H, J = 8.0 Hz), 7.01–7.06 (m, 1H), 7.18–7.22 (m, 2H), 7.33–7.39 (m, 2H), 7.86 (d, 1H, J = 7.6 Hz). ^{13}C NMR δ: 46.3, 58.0, 113.5 (d, J = 22 Hz), 115.3 (d, J = 20.5 Hz), 116.0, 118.7, 122.2, 127.6, 130.6 (d, J = 7.6 Hz), 135.5, 143.6 (d, J = 6.1 Hz), 151.3, 161.8, 164.2, 192.7. MS (EI): *m/z* (%) = 242 (17), 241 (M^+, 100), 146 (88). HRMS (EI): *m/z* calcd for $C_{15}H_{12}NOF$: 241.0903, found: 241.0905.

2-(2-chlorophenyl)-2,3-dihydroquinolin-4(1H)-one **(2m)**: Pale yellow solid. M.p. 145–147 °C (Lit.[7] m.p. 146–147 °C). IR (cm^{-1}): 3286 (NH), 1650 (C=O). ^1H NMR δ: 2.77 (dd, 1H, J_1 = 12.4, J_2 = 16.4 Hz), 2.94 (dd, 1H, J_1 = 4.0, J_2 = 16.4 Hz), 4.56 (br s, 1H, NH), 5.26 (dd, 1H, J_1 = 4.4, J_2 = 12.4 Hz), 6.73–7.25 (m, 2H), 7.26–7.41 (m, 4H), 7.67 (dd, 1H, J_1 = 1.6, J_2 = 7.6 Hz), 7.88 (dd, 1H, J_1 = 0.8, J_2 = 7.6 Hz). ^{13}C NMR δ: 44.0, 54.2, 116.0, 118.6, 119.0, 127.4, 127.5, 127.5, 129.3, 130.0, 132.7, 135.4, 138.3, 151.5, 192.8. MS (ESI): *m/z* = 256.4 (M^+-1).

2-(thiophen-2-yl)-2,3-dihydroquinolin-4(1H)-one[19] **(2n)**: Pale yellow solid. M.p. 135–137 °C. IR (cm^{-1}): 3333 (NH), 1657 (C=O). ^1H NMR δ: 2.88–2.98 (m, 2H), 4.67 (br s, 1H, NH), 5.04 (dd, 1H, J_1 = 5.6, J_2 = 11.2 Hz), 6.71–6.80 (m, 1H), 6.80–6.82 (m, 1H), 6.98–7.00(m, 1H), 7.06 (t, 1H, J = 2.4 Hz), 7.27–7.36 (m, 2H), 7.87 (dd, 1H, J_1 = 1.6, J_2 = 8.0 Hz). ^{13}C NMR δ: 47.0, 53.7, 116.0, 118.8, 119.3, 125.0, 125.1, 126.9, 127.6, 135.4, 144.5, 150.8, 192.6. MS (EI): *m/z* (%) = 230 (23), 229 (M^+, 92), 228 (100), 146 (100).

2-tert-butyl-2,3-dihydroquinolin-4(1H)-one **(2o)**: Pale white solid. M.p. 149–150 °C. IR (cm^{-1}): 3354 (NH), 1659 (C=O). ^1H NMR δ: 1.02 (m, 9H, CH3), 2.51(dd, 1H, J_1 = 14.0, J_2 = 16.0 Hz), 2.65 (dd, 1H, J_1 = 3.6, J_2 = 12.0 Hz), 3.33 (dd, 1H, J_1 = 3.6, J_2 = 14.0 Hz), 4.34(br s, 1H, NH), 6.68–6.74 (m, 2H), 7.26–7.32 (m, 1H), 7.81 (dd, 1H, J_1 = 1.6, J_2 = 8.0 Hz). ^{13}C NMR δ: 25.9, 33.2, 39.5, 62.2, 115.9, 117.9, 118.8, 127.4, 135.1, 152.0, 194.7. MS (EI): *m/z* (%) = 204 (2), 203 (M^+, 8), 146 (100). HRMS (EI): *m/z* calcd for $C_{13}H_{17}NO$: 203.1310, found: 203.1320.

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