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Superelectrophilic activation of *N*-aryl amides of 3-arylpropynoic acids: synthesis of quinolin-2(1*H*)-one derivatives

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ABSTRACT

The superelectrophilic activation of *N*-aryl amides of 3-arylpropynoic acids by Bronsted superacids (CF_3SO_3H, HSO_3F) or strong Lewis acids AlX_3 (X=Cl, Br) results in the formation of 4-aryl quinolin-2(1*H*)-ones in quantitative yields. The vinyl triflates or vinyl chlorides may be formed as additional reaction products. The investigated amides in reactions with benzene give 4,4-diaryl 3,4-dihydroquinolin-2-(1*H*)-ones under the superelectrophilic activation. 4-Aryl quinolin-2(1*H*)-ones in $POCl_3$ are converted into 4-aryl 2-chloroquinolines. 4-Fluorophenyl-4-phenyl 3,4-dihydroquinolin-2-(1*H*)-one give N-formylation products in a yield of 79% under the Vilsmeier–Haack reaction conditions.

1. Introduction

Substituted quinolin-2(1*H*)-ones are of a great theoretical and practical value. They possess different kinds of biological activities: antiviral, antitumoral, antibacterial, antiatherosclerotic, and others.[1–3] In particular, 4-aryl quinolin-2(1*H*)-ones are inhibitors of acyl-coenzyme A, and cholesterol acyl-transferase; they are potent openers of the high conductive calcium-activated K^+-channels.[4] Also some 4-aryl quinolin-2(1*H*)-ones were isolated from various *Penicillium* fungi.[5]

Due to the importance of quinolin-2(1*H*)-ones, several approaches for their synthesis have been developed. One of these methods is based on the Pd-catalyzed intramolecular cyclization of *N*-aryl amides of acetylene carboxylic acids.[6] Other methods are inter- or intramolecular quinolin-2(1*H*)-one ring closure from various compounds.[7]

N-Aryl amides of acetylene carboxylic acids under the catalysis by Lewis acid $Hf(OTf)_4$ in ionic liquids give quinolin-2(1*H*)-ones.[8] The same transformation should be caused by strong Bronsted and Lewis acids. But, up to the moment, there is just one example of such reaction. The only investigated object is unsubstituted *N*-phenylamide of 3-phenylpropynoic acid **1a**, which was converted into 4-phenyl quinolin-2(1*H*)-one **2a** under the action of polyphosphoric acid,[9] triflic acid CF_3SO_3H (TfOH),[10] $AlCl_3$,[11] zeolite H-USY,[10] polymer Nafion SAC-13[10] (Table 1, entries 1–3, 7, 16). There is no literature data on the similar transformation of any other substituted *N*-aryl amides of 3-arylpropynoic acids.

Previously we have shown[12–16] that superelectrophilic activation by Bronsted superacids (HSO_3F, TfOH) or strong Lewis acids (aluminium halides $AlCl_3$, $AlBr_3$) is an effective and simple way for intramolecular cyclization of various acetylene compounds. Superelectrophilic activation of organic compounds is a method of generating highly reactive di- (three, and even more) cationic species by protonation of organic molecule basic centres with superacids or by coordination of these basic centres with strong Lewis acids.[17] Thus, we carried out the following synthesizes: 3-arylindenones[12] from 1,3-diarylpropynones; indenes[13] from acetylene carbonyl compounds or propargylic alcohols; coumarins[14] or thiocoumarins[15] from aryl (or thio-aryl) esters of 3-arylpropynoic acids. In our preliminary communications[18,19] the transformations of *N*-phenyl, *N*-3-methylphenyl and *N*-4-methylphenyl amides of 3-phenylpropynoic acid into 4-aryl (4,4-diaryl) quinolin-2(1*H*)-one derivatives have been described.

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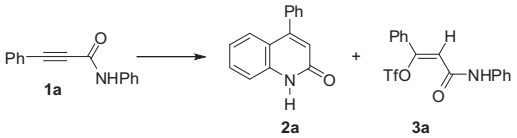
0040-4020/

Table 1
Transformations of *N*-phenylamide of 3-phenylpropynoic acid **1a** in various acidic systems



Entry	Reaction conditions	Reaction products (yield, %)
1[a]	Polyphosphoric acid (65 equiv), 120°C, 0.5 h	**2**a (81%)
2[b]	Zeolite H-USY (10 equiv), C_6H_6, 130 °C, 1 h	**2a** (95%)
3[b]	Nafion SAC-13 (10 equiv), C_6H_6, 130 °C, 3 h	**2a** (70%)
4	TfOH (35 equiv), 20 °C, 24 h	**1a** (40%)+**2a** (38%)+**3a** (17%)
5	TfOH (35 equiv), 20 °C, 40 h	**1a** (10%)+**2a** (72%)+**3a** (11%)
6	TfOH (35 equiv), 20 °C, 90 h	**2a** (86%)+**3a** (8%)
7[c]	TfOH (40 equiv), 25 °C, 100 h	**2a** (97%)
8	TfOH (35 equiv), 20 °C, 30 days	**2**a (88%)+**3**a (3%)
9	TfOH (35 equiv), 50 °C, 0.5 h	**1**a (50%)+**2**a (33%)+**3**a (14%)
10	TfOH (35 equiv), 50 °C, 2 h	**1**a (10%)+**2**a (52%)+**3**a (30%)
11	TfOH (35 equiv), 50 °C, 5 h	**2**a (80%)+**3**a (10%)
12	FSO_3H (25 equiv), −75 °C, 5 h	**2a** (98%)
13	FSO_3H (25 equiv), −50 °C, 1 h	Oligomers
14	TfOH–SbF_5 (H_0 ~−18) (25 equiv), −30 °C, 0.75 h	Oligomers
15	H_2SO_4 (270 equiv), 20 °C, 7 h	**2a** (57%)+$PhCOCH_2CONHPh$ **5a** (37%)
16[c]	$AlCl_3$ (5 equiv), CH_2Cl_2, 25 °C, 10 h	**2a** (61%)
17	$AlCl_3$ (5 equiv), CH_2Cl_2, 20 °C, 10 h	**2a** (79%)
18	$AlBr_3$ (5 equiv), CH_2Cl_2, 20 °C, 10 h	**2a** (90%)

[a] Data from Ref. 9.
[b] Data from Ref. 10.
[c] Data from Ref. 11.

The aim of this work is a systematic study of reactivity and reaction pathways of the series of *N*-aryl amides of 3-arylpropynoic acids, bearing different electron donor–acceptor substituents in aromatic rings, under the superelectrophilic activation conditions by Bronsted superacids TfOH, FSO_3H or strong Lewis acids AlX_3 (X=Cl, Br).

2. Results and discussion

The protonation of amides **1** on the oxygen atom of an amide group and on the carbon atom of acetylene bond in superacids or coordination interaction of these basic centres with strong Lewis acids leads to the formation of superelectrophilic dications **I** (Scheme 1). These species can react in the following concurrent directions. The first one is an intramolecular cyclization into quinolin-2(1*H*)-ones **2**, as a result of vinyl cationic centre attack to the internal π-nucleophile—aryl moiety of group NHAr (Scheme 1, path *a*). The second route is intermolecular addition of triflate-anion from TfOH or halogenide-ion from associated forms of aluminium halides Al_nHlg_{3n} with the formation of vinyl triflates **3** or vinyl halogenides **4**, respectively (Scheme 1, path *b*). The third reaction pathway may take place in the presence of arene molecules, as external π-nucleophiles (Scheme 1, path *c*). This way includes alkenylation of arenes by species **I**, leading to structures **II**, which can be further diprotonated to the cations **III** and transformed into compounds **6**.

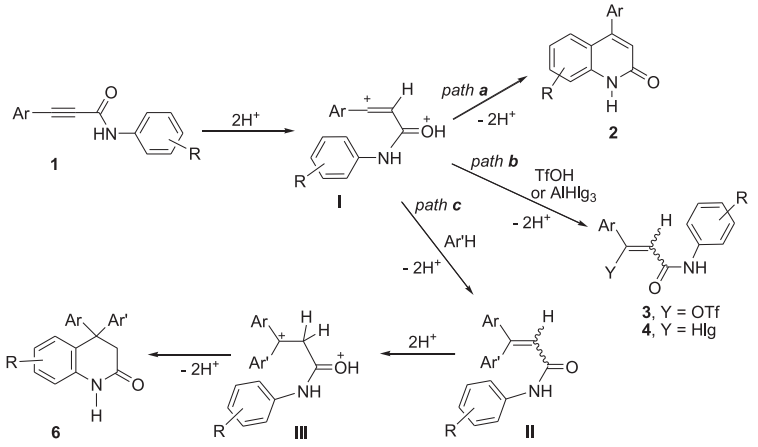
Reactions of the series of *N*-aryl amides of 3-arylpropynoic acids with TfOH, FSO_3H or $AlCl_3$, $AlBr_3$ have been studied. Initial amides **1a–z**, reaction conditions, and reaction products 4-aryl quinolin-2(1*H*)-ones **2a–x**, vinyl triflates **3a–g**, vinyl chlorides **4a–f**, keto-amides **5a–c**, and 4,4-diaryl 3,4-dihydroquinolin-2-(1*H*)-ones **6a–d** are presented in Tables 1–4. It is important that in most cases the whole yields of the reaction products are almost quantitative up to 95–98% (Tables 1–4).

Structures of the compounds **2a–x**, **3a–g**, **4a–f**, **5a–c**, **6a–d** have been determined by ^1H, ^{13}C, ^{19}F NMR, HRMS methods (see Experimental section), and X-ray analysis for compound **2b** (Fig. 1).

In some cases we failed to separate quinolinones **2**, vinyl triflates **3**, and vinyl chlorides **4** into individual compounds by usual column chromatography on silica gel due to high polarity of the group CONH in these compounds. The obtained mixtures were analyzed by NMR, and HRMS methods to identify individual components. In ^1H NMR spectra the identification of the compounds was performed on the basis of characteristic chemical shifts of the vinyl protons. Thus, for 4-aryl quinolin-2(1*H*)-ones **2a–x** the signal of this proton lays in the area of δ 6.60–6.70 ppm, for vinyl triflates **3a–g**—6.30–6.38 ppm, and for vinyl chlorides **4a–f**—6.41–6.63 ppm (see Experimental).

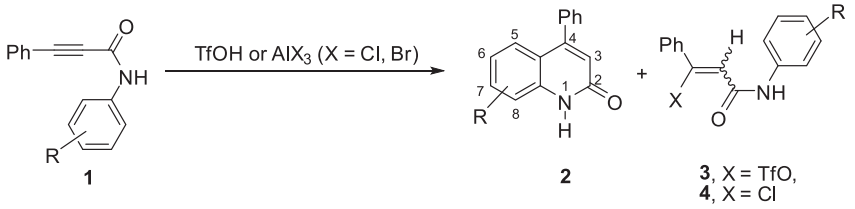
Based on our previous study[20] on triflic acid addition to acetylene compounds, the stereochemistry of vinyl triflates **3a–g** was assigned as *Z*-configuration. Additionally, stereo-chemical structures for the compounds *Z*-**3f** and *Z*-**4c** were confirmed by NOESY and ROESY experiments. The observed correlations of vinyl protons with *ortho*-protons of the phenyl ring reveal unambiguously *Z*-orientation of the substituents at the double bond (Fig. 2).

Transformations of the unsubstituted amide **1a** in various acidic systems are shown in Table 1. In TfOH at 20 °C for 24 h the amide **1a** gives 4-phenyl quinolin-2(1*H*)-one **2a** and vinyl triflate **3a** in yields of 38 and 17%, respectively. However, incomplete conversion of the initial compound takes place (the amide **1a** was recovered in a yield



Scheme 1. Different reaction pathways of compounds **1** through an intermediate formation of cations **I** under the superelectrophilic activation conditions.

Table 2
Transformations of *N*-aryl amides of 3-phenylpropynoic acid **1b**–**r** under the action of TfOH or AlX_3 (X=Cl, Br)



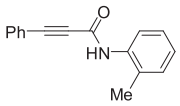
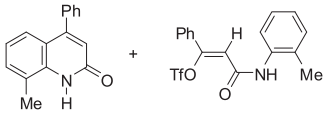
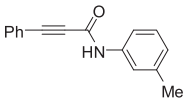
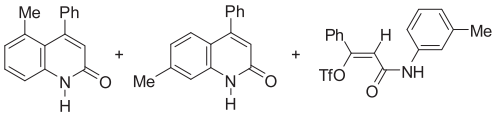
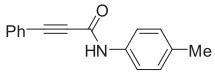
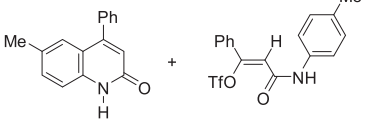
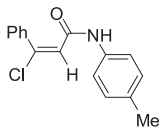
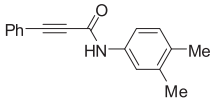
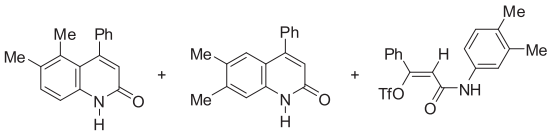
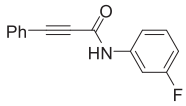
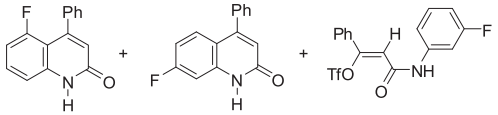
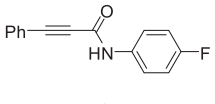
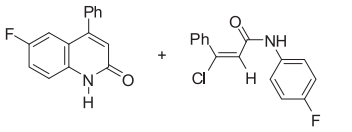
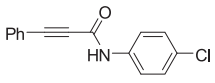
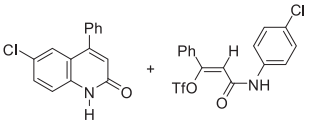
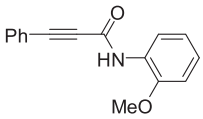
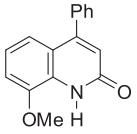
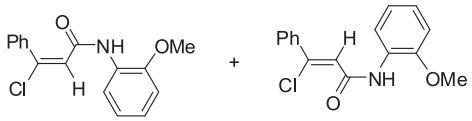
Entry	Initial compound	Reaction conditions	Reaction products (yield, %)
1	 **1b**	TfOH, 20 °C, 92 h	 **2b** (82%) **3b** (17%)
2	**1b**	$AlCl_3$, CH_2Cl_2, 20 °C, 10 h	**2b** (90%)
3	 **1c**	TfOH, 20 °C, 72 h	**1c** (20%) +  **2c** (8%) **2d** (40%) **3c** (5%)
4	**1c**	TfOH, 20 °C, 90 h	**2c** (16%)+**2d** (78%)+**3c** (5%)
5	**1c**	TfOH, 20 °C, 30 days	**2c** (14%)+**2d** (80%)+**3c** (3%)
6	**1c**	$AlCl_3$, CH_2Cl_2, 20 °C, 10 h	**2c** (26%)+**2d** (64%)
7	**1c**	$AlBr_3$, CH_2Cl_2, 20 °C, 10 h	**2c** (32%)+**2d** (64%)
8	 **1d**	TfOH, 20 °C, 70 h	**1d** (30%) +  **2e** (56%) **3d** (6%)
9	**1d**	TfOH, 20 °C, 90 h	**2e** (94%)+**3d** (5%)
10	**1d**	$AlCl_3$, CH_2Cl_2, 20 °C, 10 h	**2e** (93%) +  *E*-**4a** (6%)

Table 2 (*continued*)

Entry	Initial compound	Reaction conditions	Reaction products (yield, %)
11	 **1e**	TfOH, 20 °C, 72 h	 **2f** (19%) **2g** (74%) **3e** (6%)
12	**1e**	$AlCl_3$, CH_2Cl_2, 20 °C, 8 h	**2f** (20%)+**2g** (75%)
13	 **1f**	TfOH, 20 °C, 92 h	 **2h** (5%) **2i** (58%) **3f** (36%)
14	**1f**	$AlCl_3$, CH_2Cl_2, 20 °C, 24 h	**2h** (16%)+**2i** (78%)
15	 **1g**	$AlCl_3$, CH_2Cl_2, 20 °C, 10 h	 **2j** (78%) *E*-**4b** (6%)
16	**1g**	TfOH, 20 °C, 92 h	Oligomers
17	**1g**  **1h**	TfOH, 20 °C, 92 h	 **2k** (27%) **3g** (66%)
18	**1h**	$AlCl_3$, CH_2Cl_2, 20 °C, 24 h	**2k** (96%)
19	 **1i**	TfOH, 20 °C, 92 h	 **2l** (20%)
20	**1i**	$AlCl_3$, CH_2Cl_2, 20 °C, 10 h	**2l** (59%) +  *E*-**4c** (14%) *Z*-**4c** (14%)

(*continued on next page*)

Table 2 (*continued*)

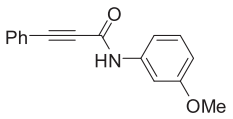
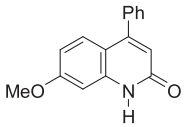
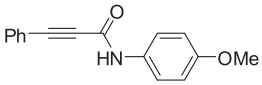
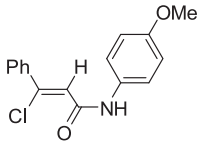
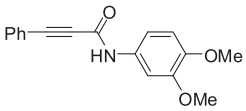
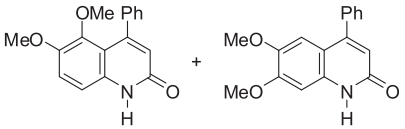
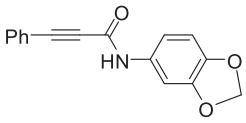
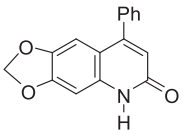
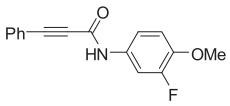
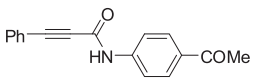
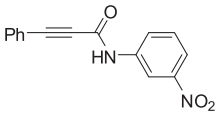
Entry	Initial compound	Reaction conditions	Reaction products (yield, %)
21	 **1j**	TfOH, 20 °C, 95 h	 **2m** (40%)
22	 **1k**	$AlCl_3$, CH_2Cl_2, 20 °C, 10 h	 *Z*-**4d** (69%)
23	 **1l**	$AlCl_3$, CH_2Cl_2, 20 °C, 8 h	 **2n** (32%) **2o** (67%)
24	**1l**	TfOH, 20 °C, 92 h	Oligomers
25	 **1m**	$AlCl_3$, CH_2Cl_2, 20 °C, 8 h	 **2p** (48%)
26	**1m**	TfOH, 20 °C, 92 h	Oligomers
27	 **1n**	TfOH, 20 °C, 92 h	Oligomers
28	 **1o**	TfOH, 20 °C, 92 h	Oligomers
29	 **1p**	TfOH, 20 °C, 12 h	Oligomers

Table 2 (*continued*)

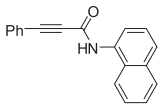
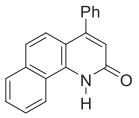
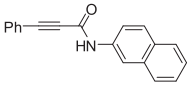
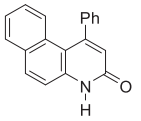
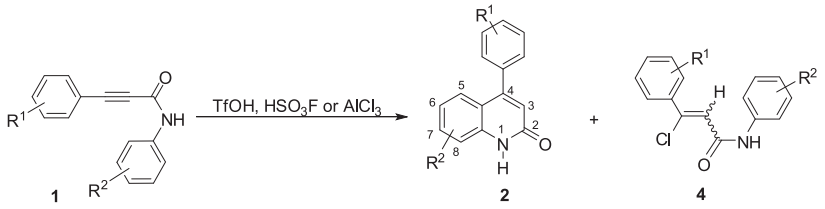
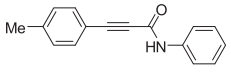
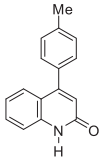
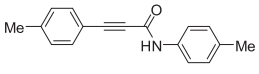
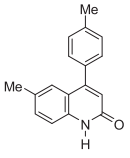
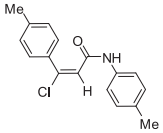
Entry	Initial compound	Reaction conditions	Reaction products (yield, %)
30	 **1q**	TfOH, 20 °C, 23 h	 **2q** (40%)
31	 **1r**	$AlCl_3$, CH_2Cl_2, 20 °C, 8 h	 **2r** (32%)

Table 3
Transformations of *N*-aryl amides of 3-arylpropynoic acids **1s**–**y** under the action of TfOH, HSO_3F or $AlCl_3$



Entry	Initial compound	Reaction conditions	Reaction products (yield, %)
1	 **1s**	TfOH, 20 °C, 8 h	 **2s** (93%)
2	**1s**	HSO_3F, −75 °C, 0.7 h	Oligomers
3	**1s**	$AlCl_3$, CH_2Cl_2, 20 °C, 2 h	**2s** (88%)
4	 **1t**	TfOH, 20 °C, 5 h	 **2t** (98%)
5	**1t**	$AlCl_3$, CH_2Cl_2, 20 °C, 2 h	**2t** (67%) +  *E*-**4e** (10%)

(*continued on next page*)

Table 3 (*continued*)

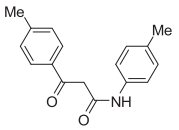
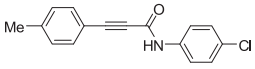
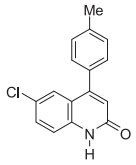
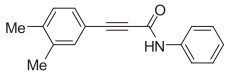
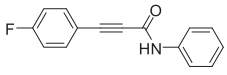
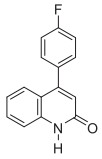
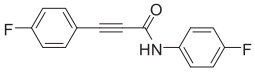
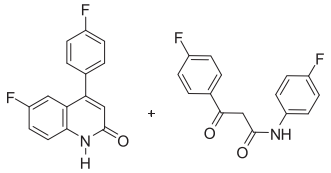
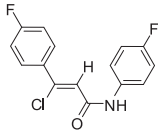
Entry	Initial compound	Reaction conditions	Reaction products (yield, %)
6	**1t**	H_2SO_4, 20 °C, 14 h	**2t** (12%) +  **5b** (54%)
7	 **1u**	TfOH, 20 °C, 10 h	 **2u** (89%)
8	 **1v**	TfOH, 20 °C, 3 h	Oligomers
9	**1v**	$AlCl_3$, CH_2Cl_2, 20 °C, 1 h	Oligomers
10	 **1w**	TfOH, 20 °C, 92 h	 **2v** (89%)
11	**1w**	$AlCl_3$, CH_2Cl_2, 20 °C, 10 h	**2v** (98%)
12	 **1x**	TfOH, 20 °C, 122 h	 **2w** (28%) **5c** (22%)
13	**1x**	$AlCl_3$, CH_2Cl_2, 20 °C, 10 h	**2w** (10%) +  *Z*-**4f** (55%)

Table 3 (*continued*)

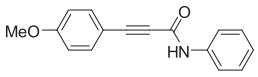
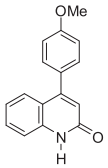
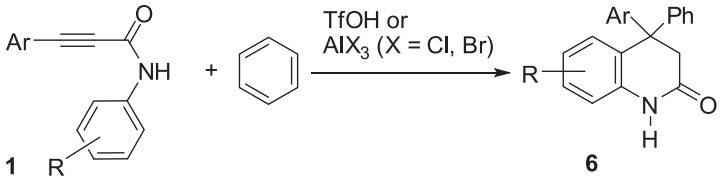
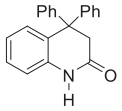
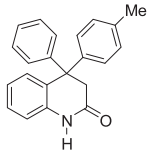
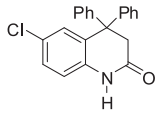
Entry	Initial compound	Reaction conditions	Reaction products (yield, %)
14	 **1y**	TfOH, 20 °C, 2 h	 **2x** (75%)
15	**1y**	HSO_3F, −75 °C, 0.4 h	Oligomers
16	**1y**	$AlCl_3$, CH_2Cl_2, 20 °C, 1 h	**1y** (50%)+**2x** (45%)
17	**1y**	$AlCl_3$, CH_2Cl_2, 20 °C, 10 h	**1y** (55%)+**2x** (36%)

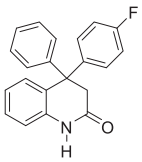
Table 4
Transformations of amides **1a**,**s**,**h**,**w** under the action of TfOH or $AlCl_3$ (X=Cl, Br) in the presence of benzene



Entry	Initial compound	Reaction conditions	Reaction products (yield, %)
1	**1a**	C_6H_6, TfOH, 20 °C, 75 h	**2a** (20%) + **3a** (10%) +  **6a** (40%)
2	**1a**	C_6H_6, $AlCl_3$, 80 °C, 1 h	**2a** (8%)+**6a** (91%)
3	**1a**	C_6H_6, $AlBr_3$, 80 °C, 1 h	**2a** (65%)+**6a** (34%)
4	**1s**	C_6H_6, TfOH, 20 °C, 8 h	**2a** (89%)+**2s** (8%)
5	**1s**	C_6H_6, $AlBr_3$, 20 °C, 3 h	**2a** (29%) + **2s** (10%) +  **6b** (5%)
6	**1h**	C_6H_6, $AlBr_3$, 20 °C, 8 h	 **6c** (53%)

(*continued on next page*)

Table 4 (*continued*)

Entry	Initial compound	Reaction conditions	Reaction products (yield, %)
7	**1h**	C_6H_6, $AlBr_3$, 80 °C, 1 h	**2k** (19%)+**6c** (80%)
8	**1w**	C_6H_6, $AlBr_3$, 80 °C, 1 h	**2a** (20%) + **2v** (34%) +  **6d** (39%)

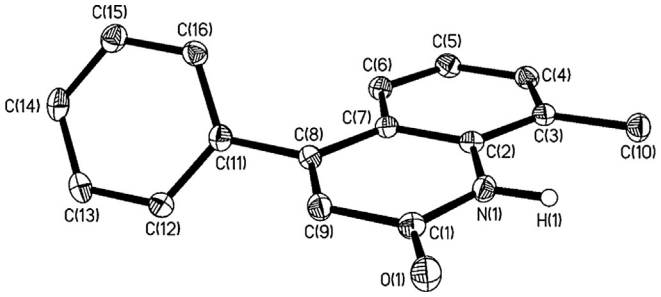


Fig. 1. Molecular structure of compound **2b**.

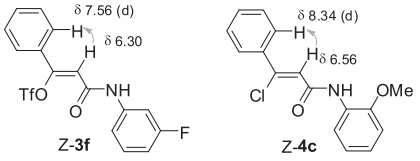


Fig. 2. NOESY and ROESY data for compounds *Z*-**3f**, and *Z*-**4c** (arrows show the observed correlations).

of 40% after the reaction) (Table 1, entry 4). The increase of reaction time leads to increased conversion of compound **1a** and to the increase of the yield of quinolin-2(1*H*)-one **2a** and to the decrease of the yield of triflate **3a** (Table 1, entries 5–8). On increasing the reaction temperature from 20 up to 50 °C the higher yields of the triflate **3a** have been obtained (Table 1, entries 9–11). For both temperatures 20 and 50 °C the reaction time increase results in the decreasing amount of the triflate **3a** and in the increasing amount of quinolin-2(1*H*)-one **2a** (Table 1, entries 4–8, and 9–11). These data reveal that formation of the triflate **3a** is reversible, but this process needs higher activation energy, compared to the formation of compound **2a**. During the reaction the triflate **3a** is converted to the thermodynamically more stable product **2a**. Additional proof of this statement is the observed quantitative transformations of the triflates **3a**,**b** into the quinolinones **2a**,**b** in TfOH at 50 °C for 8 and 5 h correspondingly (structures of compounds **2b**, **3b** are given in Table 2).

It should be noted, when AlX_3 (X=Cl, Br) are used, protons appear in the reaction system after the deprotonation of *N*-aryl ring of species **1** under the formation of compounds **2**. Also a catalytic amount of protic superacids (HHal–$AlnHal_{3n}$ or H_2O–$AlnHal_{3n}$) is normally present in such reaction media due to traces of water in the starting materials. The acid strength of HHal-$AlnHal_{3n}$ (Hal=Br, Cl) is estimated to be −15 to −18 in Hammet acidity function H_0 scale.[17b]

The use of the superacid FSO_3H (−75 °C, 5 h), having H_0 value ~−15, higher than TfOH (H_0 ~−14),[17b] leads to the quantitative formation of the quinolin-2(1*H*)-one **2a** (Table 1, entry 12). No corresponding vinyl fluorosulfonate is obtained due to lower nucleophilicity of FSO_3H, compared to TfOH (contribution of only path *a* in Scheme 1 for FSO_3H). However, in FSO_3H at higher temperature −50 °C (Table 1, entry 13) or in the more acidic system TfOH–SbF_5 (H_0 ~−18) (Table 1, entry 14) the amide **1a** is converted to mixtures of oligomeric products. On the other hand, in less acidic sulfuric acid H_2SO_4 (H_0 ~−12) two reaction products are formed: the quinolin-2(1*H*)-one **2a** and keto-amide **5a** (Table 1, entry 15). The latter is formally the product of triple bond hydration in H_2SO_4. Compound **5a** may be formed as a result of hydrolysis of the corresponding vinyl sulfonate under aqueous reaction work-up (see Experimental). Formation of compound **5a** in 37% yield in this reaction shows the contribution of the path *b* in the reactivity of the corresponding species **I** (Scheme 1). In general, triflate **3a** is formed by nucleophilic attack by the triflate-anion or the triflic acid molecule.

In reactions with strong Lewis acids $AlCl_3$ or $AlBr_3$, the substrate **1a** gives the only product of intramolecular cyclization **2a** in yields of 79–90% (Table 1, entries 16 and 17). No corresponding vinyl halogenides are formed in these cases.

Then we investigated reactions of the amides **1b**–**z**, having substituents in both arene rings (Tables 2 and 3). Table 2 contains data on the transformations of phenylpropynoic acid amides **1b**–**r**, bearing various electron donor–acceptor groups in the *N*-aryl ring only. Amides **1b**–**e** with electron-donating methyl groups are completely converted in TfOH at 20 °C for ~70–90 h to the corresponding quinolinones **2b**–**g** in high yields up to 94% (Table 2, entries 1, 3–5, 8, 9, 11). Small amounts (3–17%) of vinyl triflates **3b**–**e** also appeared due to the reaction of species **I** in the path *b* in Scheme 1. This pathway may be suppressed by the use of AlX_3 (X=Cl, Br) that leads to the quantitative formation (90–96%) of quinolinones **2b**–**g** (Table 2, entries 2, 6, 7, 10, 12).

Introduction of halogens in the amides **1f**–**h** leads to an increase in the amounts of the vinyl triflates (up to 66%) in reactions in TfOH (Table 2, entries 13, 17). It is due to electron-withdrawing properties of halogen atoms that hamper the electrophilic attack of the cations **I** into the *N*-aryl moiety (path *a* in Scheme 1), and interaction of these cations with nucleophilic surroundings prevails (path *b* in Scheme 1). Again, the use of Lewis acids $AlCl_3$, instead of TfOH, assists to minimize the formation of vinyl-type products, like chloride **4b** (yield 6%) (Table 2, entries 14, 15, 18).

ortho- and *meta*-methoxy substituted compounds **1i**,**j** are converted to quinolinones **2l**,**m** in TfOH in moderate yields 20–40% (Table 2, entries 19, 21). *para*-Methoxy **1k**,**n** and more electron rich dimethoxy **1l** and methylenedioxy **1m** derivatives give oligomeric products in TfOH (Table 2, entries 24, 26, 27). Carrying out the reactions of these compounds with $AlCl_3$ allows access to desirable quinolinones **2n**–**p** (Table 2, entries 23, 24). For mono-methoxy substrates **1i** and **1k** reactions with $AlCl_3$ give the corresponding vinyl chlorides **4c** and **4d** (Table 2, entries 20, 22), the latter is the only reaction product. In these cases the formation of large amounts of vinyl chlorides may be caused by coordination of $AlCl_3$ on oxygen atom of methoxy group that deactivates the *N*-arene ring for electrophilic attack in the path *a* and guides the reaction into the path *b* (Scheme 1).

Transformations of amides **1o**,**p**, containing strong electron-withdrawing groups COMe and NO_2, result in the formation of oligomers (Table 2, entries 28, 29), instead of expected vinyl triflates. It probably happens because of the protosolvolytic cleavage of C–N bond in *N*-aryl amido group, as it was recently found for the series of *N*-*para*-nitrophenyl amides of various carboxylic acids.[21]

And finally for this series of the *N*-aryl substituted amides, α- and β-naphthyl substances **1q**,**r** lead to quinolinones **2q**,**r** under the action of both TfOH and $AlCl_3$ (Table 2, entries 30, 31).

It should be noted that amides **1c**,**1e**,**1f** and **1l** give pairs of isomeric quinolinones **2c**,**d**, **2f**,**g**, **2h**,**i** and **2n**,**o**, respectively (Table 2, entries 3–7, 11–14, 23) that are formed as a result of electrophilic substitution in alternative positions of *N*-aryl ring. The ratio of isomers depends on the superelectrophilic activator TfOH or AlX_3 (X=Cl, Br). In general, the reactions under the action of AlX_3 (X=Cl, Br) are less selective (compare the isomer ratios in entries 4,5 and 6,7; 11 and 12; 13 and 14 in Table 2).

Next step in this study has been the investigation of the reactions of amides **1s**–**z**, bearing substituents in arene ring, conjugated with acetylene bond (Table 3). Amides of *para*-tolylpropynoic acid **1s**–**u** are readily cyclized into corresponding quinolinones **2s**–**u** in TfOH or with $AlCl_3$ for 2–10 h at 20 °C in high yields (Table 3, entries 1, 3–5, 7). Under the action of $AlCl_3$ compound **1t** gives additionally small amount of vinyl chloride **4e** (Table 3, entry 5). Electron-donating *para*-methyl group in the amide **1t** facilitates the protonation of triple bond. And we have checked the transformation of this substance in sulfuric acid (Table 3, entry 6). Indeed, the quinolinone **2t** is formed in low yield 12% only. The main reaction product is keto-amide **5b** (54%), which is formed analogously to compound **5a** from amide **1a** (see Table 1, entry 15). More electron rich amide **1v** with two methyl groups undergoes oligomerization under the reaction conditions (Table 3, entries 8, 9).

para-Fluorinated derivative **1w** leads to quinoline **2v** in excellent yield (Table 3, entries 10, 11). Introduction of one more fluorine atom in another *N*-aryl ring in compound **1x** makes the electrophilic cyclization more difficult. In this case the yield of quinoline **2w** is 8–10% (Table 3, entries 12, 13), and the main reaction products are compounds **4f** and **5c**, formed from the corresponding cation **I** in the pathway *b* in Scheme 1.

In TfOH methoxy substituted amide **1y** gives cyclization product **2x** during 2 h at 20 °C (Table 3, entry 14), in FSO_3H oligomerization takes place (Table 3, entry 15). Surprisingly, but in the reaction with $AlCl_3$ conversion of compound **1y** is incomplete even after 10 h at 20 °C (Table 3, entries 16, 17). That is caused by coordination of $AlCl_3$ on the oxygen atom of methoxy group, that makes such coordinated methoxy group a strong electron-withdrawing substituent, which seriously hampers the protonation on acetylene bond.

The data obtained in Tables 1–3 allow to bring some regularities, concerning the influence of the superelectrophilic activator on the investigated reactions. Thus, for most cases Lewis acids AlX_3 (X=Cl, Br) promote intramolecular cyclization (path *a* in Scheme 1) to a greater extent than Bronsted superacids (TfOH, FSO_3H). In TfOH the formation of vinyl triflates is often observed (path *b* in Scheme 1). Usually transformations with AlX_3 (X=Cl, Br) take less time, in comparison to TfOH, at the same temperature.

One may also state reaction restrictions, depending on the structure of the initial amides. Compounds **1o**,**p** (Table 2, entries 28, 29), bearing strong electron-withdrawing groups in *N*-arene ring, or **1v** (Table 3, entry 8), dimethylated in arylacetylene moiety, are converted to oligomers. The presence of other donor or acceptor substituents in the structures of amides **1** allows to achieve their intramolecular cyclization into quinolin-2(1*H*)-ones **2** under the action of either Bronsted superacids or strong Lewis acids in various yields.

Finally, we have carried out reactions of the selected amides **1a**,**s**,**h**,**w** with benzene to check the reactions of the cations **I** in the presence of external π-nucleophiles (Scheme 1). In our preliminary communication[19] transformations of the amide **1a** and benzene into 4,4-diphenyl 3,4-dihydroquinolin-2-(1*H*)-one **6a** have been studied (Table 4, entries 1–3). It has been shown that under the superelectrophilic activation conditions compound **6a** is formed through an addition of benzene to acetylene bond in the pathway *c* (Scheme 1), rather than through addition of benzene to quinolinone **2a**.[19]

In the system TfOH–benzene the amide **1a** gives products of all three concurrent pathways *a*, *b*, and *c* (Scheme 1): quinolinone **2a**, vinyl triflate **3a**, and dihydroquinolinone **6a** (Table 4, entry 1). Upon using $AlCl_3$ or $AlBr_3$ the reaction path *b* (Scheme 1) is completely supressed, only compounds **2a** and **6a** are formed (Table 4, entries 2, 3).

Reaction of *para*-methyl substituted amide **1s** with benzene in TfOH leads to quinolinones **2a** and **2s** (Table 4, entry 4), the former is a product of aryl groups exchange. No dihydroquinolinone is formed under this Bronsted acid activation. The corresponding dihydroquinolinone **6b** was obtained in the system $AlBr_3$–benzene in low yield 5% (Table 4, entry 5).

Amide **1h**, bearing *para*-chloro substituent in *N*-aryl ring, also gives two kinds of products: quinolinone **2k** and dihydroderivative **6c** under the activation by $AlBr_3$ (Table 4, entries 6, 7). The best yield (80%) of compound **6c** was obtained at high reaction temperature 80 °C (Table 4, entry 7). In the system $AlBr_3$–benzene fluorinated amide **1w** leads to the formation of dihydroquinolinone **6d** along with concurrent reaction products **2a** (aryl groups exchange) and **2v** (Table 4, entry 8).

So, reactions of the amides **1** with benzene under the superelectrophilic activation conditions open a new way to 4,4-diaryl 3,4-dihydroquinolin-2-(1*H*)-ones **6** (Table 4), which are difficult to access.

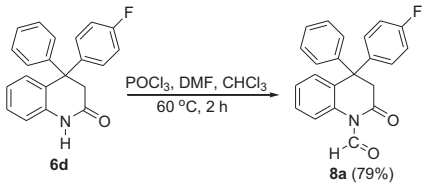
To demonstrate the synthetic potential of the obtained compounds **2** and **6** we carried out some of their reactions. 4-Aryl quinolin-2(1*H*)-ones **2c**,**d**,**m** in neat $POCl_3$ were converted into 4-aryl 2-chloroquinolines **7a**–**c**, correspondingly (Scheme 2), by known procedure.[22] Compounds **7** are of a great demand for the synthesis of diheteroarylamine ligands[23a] and pharmaceutical substances.[23b,c]

2c,d,m **7a,b,c** (60-68%)

7: R = 5-CH_3 (**a**), 7-CH_3(**b**), 7-OCH_3(**c**)

Scheme 2. Transformation of 4-aryl quinolin-2(1*H*)-ones **2c**,**d**,**m** into 4-aryl 2-chloroquinolines **7a**–**c**, correspondingly.

3,4-Dihydroquinolin-2-(1*H*)-one **6d** was transformed into the formylated derivative **8a** in the system $POCl_3$–DMF–$CHCl_3$ under the Vilsmeier–Haack reaction conditions (Scheme 3). This is an example of the N-formylation of the such kind of 3,4-dihydroquinolin-2-(1*H*)-one structures. Two carbonyl groups in these compounds can be used for various heterocyclic systems construction.



Scheme 3. N-Formylation of compound **6d**.

3. Conclusions

Efficient methods for the synthesis of 4-aryl quinolin-2(1*H*)-ones and 4,4-diaryl 3,4-dihydroquinolin-2-(1*H*)-ones have been developed on the basis of superelectrophilic activation of *N*-aryl amides of 3-arylpropynoic acids by Bronsted superacids (CF_3SO_3H, HSO_3F) or strong Lewis acids AlX_3 (X=Cl, Br). These transformations proceed at room temperature for 1–92 h with high yields of the reaction products.

Additionally 4-aryl quinolin-2(1*H*)-ones have been converted into 2-chloro-4-aryl quinolines in neat $POCl_3$ at 100 °C for 2 h. N-Formylation of the 4,4-diaryl 3,4-dihydroquinolin-2-(1*H*)-ones can be achieved in the system $POCl_3$–DMF–$CHCl_3$ at 60 °C for 2 h.

4. Experimental section

4.1. General

The NMR spectra of compounds solutions in $CDCl_3$ were recorded on a Bruker AM-500 or Bruker-400 spectrometers at 25 °C (at 500 or 400, 470 and 125 or 100 MHz for ^1H, ^{19}F and ^{13}C NMR spectra, respectively). The residual proton-solvent peak $CDCl_3$ (δ 7.26 ppm) for ^1H NMR spectra, the carbon signal of $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR spectra, and the signal of $CFCl_3$ (δ 0.0 ppm) for ^{19}F NMR spectra were used as references. IR spectra of compounds solutions in $CHCl_3$ were recorded with a spectrometer FSM-1201. CHN analysis was carried out on a machine EA-300 Euro-Vektor. HRMS was carried out at an instrument Bruker MicroTOF (ESI). Chromato-mass-spectrometry data were obtained at a machine G2570A GC/MSD Agilent Technologies 6850c with a column HP-5MS (3 m×0.25 mm), a thickness of the stationary phase 0.25 μm. The preparative reactions were monitored by thin-layer chromatography carried out on silica gel plates (Silufol UV-254) using UV light for detection. Column chromatography was performed on silica gel Chemapol 40/100 (0.04–0.10 mm) with hexanes/ethyl acetate mixture elution.

Initial N-aryl amides of 3-arylpropynoic acids ***1a–y*** were synthesized by reaction of anilines with 3-arylprop-2-ynoyl chlorides at a molar ratio of 2:1 in benzene solution at 50 °C for 30 min, or by interaction of 3-arylpropynoic acids with anilines in the presence of dicyclohexyl carbodiimide.[24]

4.2. General procedure for the transformation of amides 1a–y in Bronsted superacids TfOH or HSO_3F (Tables 1–3)

A solution of amide **1** (1 mmol) in TfOH (3 mL) was stirred at 20 °C for the time as indicated in Tables 1–3. The mixture was poured into ice water (30 mL) and extracted with chloroform (3×30 mL). The extracts were combined, washed with water, a saturated aqueous solution of $NaHCO_3$, and water again, and dried over Na_2SO_4, the solvent was distilled off under reduced pressure, and the residue was recrystallized from ethanol or subjected to chromatographic separation on silica gel using hexane/ethyl acetate as an eluent.

Analogously the reactions were carried out in HSO_3F at −75 or −50 °C for 0.4–5 h (see Tables 1 and 3). Reaction mixture was quenched with concentrated aqueous hydrochloric acid frozen down to −80 °C (30 mL), then diluted with water (50 mL), extracted and worked-up as described above.

4.3. General procedure for the transformation of amides 1a–y under the action of strong Lewis acids $AlCl_3$ or $AlBr_3$ (Tables 1–3)

Amide **1** (1 mmol) was added to the solution of $AlBr_3$ or $AlCl_3$ (5.0 mmol) in CH_2Cl_2 (20 mL). Reaction mixture was stirred at 20 °C for the time as indicated in Tables 1–3. The mixture was quenched with ice water (50 mL) extracted and worked-up as described above.

4.4. General procedure for the transformation of amides 1a,s,h,w in TfOH in the presence of benzene (Table 4)

Amide **1** (1 mmol) was added to the mixture of TfOH (2 mL) and benzene (1 mL). Reaction mixture was stirred at 20 °C for the time as indicated in Table 4. The mixture was poured into ice water (30 mL), extracted and worked-up as described above.

4.5. General procedure for the transformation of amides 1a,s,h,w under the action of strong Lewis acids $AlCl_3$ or $AlBr_3$ in the presence of benzene (Table 4)

Amide **1** (1 mmol) was added to the solution of $AlBr_3$ or $AlCl_3$ (5.0 mmol) in benzene (10 mL). Reaction mixture was stirred at 20 or 80 °C for the time as indicated in Table 4. The mixture was quenched with ice water (50 mL), extracted and worked-up as described above.

4.5.1. Physical–chemical characteristics of the obtained compounds. Characteristics of *N*-phenylamide of 3-phenylpropynoic acid **1a**, *N*-3-methylphenylamide of 3-phenylpropynoic acid **1c**, *N*-4-methylphenylamide of 3-phenylpropynoic acid **1d**, 4-phenylquinolin-2(1*H*)-one **2a** (Table 1), 6-methyl-4-phenylquinolin-2(1*H*)-one **2e** (Table 2, entries 9, 10), 7-methyl-4-phenylquinolin-2(1*H*)-one **2d** (Table 2, entries 3–7), *N*-3-phenylamide of 3-trifluoromethylsulfonyloxy-3-phenylpropenoic acid **3a** (Table 1) are given in our preliminary communication,[18] and properties of 4,4-diphenyl-3,4-dihydroquinolin-2-(1*H*)-one **6a** (Table 4, entries 1–3) are presented in our previous work.[19]

4.5.2. N-2-Methylphenylamide of 3-phenylpropynoic acid ***1b****.* Yield 58%. Mp 131–133 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=2.33 (s, 3H, Me), 7.11 (t, *J*=7.4 Hz, 1H, Ar), 7.22 (t, *J*=7.4 Hz, 2H, Ar), 7.38 (d, *J*=8.1 Hz, 1H, Ar), 7.39 (d, *J*=7.4 Hz, 2H, Ar), 7.43 (d, *J*=8.1 Hz, 1H, Ar). 7.59 (d, *J*=8.1 Hz, 2H, Ar), 7.86 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=17.8, 83.4, 85.6, 120.0, 123.3, 125.8, 126.8, 128.5, 129.1, 130.2, 130.6, 132.6, 134.9, 151.2; IR (ν, cm^{-1}): 3228, 2213, 1635; MS: *m*/*z* (%)=235 (33) [M^+], 129 (100). Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.74; H, 5.60; N, 5.90.

4.5.3. N-(3,4-Dimethylphenyl)amide of 3-phenylpropynoic acid ***1e****.* Yield 54%. Mp 125–127 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=2.22 (s, 3H, Me), 2.25 (s, 3H, Me), 7.09 (d, *J*=8.1 Hz, 1H, Ar), 7.27

(d, J=8.1 Hz, 1H, Ar), 7.34 (s, 1H, Ar), 7.37 (t, J=7.4 Hz, 2H, Ar), 7.43 (t, J=7.4 Hz, 1H, Ar), 7.49 (s, 1H, NH), 7.56 (d, J=7.4 Hz, 2H, Ar). Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.87; H, 6.09; N, 5.66.

4.5.4. N-(3-Fluorophenyl)amide of 3-phenylpropynoic acid ***1f***. Yield 40%. Mp 113–115 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=6.83 (t, J=7.5 Hz, 1H, Ar), 7.23 (t, J=8.1 Hz, 1H, Ar), 7.27 (t, J=8.1 Hz, 1H, Ar), 7.34 (t, J=7.5 Hz, 2H, Ar), 7.42 (t, J=7.5 Hz, 1H, Ar), 7.53 (d, J=8.1 Hz, 3H, Ar), 7.91 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=83.1, 86.3, 107.5 (d, J=26.7 Hz), 111.6 (d, J=21.2 Hz), 115.0 (d, J=2.7 Hz), 119.7, 128.6, 130.2 (d, J=9.3 Hz), 130.5, 132.6, 138.8 (d, J=10.9 Hz), 151.0, 162.9 (d, J=244.0 Hz); ^{19}F NMR (500 MHz, $CDCl_3$, 25 °C): δ=−107.66 (dd, J=17, 9 Hz, 1F); IR (ν, cm^{-1}): 3245, 2212, 1644; MS: m/z (%)=239 (25) [M$^+$], 129 (100). Anal. Calcd for $C_{15}H_{10}FNO$: C, 75.30; H, 4.21; N, 5.85. Found: C, 75.23; H, 4.16; N, 5.92.

4.5.5. N-(4-Fluorophenyl)amide of 3-phenylpropynoic acid ***1g***. Yield 54%. Mp 142–144 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=7.03 (t, J=8.6 Hz, 2H, Ar), 7.36 (t, J=7.6 Hz, 2H, Ar), 7.44 (t, J=7.6 Hz, 1H, Ar), 7.52–7.54 (m, 4H, Ar), 7.68 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=83.2, 86.1, 115.8 (d, J=22.4 Hz), 119.8, 121.8 (d, J=7.8 Hz), 128.6, 130.6, 132.6, 133.3 (d, J=2.6 Hz), 151.1, 159.7 (d, J=243.2 Hz); IR (ν, cm^{-1}): 3259, 2211, 1638. Anal. Calcd for $C_{15}H_{10}FNO$: C, 75.30; H, 4.21; N, 5.85. Found: C, 75.35; H, 4.24; N, 5.79.

4.5.6. N-(4-Chlorophenyl)amide of 3-phenylpropynoic acid ***1h***. Yield 75%. Mp 186–188 °C (lit.[25] 186 °C); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=7.30 (d, J=8.7 Hz, 2H, Ar), 7.37 (t, J=7.4 Hz, 2H, Ar), 7.44 (t, J=7.4 Hz, 1H, Ar), 7.52 (d, J=8.7 Hz, 2H, Ar), 7.56 (d, J=7.4 Hz, 2H, Ar), 7.61 (s, 1H, NH); IR (ν, cm^{-1}): 3280, 2214, 1635.

4.5.7. N-(2-Methoxyphenyl)amide of 3-phenylpropynoic acid ***1i***. Yield 59%. Mp 97–99 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=3.92 (s, 3H, OMe), 6.90 (d, J=8.2 Hz, 1H, Ar), 6.98 (t, J=7.5 Hz, 1H, Ar), 7.08 (t, J=7.5 Hz, 1H, Ar), 7.38 (t, J=7.5 Hz, 2H, Ar), 7.42–7.45 (m, 1H, Ar), 7.60 (d, J=8.2 Hz, Ar), 8.15 (s, 1H, NH), 8.37 (d, J=8.2 Hz, 1H, Ar); IR (ν, cm^{-1}): 3290, 2209, 1653; MS: m/z (%)=251 (37) [M$^+$], 220 (18), 129 (100). Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.52; H, 5.17; N, 5.52.

4.5.8. N-(3-Methoxyphenyl)amide of 3-phenylpropinoic acid ***1j***. Yield 70%. Oily compound; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=3.82 (s, 3H, OMe), 6.70 (d, J=8.2 Hz, 1H, Ar), 7.05 (d, J=7.4 Hz, 1H, Ar), 7.24 (t, J=8.2 Hz, 1H, Ar), 7.31 (s, 1H, Ar), 7.38 (t, J=7.4 Hz, 2H, Ar), 7.45 (t, J=7.4 Hz, 1H, Ar), 7.57 (d, J=8.2 Hz, 2H, Ar), 7.65 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=55.3, 83.5, 85.7, 105.8, 110.7, 112.1, 119.9, 128.5, 129.8, 130.3, 132.6, 138.6, 151.0, 160.2; IR (ν, cm^{-1}): 3267, 2217, 1638. Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.45; H, 5.18; N, 5.65.

4.5.9. N-(4-Methoxyphenyl)amide of 3-phenylpropynoic acid ***1k***. Yield 63%. Mp 125–126 °C (lit.[26] 122–124 °C); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=3.79 (s, 3H, OMe), 6.87 (d, J=7.5 Hz, 2H, Ar), 7.36 (t, J=7.2 Hz, 2H, Ar), 7.42 (t, J=7.5 Hz, 1H, Ar), 7.47 (d, J=7.5 Hz, 2H, Ar), 7.55 (d, J=7.2 Hz, 2H, Ar), 7.60 (s, 1H, NH); IR (ν, cm^{-1}): 3263, 2210, 1634.

4.5.10. N-(3,4-Dimethoxyphenyl)amide of 3-phenylpropynoic acid ***1l***. Yield 85%. Mp 142–144 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=3.85 (s, 3H, OMe), 3.87 (s, 3H, OMe), 6.81 (d, J=8.6 Hz, 1H, Ar), 6.97 (d, J=8.6 Hz, 1H, Ar), 7.32 (s, 1H, Ar), 7.36 (t, J=7.4 Hz, 2H, Ar), 7.41 (d, J=7.4 Hz, 1H, Ar), 7.54 (d, J=7.4 Hz, 2H, Ar), 7.64 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=55.9, 56.0, 83.5, 85.5, 104.9, 111.3, 112.1, 120.0, 128.5, 130.2, 131.0, 132.5, 146.3, 149.0, 150.9; IR (ν, cm^{-1}): 3210, 2210, 1637. Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.63; H, 5.30; N, 4.95.

4.5.11. N-(3,4-Methylendioxyphenyl)amide of 3-phenylpropynoic acid ***1m***. Yield 91%. Mp 145–148 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=5.95 (s, 2H, OCH_2O), 6.75 (d, J=8.4 Hz, 1H, Ar), 6.86 (dd, J=8.4, 2.1 Hz, 1H, Ar), 7.26 (d, J=2.1 Hz, 1H, Ar), 7.36 (t, J=7.4 Hz, 2H, Ar), 7.43 (t, J=7.4 Hz, 1H, Ar), 7.55 (d, J=7.4 Hz, 2H, Ar), 7.56 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=83.4, 85.7, 101.4, 102.8, 108.1, 113.3, 120.0, 128.5, 130.2, 131.5, 132.6, 144.7, 147.9, 151.0. Anal. Calcd for $C_{16}H_{11}NO_3$: C, 72.45; H, 4.18; N, 5.28. Found: C, 72.51; H, 4.13; N, 5.30.

4.5.12. N-(3-Fluoro-4-methoxyphenyl)amide of 3-phenylpropynoic acid ***1n***. Yield 54%. Mp 135–137 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=3.86 (s, 3H. OMe), 6.89 (t, J=8.9 Hz, 1H, Ar), 7.21 (d, J=8.9 Hz, 1H, Ar), 7.35 (t, J=7.6 Hz, 2H, Ar), 7.42 (t, J=7.6 Hz, 1H, Ar), 7.47 (dd, J=12.6, 2.6 Hz, 1H, Ar), 7.53 (d, J=7.6 Hz, 2H, Ar), 7.74 (s, 1H, NH); IR (ν, cm^{-1}): 3262, 2211, 1635. Anal. Calcd for $C_{16}H_{12}FNO_2$: C, 71.37; H, 4.49; N, 5.20. Found: C, 71.43; H, 4.45; N, 5.25.

4.5.13. N-(3-Acetylphenyl)amide of 3-phenylpropynoic acid ***1o***. Yield 63%. Mp 142–144 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=2.58 (s, 3H, Me), 7.38 (d, J=7.1 Hz, 2H, Ar), 7.45 (d, J=7.1 Hz, 1H, Ar), 7.56 (d, J=7.9 Hz, 2H, Ar), 7.67 (d, J=7.9 Hz, 2H, Ar), 7.84 (s, 1H, NH), 7.96 (d, J=7.9 Hz, 2H, Ar); IR (ν, cm^{-1}): 3280, 2209, 1667. Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.50; H, 4.95; N, 5.36.

4.5.14. N-(3-Nitrophenyl)amide of 3-phenylpropynoic acid ***1p***. Yield 73%. Mp 135–137 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=7.36 (t, J=7.6 Hz, 2H, Ar), 7.45 (t, J=7.6 Hz, 1H, Ar), 7.49–7.56 (m, 3H, Ar), 7.97–8.03 (m, 3H, Ar), 8.41 (s, 1H, NH); IR (ν, cm^{-1}): 3260, 2211, 1650. Anal. Calcd for $C_{15}H_{10}N_2O_3$: C, 67.67; H, 3.79; N, 10.52. Found: C, 67.72; H, 3.73; N, 10.48.

4.5.15. N-(1-Naphthyl)amide-3-phenylpropynoic acid ***1q***. Yield 71%. Mp 160–161 °C (lit.[25] 164 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=7.41 (d, J=7.2 Hz, 1H, Ar), 7.47–7.56 (m, 4H, Ar), 7.63 (d, J=7.2 Hz, 2H, Ar), 7.73 (d, J=8.1 Hz, 1H, Ar), 7.88–8.01 (m, 4H, Ar), 8.04 (s, 1H, NH); IR (ν, cm^{-1}): 3219, 2214, 1631.

4.5.16. N-(2-Naphthyl)amide of 3-phenylpropynoic acid ***1r***. Yield 71%. Mp 132–133 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=7.34 (t, J=7.6 Hz, 2H, Ar), 7.41–7.42 (m, 2H, Ar), 7.46 (t, J=7.6 Hz, 1H, Ar), 7.51 (dd, J=8.4, 2.1 Hz, 1H, Ar), 7.56 (d, J=7.6 Hz, 2H, Ar), 7.78 (t, J=8.4 Hz, 4H, Ar), 7.92 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=83.5, 86.0, 117.2, 119.6, 119.9, 125.3, 126.6, 127.5, 127.8, 128.5, 128.9, 130.3, 130.9, 132.6, 133.7, 134.8, 151.2; IR (ν, cm^{-1}): 3253, 2211, 1633. Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.14; H, 4.90; N, 5.12.

4.5.17. N-Phenylamide of 3-(4-methylphenyl)propynoic acid ***1s***. Yield 53%. Mp 114–116 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=2.38 (s, 3H, Me), 7.14 (t, J=7.4 Hz, 1H, Ar), 7.17 (d, J=7.4 Hz, 2H, Ar), 7.34 (t, J=7.4 Hz, 2H, Ar), 7.46 (d, J=8.0 Hz, 2H, Ar), 7.56 (d, J=8.0 Hz, 2H, Ar), 7.62 (s, 1H, NH); IR (ν, cm^{-1}): 3263, 2208, 1639. Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.65; H, 5.62; N, 5.89.

4.5.18. N-(4-Methylphenyl)amide of 3-(4-methylphenyl)propynoic acid ***1t***. Yield 59%. Mp 154–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=2.32 (s, 3H, Me), 2.38 (s, 3H, Me), 7.14 (d, J=8.1 Hz, 2H, Ar), 7.17 (d, J=8.1 Hz, 2H, Ar), 7.45 (d, J=8.1 Hz, 4H, Ar), 7.68 (s, 1H, NH);

IR (ν, cm^{-1}): 3260, 2207, 1635. Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.85; H, 6.01; N, 5.68.

4.5.19. N-(4-Chlorophenyl)amide of 3-(4-methylphenyl)propynoic acid ***1u***. Yield 57%. Mp 197–199 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=2.38 (s, 3H, Me), 7.17 (d, J=7.8 Hz, 2H, Ar), 7.29 (d, J=8.6 Hz, 2H, Ar), 7.45 (d, J=7.8 Hz, 2H, Ar), 7.51 (d, J=8.6 Hz, 2H, Ar), 7.59 (s, 1H, NH); IR (ν, cm^{-1}): 3261, 2207, 1625. Anal. Calcd for $C_{16}H_{12}ClNO$: C, 71.25; H, 4.48; N, 5.19. Found: C, 71.19; H, 4.54; N, 5.13.

4.5.20. N-Phenylamide of 3-(3,4-dimethylphenyl)propynoic acid ***1v***. Yield 62%. Mp 124–125 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=2.18 (s, 3H, Me), 2.21 (s, 3H, Me), 7.06 (d, J=8.5 Hz, 1H, Ar), 7.11–7.13 (m, 2H, Ar), 7.24 (s, 1H, Ar), 7.30 (t, J=7.6 Hz, 2H, Ar), 7.36 (d, J=7.6 Hz, 2H, Ar), 7.38 (s, 1H, NH); IR (ν, cm^{-1}): 3264, 2209, 1655. Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.79; H, 6.10; N, 5.70.

4.5.21. N-Phenylamide of 3-(4-fluorophenyl)propynoic acid ***1w***. Yield 90%. Mp 120–122 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=7.06 (t, J=8.6 Hz, 2H, Ar), 7.14 (t, J=7.6 Hz, 1H, Ar), 7.35 (t, J=7.6 Hz, 2H, Ar), 7.53–7.56 (m, 4H, Ar), 7.67 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=83.3, 84.8, 116.0 (d, J=21.1 Hz), 116.01 (d, J=3.5 Hz), 120.0124.9, 129.1 (d, J=4.1 Hz), 134.8 (d, J=8.7 Hz), 137.3, 151.0, 163.6 (d, J=251.4 Hz); IR (ν, cm^{-1}): 3260, 2212, 1640. Anal. Calcd for $C_{15}H_{10}FNO$: C, 75.30; H, 4.21; N, 5.85. Found: C, 75.35; H, 4.24; N, 5.79.

4.5.22. N-(4-Fluorophenyl)amide of 3-(4-fluorophenyl)propynoic acid ***1x***. Yield 98%. Mp 148–150 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=7.02–7.09 (m, 4H, Ar), 7.51–7.57 (m, 4H, Ar), 7.61 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=83.1, 85.0, 115.8 (d, J=22.6 Hz), 116.1 (d, J=22.1 Hz), 121.8 (d, J=7.9 Hz), 129.1 (d, J=8.7 Hz), 133.3 (d, J=2.6 Hz), 134.8 (d, J=8.8 Hz), 151.0, 159.7 (d, J=243.3 Hz), 163.7 (d, J=251.7 Hz); IR (ν, cm^{-1}): 3244, 2213, 1638. Anal. Calcd for $C_{15}H_9F_2NO$: C, 70.04; H, 3.53; N, 5.45. Found: C, 70.09; H, 3.48; N, 5.43.

4.5.23. N-Phenylamide of 3-(4-methoxyphenyl)propynoic acid ***1y***. Yield 44%. Mp 95–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=3.84 (s, 3H, OMe), 6.89 (d, J=8.9 Hz, 2H, Ar), 7.13 (t, J=7.8 Hz, 1H, Ar), 7.35 (t, J=7.8 Hz, 2H, Ar), 7.53 (d, J=8.9 Hz, 2H, Ar), 7.56 (d, J=8.1 Hz, 2H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=55.4, 82.8, 86.4, 111.8, 114.3, 119.9, 124.7, 129.1, 134.4, 137.5, 151.3, 161.2; IR (ν, cm^{-1}): 3266, 2211, 1638. Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.45; H, 5.16; N, 5.63.

4.5.24. 8-Methyl-4-phenylquinolin-2(1H)-one ***2b*** *(Table 2, entries 1, 2).* Mp 218–221 °C (lit.[27] 222–223 °C); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=2.53 (s, 3H, Me), 6.61 (s, 1H, HC=), 7.05 (t, J=7.6 Hz, 1H, Ar), 7.35–7.39 (m, 2H, Ar), 7.41–7.43 (m, 2H, Ar), 7.47–7.49 (m, 3H, Ar), 10.36 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=17.3, 119.5, 120.6, 122.1, 123.8, 125.1, 128.5, 128.7, 128.8, 131.9, 137.1, 137.3, 153.8, 163.0.

4.5.25. X-ray crystallographic study of ***2b***. Intensity data for **2b** was collected at 150 K on a Smart Apex diffractometer with graphite monochromated Mo Kα radiation (λ=0.71073 Å) in the ω scan mode (ω=0.3°, 10 s on each frame). The intensity data were integrated by SAINT program.[28] SADABS[29] was used to perform area-detector scaling and absorption corrections. The structure **2b** was solved by direct method and was refined on F^2 using all reflections with SHELXTL package.[30] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and refined in the 'riding-model'. X-ray data for **2b**: $C_{16}H_{13}NO$, crystal size 0.35×0.10×0.10 mm, M=235.27, monoclinic, a=12.1961(4) Å, b=10.2640(4) Å, c=24.4896(9) Å, β=90.089(2)°, V=1155.16(18) $Å^3$, space group $P2_1/n$, Z=4, $F(000)$=496, d_{calcd}=1.353 g cm^{-1}, μ=0.085 mm^{-1}, θ=2.41–26.00°, reflection collected 6908, independent reflection 2256 (R_{int}=0.0325), GOF (F^2)=1.019, R_1=0.0469 [$I>2\sigma(I)$], wR_2=0.1198, largest diff. peak and hole 0.262/−0.168 e $Å^{-3}$. CCDC 983969 (**2b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk).

4.5.26. 5-Methyl-4-phenylquinolin-2(1H)-one ***2c***. Compound **2c** (Table 2, entries 3–7) was obtained in a mixture with compound **2d**. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, from the spectrum of the mixture): δ=2.43 (s, 3H, Me), 6.57 (s, 1H, HC=), 6.93 (d, J=7.1 Hz, 1H, Ar), 7.32–7.48 (m, 7H, Ar), 12.76 (s, 1H, NH).

4.5.27. 5,6-Dimethyl-4-phenylquinolin-2(1H)-one ***2f*** *and 6,7-dimethyl-4-phenylquinolin-2(1H)-one* ***2g***. Compounds **2f** and **2g** (Table 2, entries 11, 12) were obtained as a mixture with mp 255–257 °C (for the ratio ~1:3.5). Compound **2f**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, from the spectrum of the mixture): δ=2.25 (s, 3H, Me), 2.27 (s, 3H, Me), 6.60 (s, 1H, HC=), 12.79 (s, 1H, NH). Compound **2g**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, from the spectrum of the mixture): δ=2.22 (s, 3H, Me), 2.34 (s, 3H, Me), 6.63 (s, 1H, HC=), 12.79 (s, 1H, NH). For the mixture of compounds **2f**,**g**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=7.27–7.32 (m, Ar), 7.41–7.45 (m, Ar), 7.49–7.50 (m, Ar), 7.60–7.63 (m, Ar). HRMS (ES^+): calcd for $C_{17}H_{16}NO$, 250.1226; found 250.1237.

4.5.28. 5-Fluoro-4-phenylquinolin-2(1H)-one ***2h*** *and 7-Fluoro-4-phenylquinolin-2(1H)-one* ***2i***. Compounds **2h** and **2i** (Table 2, entries 13, 14) were obtained as a mixture with mp 258–260 °C (for the ratio ~1:11). Compound **2h**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, from the spectrum of the mixture): δ=6.58 (s, 1H, HC=), 6.90–7.54 (m, 8H, Ar), 12.09 (s, 1H, NH). Compound **2i**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, from the spectrum of the mixture): δ=6.63 (s, 1H, HC=), 6.90 (td, J=8.7, 2.2 Hz, 1H, Ar), 7.21 (dd, J=9.3, 2.2 Hz, 1H, Ar), 7.43–7.45 (m, 2H, Ar), 7.50–7.54 (m, 4H, Ar), 12.77 (s, 1H, NH). For the mixture of compounds **2h**,**i**: HRMS (ES^+): calcd for $C_{15}H_{11}FNO$, 240.0819; found 240.0831.

4.5.29. 6-Fluoro-4-phenylquinolin-2(1H)-one ***2j*** *(Table 2, entry 15).* Mp 160–163 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=6.63 (s, 1H, HC=), 7.05 (t, J=8.0 Hz, 2H, Ar), 7.42–7.44 (m, 3H, Ar), 7.56–7.59 (m, 2H, Ar), 7.66–7.67 (m, 2H, Ar), 8.02 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=111.8 (d, J=24.8 Hz), 119.2 (d, J=24.8 Hz), 123.7, 126.8, 128.6, 128.8, 129.0, 129.2, 130.7, 130.8, 131.2, 146.0, 159.1; ^{19}F NMR (500 MHz, $CDCl_3$, 25 °C): δ=−113.92 to −113.98 (m, 1F). Anal. Calcd for $C_{15}H_{10}FNO$: C, 75.30; H, 4.21; N, 5.85. Found: C, 75.25; H, 4.27; N, 5.89.

4.5.30. 6-Chloro-4-phenylquinolin-2(1H)-one ***2k*** *(Table 2, entries 17, 18).* Mp 258–260 °C (lit.[31] 260–263 °C); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=6.69 (s, 1H, HC=), 7.42–7.45 (m, 3H, Ar), 7.47–7.49 (m, 1H, Ar), 7.50–7.54 (m, 4H, Ar), 12.36 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=118.1, 120.7, 121.6, 126.0, 128.2, 128.8, 128.9, 129.2, 131.0, 136.3, 137.3, 152.7, 163.9.

4.5.31. 8-Methoxy-4-phenylquinolin-2(1H)-one ***2l*** *(Table 2, entries 19, 20).* Oily compound; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ=3.90 (s, 3H, OMe), 6.66 (s, 1H, HC=), 6.90 (d, J=8.2 Hz, 1H, Ar), 6.99 (t, J=7.6 Hz, 2H, Ar), 8.75 (s, 1H. NH), 7.08 (t, J=7.6 Hz, 1H, Ar), 7.58 (d,

J=7.6 Hz, 2H, Ar), 7.36–7.39 (m, 2H, Ar); HRMS (ES^+): calcd for $C_{16}H_{14}NO_2$, 252.1019; found 252.1021.

4.5.32. 7-Methoxy-4-phenylquinolin-2(1H)-one ***2m*** *(Table 2, entry 21).* Mp 230–232 °C (lit.[32] 232–233 °C); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ=3.86 (s, 3H, OMe), 6.50 (s, 1H, HC=), 6.73 (d, J=8.8 Hz, 1H, Ar), 6.90 (s, 1H, Ar), 7.36–7.41 (m, 3H, Ar), 7.43–7.45 (m, 3H, Ar), 11.81 (s, 1H, NH); IR (ν, cm^{-1}): 3300, 1651; MS (ES): m/z (%)=251 (100) $[M]^+$, 208 (20), 181 (18), 124 (28), 109 (18).

4.5.33. 5,6-Dimethoxy-4-phenylquinolin-2(1H)-one ***2n*** *and 6,7-dimethoxy-4-phenylquinolin-2(1H)-one* ***2o****.* Compounds **2n** and **2o** (Table 2, entry 23) were obtained as a mixture. Compound **2n**: ^1H NMR (500 MHz, $CDCl_3$, 25 °C, from the spectrum of the mixture): δ=3.84 (s, 3H, OMe), 3.87 (s, 3H, OMe), 6.63 (s, 1H, HC=), 8.21 (s, 1H, NH). Compound **2o**: ^1H NMR (500 MHz, $CDCl_3$, 25 °C, from the spectrum of the mixture): δ=3.83 (s, 3H, OMe), 3.84 (s, 3H, OMe), 6.64 (s, 1H, HC=), 8.27 (s, 1H, NH). For the mixture of compounds **2n**,**o**: ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=6.75–6.84 (m, Ar), 7.15–7.19 (m, Ar), 7.36–7.38 (m, Ar), 7.57–7.62 (m, Ar); HRMS (ES^+): calcd for $C_{17}H_{15}NNaO_3$ 304.0950; found 304.0949.

4.5.34. 7,8-Methylenedioxy-4-phenylquinolin-2(1H)-one ***2p*** *(Table 2, entry 25).* Oily compound; ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=5.95 (s, 1H, CH_2), 6.62 (s, 1H, HC=), 7.33–7.41 (m, 5H, Ar), 7.45 (d, J=7.4 Hz, 1H, Ar), 7.64 (d, J=6.9 Hz, 1H, Ar), 8.08 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=116.7, 122.6, 123.0, 123.9, 124.0, 128.0, 129.1, 129.2, 129.4, 129.6, 129.7, 133.39, 133.41, 134.8, 136.6, 138.2, 162.2. Anal. Calcd for $C_{16}H_{11}NO_3$: C, 72.45; H, 4.18; N, 5.28. Found: C, 72.50; H, 4.22; N, 5.24.

4.5.35. 4-Phenylbenzo[h]quinolin-2(1H)-one ***2q*** *(Table 2, entry 30).* Mp 220–222 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ=6.80 (s, 1H, HC=), 7.48 (d, J=7.4 Hz, 3H, Ar), 7.53–7.54 (m, 5H, Ar), 7.66 (t, J=7.4 Hz, 1H, Ar), 7.71 (t, J=7.4 Hz, 1H, Ar), 7.88 (d, J=8.1 Hz, 1H, Ar), 8.70 (d, J=8.1 Hz, 1H, NH); IR (ν, cm^{-1}): 3300, 1653; MS (ES): m/z (%)=271 (100) $[M]^+$, 270 (24), 243 (16), 215 (14), 139 (10), 77 (8). Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.07; H, 4.87; N, 5.21.

4.5.36. 4-Phenylbenzo[f]quinolin-2(1H)-one ***2r*** *(Table 2, entry 31).* Mp 300–302 °C (lit.[33] 305–307 °C); ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=6.71 (s, 1H, HC=), 7.10 (t, J=7.6 Hz, 1H, Ar), 7.29 (d, J=8.2 Hz, 2H, Ar), 7.33–7.36 (m, 4H, Ar), 7.49–7.50 (m, 4H, Ar), 13.43 (s, 1H, NH).

4.5.37. 4-(4-Methylphenyl)quinolin-2(1H)-one ***2s*** *(Table 3, entries 1, 3).* Mp 226–228 °C (lit.[34] 229–231 °C); ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=2.44 (s, 3H, Me), 6.70 (s, 1H,=CH), 7.15 (t, J=8.0 Hz, 1H, Ar), 7.31 (d, J=7.5 Hz, 2H, Ar), 7.35 (d, J=7.5 Hz, 2H, Ar), 7.48–7.51 (m, 1H, Ar), 7.55 (d, J=8.0 Hz, 1H, Ar), 7.58 (d, J=8.0 Hz, 1H, Ar), 12.89 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=21.2, 116.8, 119.8, 120.1, 122.7, 126.7, 128.8, 129.3, 130.7, 134.1, 138.8, 138.9, 153.9, 164.1.

4.5.38. 6-Methyl-4-(4-methylphenyl)quinolin-2(1H)-one ***2t*** *(Table 3, entry 4).* Mp 228–230 °C (lit.[35] 231–232 °C); ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=2.34 (s, 3H, Me), 2.46 (s, 3H, Me), 6.65 (s. 1H, HC=), 7.30–7.41 (m, 7H, Ar), 12.30 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=21.0, 21.3, 116.7, 119.7, 126.2, 127.1, 128.7, 129.3, 132.2, 132.3, 134.3, 136.8, 138.7, 153.6, 163.8.

4.5.39. 7-Chloro-4-(4-methylphenyl)quinolin-2(1H)-one ***2u*** *(Table 3, entry 7).* Mp 250–252 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=2.46 (s, 3H, Me), 6.69 (s, 1H, =CH), 7.33 (s, 4H, Ar), 7.46 (s, 2H, Ar), 7.55 (s, 1H, Ar), 12.69 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=22.1, 119.1, 122.1, 126.8, 127.8, 129.4, 129.6, 129.8, 130.3, 132.0, 133.9, 137.8, 140.2, 165.1. HRMS (ES^+): calcd for $C_{16}H_{16}ClNO$, 270.0680; found 270.0689.

4.5.40. 4-(4-Fluorophenyl)quinolin-2(1H)-one ***2v*** *(Table 3, entries 10, 11).* Mp 247–248 °C (lit.[36] 247–248 °C); ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=6.67 (s, 1H, HC=), 7.18–7.23 (m, 3H, Ar), 7.43–7.46 (m, 2H, Ar), 7.50–7.53 (m, 3H, Ar), 12.51 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=115.7 (d, J=21.4 Hz), 116.9, 119.5, 120.7, 122.7, 126.4, 128.4, 128.9, 130.6 (d, J=8.0 Hz), 130.9, 133.0 (d, J=3.1 Hz), 138.9, 152.5, 162.1, 164.0; ^{19}F NMR (470 MHz, $CDCl_3$, 25 °C): δ=−109.09 to −109.02 (m).

4.5.41. 6-Fluoro-4-(4-fluorophenyl)quinolin-2(1H)-one ***2w*** *(Table 3, entries 12, 13).* Mp 292–294 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=6.67 (s, 1H, HC=), 7.18–7.23 (m, 2H, Ar), 7.27–7.30 (m, 1H, Ar), 7.41–7.46 (m, 4H, Ar), 12.42 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=110.3, 111.7 (d, J=23.6 Hz), 116.0 (dd, J=21.7, 4.7 Hz), 118.1 (d, J=8.5 Hz), 119.2 (d, J=24.5 Hz), 122.0, 125.9, 128.3, 130.5 (d, J=8.5 Hz), 131.1, 132.5 (d, J=3.6 Hz), 135.3; ^{19}F NMR (470 MHz, $CDCl_3$, 25 °C): δ=−115.38 to −115.33 (m), −108.53 to −108.47 (m). Anal. Calcd for $C_{15}H_9F_2NO$: C, 70.04; H, 3.53; N, 5.45. Found: C, 69.98; H, 3.58; N, 5.49.

4.5.42. 4-(4-Methoxyphenyl)quinolin-2(1H)-one ***2x*** *(Table 3, entries 14–17).* Mp 252–254 °C (lit.[37] 231–233 °C); ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=3.89 (s, 3H, OMe), 6.63 (s, 1H, HC=), 7.03 (d, J=8.6 Hz, 2H, Ar), 7.16 (t, J=7.4 Hz, 1H, Ar), 7.33 (d, J=7.4 Hz, 1H, Ar), 7.40 (t, J=8.6 Hz, 1H, Ar), 7.50 (t, J=7.4 Hz, 1H, Ar), 7.60 (d, J=7.4 Hz, 1H, Ar), 10.69 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=55.4, 114.1, 116.7, 119.8, 122.6, 126.8, 128.6, 128.9, 129.4, 130.2, 130.6, 138.8, 153.3, 160.2; IR (ν, cm^{-1}): 3300, 1657; MS (ES): m/z (%)=251 (100) $[M]^+$, 250 (26), 236 (17), 220 (7), 208 (21).

4.5.43. N-2-Methylphenylamide of 3-trifluoromethylsulfonyloxy-3-phenylpropenoic acid ***3b*** *(Table 2, entry 1).* Mp 153–154 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=2.31 (s, 3H, Me), 6.37 (s, 1H, HC=), 7.11 (t, J=7.4 Hz, 1H, Ar), 7.36 (s, 1H, Ar), 7.46–7.54 (m, 3H, Ar), 7.60 (d, J=7.4 Hz, 2H, Ar), 9.37 (s, 1H, NH); ^{19}F NMR (470 MHz, $CDCl_3$, 25 °C): δ=−70.30 (s, CF_3); HRMS (ES^+): calcd for $C_{17}H_{15}F_3NO_4S$, 386.0668; found 386.0653.

4.5.44. N-3-Methylphenylamide of 3-trifluoromethylsulfonyloxy-3-phenylpropenoic acid ***3c****.* Compound **3c** was obtained in a mixture with compounds **2c**,**d** (Table 2, entries 3–5). ^1H NMR (500 MHz, $CDCl_3$, 25 °C, selected signals from the spectrum of the mixture): δ=2.35 (s, Me), 6.33 (s, 1H, HC=); ^{19}F NMR (470 MHz, $CDCl_3$, 25 °C): δ=−70.37 (s, CF_3); HRMS (ES^+): calcd for $C_{17}H_{15}F_3NO_4S$, 386.0668; found 386.0673.

4.5.45. N-4-Methylphenylamide of 3-trifluoromethylsulfonyloxy-3-phenylpropenoic acid ***3d****.* Compound **3d** was obtained in a mixture with the compounds **2e** (Table 2, entries 8, 9). ^1H NMR (500 MHz, $CDCl_3$, 25 °C, from the spectrum of the mixture): δ=2.33 (s, Me), 6.37 (s, 1H, HC=), 7.10–7.60 (m, 9H, Ar), 7.94 (s, 1H, NH); HRMS (ES^+): calcd for $C_{17}H_{14}F_3NO_4S$, 386.0668; found 386.0644.

4.5.46. N-3,4-Dimethylphenylamide of 3-trifluoromethylsulfonyloxy-3-phenylpropenoic acid ***3e****.* Compound **3e** was obtained in a mixture with compounds **2g**,**f** (Table 2, entry 11). ^1H NMR (500 MHz, $CDCl_3$, 25 °C, selected signals from the spectrum of the mixture): δ=2.25 (s, Me), 2.35 (s, Me), 6.33 (s, 1H, HC=); ^{19}F NMR (470 MHz, $CDCl_3$, 25 °C): δ=−70.31 (s, CF_3); HRMS (ES^+): calcd for $C_{18}H_{17}F_3NO_4S$, 400.0825; found 400.0806.

4.5.47. N-3-Fluorophenylamide of 3-trifluoromethylsulfonyloxy-3-phenylpropenoic acid ***3f*** *(Table 2, entry 13).* Mp 136–138 °C; ^1H

NMR (500 MHz, $CDCl_3$, 25 °C): δ=6.39 (s, 1H, HC=), 6.80 (s, 1H, Ar), 7.21–7.25 (m, 2H, Ar), 7.40–7.22 (m, 2H, Ar), 7.46–7.52 (m, 4H, Ar), 8.06 (s,1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=108 (d, *J*=25.8 Hz), 112 (d, *J*=21 Hz), 114.4, 115.8, 118.4 (q, *J*=318 Hz), 126.5, 129.2, 130.3 (d, *J*=9.8 Hz), 131.8, 131.83 (d, *J*=7.6 Hz), 138.7 (d, *J*=10.7 Hz), 153.2, 160.5, 163.1 (d, *J*=244 Hz); ^{19}F NMR (470 MHz, $CDCl_3$, 25 °C): δ=−107.84 (m, 1F), −70.36 (s, CF_3); HRMS (ES^+): calcd for $C_{16}H_{12}F_4NO_4S$, 389.0345; found 390.0406.

4.5.48. N-4-Chlorophenylamide of 3-trifluoromethylsulfonyloxy-3-phenylpropenoic acid ***3g*** *(Table 2, entry 17).* Mp 134–136 °C (lit.[38] 130 °C); ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=6.31 (s, 1H, HC=), 7.25–7.30 (m, 2H, Ar), 7.45–7.57 (m, 2H, Ar), 7.51–7.57 (m, 5H, Ar), 7.65 (s, 1H, NH); ^{19}F NMR (470 MHz, $CDCl_3$, 25 °C): δ=−70.39 (s, CF_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=114.6, 118.4 (q, *J*=319 Hz, CF_3), 121.7, 126.5, 129.17, 129.2, 129.23, 131.8, 131.9, 135.9, 153.1, 160.3; IR (*ν*, cm^{-1}): 3400, 1670.

4.5.49. (E)-N-4-Methylphenylamide of 3-chloro-3-phenylpropenoic acid ***4a****.* Compound **4a** was obtained in a mixture with compound **2e** (Table 2, entry 10). Mp lit.[39] 142 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C, selected signals from the spectrum of the mixture): δ=2.34 (s, 3H, Me), 6.48 (s, 1H, HC=), 8.42 (s, 1H, NH); HRMS (ES^+): calcd for $C_{16}H_{15}ClNO$, 272.0837; found 272.0849.

4.5.50. (E)-N-4-Fluorophenylamide of 3-chloro-3-phenylpropenoic acid ***4b****.* Compound **4b** was obtained in a mixture with compound **2j** (Table 2, entry 15). ^1H NMR (500 MHz, $CDCl_3$, 25 °C, selected signals from the spectrum of the mixture): δ=6.47 (s, 1H, HC=), 6.89–7.54 (m, 9H, Ar); HRMS (ES^+): calcd for $C_{15}H_{12}ClFNO$, 276.0586; found 276.0579.

4.5.51. (E/Z)-N-2-Methoxyphenylamide of 3-chloro-3-phenylpropenoic acid ***4c****.* Compound **4c** was obtained (*E*/*Z*-ratio 1:1) in a mixture with compound **2l** (Table 2, entry 20). ^1H NMR (500 MHz, $CDCl_3$, 25 °C, from the spectrum of the mixture): δ=3.61 (s, OMe, *Z*-), 3.90 (s, OMe, *E*-), 6.50 (s, 1H, HC=, *Z*-), 6.55 (s, 1H, HC=, *E*-), 8.19 (s, NH, *E*- and *Z*-), 7.36–7.39 (m, Ar, *E*- and *Z*-), 7.51 (t, *J*=8.2 Hz, Ar, *E*- and *Z*-), 7.67–7.68 (m, Ar, *E*- and *Z*-). For the *E*/*Z*-mixture: HRMS (ES^+): calcd for $C_{16}H_{15}ClNO_2$, 288.0786; found 288.0781.

4.5.52. (Z)-N-3-Methoxyphenylamide of 3-chloro-3-phenylpropenoic acid ***4d*** *(Table 2, entry 22).* Mp 140–141 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=3.80 (s, 3H, OMe), 6.63 (s, 1H, HC=), 6.89 (d, *J*=9.0 Hz, 2H, Ar), 7.42–7.43 (m, 2H, Ar), 7.52 (d, *J*=9.0 Hz, 2H, Ar), 7.65–7.67 (m, 2H, Ar), 7.95 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=55.4, 114.1, 120.8, 121.9, 122.0, 127.0, 128.4, 128.5, 130.2, 130.6, 132.4, 136.9, 156.6, 162.1; HRMS (ES^+): calcd for $C_{16}H_{15}ClNO_2$, 288.0786; found 288.0726.

4.5.53. (E)-N-4-Methylphenylamide of 3-chloro-3-(4-methylphenyl) propenoic acid ***4e****.* Compound **4e** was obtained in a mixture with compound **2t** (Table 3, entry 5). ^1H NMR (500 MHz, $CDCl_3$, 25 °C, from the spectrum of the mixture): δ=2.31 (s, 3H, Me), 2.37 (s, 3H, Me), 6.44 (s, 1H, HC=), 7.12 (d, *J*=7.6 Hz, 2H, Ar), 7.17 (d, *J*=7.6 Hz, 2H, Ar), 7.32 (d, *J*=8.0 Hz, 2H, Ar), 7.50 (d, *J*=8.0 Hz, 2H, Ar), 8.25 (s, 1H, NH); For the mixture: HRMS (ES^+): calcd for $C_{17}H_{17}ClNO$, 286.0993; found 286.0984.

4.5.54. (Z)-N-3-Fluorophenylamide of 3-chloro-3-(4-fluorophenyl) propenoic acid ***4f*** *(Table 3, entry 13).* Mp 148–150 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=6.57 (s, 1H, HC=), 7.03 (t, *J*=8.6 Hz, 2H, Ar), 7.10 (t, *J*=8.6 Hz, 2H, Ar), 7.56 (q, *J*=8.6, 5.1 Hz, 2H, Ar), 7.63 (q, *J*=8.6, 5.1 Hz, 2H, Ar), 8.07 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=115.7 (d, *J*=6.2 Hz), 115.8 (d, *J*=6.2 Hz), 120.7, 122.0 (d, *J*=7.8 Hz), 129.1 (d, *J*=8.6 Hz), 133.0 (d, *J*=3.6 Hz), 133.4, 160.6, 162.0, 163.0, 165.0; ^{19}F NMR (470 MHz, $CDCl_3$, 25 °C): δ=−113.84 to −113.78 (m), −106.13 to −106.07 (m); HRMS (ES^+): calcd for $C_{15}H_{11}ClF_2NO$, 294.0492; found 294.0483.

4.5.55. N-Phenylamide of 3-oxo-3-phenylpropanoic acid ***5a*** *(Table 1, entry 15).* Mp 104–106 °C (lit.[40] 105–106 °C); ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=4.12 (s, 2H, CH_2), 7.11 (t, *J*=7.6 Hz, 1H, Ar), 7.33 (t, *J*=7.6 Hz, 2H, Ar), 7.55–7.65 (m, 5H, Ar), 8.04 (d, *J*=7.6 Hz, 2H, Ar), 9.29 (s, 1H, NH).

4.5.56. N-4-Methylphenylamide of 3-(4-methylphenyl)-3-oxopropanoic acid ***5b*** *(Table 3, entry 6).* Mp 130–132 °C (lit.[41] 130–131 °C); ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=2.30 (s, 3H, Me), 2.42 (s, 3H, Me), 4.07 (s, 2H, CH_2), 7.11 (d, *J*=8.2 Hz, 2H, Ar), 7.29 (d, *J*=8.2 Hz, 2H, Ar), 7.45 (d, *J*=8.2 Hz, 2H, Ar), 7.92 (d, *J*=8.2 Hz, 2H, Ar), 9.25 (s, 1H, NH).

4.5.57. N-4-Fluorophenylamide of 3-(4-fluorophenyl)-3-oxopropanoic acid ***5c*** *(Table 3, entry 12).* Mp 125–127 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=4.07 (s, 2H, CH_2), 7.02 (t, *J*=8.6 Hz, 2H, Ar), 7.19 (t, *J*=8.6 Hz, 2H, Ar), 7.51–7.53 (m, 2H, Ar), 8.05–8.08 (m, 2H, Ar), 9.21 (s, 1H, NH); HRMS (ES^+): calcd for $C_{15}H_{11}FNO_2$, 276.0831; found 276.0834.

4.5.58. 4-(4-Methylphenyl)-4-phenyl-3,4-dihydroquinolin-2-(1H)-one ***6b*** *(Table 4, entry 5).* Mp 220–222 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=2.33 (s, 3H, Me), 3.38 (s, 2H, CH_2), 6.78 (d, *J*=8.1 Hz, 1H, Ar), 6.84 (d, *J*=7.4 Hz, 1H, Ar), 6.94 (d, *J*=8.1 Hz, 2H, Ar), 6.99 (t, *J*=7.4 Hz, 1H, Ar), 7.05–7.11 (m, 4H, Ar), 7.23 (t, *J*=8.1 Hz, 2H, Ar), 7.29 (t, *J*=7.4 Hz, 2H, Ar), 7.74 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=20.9, 29.7, 44.5, 116.2, 123.0, 127.0, 128.1, 128.3, 128.5, 128.6, 129.1, 129.4, 131.4, 136.7, 137.0, 140.5, 143.9, 170.3–170.4 (m); IR (*ν*, cm^{-1}): 3300, 1650; MS (ES): *m*/*z* (%)=314 (28) [MH^+], 313 (100) [$M]^+$, 270 (19), 236 (94), 222 (66), 194 (19), 178 (23), 165 (17). Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.36; H, 6.05; N, 4.51.

4.5.59. 6-Chloro-4,4-diphenyl-3,4-dihydroquinolin-2-(1H)-one ***6c*** *(Table 4, entries 6, 7).* Mp 250–252 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=3.37 (s, 2H, CH_2), 6.75 (d, *J*=8.4 Hz, 1H, Ar), 6.80 (s, 1H, Ar), 7.03 (d, *J*=7.1 Hz, 4H, Ar), 7.20 (dd, *J*=8.4, 2.2 Hz, 1H, Ar), 7.27–7.31 (m, 6H, Ar), 8.32 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=29.7, 44.2, 117.4, 127.3, 128.3, 128.5, 128.5, 129.2, 133.0, 135.7, 142.8, 170.1; HRMS (ES^+): calcd for $C_{21}H_{16}ClNO$, 334.0943; found 334.0903.

4.5.60. 4-(4-Fluorophenyl)-4-phenyl-3,4-dihydroquinolin-2-(1H)-one ***6d*** *(Table 4, entry 8).* Mp 221–223 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ=3.38 (d, 1H, CH_2), 3.39 (d, 1H, CH_2), 6.81 (t, *J*=7.2 Hz, 2H, Ar), 6.94–7.05 (m, 7H, Ar), 7.22–7.30 (m, 4H, Ar), 8.27 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ=44.6, 51.3, 115.1 (d, *J*=21.0 Hz), 116.3, 123.1, 127.2, 128.3, 128.4, 128.5, 129.2, 130.2 (d, *J*=8.0 Hz), 131.0, 137.0, 139.3, 143.5, 161.7 (d, *J*=245.3 Hz). 170.2; HRMS (ES^+): calcd for $C_{21}H_{16}FNO$, 318.1289; found 318.1297.

4.5.61. 2-Chloro-5-methyl-4-phenylquinoline ***7a*** *and 2-chloro-7-methyl-4-phenylquinoline* ***7b****.* Compounds **7a** and **7b**, as mixture of isomers (Scheme 2), were obtained from the mixture of the isomeric compounds **2c**,**d** in a yield of 68% by a known method.[22] Compound **7a**: ^1H NMR (400 MHz, $CDCl_3$, 25 °C, from the spectrum of the mixture): δ=2.03 (s, 3H, CH_3), 7.14–7.39 (m, 2H, Ar), 7.30 (s, 1H, H^3), 7.49–7.60 (m, 5H, Ar), 7.80 (d, *J*=8.6 Hz, 1H, H^5). Compound **7b**: ^1H NMR (400 MHz, $CDCl_3$, 25 °C, from the spectrum of the mixture): δ=2.60 (s, 3H, CH_3), 7.14–7.39 (m, 1H, Ar), 7.32 (s, $1H^3$), 7.49–7.60 (m, 5H, Ar), 7.90 (s, $1H^8$), 8.01 (d, *J*=8.4 Hz, $1H^8$).

HRMS (ES^+) (for the mixture of isomers): calcd for $C_{16}H_{12}ClN$, 254.0737; found 254.0731.

4.5.62. 2-Chloro-7-methoxy-4-phenylquinoline ***7c****.* Compound **7c** (Scheme 2) was obtained from compound **2m** in a yield of 60% by a known method.[22] Mp 104–105 °C (lit.[42] 108–108.5 °C); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ=3.95 (s, 3H, OCH_3), 7.14 (dd, J=9.2, 2.6 Hz, $1H^6$), 7.22 (s, $1H^3$), 7.42 (d, J=2.6 Hz, $1H^8$), 7.45–7.54 (m, 5H, Ph), 7.75 (d, J=9.2 Hz, $1H^5$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=55.6, 107.3, 119.7, 119.8, 120.6, 127.0, 128.7, 128.9, 129.3, 137.0, 150.3, 150.7, 151.4, 161.4.

4.5.63. 4-(4-Fluorophenyl)-1-formyl-4-phenyl-3,4-dihydroquinolin-2-(1H)-one ***8a*** *(Scheme 3).* A solution of $POCl_3$ (0.029 g, 0.19 mmol) and DMF (0.016 g, 0.22 mmol) in $CHCl_3$ (0.5 mL) was stirred at room temperature for 1 h. Compound **6d** (26 mg, 0.082 mmol) was added to the solution and the reaction mixture was stirred at 60 °C for 2 h. Then solvent was distilled off under vacuum, and firstly ice water (2 mL) and then sodium acetate (0.018 g) were added to the mixture. The obtained mixture was heated at 90 °C for 15 min with sodium acetate addition to keep the solution pH at about 6. After cooling down of the solution the formed precipitate was filtered off, and dissolved in CH_2Cl_2 (10 mL). The solution in CH_2Cl_2 was dried over Na_2SO_4, solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (eluents: hexane/ethyl acetate in the ratios 25:5 to 25:9). Yield 79%. Mp 141–143 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ=3.52 (d, J=15.6 Hz, 1H, CH_2), 3.59 (d, J=15.6 Hz, 1H, CH_2), 6.73 (dd, J=1.4, 7.8 Hz, 1H, H^5), 7.18 (td, J=1.2, 7.7 Hz, 1H, H^6), 6.99–7.02 (m, 6H, Ar), 7.30–7.35 (m, 3H, Ar), 7.39 (td, J=1.5, 8.2 Hz, 1H, H^7), 7.89 (dd, J=0.9, 8.2 Hz, 1H, H^8), 9.37 (s, 1H, C*H*=O); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=46.5, 50.6, 115.7 (d, J=21 Hz), 123.2, 126.5, 127.8, 128.0, 128.5, 128.6, 128.9, 130.3 (d, J=8 Hz), 133.2, 136.4, 138.4 (d, J=3 Hz), 142.4, 160.1, 162.0 (d, J=247 Hz), 172.4; ^{19}F (376 MHz, $CDCl_3$, 25°C): δ=−114.6 to −114.7 (m, 1F); HRMS (ES^+): calcd for $C_{22}H_{16}FNO_2$, 346.1238; found, 346.1228.

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Supplementary data

These data include ^1H, ^{13}C, and ^{19}F NMR spectra of the obtained compounds. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.07.028.

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