Chlorotrimethylsilane-Mediated Synthesis of Functionalized Fused Pyridines: Reaction of 3-Formylchromones with Electron-Rich Aminoheterocycles

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Abstract: The reaction of 3-formylchromones with aminoheterocycles was investigated. A simple and flexible general procedure for annulation of 5-(2-hydroxybenzoyl)pyridines was proposed. The best reaction conditions were found to be heating the reaction mixture in DMF in the presence of Me_3SiCl as a promoter and water as scavenger.

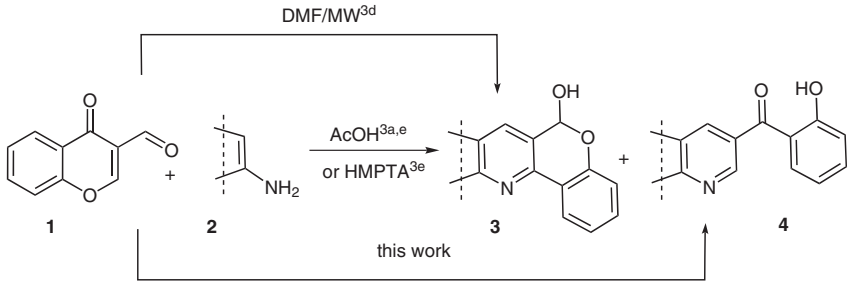
Key words: 3-formylchromones, aminoheterocycles, anilines, fused pyridines, quinolines, cyclization, chlorotrimethylsilane

Readily available 3-formylchromones have three electrophilic centers in their structure: electrophilic C-4 carbon atom, formyl function at C-3, and unsaturated C-2 carbon atom, which are able to undergo Michael addition of nucleophiles.[1] The 3-formylchromones are used for constructing different heterocyclic systems by reacting with various binucleophiles. As a rule, 1,2-binucleophiles such as hydrazines, hydroxylamines, and 1,3-*NCN*-binucleophiles such as amidines and amino heterocycles afford 2-hydroxybenzoyl-containing pyrazoles, isoxazoles, and pyrimidines.[2,3]

Continuing our research on cyclization of 3-formylchromones with binucleophiles aimed at the synthesis of new scaffolds and small libraries around them,[4] we searched for new binucleophiles that can be used in the reaction to produce new pharmaceutically relevant scaffolds. Among the 1,3-*CCN*-binucleophiles, π-electron-rich aminoheterocycles are the best candidates; moreover, we have used them previously in electrophilic functionalization.[5] As the electrophilic component bearing three reactive centers could react by different reactive modes, we might expect a mixture of products in the reaction. Indeed, two types of products **3** and **4** are formed in the reaction (Scheme 1). Formation of type **4** fused pyridines has been described in the case of 5-aminopyrazoles,[3a,c] 3-(4-pyridyl)-5-aminooxazole,[3a] and 2-aminoquinilin-4-one.[3a] In the case of 6-aminouracils, either solely type **3** pyridines (MW irradiation)[3d] or a mixture of types **3** and **4** pyridines (AcOH or HMPTA as a solvent)[3e] were formed. Primary push–pull enamines also formed only type **3** pyridines.[3a,f]

We were interested in the elaboration of a general and facile preparative method for the synthesis of type **4** structures starting from 3-formylchromones. Earlier we have shown the advantages of using TMSCl in the cyclization of formylchromones with cyanoacetamides.[4] Therefore we decided to use TMSCl as a promoter and water scavenger in the reaction with aminoheterocycles. Among the available electron-rich aminoheterocycles and push–pull enamines, we have chosen the most widely studied 5-aminopyrazoles and 6-aminouraciles in which the *ortho*-carbon atom possesses an increased nucleophilicity to exemplify the general procedure.

3-Formylchromone (**1**) reacted with 5-aminopyrazoles **5a–h** and 6-aminouracils **6a–d** and **7** regioselectively on using four equivalents of TMSCl in DMF at 100 °C. Pyridines **8a–h**, **9a–d** and **10**, respectively, were formed exclusively in almost quantitative yields (Scheme 2, Table 1). It should be noted that *N*1-unsubstituted ami-



Scheme 1

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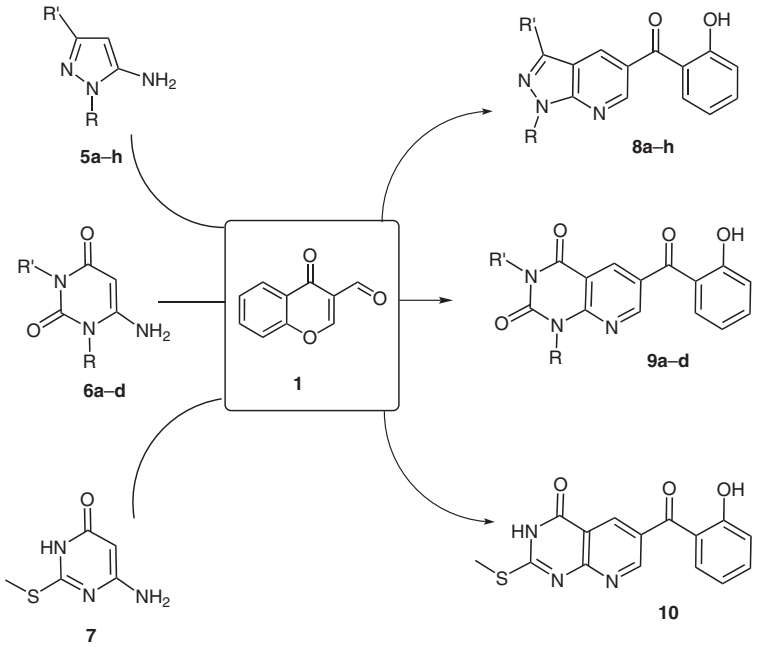

Scheme 2

nopyrazole **5c** reacted exclusively as a *CCN*-binucleophile forming pyrazolopyridine **8c** under our conditions, unlike previous reports.[3b,g]

The formation of pyrazolopyridine **8c** instead of isomeric pyrazolopyrimidine suggests that in our case the transformation involves different intermediates. We suppose that in the first step, one equivalent of TMSCl reacts with 3-formylchromone (**1**) in DMF at 100 °C to form chloride **12**. This assumption is in accordance with the results of 3-formylchromone silylation reported by Iwasaki and coworkers.[6] In the second step, adduct **12** reacts with aminoheterocycle **2** by attacking a nucleophilic carbon atom affording the addition product **13** followed by cyclization and hydrolysis of intermediate *o*-(trimethylsilyl)pyridine **14** to give the desired pyridine **4** (Scheme 3).

Table 1 Fused Pyridines **8**–**10** Prepared

Starting compound	Product[a]	R	R′	Yield (%)[b]	Mp (°C)[c] (solvent) [Lit.]	M + 1[d]	^{1}H NMR (DMSO-d_6/TMS) δ, *J* (Hz)
5a	**8a**	Me	Me	90	156–157 (MeOH)	268	2.53 (3 H, s, CH_3), 4.03 (3 H, s, NCH_3), 6.90 (1 H, t, $^3J_{H,H}$ = 7.8, CH), 6.98 (1 H, d, $^3J_{H,H}$ = 7.8 CH), 7.31 (1 H, d, $^3J_{H,H}$ = 7.8, CH), 7.48 (1 H, t, $^3J_{H,H}$ = 7.8, CH), 8.56 (1 H, d, $^4J_{H,H}$ = 1.5, 4-H, pyridyl), 8.91 (1 H, d, $^4J_{H,H}$ = 1.5, 2-H, pyridyl), 10.35 (1 H, br s, OH)
5b	**8b**	Ph	Me	94	126–127 [120–121][3c] (MeOH + DMF)	330	2.63 (3 H, s, CH_3), 7.00 (2 H, t + d, $^3J_{H,H}$ = 8.0, CH), 7.34 (1 H, t, $^3J_{H,H}$ = 7.6, CH), 7.50 (2 H, t + d, $^3J_{H,H}$ = 8.0, CH), 7.55 (2 H, t, $^3J_{H,H}$ = 7.6, CH), 8.23 (2 H, d, $^3J_{H,H}$ = 7.6, CH), 8.64 (1 H, d, $^4J_{H,H}$ = 1.6, 4-H, pyridyl), 8.90 (1 H, d, $^4J_{H,H}$ = 1.6, 2-H, pyridyl), 10.38 (1 H, br s, OH)
5c	**8c**	H	Me	90	195–196 (MeOH)	254	2.52 (3 H, s, CH_3), 7.00 (2 H, t + d, $^3J_{H,H}$ = 8.0, CH), 7.46 (2 H, t + d, $^3J_{H,H}$ = 8.0, CH), 8.52 (1 H, d, $^4J_{H,H}$ = 1.6, 4-H, pyridyl), 8.78 (1 H, d, $^4J_{H,H}$ = 1.6, 2-H, pyridyl), 10.26 (1 H, br s, OH), 13.63 (1 H, br s, NH)
5d	**8d**	H	OH	96	274–275 (MeOH + DMF)	256	6.99 (2 H, t + d, $^3J_{H,H}$ = 8.0, CH), 7.38 (1 H, dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.2, CH), 7.44 (1 H, td, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.2, CH), 8.40 (1 H, d, $^4J_{H,H}$ = 1.6, 4-H, pyridyl), 8.79 (1 H, d, $^4J_{H,H}$ = 1.6, 2-H, pyridyl), 10.24 (1 H, br s, OH), 12.71 (1 H, br s, OH), 13.50 (1 H, br s, NH)

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Table 1 Fused Pyridines **8**–**10** Prepared (continued)

Starting compound	Product[a]	R	R′	Yield (%)[b]	Mp (°C)[c] (solvent) [Lit.]	M + 1[d]	^{1}H NMR (DMSO-d_6/TMS) δ, *J* (Hz)
5e	**8e**	Ph	*t*-Bu	87	132–133 (MeOH + DMF)	372	1.52 (9 H, s, *t*-C_4H_9), 7.00 (1 H, t, $^3J_{H,H}$ = 7.6, CH), 7.04 (1 H, d, $^3J_{H,H}$ = 7.6, CH), 7.36 (1 H, t, $^3J_{H,H}$ = 8.4, CH), 7.51 (2 H, m, CH), 7.59 (2 H, t, $^3J_{H,H}$ = 8.4, CH), 8.25 (2 H, d, $^3J_{H,H}$ = 8.4, CH), 8.72 (1 H, d, $^4J_{H,H}$ = 1.6, 4-H, pyridyl), 8.90 (1 H, d, $^4J_{H,H}$ = 1.6, 2-H, pyridyl), 10.47 (1 H, s, OH)
5f	**8f**	Ph	cyclo-pentyl	90	136–137 (MeOH + DMF)	384	1.68 (2 H, m, CH_2), 1.78 (2 H, m, CH_2), 1.97 (2 H, m, CH_2), 2.16 (2 H, m, CH_2), 3.33 (1 H, qt, $^3J_{H,H}$ = 6.4, CH), 6.99 (1 H, t, $^3J_{H,H}$ = 8.8, CH), 7.03 (1 H, d, $^3J_{H,H}$ = 8.8, CH), 7.35 (1 H, t, $^3J_{H,H}$ = 8.0, CH), 7.48 (2 H, m, CH), 7.58 (2 H, t, $^3J_{H,H}$ = 8.0, CH), 8.25 (2 H, d, $^3J_{H,H}$ = 8.0, CH), 8.64 (1 H, d, $^4J_{H,H}$ = 1.6, 4-H, pyridyl), 8.91 (1 H, d, $^4J_{H,H}$ = 1.6, 2-H, pyridyl), 10.43 (1 H, br s, OH)
5g	**8g**	Ph	Ph	93	167–168 (MeOH + DMF)	392	7.01 (1 H, t, $^3J_{H,H}$ = 8.0, CH), 7.03 (1 H, d, $^3J_{H,H}$ = 8.0, CH), 7.41 (1 H, t, $^3J_{H,H}$ = 7.6, CH), 7.52 (3 H, m, CH), 7.62 (4 H, m, CH), 8.07 (2 H, d, $^3J_{H,H}$ = 7.6, CH), 8.32 (2 H, d, *J* = 8.0, CH), 8.83 (1 H, d, $^4J_{H,H}$ = 1.5, 4-H, pyridyl), 8.97 (1 H, d, $^4J_{H,H}$ = 1.5, 2-H, pyridyl), 10.52 (1 H, br s, OH)
5h	**8h**	$(CH_2)_2OH$	Ph	85	149–150 (MeOH)	360	4.00 (2 H, t, $^3J_{H,H}$ = 6.2, OCH_2), 4.47 (2 H, t, $^3J_{H,H}$ = 6.2, NCH_2), 4.98 (1 H, br s, OH), 6.97 (2 H, t + d, $^3J_{H,H}$ = 8.0, CH), 7.43 (2 H, t + d, $^3J_{H,H}$ = 8.0, CH), 7.60 (3 H, m, CH), 7.74 (2 H, d, $^3J_{H,H}$ = 8.1, CH), 8.23 (1 H, d, $^4J_{H,H}$ = 1.8, 4-H, pyridyl), 8.97 (1 H, d, $^4J_{H,H}$ = 1.8, 2-H, pyridyl), 10.36 (1 H, s, OH)
6a	**9a**	H	H	95	292–293 [>300][3e] (MeOH + DMF)	284	6.99 (2 H, m, CH), 7.40 (1 H, dd, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.2, CH), 7.47 (1 H, td, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.2, CH), 8.36 (1 H, d, $^4J_{H,H}$ = 2.2, 4-H, pyridyl), 8.88 (1 H, d, $^4J_{H,H}$ = 2.2, 2-H, pyridyl), 10.33 (1 H, br s, OH), 11.90 (1 H, br s, NH)
6b	**9b**	Me	H	96	244–245 (MeOH + DMF)	298	3.52 (3 H, s, NCH_3), 6.98 (1 H, t, $^3J_{H,H}$ = 8.2, CH), 7.02 (1 H, d, $^3J_{H,H}$ = 8.2, CH), 7.41 (1 H, dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.6, CH), 7.41 (1 H, td, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 1.6, CH), 8.42 (1 H, d, $^4J_{H,H}$ = 2.3, 4-H, pyridyl), 8.97 (1 H, d, $^4J_{H,H}$ = 2.3, 2-H, pyridyl), 10.40 (1 H, br s, OH), 11.64 (1 H, s, NH), 12.09 (1 H, s, NH)
6c	**9c**	Me	Me	91	211–212 [>300][3e] (MeOH + DMF)	312	3.29 (3 H, s, NCH_3), 3.59 (3 H, s, NCH_3), 6.99 (1 H, t, $^3J_{H,H}$ = 8.4, CH), 7.01 (1 H, d, $^3J_{H,H}$ = 8.4, CH), 7.41 (1 H, dd, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 1.2, CH), 7.47 (1 H, td, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 1.2, CH), 8.48 (1 H, d, $^4J_{H,H}$ = 1.6, 4-H, pyridyl), 8.98 (1 H, d, $^4J_{H,H}$ = 1.6, 2-H, pyridyl), 10.37 (1 H, br s, OH)
6d	**9d**	CH_2Ph	Me	94	184–185 (MeOH + DMF)	388	3.32 (3 H, s, NCH_3), 5.48 (2 H, s, NCH_2), 7.00 (2 H, m, CH), 7.23 (1 H, t, $^3J_{H,H}$ = 7.2, CH), 7.29 (2 H, t, $^3J_{H,H}$ = 7.2, CH), 7.36 (2 H, d, $^3J_{H,H}$ = 7.2, CH), 7.42 (1 H, d, $^3J_{H,H}$ = 7.6, CH), 7.50 (1 H, t, $^3J_{H,H}$ = 7.6, CH), 8.53 (1 H, d, $^4J_{H,H}$ = 1.6, 4-H, pyridyl), 8.96 (1 H, d, $^4J_{H,H}$ = 1.6, 2-H, pyridyl), 10.38 (1 H, s, OH)
7	**10**	–	–	89	175–176 (MeOH + DMF)	314	2.63 (3 H, s, SCH_3), 6.98 (2 H, t + d, $^3J_{H,H}$ = 8.0, CH), 7.46 (2 H, t + d, $^3J_{H,H}$ = 8.0, CH), 8.53 (1 H, d, $^4J_{H,H}$ = 1.6, 4-H, pyridyl), 9.08 (1 H, d, $^4J_{H,H}$ = 1.6, 2-H, pyridyl), 10.37 (1 H, s, OH), 13.09 (1 H, br s, NH)

[a] Satisfactory microanalysis obtained: C ± 0.33; H ± 0.45; N ± 0.25. ^{13}C NMR spectral data of the products are given in the experimental.
[b] Yields refer to pure isolated product.
[c] Melting points are uncorrected.
[d] APCI MS, Agilent 1100/DAD/MSD VL G1965a instrument.

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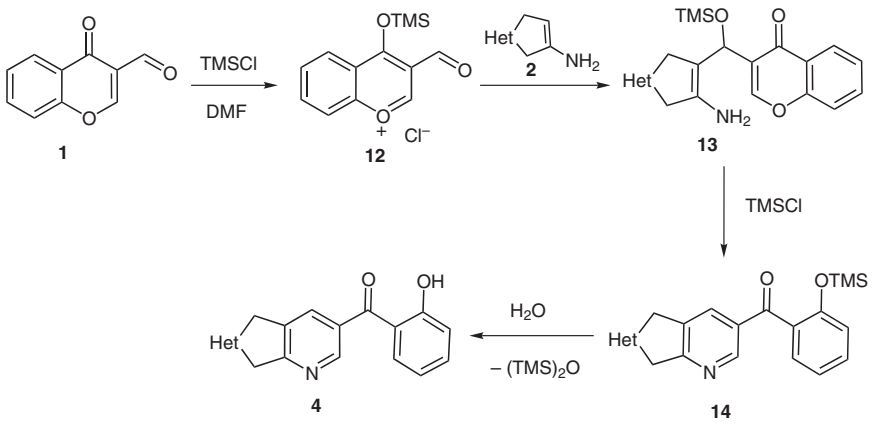
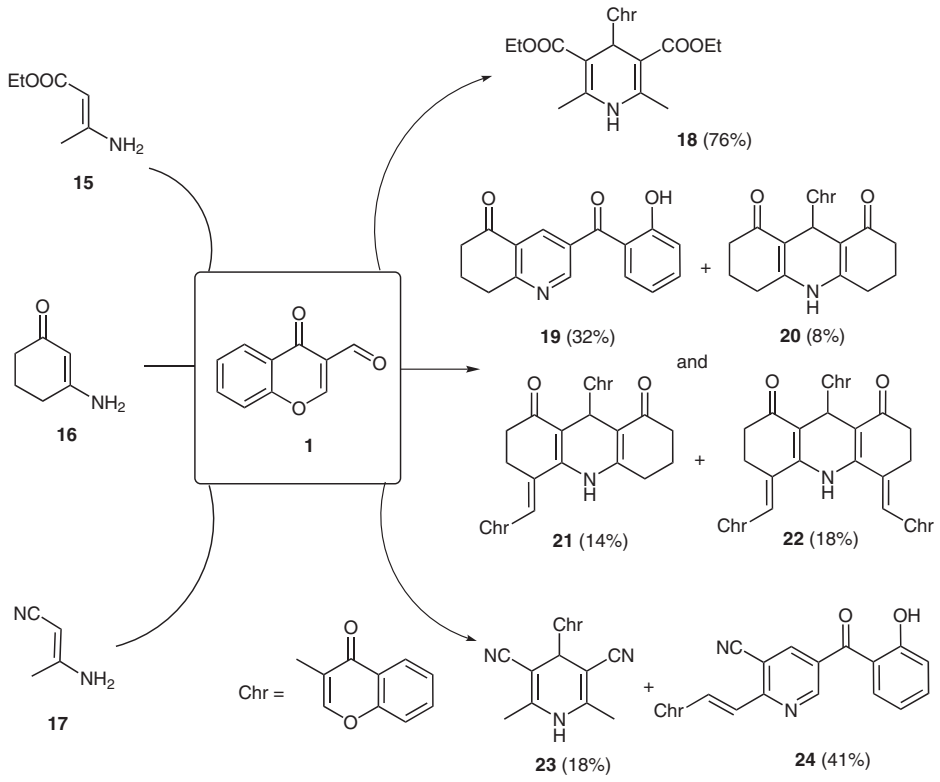


Scheme 3

Under the standard conditions, push–pull enamines react with 3-formylchromones giving unidentifiable mixture of products;[4] therefore we sought reaction conditions that minimize destruction of the starting enamines. At room temperature, ethyl β-aminocrotonate (**15**) gives a mixture which, according to LC/MS data, consists of Hantzsch product **18** (76%) that was isolated in 45% preparative yield. At the same time, β-aminocyclohexenone (**16**) affords a hard-to-separate mixture of at least four products, i.e., target pyridine **19** (~32%) and three Hantzsch products **20** (~8%), **21** (~14%) and **22** (~18%). Under the same conditions β-aminocrotonitrile (**17**) yields a multi-component mixture containing Hantzsch product **20** (~18%) and compound **21** (~41%) which is the product of condensation of the target pyridine with another 3-formylchromone molecule (Scheme 4).

With other aminoheterocycles, using the same reaction conditions we obtained products **29**–**32** of 5-amino-3-methylisoxazoles **25a**–**c**, 5-amino-3-methylisothiazole **26**, aminofuran **27**, and 2-aminothiophene **28** in good yields (Scheme 5, Table 2).



Scheme 4

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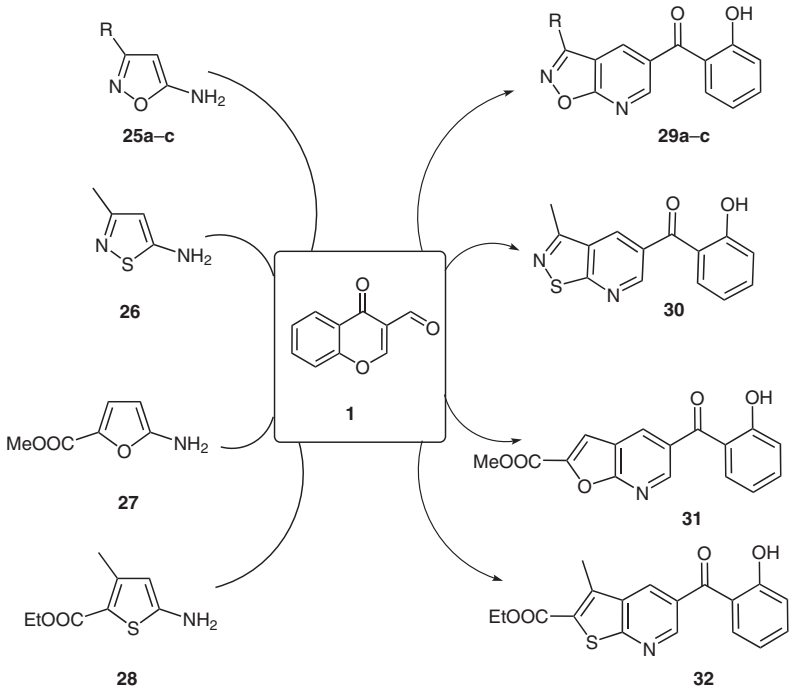

Scheme 5

Table 2 Fused Pyridines **29**–**32** Prepared

Starting compound[a]	Product	R	Yield (%)[b]	Mp (°C)[c] (solvent) [Lit]	M + 1[d]	^{1}H NMR (DMSO-d_6/TMS) δ, J (Hz)
25a	**29a**	Me	91	160–161 (EtOH)	255	2.64 (3 H, s, CH_3), 6.94 (1 H, t, $^3J_{H,H}$ = 8.0, CH), 7.00 (1 H, d, $^3J_{H,H}$ = 8.0, CH), 7.47 (2 H, t + d, $^3J_{H,H}$ = 8.0, CH), 8.68 (1 H, d, $^4J_{H,H}$ = 1.6, 4-H, pyridyl), 8.86 (1 H, d, $^4J_{H,H}$ = 1.6, 2-H, pyridyl), 10.53 (1 H, br s, OH)
25b	**29b**	*i*-Pr	87	106–107 (EtOH)	283	1.41 [6 H, d, $^3J_{H,H}$ = 7.2, $CH(CH_3)_2$], 3.36 [1 H, hep, $^3J_{H,H}$ = 7.2, $CH(CH_3)_2$], 7.01 (2 H, t + d, $^3J_{H,H}$ = 8.4, CH), 7.50 (2 H, m, CH), 8.78 (1 H, d, $^4J_{H,H}$ = 1.6, 4-H, pyridyl), 8.88 (1 H, d, $^4J_{H,H}$ = 1.6, 2-H, pyridyl), 10.52 (1 H, br s, OH)
25c	**29c**	Ph	90	172–173 (MeOH)	317	7.01 (2 H, m, CH), 7.52 (2 H, m, CH), 7.65 (3 H, m, CH), 8.05 (2 H, m, CH), 8.85 (1 H, d, $^4J_{H,H}$ = 1.9, 4-H, pyridyl), 8.97 (1 H, d, $^4J_{H,H}$ = 1.9, 2-H, pyridyl), 10.50 (1 H, s, OH)
26	**30**	–	89	142–143 (MeOH)	271	2.76 (3 H, s, CH_3), 7.01 (2 H, m, CH), 7.51 (2 H, m, CH), 8.79 (1 H, d, $^4J_{H,H}$ = 1.2, 4-H, pyridyl), 9.00 (1 H, d, $^4J_{H,H}$ = 1.2, 2-H, pyridyl), 10.49 (1 H, s, OH)
27	**31**	–	50	148–149 (MeOH)	298	3.93 (3 H, s, CO_2CH_3), 7.00 (2 H, m, CH), 7.45 (1 H, d, $^3J_{H,H}$ = 7.7, CH), 7.48 (1 H, t, $^3J_{H,H}$ = 7.7, CH), 7.88 (1 H, s, CH), 8.57 (1 H, d, $^4J_{H,H}$ = 2.0, 4-H, pyridyl), 8.81 (1 H, d, $^4J_{H,H}$ = 2.0, 2-H, pyridyl), 10.37 (1 H, br s, OH)
28	**32**	–	95	137–138 (MeOH + DMF)	342	1.35 (3 H, t, $^3J_{H\ H}$ = 6.8, CH_2CH_3), 2.74 (3 H, s, CH_3), 4.36 (2 H, q, $^3J_{H,H}$ = 6.8, CH_2CH_3), 6.99 (1 H, t, $^3J_{H,H}$ = 7.6, CH), 7.01 (1 H, d, $^3J_{H,H}$ = 7.6, CH), 7.50 (2 H, m, CH), 8.61 (1 H, d, $^4J_{H,H}$ = 1.6, 4-H, pyridyl), 8.90 (1 H, d, $^4J_{H,H}$ = 1.6, 2-H, pyridyl), 10.48 (1 H, br s, OH)

[a] Satisfactory microanalysis obtained: C ± 0.33; H ± 0.45; N ± 0.25. ^{13}C NMR spectral data of the products are given in the experimental.
[b] Yields refer to pure isolated product.
[c] Melting points are uncorrected.
[d] APCI MS, Agilent 1100/DAD/MSD VL G1965a instrument.

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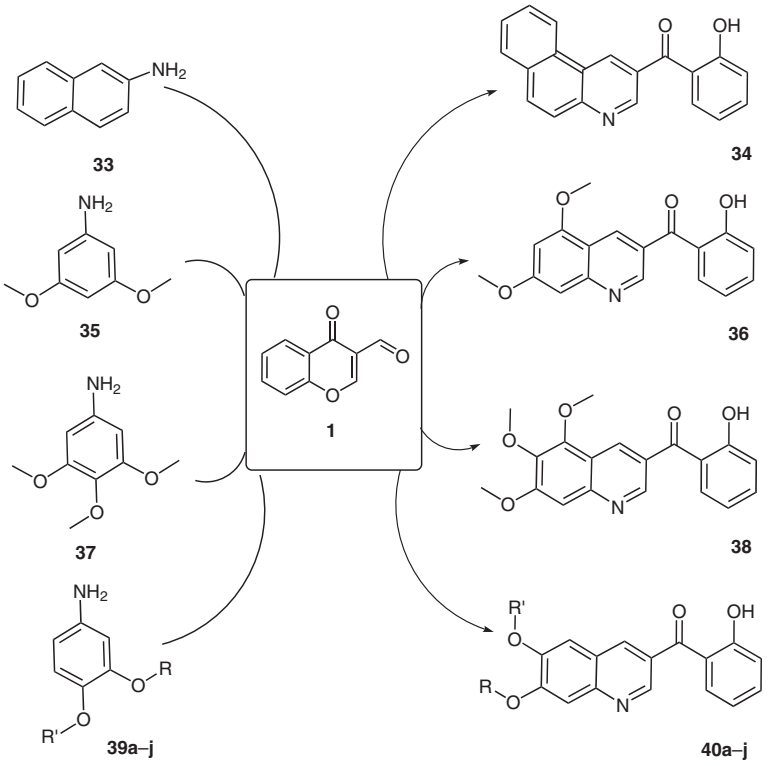
We applied the procedure to anilines for the assembly of quinolines in a similar way. Using chlorotrimethylsilane we succeeded in reacting 3-formylchromone with β-naphthylamine (**33**), which undergoes reaction involving the α-carbon atom of naphthalene ring[7] and gets converted into benzo[*f*]quinoline **34**. In our previous work[5b] dedicated to electrophilic funtionalization of electron-rich aminoheterocycles with trifluoromethyl-containing β-diketones, *m*-dimethylaminoaniline, 3,5-dimethoxyaniline, and 1,2,3,3-tetramethyl-2,3-dihydro-1*H*-6-indolylamine afford the corresponding quinolines. Under mentioned conditions *m*-dimethylaminoaniline and 1,2,3,3-tetramethyl-2,3-dihydro-1*H*-6-indolylamine decompose. At the same time 3,5-dimethoxyaniline (**35**), 3,4,5-trimethoxyaniline (**37**) and 3,4-dialkoxyanilines **39a–j** having less nucleophilic α-carbon atom gave quinolines **36**, **38** and **40a–j** in low to good yields (Scheme 6, Table 3).

It should be noted that till the present moment, starting from 3-formylchromones and anilines, only Schiff bases and 1,4-adducts of two molecules of aniline and 3-formylchromone are described in the literature.[8] The structure of new substances was confirmed by ^{1}H NMR, ^{13}C NMR, IR spectroscopy, APCI MS spectrometry, and elemental analyses.

In conclusion we have elaborated a new general procedure for reaction of 3-formylchromone with electron-rich aminoheterocycles which results in the sole formation of fused 3-(2-hydroxybenzoyl)pyridines. Under mentioned conditions 5-aminopyrazoles, 6-aminouracils, 5-aminoisoxazoles, 5-aminoisothiazole, 5-aminofuran and 2-aminothiophene give cyclization products in high yields. An additional reaction of 3-formylchromone with anilines leads to quinolines. The limitation of the procedure is the stability of the corresponding 1,3-*CCN*-binucleophiles in DMF-TMSCl medium at the reaction temperature. The procedure is very simple and could be easily adapted to semi-automated solution-phase parallel synthesis of fused pyridine libraries.

All commercially available starting materials (Aldrich, Fluka, Enamine LTD) were used without additional purification. All solvents were purified by standard methods. No precautions were taken to exclude ambient moisture in procedures carried out under open atmosphere. ^{1}H NMR (400 MHz) spectra were recorded on a Varian Mercury-400 spectrometer with TMS as an internal standard. ^{13}C NMR (125 MHz) spectra were recorded on a Bruker Avance drx 500 spectrometer with TMS as an internal standard. ^{19}F NMR (470 MHz) were recorded on a Bruker Avance DRX 500 spectrometer with $CFCl_3$ as an internal standard. HPLC APCI MS spectra were recorded on an Agilent 1100/DAD/MSD VL G1965a instrument. IR spectra were recorded on a Nexus-470 spectrometer. Branson 2510E-MT ultrasonic bath was used.

Commercially unavailable 3-formylchromone (**1**)[9] and starting aminoheterocycles (5-aminopyrazoles **5a–h**,[10] 6-aminouracyls **6a–d** and **7**,[11] 5-aminoisoxazoles **25a–c**,[12] 5-aminofuran **27**,[13] 2-aminothiophene **28**[14]), anilines **39c–e** and **39h**,[15] aniline **39i**,[16] and aniline **39j**[17] were prepared according to the literature.



Scheme 6

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Table 3 Quinolines **34**,**36**,**38** Prepared

Anilines	Product[a]	R	R′	Yield (%)[b]	Mp (°C)[c] (solvent)	M + 1[d]	^{1}H NMR (DMSO-d_6/TMS) δ, J (Hz)
33	**34**	–	–	94	154–155 (MeOH + DMF)	300	7.01 (1 H, t, $^3J_{H,H}$ = 8.0, CH), 7.06 (1 H, d, $^3J_{H,H}$ = 8.0, CH), 7.53 (1 H, d, $^3J_{H,H}$ = 8.0, CH), 7.56 (1 H, t, $^3J_{H,H}$ = 8.0, CH), 7.77 (2 H, m, CH), 8.00 (1 H, d, $^3J_{H,H}$ = 9.2, CH), 8.11 (1 H, dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 1.2, CH), 8.27 (1 H, d, $^3J_{H,H}$ = 9.2, CH), 8.83 (1 H, d, $^3J_{H,H}$ = 8.8, CH), 9.14 (1 H, d, $^4J_{H,H}$ = 1.6, 4-H, pyridyl), 9.44 (1 H, d, $^4J_{H,H}$ = 1.6, 2-H, pyridyl), 10.56 (1 H, br s, OH)
35	**36**	–	–	30	157–158 (EtOH)	310	3.99 (3 H, s, OCH_3), 4.00 (3 H, s, OCH_3), 6.90 (1 H, d, $^4J_{H,H}$ = 1.9, CH), 7.00 (1 H, t, $^3J_{H,H}$ = 7.9, CH), 7.06 (1 H, d, $^3J_{H,H}$ = 7.9, CH), 7.21 (1 H, d, $^4J_{H,H}$ = 1.9, CH), 7.46–7.51 (2 H, m, CH), 8.84 (1 H, d, $^4J_{H,H}$ = 2.0, CH), 9.17 (1 H, d, $^4J_{H,H}$ = 2.0, CH), 10.48 (1 H, br s, OH)
37	**38**	–	–	85	163–164 (MeOH + DMF)	340	3.90 (3 H, s, OCH_3), 4.04 (6 H, s, 2 OCH_3), 7.00 (1 H, t, $^3J_{H,H}$ = 8.0, CH), 7.07 (1 H, d, $^3J_{H,H}$ = 8.0, CH), 7.45–7.52 (3 H, m, CH), 8.75 (1 H, d, $^4J_{H,H}$ = 2.0, 4-H, pyridyl), 9.07 (1 H, d, $^4J_{H,H}$ = 2.0, 2-H, pyridyl), 10.49 (1 H, br s, OH)
39a	**40a**	H	Me	91	207–208 (MeOH + DMF)	296	3.95 (3 H, s, OCH_3), 7.01 (1 H, t, $^3J_{H,H}$ = 8.7, CH), 7.09 (1 H, d, $^3J_{H,H}$ = 8.7, CH), 7.49–7.52 (2 H, m, CH), 7.77 (1 H, s, CH), 7.88 (1 H, s, CH), 9.02 (2 H, m, 2-H, 4-H, pyridyl), 10.56 (1 H, br s, OH), 12.16 (1 H, br s, OH)
39b	**40b**	Me	Me	93	140–141 (MeOH + DMF)	310	3.91 (3 H, s, OCH_3), 4.00 (3 H, s, OCH_3), 6.99 (1 H, t, $^3J_{H,H}$ = 8.2, CH), 7.04 (1 H, d, $^3J_{H,H}$ = 8.2, CH), 7.46–7.51 (2 H, m, CH), 7.55 (1 H, s, CH), 7.71 (1 H, s, CH), 8.72 (1 H, d, $^4J_{H,H}$ = 1.9, 4-H, pyridyl), 9.04 (1 H, d, $^4J_{H,H}$ = 1.9, 2-H, pyridyl), 10.45 (1 H, br s, OH)
39c	**40c**	Me	Et	88	140–141 (MeOH + DMF)	324	1.41 (3 H, t, $^3J_{H,H}$ = 7.0, OCH_2CH_3), 4.02 (3 H, s, OCH_3), 4.20 (2 H, q, $^3J_{H,H}$ = 7.0, OCH_2CH_3), 7.00 (1 H, t, $^3J_{H,H}$ = 8.0, CH), 7.06 (1 H, d, $^3J_{H,H}$ = 8.0, CH), 7.48–7.52 (2 H, m, CH), 7.63 (1 H, s, CH), 7.78 (1 H, s, CH), 8.87 (1 H, d, $^4J_{H,H}$ = 1.8, 4-H, pyridyl), 9.08 (1 H, d, $^4J_{H,H}$ = 1.8, 2-H, pyridyl), 10.49 (1 H, br s, OH)
39d	**40d**	Et	Et	86	137–138 (MeOH)	338	1.40 (3 H, t, $^3J_{H,H}$ = 6.9, OCH_2CH_3), 1.43 (3 H, t, $^3J_{H,H}$ = 6.9, OCH_2CH_3), 4.18 (2 H, q, $^3J_{H,H}$ = 6.9, OCH_2CH_3), 4.26 (2 H, q, $^3J_{H,H}$ = 6.9, OCH_2CH_3), 6.99 (1 H, t, $^3J_{H,H}$ = 8.1, CH), 7.03 (1 H, d, $^3J_{H,H}$ = 8.1, CH), 7.44–7.49 (3 H, m, CH), 7.63 (1 H, s, CH), 8.61 (1 H, d, $^4J_{H,H}$ = 1.9, 4-H, pyridyl), 8.99 (1 H, d, $^4J_{H,H}$ = 1.9, 2-H, pyridyl), 10.39 (1 H, br s, OH)
39e	**40e**	Pr	Pr	80	125–126 (MeOH)	366	1.01 (6 H, m, 2 $OCH_2CH_2CH_3$), 1.81 (4 H, m, 2 $OCH_2CH_2CH_3$), 4.05 (2 H, q, $^3J_{H,H}$ = 6.6, $OCH_2CH_2CH_3$), 4.14 (2 H, q, $^3J_{H,H}$ = 6.6, $OCH_2CH_2CH_3$), 6.98 (1 H, t, $^3J_{H,H}$ = 8.2, CH), 7.01 (1 H, d, $^3J_{H,H}$ = 8.2, CH), 7.42–7.48 (3 H, m, CH), 7.54 (1 H, s, CH), 8.46 (1 H, d, $^4J_{H,H}$ = 1.9, 4-H, pyridyl), 8.92 (1 H, d, $^4J_{H,H}$ = 1.9, 2-H, pyridyl), 10.35 (1 H, br s, OH)
39f	**40f**	-CH_2-		90	148–149 (MeOH + DMF)	294	6.28 (2 H, m, CH_2), 6.98 (1 H, t, $^3J_{H,H}$ = 8.0, CH), 7.01 (1 H, d, $^3J_{H,H}$ = 8.0, CH), 7.44–7.49 (3 H, m, CH), 7.57 (1 H, s, CH), 8.55 (1 H, d, $^4J_{H,H}$ = 1.9, 4-H, pyridyl), 8.92 (1 H, d, $^4J_{H,H}$ = 1.9, 2-H, pyridyl), 10.41 (1 H, br s, OH)
39g	**40g**	-$(CH_2)_2$-		91	136–137 (MeOH + DMF)	308	4.45 (4 H, m, OCH_2CH_2O), 7.00 (1 H, t, $^3J_{H,H}$ = 8.0, CH), 7.05 (1 H, d, $^3J_{H,H}$ = 8.0, CH), 7.49 (2 H, m, CH), 7.58 (1 H, s, CH), 7.75 (1 H, s, CH), 8.75 (1 H, d, $^4J_{H,H}$ = 1.6, 4-H, pyridyl), 9.03 (1 H, d, $^4J_{H,H}$ = 1.6, 2-H, pyridyl), 10.48 (1 H, br s, OH)

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Table 3 Quinolines **34**,**36**,**38** Prepared (continued)

Anilines	Product[a]	R	R′	Yield (%)[b]	Mp (°C)[c] (solvent)	M + 1[d]	^{1}H NMR (DMSO-d_6/TMS) δ, J (Hz)
39h	**40h**	-(CH$_2$)$_3$-		85	131–132 (MeOH + DMF)	322	2.21 (2 H, qt, $^3J_{H,H}$ = 6.8, CH$_2$CH_2CH$_2$), 4.27 (2 H, t, $^3J_{H,H}$ = 6.0, OCH_2CH$_2$), 4.34 (2 H, t, $^3J_{H,H}$ = 6.0, OCH_2CH$_2$), 7.00 (2 H, m, CH), 7.47 (2 H, m, CH), 7.56 (1 H, s, CH), 7.73 (1 H, s, CH), 8.54 (1 H, d, $^4J_{H,H}$ = 2.1, 4-H, pyridyl), 8.96 (1 H, d, $^4J_{H,H}$ = 2.1, 2-H, pyridyl), 10.40 (1 H, br s, OH)
39i	**40i**	-CF$_2$-		87	119–120 (MeOH + DMF)	330	7.01 (2 H, m, CH), 7.49 (2 H, m, CH), 8.04 (1 H, s, CH), 8.16 (1 H, s, CH), 8.71 (1 H, d, $^4J_{H,H}$ = 2.0, 4-H, pyridyl), 9.08 (1 H, d, $^4J_{H,H}$ = 2.0, 2-H, pyridyl), 10.39 (1 H, br s, OH)
39j	**40j**			82	105–106 (MeOH)	348	1.84 (4 H, m, CH), 2.15 (4 H, m, CH), 6.99 (2 H, m, CH), 7.38 (1 H, s, CH), 7.44–7.50 (3 H, m, CH), 8.46 (1 H, d, $^4J_{H,H}$ = 1.8, 4-H, pyridyl), 8.88 (1 H, d, $^4J_{H,H}$ = 1.8, 2-H, pyridyl), 10.36 (1 H, s, OH)

[a] Satisfactory microanalysis obtained: C ± 0.33; H ± 0.45; N ± 0.25. ^{13}C NMR spectral data of the products are given in the experimental.
[b] Yields refer to pure isolated product.
[c] Melting points are uncorrected.
[d] APCI MS, Agilent 1100/DAD/MSD VL G1965a instrument.

Fused Pyridines 8–10, 29–32 from 3-Formylchromone (1) and Aminoheterocycles 5–7, 25–28; General Procedure

Aminoheterocycle **5a–h**, **6a–d**, **7**, **25a–c**, **26–28** (4 mmol) and 3-formylchromone **1** (696 mg, 4 mmol) were placed into a 25 mL ace pressure tube and dissolved in DMF (10 mL). Chlorotrimethylsilane (1.738 g, 16 mmol) was added dropwise to the solution. The tube was thoroughly sealed and heated on a water-bath for 6–8 h. After cooling, the flask was opened (**caution!** excessive pressure inside), the mixture was poured into H_2O (30 mL) and allowed to stand at r.t. in an ultrasonic bath for 1 h. The precipitate formed was filtered and washed with small amount of MeOH. Recrystallization from an appropriate solvent yielded targeted compounds **8a–h**, **9a–d**, **10**, **29a–c**, **30–32** (Tables 1 and 2).

8a

IR (KBr): 3600–3275 (br, OH), 3061, 3030, 2981, 2922, 1630 (C=O), 1591, 1481, 1296, 1217, 816, 768, 640 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 12.0, 33.5, 113.8, 116.9, 119.3, 124.8, 126.3, 130.6, 132.2, 133.5, 142.4, 150.2, 151.3, 156.8, 195.4.

8b

IR (KBr): 3600–3275 (br, OH), 3059, 3045, 2953, 2916, 1632 (C=O), 1593, 1510, 1483, 1308, 1248, 1201, 742 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 21.2, 116.1, 116.9, 119.4, 120.4, 124.6, 126.0, 127.5, 129.2, 130.8, 132.5, 133.8, 138.7, 145.0, 150.8, 150.8, 156.9, 195.0.

8c

IR (KBr): 3600–3350 (br, OH, NH), 3172, 3134, 3034, 2918, 1623 (C=O), 1587, 1481, 1441, 1304, 1240, 910, 768 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 12.2, 113.4, 116.8, 119.3, 125.0, 126.2, 130.5, 131.9, 133.3, 143.4, 150.3, 153.3, 156.6, 195.4.

8d

IR (KBr): 3600–3350 (br, OH, NH), 3107, 3066, 3007, 2926, 1645, 1630 (C=O), 1606, 1333, 1308, 1242, 752 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 104.3, 117.1, 119.8, 125.6, 125.8, 130.6, 133.3, 133.4, 151.3, 153.1, 155.7, 156.6, 195.4.

8e

IR (KBr): 3610–3290 (br, OH), 3074, 2962, 2927, 1623 (C=O), 1587, 1506, 1306, 1252, 1223, 1163, 939, 756, 687 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 30.1, 34.6, 114.2, 117.3, 119.9, 121.3, 124.9, 126.6, 127.5, 129.7, 131.3, 133.9, 134.4, 139.1, 150.8, 151.8, 155.7, 157.3, 195.3.

8f

IR (KBr): 3600–3120 (br, OH), 3068, 2954, 1632 (C=O), 1597, 1510, 1483, 1423, 1290, 1250, 1182, 947, 764 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 25.7, 32.2, 38.2, 115.5, 117.3, 119.9, 121.0, 125.0, 126.5, 127.7, 129.7, 131.3, 132.9, 134.3, 139.2, 151.2, 151.6, 152.4, 157.4, 195.4.

8g

IR (KBr): 3550–3300 (br, OH), 3059, 3039, 2922, 1628 (C=O), 1591, 1504, 1481, 1413, 1340, 1250, 1205, 748 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 114.5, 117.4, 120.0, 121.7, 124.7, 127.2, 127.7, 128.9, 129.8, 129.9, 131.6, 131.8, 133.4, 134.6, 138.9, 145.8, 151.3, 151.8, 157.6, 195.4.

8h

IR (KBr): 3600–3200 (br, OH), 3055, 2953, 2924, 2877, 1622 (C=O), 1597, 1483, 1458, 1333, 1302, 1236, 1160, 1072, 910, 771, 708, 650 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 53.7, 60.3, 112.3, 117.2, 119.9, 125.3, 127.5, 128.1, 129.8, 130.2, 130.4, 131.0, 133.9, 134.1, 140.2, 152.0, 156.9, 158.3, 195.5.

9a

IR (KBr): 3600–3350 (br, OH, NH), 3172, 3064, 2926, 2829, 1716 (uracyl C=O), 1699 (uracyl C=O), 1628 (C=O), 1605, 1485, 1446, 1340, 1254, 918, 800, 769, 658 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 109.8, 117.2, 120.0, 125.0, 128.6, 130.8, 134.1, 137.9, 150.8, 155.1, 155.8, 156.7, 162.5, 194.0.

9b

IR (KBr): 3600–3300 (br, OH, NH), 3176, 3128, 3049, 2929, 2845, 1716 (uracyl C=O), 1687 (uracyl C=O), 1624 (C=O), 1595, 1495, 1468, 1329, 1288, 1240, 798, 771 cm^{-1}.

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^{13}C NMR (125 MHz, DMSO-d_6): δ = 29.1, 111.0, 117.3, 120.0, 124.9, 128.3, 130.8, 134.2, 137.9, 151.0, 154.5, 155.1, 156.8, 161.4, 193.9.

9c

IR (KBr): 3600–3250 (br, OH), 3045, 2956, 2927, 1714, 1662, 1623 (C=O), 1600, 1497, 1454, 1329, 1288, 1153, 769 cm[1].

^{13}C NMR (125 MHz, DMSO-d_6): δ = 28.7, 30.0, 110.2, 117.3, 120.0, 124.8, 128.5, 130.9, 134.3, 138.3, 151.3, 153.1, 155.1, 156.9, 161.0, 193.9.

9d

IR (KBr): 3600–3200 (br, OH), 3062, 3034, 2962, 2926, 1713, 1668, 1624 (C=O), 1608, 1593, 1497, 1340, 1242, 764 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 28.8, 45.8, 110.4, 117.3, 120.0, 124.9, 127.6, 127.8, 128.8, 128.9, 130.9, 134.3, 137.3, 138.5, 151.3, 152.8, 155.1, 156.8, 161.0, 193.9.

10

IR (KBr): 3600–3275 (br, OH, NH), 3176, 3074, 3010, 2895, 2821, 1687 (uracyl C=O), 1624 (C = O), 1599, 1566, 1483, 1342, 1294, 1252, 1219, 1153, 987, 897, 814, 758, 646 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 13.6, 114.7, 117.3, 120.0, 124.9, 130.3, 130.9, 134.3, 137.6, 156.0, 156.9, 160.3, 161.9, 164.1, 194.4.

29a

IR (KBr): 3600–3300 (br, OH), 3086, 2972, 2926, 1623 (C=O), 1603, 1587, 1485, 1446, 1290, 1252, 1221, 976, 901, 764 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 10.5, 113.31, 117.0, 119.5, 124.2, 130.4, 130.9, 134.2, 134.5, 152.5, 157.0, 157.4, 170.0, 194.4.

29b

IR (KBr): 3600–3200 (br, OH), 3059, 2978, 2931, 1630 (C=O), 1601, 1483, 1448, 1356, 1304, 1244, 1159, 764 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 21.0, 27.1, 112.3, 117.5, 120.0, 124.5, 130.8, 131.5, 134.8, 134.9, 152.8, 157.6, 165.2, 170.7, 194.8.

29c

IR (KBr): 3600–3300 (br, OH), 3172, 3059, 3032, 2960, 1622 (C=O), 1599, 1489, 1441, 1390, 1346, 1308, 1244, 1157, 903, 885, 744, 690, 644 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 111.7, 117.5, 120.1, 124.2, 127.7, 128.3, 130.1, 131.7, 131.8, 131.9, 135.1, 135.2, 153.0, 157.8, 158.4, 171.1, 194.7.

30

IR (KBr): 3600–3330 (br, OH), 3064, 3028, 2981, 2958, 2924, 1626 (C=O), 1589, 1479, 1446, 1352, 1302, 1246, 1209, 860, 777, 750 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 18.3, 117.5, 120.0, 124.5, 127.5, 130.6, 131.6, 133.7, 134.9, 151.4, 157.8, 164.4, 174.3, 195.5.

31

IR (KBr): 3600–3300 (br, OH), 3145, 3107, 3068, 2964, 1749 (ester C=O), 1626 (C=O), 1595, 1572, 1437, 1381, 1213, 1161, 818, 762, 733, 652 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 53.2, 114.5, 117.3, 119.2, 119.9, 124.9, 131.1, 131.4, 134.4, 135.3, 145.8, 149.5, 157.2, 159.1, 163.2, 195.4.

32

IR (KBr): 3600–3250 (br, OH), 3050, 2985, 2939, 1718 (ester C=O), 1626 (C=O), 1603, 1579, 1444, 1306, 1240, 1142, 1072, 766, 750 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 12.9, 14.1, 61.7, 117.0, 119.5, 124.0, 127.1, 130.3, 131.0, 132.7, 134.3, 139.9, 150.2, 157.3, 162.1, 162.9, 195.3.

Quinolines 34, 36, 38, 40 from 3-Formylchromone (1) and Anilines 33, 35, 37, 39; General Procedure

Aniline **33**, **35**, **37** or **39a–j** (4.4 mmol) and 3-formylchromone **1** (696 mg, 4 mmol) were placed in a 25 mL ace pressure tube and dissolved in DMF (10 mL). Chlorotrimethylsilane (1.738 g, 16 mmol) was added dropwise to the solution. The tube was thoroughly sealed and heated on a water-bath for 12 h. After cooling, the flask was opened (**caution!** excessive pressure inside), the mixture was poured into H_2O (30 mL) and allowed to stand at r.t. in an ultrasonic bath for 1 h. The precipitate formed was filtered and washed with MeOH (3 mL). Recrystallization from an appropriate solvent yielded targeted compounds **34**, **36**, **38**, **40a–j** (Table 3).

34

IR (KBr): 3600–3300 (br, OH), 3070, 3051, 1624 (C=O), 1601, 1581, 1483, 1387, 1336, 1298, 1244, 1217, 957, 831, 818, 756, 719 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 117.1, 119.6, 123.4, 123.9, 124.1, 127.3, 128.1, 128.1, 128.9, 129.5, 130.9, 131.3, 131.4, 132.1, 133.3, 134.4, 149.2, 149.6, 157.6, 195.9.

36

IR (KBr): 3600–3300 (br, OH), 3070, 3012, 2927, 1630 (C=O), 1605, 1579, 1477, 1419, 1294, 1246, 1165, 974, 856, 771, 712 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 56.8, 57.3, 97.0, 100.7, 115.9, 117.4, 120.0, 124.8, 127.9, 131.1, 134.4, 136.5, 148.5, 153.6, 157.0, 157.6, 165.9, 193.7.

38

IR (KBr): 3600–3300 (br, OH), 3068, 2997, 2949, 1635 (C=O), 1603, 1487, 1452, 1417, 1381, 1290, 1248, 1155, 1111, 1045, 931, 892, 818, 764 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 57.3, 61.7, 62.5, 100.8, 117.5, 118.8, 120.0, 124.6, 128.7, 131.3, 134.6, 136.0, 141.9, 142.8, 147.1, 148.1, 157.4, 160.3, 193.9.

40a

IR (KBr): 3600–3330 (br, OH), 3059, 2976, 2845, 1620 (C=O), 1605, 1524, 1460, 1363, 1271, 1236, 1163, 997, 920, 876, 773, 638 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 56.7, 104.9, 108.6, 117.5, 120.0, 123.7, 124.6, 128.4, 131.1, 134.5, 139.9, 142.0, 142.8, 151.8, 157.0, 157.2, 193.4.

40b

IR (KBr): 3600–3250 (br, OH), 3062, 3028, 2974, 2947, 1649 (C=O), 1624, 1605, 1506, 1462, 1354, 1281, 1246, 1157, 1005, 912, 756 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 56.6, 56.8, 105.1, 107.9, 117.4, 119.9, 123.4, 124.9, 129.2, 131.1, 134.3, 139.5, 143.4, 145.5, 151.1, 155.9, 157.2, 194.9.

40c

IR (KBr): 3600–3250 (br, OH), 3057, 2983, 2926, 1637 (C=O), 1605, 1506, 1473, 1456, 1282, 1246, 1165, 1012, 914, 750 cm^{-1}.

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^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.8, 57.0, 65.1, 102.7, 108.6, 117.5, 120.0, 124.2, 124.6, 129.4, 131.2, 134.6, 140.2, 141.6, 143.5, 150.8, 157.0, 1573, 193.7.

40d

IR (KBr): 3600–3270 (br, OH), 3057, 2981, 2929, 1620 (C=O), 1581, 1498, 1466, 1394, 1344, 1294, 1244, 1157, 1038, 935, 773 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.8, 14.9, 64.7, 65.0, 106.3, 108.4, 117.4, 119.9, 123.1, 125.0, 129.0, 131.0, 134.1, 138.8, 144.2, 146.0, 150.2, 154.9, 157.2, 195.3.

40e

IR (KBr): 3600–3150 (br, OH), 3082, 2966, 2937, 1624 (C=O), 1585, 1497, 1468, 1296, 1238, 1157, 1001, 918, 764 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 10.8, 10.8, 22.3, 22.3, 70.3, 70.3, 108.4, 117.3, 119.8, 122.5, 125.3, 128.8, 130.9, 133.9, 137.0, 146.8, 147.6, 150.0, 154.3, 157.2, 196.3.

40f

IR (KBr): 3600–3200 (br, OH), 3057, 2922, 1624, 1587, 1468, 1348, 1244, 1032, 904, 756 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 103.3, 104.5, 104.6, 117.4, 119.8, 124.4, 125.0, 129.3, 131.1, 134.2, 138.0, 147.3, 147.4, 149.0, 153.5, 157.4, 195.8.

40g

IR (KBr): 3600–3200 (br, OH), 3057, 2924, 1637 (C=O), 1604, 1498, 1458, 1290, 1246, 1065, 901, 744 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 64.1, 64.8, 110.6, 114.0, 117.0, 119.5, 122.9, 124.3, 128.8, 130.8, 134.0, 139.3, 145.5, 146.3, 150.2, 157.0, 194.4.

40h

IR (KBr): 3600–3320 (br, OH), 3076, 2943, 2854, 1643 (C=O), 1606, 1495, 1452, 1394, 1350, 1298, 1252, 1213, 987, 901, 746 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 31.1, 71.1, 117.4, 118.4, 119.5, 119.9, 123.8, 124.9, 129.8, 131.2, 134.3, 137.6, 146.6, 149.0, 152.4, 156.6, 157.6, 196.1.

40i

IR (KBr): 3600–3250 (br, OH), 3059, 2956, 2922, 1626 (C=O), 1603, 1489, 1468, 1448, 1244, 1205, 1157, 1036, 908, 756 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 108.1, 108.5, 117.4, 119.9, 124.6, 124.8, 130.6, 131.2, 131.5 (t, $^1J_{C,F}$ = 255 Hz), 134.5, 138.5, 143.2, 146.9, 147.4, 149.7, 157.5, 195.8.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –51.4.

40j

IR (KBr): 3600–3320 (br, OH), 3047, 2966, 2941, 2881, 2850, 1662 (C=O), 1603, 1471, 1338, 1244, 1209, 1155, 1090, 908, 756 cm^{-1}.

^{13}C NMR (125 MHz, DMSO-d_6): δ = 23.1, 37.0, 104.3, 105.1, 117.3, 119.8, 124.0, 125.1, 129.0, 129.7, 131.1, 134.1, 137.2, 147.9, 148.2, 148.4, 152.6, 157.4, 196.2.

Compound 18 from 3-Formylchromone (1) and Ethyl β-Aminocrotonate (15)

Ethyl β-aminocrotonate (**15**; 517 mg, 4 mmol) and 3-formylchromone (**1**; 696 mg, 4 mmol) were placed in a 25 mL ace pressure tube and dissolved in DMF (10 mL). Chlorotrimethylsilane (1.738 g, 16 mmol) was added dropwise to the solution. The tube was thoroughly sealed and allowed to stand at r.t. in an ultrasonic bath for 1 h and then allowed to stand at r.t. for 2 d. The mixture was poured into H_2O (30 mL) and allowed to stand at r.t. in an ultrasonic bath for 1 h. The precipitate formed was filtered and washed with small amount of *i*-PrOH (2 mL). Two recrystallization from MeOH–DMF yielded targeted compound **18**; yield: 357 mg (45%); mp 239–240 °C (Lit.[18a] mp 248–250 °C).

^{1}H NMR and IR spectral data of compound **18** were in agreement with the literature data.[18]

^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.7, 18.7, 59.3, 98.6, 118.7, 124.7, 125.6, 127.2, 134.1, 147.1, 155.0, 155.8, 167.4, 175.5.

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