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Eco-friendly synthesis of fused pyrano[2,3-*b*]pyrans *via* ammonium acetate-mediated formal oxa-[3 + 3] cycloaddition of 4*H*-chromene-3-carbaldehydes and cyclic 1,3-dicarbonyl compounds†

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Various substituted polycyclic pyrano[2,3-*b*]pyrans were synthesized *via* the condensation of 4*H*-chromene-3-carbaldehydes and their areno-condensed analogues with hetero- and carbocyclic 1,3-dicarbonyl compounds in acetic acid. Ammonium acetate was used as a green catalyst for the reaction. The process also involves the subsequent Knoevenagel condensation and 6π-electrocyclization of the 1-oxatriene intermediates formed. Fused pyridines were isolated as the products of the conjugated addition of ammonia to 1-oxatriene intermediates while using carbocyclic 1,3-dicarbonyl compounds and increasing the reaction time, indicating the reversibility of the electrocyclization stage. The calculated values of the Gibbs free energies and reaction rate constants for the 1-oxatriene – 2*H*-pyran equilibrium also testified to the irreversibility of pyrano[2,3-*b*]pyran formation in the case of using of heterocyclic 1,3-dicarbonyl compounds.

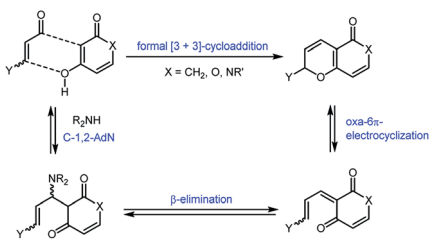
Introduction

Among the effective approaches to the synthesis of six-membered oxygen- and nitrogen-containing heterocycles are the reactions of formal [3 + 3]-cycloaddition, including the Knoevenagel condensation followed by 6π-electrocyclization.[1] The net result is the formation of a new stereocenter adjacent to the pyran oxygen atom, two σ-bonds and ring (Scheme 1).

Oxa-[3 + 3]-annulation is a powerful synthetic strategy in the preparation of natural compounds and represents a complementary approach to oxa-[4 + 2]-cycloaddition. This method has already been widely used in the synthesis of various terpenes and alkaloids.[1a–c] At the same time, the set of possible substrates is limited almost exclusively to acyclic α,β-unsaturated aldehydes. The involvement of other types of conjugated aldehydes, in particular 4*H*-chromen-3-carbaldehydes, in this type of transformation stimulates significant interest because it will provide access to the synthesis of a large number of new polycondensed heterocycles.

Despite the obvious advantages of formal oxa-[3 + 3]-cycloaddition, the use of this methodology has long been limited due to the presence of a large number of competitive processes that reduce the yield of the target product. These include competition between the 1,2- and 1,4-addition to the α,β-unsaturated aldehyde, while the ambident nature of the nucleophile can lead to the initial O- or C-attack of the conjugated system (Fig. 1). At the same time, acyclic α,β-unsaturated enones and enals usually give 1,4-addition products (Michael adducts) as the predominant or sole products.[2]

2*H*,5*H*-Pyrano[4,3-*b*]pyran-5-one and 2,6-dihydro-5*H*-pyrano[3,2-*c*]pyridin-5-one are important scaffolds that are present in many natural products with potent biological activities and structural diversity. The pyrano[3,2-*c*]quinolone moiety is a structural motif present in several pyranoquinolone alkaloids including haplophytin A,[3a] oricine[3b] and simulenoline,[3c] which



Scheme 1 The formal [3 + 3]-cycloaddition approach leading to the fused 2*H*-pyran motifs.

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Fig. 1 Possible reaction pathways of 1,3-dicarbonyl compounds with α,β-unsaturated aldehydes.

is a potent inhibitor of platelet aggregation. Among the derivatives of 2*H*-pyran-2-one and its benzo-condensed analogues are triptiliospinocoumarin,[3d] vismiaguian A,[3e] pyripyropene T,[3f] an antithrombinic sesquiterpenoid pyranocoumarin ferprenin[3g] and some others.[3h] Besides, the polycyclic acetal-fused pyrano[2,3-*b*]pyran skeleton is present in a variety of biologically active natural products, for example, welwitschin H,[3i] oleracone G[3j] and some alkaloids[3k,l] (Fig. 2).

Fused 2*H*,5*H*-pyrano[4,3-*b*]pyran-5-ones and 2,6-dihydro-5*H*-pyrano[3,2-*c*]pyridin-5-ones are important structural motifs in bioactive synthetic products. For instance, compound **A** shows phytotoxic activity,[4a] pyrones **B–E** strongly inhibit acetylcholinesterase activity, DNA synthesis, and leukemic cell growth.[4b] Pyrano[4,3-*b*]pyranone **F** is cytotoxic to neuroblastoma and melanoma cells.[4c] The tricyclic 2*H*-pyrans **G–I** may serve as lead compounds for the discovery of new drugs for the prevention and treatment of neurodegenerative diseases (for example, Alzheimer's disease).[4d,e] Pyrano[3,2-*c*]quinolone and pyrano[3,2-*c*]pyranone scaffolds **J** are present in a number of antiproliferative agents (against breast and liver cancer cell) (Fig. 3).[4f–h]

Results and discussion

3-Formyl-4*H*-chromenes and their benzo-condensed derivatives are promising starting compounds for the synthesis of a wide

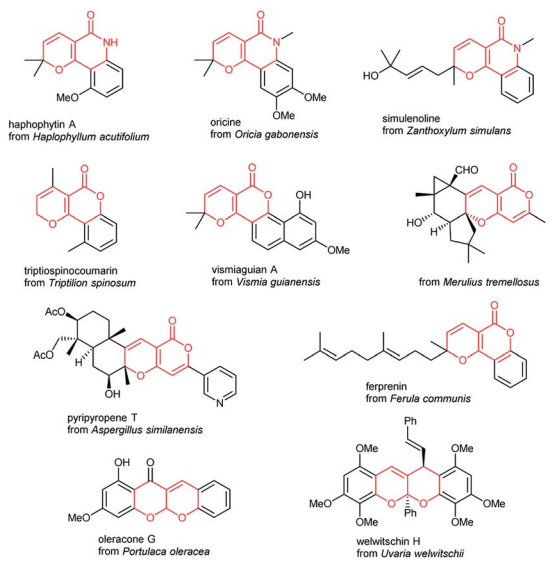


Fig. 2 Natural compounds containing fused 2*H*,5*H*-pyrano[4,3-*b*]pyran-5-one, 2,6-dihydro-5*H*-pyrano[3,2-*c*]pyridin-5-one and pyrano[2,3-*b*]pyran scaffolds.

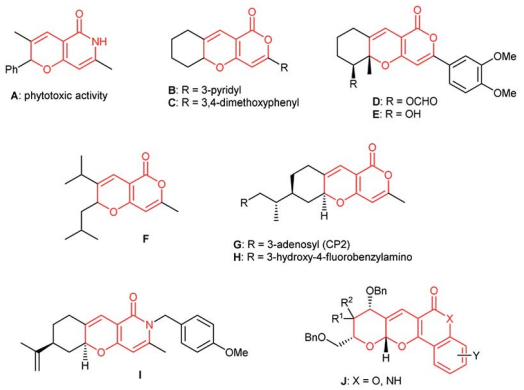
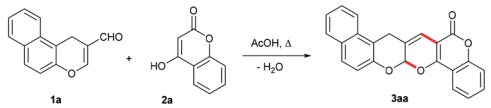


Fig. 3 Biologically active compounds containing fused 2*H*,5*H*-pyrano[4,3-*b*]pyran-5-one and 2,6-dihydro-5*H*-pyrano[3,2-*c*]pyridin-5-one scaffolds.

variety of heterocyclic systems due to the presence of two nonequivalent electrophilic centers (C-2 and carbonyl carbons). We have previously shown that the three-component condensation of 3-formyl-4*H*-chromenes, ammonium acetate and 1,3-dicarbonyl compounds leads to β-(2-hydroxybenzyl)-substituted pyridine derivatives.[5a] However, we have found that the use of the 1,3-dicarbonyl compounds of the heterocyclic series in this reaction leads to pyrano[2,3-*b*]pyrans as formal [3 + 3]-cycloaddition products. In continuation of our interest in chromene chemistry,[5] here we report an effective eco-friendly synthesis of polycyclic pyrano[2,3-*b*]pyrans from β-formyl-substituted 4*H*-chromenes, ammonium acetate and cyclic β-dicarbonyl compounds.

As a model reaction, we chose the reaction between the aldehyde **1a** and 4-hydroxycoumarin **2a**. It is known that formal [3 + 3]-cycloaddition is catalyzed by both Lewis and Brønsted acids and bases.[6] The annulation reaction of **1a** and **2a** was initially performed under refluxing conditions in AcOH with piperazine as a catalyst. As depicted in Table 1 (entry 1), **3aa** was obtained in 34% yield along with the recovery of the starting materials in 2 min in the presence of 0.2 equiv. of piperidine. Increasing the used catalyst did not affect the yield to a large extent (entry 2). However, increasing the reaction time to 30 min allowed us to isolate **3aa** in 71% yield (entry 3). A further increase in the reaction time up to 2 hours did not affect the reaction yield (entry 4). To improve the yields and reaction rates, several experimental conditions were evaluated. The use of CH_3CN, 1,2-dichloroethane, dioxane, or DMF resulted in lower yields and longer reaction times (entries 5–8). As AcOH was found to be the best solvent, we screened different catalysts. In the case of TMG, Et_3N, DBU, *N*-methylimidazole and even pyridine, we did not observe any significant differences in the yields and reaction rates (entries 9, 10, 12, 14, 16). The best results were obtained in AcOH as a solvent and in the presence of 1.0 equiv. of ammonium acetate. Under these conditions, the reaction was complete in 1 h, and the yield was 95% (entry 18). Further increase in the quantity of ammonium acetate did not affect the yield. It is important to note that the use of even 0.2 equiv. of ammonium acetate led to **3aa** in comparable yield

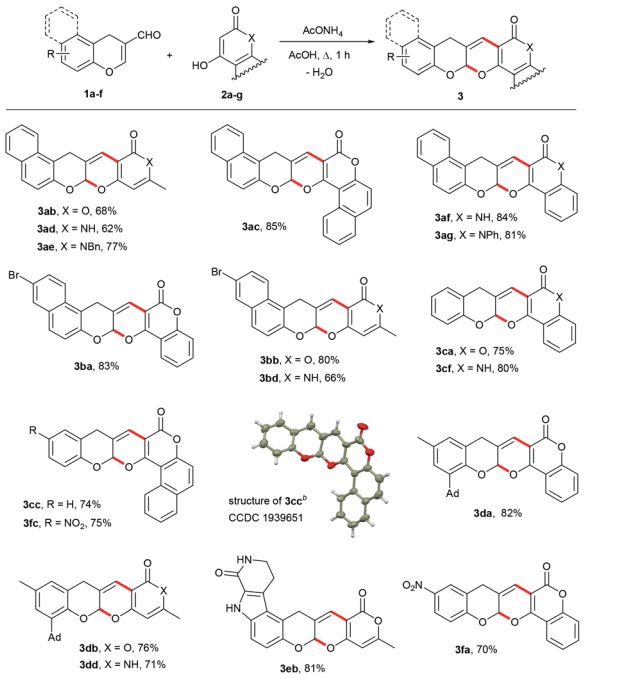
Table 1 Optimization of the reaction conditions[a]



Entry	Catalyst (x equiv.)	Time	Yield[b] (%)
1	Piperidine (0.2)	2 min	34
2	Piperidine (1.0)	2 min	39
3	Piperidine (0.2)	30 min	71
4	Piperidine (0.2)	2 h	73
5[c]	Piperidine (0.2)	5 h	40
6[d]	Piperidine (0.2)	14 h	49
7[e]	Piperidine (0.2)	14 h	46
8[f]	Piperidine (0.2)	30 min	31
9	Et_3N (0.2)	2 h	78
10	DBU (0.2)	2 h	79
11	*N*-Methylimidazole (0.2)	2 min	13
12	*N*-Methylimidazole (0.2)	2 h	74
13	TMG[g] (0.2)	2 min	13
14	TMG (1.0)	1 h	80
15	Py (0.2)	2 min	37
16	Py (1.0)	1 h	76
17	$AcONH_4$ (1.0)	20 min	89
18	**$AcONH_4$ (1.0)**	**1 h**	**95**
19	**$AcONH_4$ (0.2)**	**2 h**	**93**
20[h]	$AcONH_4$ (0.2)	2 h	52
21	*p*-TSA (1.0)	2 h	—
22	None	8 h	43
23[h]	None	1 h	46
24[h]	None	2 h	44

[a] All reactions were carried out with **1a** (1 mmol), **2a** (1 mmol) and catalyst in 3 mL of AcOH under reflux (unless otherwise indicated) and an air atmosphere. [b] Isolated yields. [c] CH_3CN. [d] 1,2-Dichloroethane. [e] 1,4-Dioxane. [f] DMF at 100 °C. [g] 1,1,3,3-Tetramethylguanidine. [h] EtOH.

Table 2 Substrate scope[a]



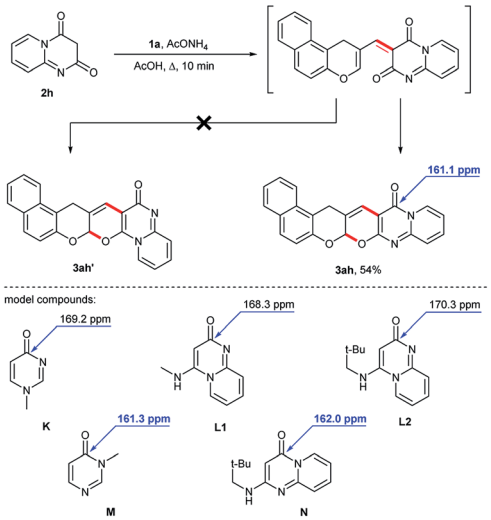
[a] All reactions were carried out with **1** (1 mmol), **2** (1 mmol) and ammonium acetate (0.2 mmol) in AcOH under reflux for 1 h. [b] X-ray with 50% probability displacement.

(entry 19). Ethanol was also used in the ammonium acetate catalyzed reaction as a solvent, but the yield of **3aa** was lower (entry 20). When we carried out the same transformation in the presence of 1.0 equiv. of *p*-TSA in AcOH, a complex mixture of unidentified products was obtained along with the starting aldehyde **1a** (entry 21). To determine the role of the catalyst, the reaction was carried out in the absence of ammonium acetate in AcOH or ethanol and **3aa** was isolated from the reaction mixture in 43–46% yield (entries 22–24). This indicates that a secondary amine, or ammonium acetate, is not necessary for this transformation, but they accelerate the reaction and increase the yields. The synthesis of compound **3aa** was repeated under optimized conditions on several different scales (up to 20 mmol), all with comparable yields.

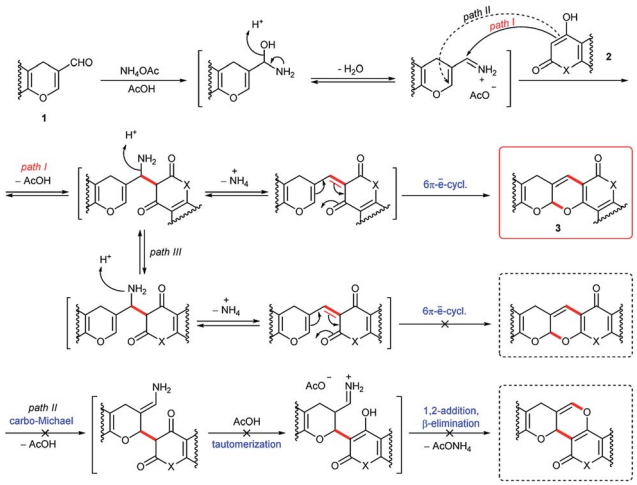
With the optimized reaction parameters, we extended this methodology to various formylchromones **1a–f** and cyclic 1,3-dicarbonyl compounds **2a–g** such as 4-hydroxy-6-methyl-2*H*-pyran-2-one, 4-hydroxy-6-methylpyridin-2(1*H*)-ones and their benzocondensed analogues. As shown in Table 2, polycyclic acetals **3** were prepared in 64–85% isolated yields. All reactions were carried out using a 1 : 1 molar ratio of chromenecarbaldehyde **1** and 1,3-dicarbonyl compound **2**. Ammonium acetate is a very cheap and nontoxic catalyst, therefore, this procedure presents a green method for the diversity-oriented synthesis of biologically active compounds.

The structures of all products were determined on the basis of their analytical data. The cyclic nature of products **3** was confirmed by the absence of phenolic OH-stretching frequencies in the IR spectra and phenolic proton signals in the ^{1}H NMR spectra. A characteristic feature of the ^{1}H NMR spectra is the presence of two one-proton singlet signals in the region of 6.62–7.03 ppm, corresponding to the acetal and olefinic protons. Methylene protons of **3** were observed, as a rule, as two separate doublets at 3.54–5.30 ppm (J_{AB} = 15.8–19.2 Hz) due to the chiral acetal center in these molecules. NH protons in the ^{1}H NMR spectra of the *N*-unsubstituted derivatives of pyridinone and quinolinone were seen as singlets at 10.93–12.20 ppm. In the ^{13}C NMR spectra of **3**, a signal in the region of 95.8–98.2 ppm was assigned to the acetal carbon atom. Methylene carbon atoms appeared at 29.8–37.2 ppm. The DEPT spectra showed that the number of protons directly attached to the carbon atoms corresponds to the assigned structures. The structure of **3cc** was also confirmed by single-crystal X-ray diffraction analysis.

We also studied the reaction of 1*H*-benzo[*f*]chromene-2-carbaldehyde **1a** with 2*H*-pyrido[1,2-*a*]pyrimidine-2,4(3*H*)-dione **2h** in the presence of ammonium acetate. In this reaction, the formation of two electrocyclic products was potentially



Scheme 2 Reaction of 1*H*-benzo[*f*]chromene-2-carbaldehyde **1a** with 2*H*-pyrido[1,2-*a*]pyrimidine-2,4(3*H*)-dione **2h**.



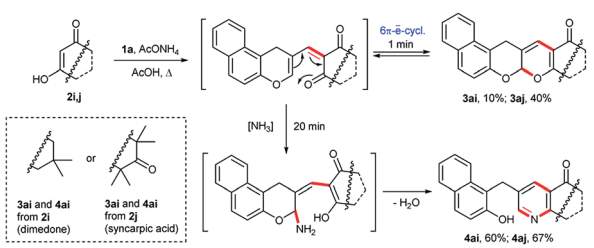
Scheme 3 Putative formal [3 + 3]-cycloaddition pathway.

possible (Scheme 2). According to NMR spectroscopy, only one cyclic regioisomer was obtained. In the ^{13}C NMR spectrum, the carbonyl carbon atom appeared at 161.1 ppm. A comparison of the chemical shifts of the carbonyl carbon atoms in the product and in model compounds[7] **K–N** was in favor of the linear condensed structure **3ah**. Thus, the carbonyl carbon atom bonded to nitrogen at the double bond was more unshielded and appeared at 168.3–170.3 ppm (pyrimidin-4(1*H*)-one **K** and 2*H*-pyrido[1,2-*a*]pyrimidin-2-ones **L1**, **L2**), while carbonyl carbons in pyrimidin-4(3*H*)-one **M** and 4*H*-pyrido[1,2-*a*]pyrimidin-4-one **N** appeared at 161.3 and 162.0 ppm respectively. This does not attribute structure **3ah′** to the formed isomer.

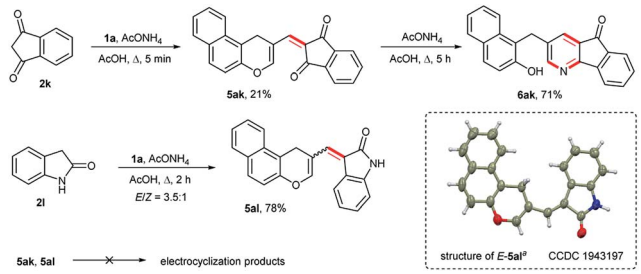
Scheme 3 outlines a proposed mechanism for the formation of fused 2*H*-pyrans **3**. The Knoevenagel condensation between the enol derivatives of the β-ketolactones or β-ketolactams **2** and the electrophilic formyl carbon atom of the chromenecarbaldehydes **1** furnishes the conjugated 1-oxatriene intermediate, which undergoes a 6π-electrocyclization to form the heterocyclic compounds. Ammonium acetate might play the role of a Lewis base (to activate the enol form of the cyclic 1,3-dicarbonyl compounds) and the role of a Brønsted acid (to activate the aldehydes *via* hydrogen bonding or immonium salt formation). It should be noted that the studied 1,3-dicarbonyl compounds are strong OH-acids. For example, the pK_a of 4-hydroxycoumarin **2a** is 4.1.[8] On the other hand, the vinyliminium ion arising from the formyl group and ammonia *in situ* is a better electrophile than **1** and undergoes selective C-1,2-addition with the 1,3-dicarbonyl compound. Thus, the activation of both partners of this reaction by the same catalyst might explain the highest yields in the case of using ammonium acetate. At the same time, the formation of the iminium salt is not obligatory. It was shown that the reaction was catalyzed not only by piperidine and ammonium acetate but also pyridine, Et_3N and *N*-methylimidazole (Table 1). Therefore, we consider that the formation of the enolate anion from **2** is more important. Both chromenecarbaldehydes **1** and cyclic 1,3-dicarbonyl compounds **2** are polydentate reagents, and several reaction modes are possible by the combination of 1,4- *vs.* 1,2-addition. Nevertheless, the reaction is regioselective and the *path II* including the initial *carbo*-Michael addition was not realized. Electrocyclization involving the carbonyl group of the lactone or lactam moiety was also not observed (*path III*).

In order to broaden the scope of the present method, we attempted this protocol using dimedone **2i** and syncarpic acid **2j** as cyclic 1,3-dicarbonyl compounds. The products of electrocyclization, **3ai**, **3aj**, were isolated in low yields when the reaction was carried out for 1 min in boiling acetic acid. However, the boiling of an equimolar mixture of reagents for 20 min resulted exclusively in 7,8-dihydroquinolin-5(6*H*)-one derivatives **4ai**, **4aj** (Scheme 4) as described in literature.[5a] Compounds **4ai**, **4aj** arose from **3ai**, **3aj** *via* an oxa-6π-electrocyclic ring-opening of **3**, a 1,6-addition of ammonia, dehydration and closure of the dihydropyran fragment. This assumption was confirmed by the fact that the isolated compound **3aj** was converted to **4aj** in 83% yield under the mentioned conditions. Since both the Knoevenagel condensation and electrocyclic ring-closure are reversible,[9] such preference could simply be a reflection of the stability of the respective products being in favour of **4**.

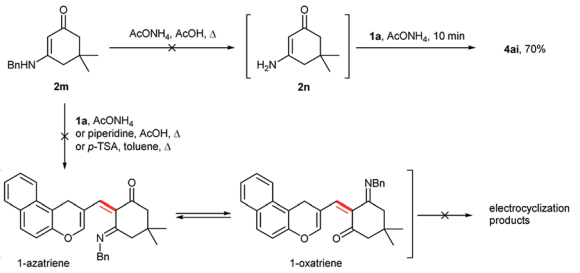
We also observed an intriguing contrast between 1,3-indandione **2k** and oxindole **2l** (Scheme 5). In the case of 1,3-



Scheme 4 Reaction of **1a** with enolizable cyclic β-diketones (dimedone and syncarpic acid).



Scheme 5 Reaction of **1a** with 1,3-indandione and oxindole. [a]X-ray with 50% probability displacement.



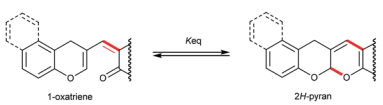
Scheme 6 Reaction of **1a** with enaminone **2m**.

indandione, the 1-oxatriene **5ak** was isolated in 21% yield after boiling for 5 min. Prolonged heating (5 h) of an equimolar mixture of reagents in AcOH in the presence of ammonium acetate gave the 1,6-addition product **6ak** of ammonia generated from ammonium acetate. No desired electrocyclization product was obtained. At the same time, the reaction of **1a** with oxindole was terminated at the stage of the Knoevenagel adduct **5al**. The last was isolated in 78% yield as a mixture of *E*- and *Z*-isomers in an approximately 3.5 : 1 molar ratio, judging from the ^{1}H NMR spectrum of the crude product. Pure *E*-indolinone was prepared by multiple recrystallizations from DMF, and its structure was confirmed by X-ray analysis. The Knoevenagel condensation products **5ak** and both *Z*- and *E*-isomers of **5al** that can undergo electrocyclization only after isomerization to the *Z*-form failed to give the fused pyrano[2,3-*b*]pyran derivatives. In contrast to the ketone carbonyls of dimedone, syncarpic acid and 1,3-indandione, it appears that the amide carbonyl of oxindole are not sufficiently electrophilic to react with ammonia. Thus, for reactions of 1,3-indandione and oxindole with **1a**, the electrocyclic ring-closure step is either very slow or is arrested and, in the case of 1,3-indandione, the 1,6-addition of ammonia either occurs faster or is more favored.

Based on the literature,[4g,9] we can presume that compounds **3** equilibrate with 1-oxatriene intermediates. The energy calculation was done to determine the energy differences between some fused pyrano[2,3-*b*]pyrans **3** and their 1-oxatriene valence tautomers. It turned out that the energy differences between 2*H*-pyran and 1-oxatriene forms of **5ak** and **5al** were significantly larger as compared to other 1,3-dicarbonyl compounds (Table 3).

We proposed that the reaction of **1a** with 3-(benzylamino)-5,5-dimethylcyclohex-2-enone **2m** by analogy with 1,3-dicarbonyl compounds would result in the formation of a formal aza- or oxa-[3 + 3]-cycloaddition product as a result of the Knoevenagel condensation and 6π-electrocyclization (Scheme 6). The use of such cyclic vinylogous amide **2m** in a formal [3 + 3]-cycloaddition, including the 1-azatriene intermediate, has already been described in the literature.[10] However, the treatment of **1a** with enaminoketone **2m** in the presence of catalytic amounts of ammonium acetate/piperidine in acetic acid or *p*-TSA in toluene under reflux resulted in the recovery of the starting material. In the presence of an excess of ammonium acetate, 7,8-dihydroquinolin-5(6*H*)-one **4ai** was isolated in 70% yield. The benzylamino fragment in enaminone **2m** was first replaced by an amino group with the formation of 3-amino-5,5-dimethylcyclohex-2-en-1-one **2n**. Then, enaminone **2n** reacted with chromene **1a** to form the Michael adduct. The subsequent opening of the dihydropyran fragment and intramolecular nucleophilic addition led to the formation of a pyridine ring.

Table 3 Gibbs free energies[a] and reaction rate constants for 1-oxatriene – 2*H*-pyran equilibrium



Compound	Δ*G*, kJ mol^{-1}	K_{eq}
3ab	−14.05	290.1
3ad	−20.73	4303.5
3ca	−9.71	50.4
3ai	−5.48	9.1
3aj	−1.65	1.9
5ak	49.02	2.6×10^{-9}
***Z*-5al**	57.63	7.9×10^{-11}

[a] Calculated at 298.15 K and 1 atm using the IEFPCM solvent model (acetic acid).

Conclusion

We have developed the first ammonium acetate-catalyzed formal oxa-[3 + 3]-annulation allowing the synthesis of a variety of fused pyrano[2,3-*b*]pyrans from cyclic β-dicarbonyl compounds and 4*H*-chromene-3-carbaldehydes. In some cases, 1-oxatriene compounds were proposed as key intermediates, and fused pyridines were isolated as 1,6-addition products of ammonia. The calculated values of the Gibbs free energies and reaction rate constants for 1-oxatriene – 2*H*-pyran equilibrium and experimental data indicated the reversibility of the electrocyclization stage, while the direction of the equilibrium shift was determined by the nature of the 1,3-dicarbonyl compound. Several new polycondensed heterocyclic systems were obtained in good yields in the green one-pot reaction. This method does not require strong bases for successful annulation, perhaps owing to the high acidity of 1,3-dicarbonyl compounds. Besides, the advantages of this eco-friendly procedure include the use of

available and inexpensive reagents, atom- and step-economy, simple reaction conditions, broad substrate scope, no metal catalysis, scalability, and easy isolation by a chromatography-free protocol.

Experimental

General information

Melting points were determined by the capillary method on an SRS OptiMelt MPA100 apparatus and were uncorrected. FTIR-spectra were obtained on a Shimadzu IR Affinity-1 spectrophotometer with the Specac Diamond ATR GS 10800-B attachment and are reported in cm^{-1}. ^1H and ^{13}C NMR spectra (including DEPT-135, HMBC, HETCOR, COSY, and NOESY experiments) were recorded on a JEOL JNM-ECX 400 spectrometer (400 and 100 MHz, respectively) in DMSO-d_6 solutions at ambient temperature unless otherwise noted, relative to the residual solvent signal [DMSO-d_6 $\delta = 2.50$ ppm (^1H), $\delta = 39.5$ ppm (^{13}C)]. Chemical shifts and coupling constants were recorded in units of parts per million and hertz, respectively. ^{13}C NMR spectroscopy of **3ac**, **3af** and **3fc** was hindered due to its poor solubility in common solvents. High-resolution mass spectra (HRMS) were recorded on an Agilent 6230 TOF instrument using an electrospray (ESI) ionization source. The reaction progress was controlled by TLC on aluminum foil-backed silica gel plates (Merck, Kiesgel 60 F254); visualization was conducted under UV light and in iodine vapor. X-ray diffraction data were collected by using STOE STADI VARI PILATUS-100K (for **3cc**), or SuperNova, Dual, Cu at zero, AtlasS2 (for **5al**) diffractometers. All commercial solvents and reagents were used without additional purification. Computational calculations were carried out using the hybrid functionals of Becke[11] and Lee, Yang and Parr.[12] The solvent effect was computed by carrying out the single-point energy calculations of the gas-phase optimized geometries using the polarized continuum model (PCM).[13] The Gaussian 03 program package[14] was used for all calculations. The reported 4*H*-chromene-3-carbaldehydes and 1*H*-benzo[*f*]chromene-2-carbaldehydes were prepared according to literature procedures.[15]

General procedure

A mixture of 3-formylchromone **1a–f** (1 mmol), 1,3-dicarbonyl compound **2a–g** (1 mmol) and ammonium acetate (15 mg, 0.2 mmol or more) in acetic acid (3 mL, unless otherwise noted) was stirred under reflux for 1 h. The progress of the reaction was monitored by TLC. After completion, the mixture was cooled to room temperature, and the formed precipitate was collected. The crude product was purified by recrystallization.

6*H*,8*H*,15*aH*-Benzo[f]pyrano[2,3-*b*:5,6-*c*′]dichromen-6-one (3aa). Yield: 95%, 336 mg. Colorless solid, mp 234–235 °C (DMF). IR ν_{max}: 1714, 1659, 1622, 1599, 1516, 1464, 1395, 1342, 1231, 1169, 1155, 1132, 1090, 1040, 1001, 970, 949, 937, 806, 766, 739. ^1H NMR (400 MHz, DMSO-d_6) (at 120 °C) δ: 4.09 (s, 2H, CH_2), 6.84 (s, 1H, H-7), 6.94 (s, 1H, H-15a), 7.09 (d, $J = 9.0$ Hz, 1H, H-14), 7.37–7.44 (m, 3H, H-2,4,11), 7.52–7.56 (m, 1H, H-10), 7.63–7.67 (m, 1H, H-3), 7.73 (d, $J = 8.7$ Hz, 1H, H-13), 7.83 (d, $J = 8.2$ Hz, 1H, H-12), 7.86 (d, $J = 8.5$ Hz, 1H, H-9), 7.92 (d, $J = 7.8$ Hz, 1H, H-1). ^{13}C NMR (100 MHz, DMSO-d_6) (at 120 °C) δ: 29.9 (CH_2), 96.9 (CH-15a), 100.3 (C-6a), 113.7 (CH-7), 114.6 (C-16b), 115.7 (C-8a), 117.1 (CH-4), 118.8 (CH-14), 122.8 (2CH-1,9), 124.7 (CH-11), 125.2 (CH-2), 126.5 (C-7a), 127.4 (CH-10), 128.8 (CH-12), 129.0 (CH-13), 129.9 (C-12a), 132.3 (C-8b), 133.2 (CH-3), 150.3 (C-14a), 153.0 (C-4a), 155.3 (C-16a), 159.7 (C=O). HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{15}O_4$ $[M + H]^+$: 355.0970, found: 355.0967.

10-Methyl-7*aH*,12*H*,14*H*-benzo[*f*]pyrano[3′,4′:5,6]pyrano[2,3-*b*]chromen-12-one (3ab). Yield: 68%, 216 mg. Colorless solid, mp 217–219 °C (AcOH). IR ν_{max}: 1706, 1637, 1624, 1573, 1516, 1443, 1427, 1390, 1359, 1330, 1257, 1236, 1215, 1204, 1148, 1071, 1060, 1042, 1006, 982, 943, 938, 907, 853, 802, 769. ^1H NMR (400 MHz, DMSO-d_6) (at 140 °C) δ: 2.23 (s, 3H), 3.99 (s, 2H), 6.20 (s, 1H), 6.67 (s, 1H), 6.71 (s, 1H), 7.04 (d, $J = 8.9$ Hz, 1H), 7.38 (t, $J = 7.1$ Hz, 1H), 7.52 (t, $J = 7.3$ Hz, 1H), 7.70 (d, $J = 9.0$ Hz, 1H), 7.79–7.84 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) (at 140 °C) δ: 20.0 (CH_3), 29.8 (CH_2), 96.7 (CH), 97.5 (C), 99.3 (CH), 113.5 (CH), 115.7 (C), 118.8 (CH), 122.8 (CH), 124.4 (C), 124.5 (CH), 127.3 (CH), 128.8 (CH), 128.9 (CH), 129.9 (C), 132.4 (C), 150.3 (C), 160.8 (C), 161.2 (C), 163.6 (C). HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{15}O_4$ $[M + H]^+$: 319.0970, found: 319.0962.

8*H*,10*H*,17*aH*-Dibenzo[*f*,*f*′]pyrano[2,3-*b*:5,6-*c*′]dichromen-8-one (3ac). The reaction was carried out in 6 mL of AcOH. Yield: 85%, 343 mg. Light-yellow solid, mp 276–277 °C (DMF). IR ν_{max}: 1697, 1622, 1597, 1557, 1514, 1464, 1393, 1344, 1217, 1169, 1144, 1076, 1049, 974, 960, 945, 814, 806, 752, 735. ^1H NMR (400 MHz, DMSO-d_6) δ: 4.12 (d, $J = 18.6$ Hz, 1H), 4.18 (d, $J = 18.6$ Hz, 1H), 6.93 (s, 1H), 7.13–7.16 (m, 2H), 7.40–7.44 (m, 1H), 7.55–7.59 (m, 2H), 7.63–7.67 (m, 1H), 7.75–7.82 (m, 2H), 7.85–7.92 (m, 2H), 8.09 (d, $J = 8.0$ Hz, 1H), 8.24 (d, $J = 8.9$ Hz, 1H), 9.26 (d, $J = 8.7$ Hz, 1H). HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{17}O_4$ $[M + H]^+$: 405.1127, found: 405.1134.

10-Methyl-7*a*,11-dihydro-12*H*,14*H*-benzo[5′,6′]chromeno[3′,2′:5,6]pyrano[3,2-*c*]pyridin-12-one (3ad). Yield: 62%, 197 mg. Colorless solid, mp 308–310 °C (DMF). IR ν_{max}: 3200–2400, 1661, 1622, 1595, 1570, 1516, 1493, 1456, 1437, 1395, 1341, 1265, 1227, 1219, 1184, 1167, 1150, 1088, 962, 934, 916, 812, 802, 741. ^1H NMR (400 MHz, DMSO-d_6) (at 140 °C) δ: 2.18 (s, 3H, CH_3), 3.94 (d, $J = 18.1$ Hz, 1H, CH_2), 4.01 (d, $J = 18.1$ Hz, 1H, CH_2), 5.83 (s, 1H, H-9), 6.61 (s, 1H, H-7a), 6.81 (s, 1H, H-13), 7.02 (d, $J = 8.9$ Hz, 1H, H-6), 7.38 (ddd, $J = 8.0$, 6.9, 1.2 Hz, 1H, H-3), 7.52 (ddd, $J = 8.0$, 6.9, 1.2 Hz, 1H, H-2), 7.69 (d, $J = 9.0$ Hz, 1H, H-5), 7.80 (d, $J = 8.0$ Hz, 1H, H-4), 7.84 (d, $J = 8.4$ Hz, 1H, H-1), 10.93 (br. s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6) (at 140 °C) δ: 19.2 (CH_3), 30.1 (CH_2), 96.6 (CH-7a), 97.2 (CH-9), 102.9 (C-12a), 114.8 (CH-13), 115.9 (C-14a), 119.0 (CH-6), 122.4 (C-13a), 122.8 (CH-1), 124.4 (CH-3), 127.3 (CH-2), 128.7 (CH-5), 128.8 (CH-4), 129.8 (C-4a), 132.5 (C-14b), 146.4 (C-10), 150.7 (C-6a), 159.0 (C-8a), 161.2 (C=O). HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{16}NO_3$ $[M + H]^+$: 318.1130, found: 318.1137.

11-Benzyl-10-methyl-7*a*,11-dihydro-12*H*,14*H*-benzo[5′,6′]chromeno[3′,2′:5,6]pyrano[3,2-*c*]pyridin-12-one (3ae). Yield: 77%, 314 mg. Colorless solid, mp 238–240 °C (DMF–MeOH). IR ν_{max}: 1672, 1641, 1622, 1589, 1572, 1439, 1412, 1339, 1223, 1204, 1152, 1117, 984, 964, 947, 806, 768, 739, 708. ^1H NMR (400 MHz,

DMSO-d_6) δ: 2.24 (s, 3H), 4.01 (s, 2H), 5.21 (d, J = 15.8 Hz, 1H), 5.30 (d, J = 15.8 Hz, 1H), 6.16 (s, 1H), 6.68 (s, 1H), 6.89 (s, 1H), 7.03–7.09 (m, 3H), 7.19–7.31 (m, 3H), 7.39 (t, J = 7.2 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.73 (d, J = 8.9 Hz, 1H), 7.83 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 20.7 (CH_3), 30.3 (CH_2), 46.7 (CH_2), 95.8 (CH), 99.4 (CH), 102.4 (C), 114.8 (CH), 115.8 (C), 119.0 (CH), 123.0 (CH), 123.4 (C), 124.6 (CH), 126.6 (2CH), 127.4 (CH), 127.6 (CH), 128.9 (2CH), 129.2 (2CH), 129.5 (C), 132.3 (C), 137.6 (C), 148.2 (C), 150.4 (C), 157.2 (C), 160.9 (C). HRMS (ESI, m/z) calcd for $C_{27}H_{22}NO_3$ $[M + H]^+$: 408.1600, found: 408.1595.

5,15*a*-Dihydro-6*H*,8*H*-benzo[5′,6′]chromeno[3′,2′:5,6]pyrano[3,2-*c*]quinolin-6-one (3af). The reaction was carried out in 6 mL of AcOH. Yield: 84%, 297 mg. Light-yellow solid, mp 339–340 °C (DMF). IR ν_{max}: 3300–2500, 1678, 1661, 1624, 1599, 1568, 1497, 1418, 1395, 1263, 1233, 1177, 1167, 1098, 1009, 964, 951, 922, 806, 743, 737, 725. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.09 (s, 2H), 6.91 (s, 1H), 6.97 (s, 1H), 7.09 (d, J = 8.9 Hz, 1H), 7.22–7.26 (m, 1H), 7.31 (d, J = 8.2 Hz, 1H), 7.39–7.43 (m, 1H), 7.51–7.57 (m, 2H), 7.75 (d, J = 8.9 Hz, 1H), 7.83–7.87 (m, 2H). 7.90 (d, J = 8.0 Hz, 1H), 11.72 (s, 1H). HRMS (ESI, m/z) calcd for $C_{23}H_{16}NO_3$ $[M + H]^+$: 354.1130, found: 354.1124.

5-Phenyl-5,15*a*-dihydro-6*H*,8*H*-benzo[5′,6′]chromeno[3′,2′:5,6]pyrano[3,2-*c*]quinolin-6-one (3ag). The reaction was carried out in 6 mL of AcOH. Yield: 81%, 348 mg. Colorless solid, mp 263–264 °C (DMF–MeOH). IR ν_{max}: 1674, 1651, 1616, 1593, 1568, 1466, 1454, 1435, 1418, 1393, 1331, 1314, 1275, 1217, 1182, 1092, 1011, 982, 961, 818, 756, 723, 694. ^{1}H NMR (400 MHz, DMSO-d_6) (at 140 °C) δ: 4.11 (s, 2H), 6.59 (d, J = 8.5 Hz, 1H), 6.93 (s, 1H), 7.00 (s, 1H), 7.10 (d, J = 8.9 Hz, 1H), 2.27–7.30 (m, 3H), 7.38–7.44 (m, 2H), 7.49–7.60 (m, 4H), 7.73 (d, J = 9.0 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 8.06 (d, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (at 140 °C) δ: 30.2 (CH_2), 96.8 (CH), 105.2 (C), 114.6 (C), 114.7 (CH), 115.9 (C), 116.2 (CH), 118.9 (CH), 122.7 (CH), 122.8 (2CH), 124.5 (CH), 126.0 (C), 127.3 (CH), 128.8 (CH), 128.9 (CH), 129.1 (CH), 129.7 (2CH), 129.9 (C), 130.3 (2CH), 131.5 (CH), 132.5 (C), 138.4 (C), 140.7 (C), 150.6 (C), 152.6 (C), 160.1 (C). HRMS (ESI, m/z) calcd for $C_{29}H_{20}NO_3$ $[M + H]^+$: 430.1443, found: 430.1440.

11-Bromo-6*H*,8*H*,15*aH*-benzo[*f*]pyrano[2,3-*b*:5,6-*c*′]dichromen-6-one (3ba). The reaction was carried out in 6 mL of AcOH. Yield: 83%, 360 mg. Colorless solid, mp 243–245 °C (AcOH). IR ν_{max}: 1717, 1659, 1622, 1585, 1516, 1464, 1395, 1344, 1227, 1167, 1155, 1001, 970, 947, 937, 806, 766, 737. ^{1}H NMR (400 MHz, DMSO-d_6) (at 110 °C) δ: 4.09 (s, 2H), 6.84 (s, 1H), 6.96 (s, 1H), 7.14 (d, J = 8.9 Hz, 1H), 7.38–7.44 (m, 2H), 7.63–7.68 (m, 2H), 7.73 (d, J = 9.0 Hz, 1H), 7.81 (d, J = 9.2 Hz, 1H), 7.92 (dd, J = 8.0, 1.8 Hz, 1H), 8.08 (d, J = 1.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (at 110 °C) δ: 29.9 (CH_2), 96.8 (CH), 100.2 (C), 113.9 (CH), 114.5 (C), 116.1 (C), 117.1 (CH), 117.8 (C), 120.1 (CH), 122.8 (CH), 125.2 (CH), 125.3 (CH), 126.0 (C), 128.3 (CH), 130.3 (CH), 130.7 (CH), 131.0 (C), 131.1 (C), 133.3 (CH), 150.7 (C), 153.0 (C), 155.3 (C), 159.7 (C). HRMS (ESI, m/z) calcd for $C_{23}H_{14}BrO_4$ $[M + H]^+$: 433.0075, found: 433.0082.

3-Bromo-10-methyl-7*aH*,12*H*,14*H*-benzo[*f*]pyrano[3′,4′:5,6]pyrano[2,3-*b*]chromen-12-one (3bb). Yield: 80%, 318 mg. Colorless solid, mp 256–257 °C (DMF). IR ν_{max}: 1726, 1711, 1670, 1636, 1582, 1572, 1501, 1449, 1422, 1393, 1333, 1217, 1206, 1148, 1072, 1001, 970, 937, 910, 876, 799. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.23 (s, 3H), 3.96 (d, J = 19.2 Hz, 1H), 4.03 (d, J = 19.2 Hz, 1H), 6.36 (s, 1H), 6.68 (s, 1H), 6.77 (s, 1H), 7.11 (d, J = 8.9 Hz, 1H), 7.65 (dd, J = 8.9, 2.1 Hz, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 9.0 Hz, 1H), 8.12 (d, J = 2.1 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 20.2 (CH_3), 29.9 (CH_2), 96.1 (CH), 97.1 (C), 99.5 (CH), 113.4 (CH), 116.1 (C), 117.7 (C), 120.2 (CH), 124.1 (C), 125.4 (CH), 128.2 (CH), 130.3 (CH), 130.7 (CH), 130.8 (C), 130.9 (C), 150.6 (C), 160.7 (C), 161.4 (C), 163.9 (C). HRMS (ESI, m/z) calcd for $C_{20}H_{14}BrO_4$ $[M + H]^+$: 397.0075, found: 397.0067.

3-Bromo-10-methyl-7*a*,11-dihydro-12*H*,14*H*-benzo[5′,6′]chromeno[3′,2′:5,6]pyrano[3,2-*c*]pyridin-12-one (3bd). Yield: 66%, 262 mg. Colorless solid, mp 317–319 °C (DMF). IR ν_{max}: 3200–2400, 1663, 1616, 1570, 1493, 1458, 1387, 1335, 1263, 1219, 1186, 1150, 1088, 959, 918, 875, 799. ^{1}H NMR (400 MHz, DMSO-d_6) (at 140 °C) δ: 2.18 (s, 3H), 3.91–4.02 (m, 2H), 5.83 (s, 1H), 6.62 (s, 1H), 6.81 (s, 1H), 7.07 (d, J = 8.9 Hz, 1H), 7.60 (d, J = 8.9 Hz, 1H), 7.69 (d, J = 9.2 Hz, 1H), 7.80 (d, J = 9.2 Hz, 1H), 8.04 (s, 1H), 10.95 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (at 140 °C) δ: 19.2 (CH_3), 30.0 (CH_2), 96.6 (CH), 97.1 (CH), 102.8 (C), 115.0 (CH), 116.3 (C), 117.5 (C), 120.3 (CH), 121.9 (C), 125.2 (CH), 128.0 (CH), 130.1 (CH), 130.6 (CH), 131.1 (C), 140.9 (C), 146.5 (C), 151.1 (C), 158.9 (C), 161.1 (C). HRMS (ESI, m/z) calcd for $C_{20}H_{15}BrNO_3$ $[M + H]^+$: 396.0235, found: 396.0231.

6*H*,8*H*,13*aH*-Pyrano[2,3-*b*:5,6-*c*′]dichromen-6-one (3ca). Yield: 75%, 228 mg. Colorless solid, mp 189–191 °C. IR ν_{max}: 1701, 1676, 1618, 1582, 1570, 1493, 1454, 1416, 1275, 1217, 1190, 1171, 1065, 1038, 1001, 968, 932, 754, 739. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 3.69 (d, J = 17.8 Hz, 1H), 3.83 (d, J = 17.8 Hz, 1H), 6.71 (s, 1H), 6.85–6.88 (m, 2H), 6.94 (t, J = 7.3 Hz, 1H), 7.11–7.14 (m, 2H), 7.37–7.41 (m, 2H), 7.64 (t, J = 7.7 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 32.3 (CH_2), 96.5 (CH), 100.0 (C), 113.3 (CH), 114.3 (C), 117.2 (CH), 117.4 (CH), 122.6 (CH), 122.8 (CH), 123.7 (C), 125.3 (CH), 126.4 (C), 128.3 (CH), 129.3 (CH), 133.4 (CH), 152.6 (C), 152.8 (C), 155.2 (C), 159.9 (C). HRMS (ESI, m/z) calcd for $C_{19}H_{13}O_4$ $[M + H]^+$: 305.0814, found: 305.0807.

8*H*,10*H*,15*aH*-Benzo[*f*′]pyrano[2,3-*b*:5,6-*c*′]dichromen-8-one (3cc). The reaction was carried out in 10 mL of AcOH. Yield: 74%, 262 mg. Light-yellow solid, mp 234–235 °C (DMF). IR ν_{max}: 1694, 1578, 1557, 1518, 1557, 1518, 1483, 1464, 1452, 1422, 1341, 1317, 1219, 1169, 1157, 1109, 1078, 1051, 1034, 1011, 980, 961, 947, 905, 866, 826, 787, 756, 745, 702. ^{1}H NMR (400 MHz, DMSO-d_6) (at 120 °C) δ: 3.79 (br. s, 2H), 6.76 (s, 1H), 6.92–6.99 (m, 2H), 7.03 (s, 1H), 7.13–7.19 (m, 2H), 7.49 (d, J = 8.9 Hz, 1H), 7.59–7.63 (m, 1H), 7.73–7.77 (m, 1H), 8.02 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 8.9 Hz, 1H), 9.21 (d, J = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (at 120 °C) δ: 31.9 (CH_2), 97.4 (CH), 100.9 (C), 108.1 (C), 114.2 (CH), 117.5 (2CH), 122.7 (CH), 124.1 (C), 125.6 (C), 126.4 (CH), 126.5 (CH), 128.3 (CH), 128.6 (C), 129.0 (CH), 129.1 (CH), 129.7 (CH), 131.3 (C), 134.9 (CH), 152.8 (C), 154.2 (C), 158.7 (C), 159.5 (C). HRMS (ESI, m/z) calcd for $C_{23}H_{15}O_4$ $[M + H]^+$: 355.0970, found: 355.0964.

5,13*a*-Dihydro-6*H*,8*H*-chromeno[3′,2′:5,6]pyrano[3,2-*c*]quinolin-6-one (3cf). The product was recrystallized from ethanol. Yield: 80%, 242 mg. Colorless solid. IR ν_{max}: 3100–2700

(NH), 1680, 1663, 1609, 1570, 1501, 1485, 1454, 1418, 1350, 1312, 1173, 1111, 1094, 1032, 1007, 966, 953, 924, 745. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 3.66 (d, J = 17.9 Hz, 1H), 3.85 (d, J = 17.9 Hz, 1H), 6.80–6.85 (m, 3H), 6.93 (t, J = 7.3 Hz, 1H), 7.09–7.14 (m, 2H), 7.22 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 11.71 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 32.6 (CH_2), 96.2 (CH), 105.0 (C), 113.4 (C), 113.9 (CH), 116.0 (CH), 117.4 (CH), 122.2 (CH), 122.3 (CH), 122.6 (CH), 123.9 (C), 125.6 (C), 128.2 (CH), 129.3 (CH), 131.7 (CH), 138.4 (C), 152.8 (C), 152.9 (C), 160.4 (C). HRMS (ESI, m/z) calcd for $C_{19}H_{14}NO_3$ $[M + H]^+$: 304.0974, found: 304.0974.

12-(Adamantan-1-yl)-10-methyl-6*H*,8*H*,13*aH*-pyrano[2,3-*b*:5,6-*c*′]dichromen-6-one (3da). Yield: 82%, 371 mg. Light-yellow solid, mp 221–223 °C (DMF). IR ν_{max}: 2903, 2845, 1722, 1676, 1618, 1570, 1493, 1454, 1412, 1342, 1321, 1288, 1271, 1213, 1177, 1139, 1105, 1045, 980, 949, 941, 924, 914, 866, 746. ^{1}H NMR (400 MHz, DMSO-d_6) (at 100 °C) δ: 1.74 (br. s, 6H), 2.03 (br. s, 3H), 2.09 (br. s, 6H), 2.20 (s, 3H), 3.64 (s, 2H), 6.58 (d, J = 1.1 Hz, 1H), 6.80 (s, 1H), 6.84–6.86 (m 2H), 7.36–7.43 (m, 2H), 7.63 (ddd, J = 8.5, 8.0, 1.6 Hz, 1H), 7.77 (dd, J = 8.0, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (at 100 °C) δ: 21.0 (CH_3), 29.2 (3CH), 32.1 (CH_2), 37.0 (C), 37.3 ($3CH_2$), 41.1 ($3CH_2$), 98.2 (CH), 100.8 (C), 113.2 (CH), 114.7 (C), 117.2 (CH), 122.2 (CH), 125.2 (CH), 125.4 (C), 126.0 (CH), 126.8 (CH), 127.0 (C), 131.5 (C), 133.2 (CH), 138.6 (C), 149.4 (C), 153.1 (C), 155.6 (C), 159.7 (C). HRMS (ESI, m/z) calcd for $C_{30}H_{29}O_4$ $[M + H]^+$: 453.2066, found: 453.2064.

7-(Adamantan-1-yl)-3,9-dimethyl-1*H*,5*aH*,11*H*-pyrano[3′,4′:5,6]pyrano[2,3-*b*]chromen-1-one (3db). Yield: 76%, 316 mg. Colorless solid, mp 236–237 °C (AcOH). IR ν_{max}: 2903, 2874, 2845, 1703, 1639, 1576, 1456, 1447, 1420, 1327, 1204, 1144, 1001, 964, 816, 764. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.68 (br. s, 6H), 2.00 (br. s, 9H), 2.17 (s, 3H), 2.20 (s, 3H), 3.54 (d, J = 17.8 Hz, 1H), 3.67 (d, J = 17.8 Hz, 1H), 6.33 (s, 1H), 6.46 (s, 1H), 6.60 (s, 1H), 6.75 (s, 1H), 6.80 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 20.1 (CH_3), 21.1 (CH_3), 28.9 (3CH), 32.2 (CH_2), 36.8 (CH), 37.0 ($3CH_2$), 40.7 ($3CH_2$), 96.9 (CH), 97.3 (C), 99.5 (CH), 112.2 (CH), 124.6 (C), 125.0 (C), 125.8 (CH), 127.1 (CH), 131.0 (C), 138.3 (C), 149.5 (C), 161.0 (C), 161.4 (C), 163.7 (C). HRMS (ESI, m/z) calcd for $C_{27}H_{29}O_4$ $[M + H]^+$: 417.2066, found: 417.2060.

7-(Adamantan-1-yl)-3,9-dimethyl-2,5*a*-dihydro-1*H*,11*H*-chromeno[3′,2′:5,6]pyrano[3,2-*c*]pyridin-1-one (3dd). Yield: 71%, 295 mg. Colorless solid, mp 213–215 °C (AcOH). IR ν_{max}: 3200–2600, 2901, 2847, 1634, 1572, 1450, 1342, 1260, 1209, 1180, 1138, 1090, 1016, 972, 949, 926, 914, 802. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.76 (br. s, 6H), 2.06 (br. s, 3H), 2.09 (br. s, 6H), 2.25 (s, 3H), 2.31 (s, 3H), 3.48 (d, J = 17.8 Hz, 1H), 3.71 (d, J = 17.8 Hz, 1H), 5.93 (s, 1H), 6.40 (s, 1H), 6.73 (d, J = 1.8 Hz, 1H), 6.75 (s, 1H), 6.88 (d, J = 1.8 Hz, 1H), 12.20 (br. s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 19.3 (CH_3), 21.0 (CH_3), 29.2 (3CH), 36.9 (C), 37.2 (CH_2), 37.2 ($3CH_2$), 40.7 ($3CH_2$), 96.8 (CH), 99.5 (CH), 103.4 (C), 113.3 (CH), 123.4 (C), 124.0 (C), 125.8 (CH), 126.6 (CH), 131.1 (C), 139.1 (C), 145.0 (C), 149.7 (C), 160.3 (C), 163.0 (C). HRMS (ESI, m/z) calcd for $C_{27}H_{30}NO_3$ $[M + H]^+$: 416.2226, found: 416.2230.

11-Methyl-2,3,5,15-tetrahydro-8*aH*,13*H*-pyrano[3″,4″:5′,6′]pyrano[3′,2′:5,6]pyrano[3,2-*e*]pyrido[3,4-*b*]indole-4,13(1*H*)-dione (3eb). Yield: 81%, 305 mg. Colorless solid, mp 298–300 °C (dec.) (AcOH). IR ν_{max}: 3400–2800, 1730, 1676, 1632, 1578, 1539, 1497, 1425, 1337, 1294, 1233, 1206, 1144, 1128, 1082, 1053, 1028, 999, 978, 962, 939, 907, 760. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.21 (s, 3H), 2.98–3.06 (m, 1H), 3.10–3.18 (m, 1H), 3.43–3.49 (m, 2H), 4.02 (s, 2H), 6.32 (s, 1H), 6.58 (s, 1H), 6.60 (s, 1H), 6.71 (d, J = 8.7 Hz, 1H), 7.13 (d, J = 8.7 Hz, 1H), 7.53 (s, 1H), 11.52 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 20.2 (CH_3), 22.5 (CH_2), 30.6 (CH_2), 41.7 (CH_2), 95.9 (CH), 97.1 (C), 99.5 (CH), 112.6 (2CH), 114.8 (C), 115.9 (CH), 118.3 (C), 123.4 (C), 125.2 (C), 128.5 (C), 133.3 (C), 146.1 (C), 160.8 (C), 161.5 (C), 162.2 (C), 163.6 (C). HRMS (ESI, m/z) calcd for $C_{21}H_{17}N_2O_5$ $[M + H]^+$: 377.1137, found: 377.1130.

10-Nitro-6*H*,8*H*,13*aH*-pyrano[2,3-*b*:5,6-*c*′]dichromen-6-one (3fa). Yield: 70%, 244 mg. Light-yellow solid, mp 257–258 °C (AcOH). IR ν_{max}: 1703, 1672, 1618, 1582, 1570, 1514, 1485, 1421, 1414, 1340, 1246, 1179, 1113, 1086, 1076, 1005, 920, 824, 746. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 3.88 (d, J = 18.1 Hz, 1H), 3.95 (d, J = 18.1 Hz, 1H), 6.81 (s, 1H), 7.04–7.10 (m, 2H), 7.40–7.44 (m, 2H), 7.65–7.69 (m, 1H), 7.89 (d, J = 7.8 Hz, 1H), 8.02 (dd, J = 8.9, 2.5 Hz, 1H), 8.12 (d, J = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 32.2 (CH_2), 96.9 (CH), 100.0 (C), 114.1 (C), 114.5 (CH), 117.3 (CH), 118.4 (CH), 122.9 (CH), 124.3 (CH), 124.4 (C), 124.8 (C), 125.3 (CH), 125.4 (CH), 133.6 (CH), 142.2 (C), 152.8 (C), 155.1 (C), 158.2 (C), 159.7 (C). HRMS (ESI, m/z) calcd for $C_{19}H_{12}NO_6$ $[M + H]^+$: 350.0665, found: 350.0660.

12-Nitro-8*H*,10*H*,15*aH*-benzo[*f*′]pyrano[2,3-*b*:5,6-*c*′]dichromen-8-one (3fc). Yield: 75%, 300 mg. Light-yellow solid, mp 284–285 °C (DMF). IR ν_{max}: 1705, 1682, 1584, 1557, 1518, 1479, 1468, 1423, 1339, 1325, 1250, 1227, 1171, 1084, 1047, 968, 922, 812, 754, 745. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 3.91 (d, J = 18.1 Hz, 1H), 3.98 (d, J = 18.1 Hz, 1H), 6.86 (s, 1H), 7.12 (d, J = 9.1 Hz, 1H), 7.22 (s, 1H), 7.52 (d, J = 8.9 Hz, 1H), 7.59–7.63 (m, 1H), 7.73–7.77 (m, 1H), 8.01–8.05 (m, 2H), 8.13 (s, 1H), 8.20 (d, J = 8.9 Hz, 1H), 9.14 (d, J = 8.7 Hz, 1H). HRMS (ESI, m/z) calcd for $C_{23}H_{14}NO_6$ $[M + H]^+$: 400.0821, found: 400.0828.

7*aH*,15*H*,17*H*-Benzo[5′,6′]chromeno[3′,2′:5,6]pyrano[2,3-*d*]pyrido[1,2-*a*]pyrimidin-15-one (3ah). A mixture of 1*H*-benzo[*f*]chromene-2-carbaldehyde **1a** (210 mg, 1 mmol), 2*H*-pyrido[1,2-*a*]pyrimidine-2,4(3*H*)-diones **2h** (162 mg, 1 mmol) and ammonium acetate (77 mg, 1 mmol) in acetic acid (4 mL) was stirred under reflux for 10 min and cooled to room temperature. The precipitate that formed was filtered, washed with acetic acid and water, dried and recrystallized from acetic acid. Yield: 54%, 191 mg. Bright-yellow solid, mp 280–282 °C. IR ν_{max}: 1690, 1668, 1636, 1622, 1597, 1576, 1526, 1489, 1454, 1429, 1387, 1283, 1223, 1180, 1155, 1121, 1082, 989, 966, 955, 930, 808, 772, 743. ^{1}H NMR (400 MHz, DMSO-d_6) (at 140 °C) δ: 4.06 (s, 2H), 6.80 (s, 1H), 6.99 (s, 1H), 7.06 (d, J = 8.9 Hz, 1H), 7.29 (t, J = 6.9 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.51–7.56 (m, 2H), 7.71 (d, J = 8.9 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.88–7.93 (m, 1H), 8.91 (d, J = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (at 140 °C) δ: 29.8 (CH_2), 92.4 (C), 97.6 (CH), 114.8 (CH), 115.6 (C), 116.4 (CH), 118.9 (CH), 122.8 (CH), 123.8 (C), 124.5 (CH),

125.5 (CH), 127.3 (CH), 128.4 (CH), 128.8 (2CH), 129.8 (C), 132.5 (C), 138.5 (CH), 150.1 (C), 150.5 (C), 155.8 (C), 161.1 (C). HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{15}N_2O_3$ $[M + H]^+$: 355.1083, found: 355.1076.

10,10-Dimethyl-7*a*,9,10,11-tetrahydro-12*H*,14*H*-benzo[*f*]chromeno[2,3-*b*]chromen-12-one (3ai). A mixture of 1*H*-benzo[*f*]chromene-2-carbaldehyde **1a** (210 mg, 1 mmol), dimedone **2i** (140 mg, 1 mmol) and ammonium acetate (77 mg, 1 mmol) in acetic acid (4 mL) was heated under reflux for 1 min. The resulting solution was poured into 15 mL of water, the precipitate was filtered off and heated to boiling with 2 mL of methanol. After hot filtration, the mother liquor was evaporated to a volume of 1 mL and stored at −30 °C overnight. The precipitate was filtered off, dissolved with heating in a minimum amount of DMF and a five-fold volume of methanol was added. The product precipitates in the form of thin colorless needles. Yield: 10%, 33 mg. Mp 161–163 °C (DMF–MeOH, 1 : 5). IR ν_{max}: 2961, 2889, 1661, 1620, 1595, 1510, 1464, 1425, 1406, 1393, 1333, 1227, 1206, 1188, 1175, 1144, 1067, 1036, 974, 955, 912, 814, 772, 752, 741. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.00 (s, 3H), 1.03 (s, 3H), 2.20 (d, J = 15.8 Hz, 1H), 2.29 (d, J = 15.8 Hz, 1H), 2.48 (d, J = 18.1 Hz, 1H), 2.56 (d, J = 18.1 Hz, 1H), 3.94 (s, 2H), 6.64 (s, 1H), 6.68 (s, 1H), 7.05 (d, J = 8.9 Hz, 1H), 7.39 (ddd, J = 8.0, 6.9, 1.2 Hz, 1H), 7.53 (ddd, J = 8.5, 7.1, 1.4 Hz, 1H), 7.72 (d, J = 8.9 Hz, 1H), 7.79–7.84 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 27.8 (CH_3), 28.9 (CH_3), 29.8 (CH_2), 32.6 (C), 40.9 (CH_2), 50.3 (CH_2), 96.5 (CH), 108.4 (C), 112.5 (CH), 115.8 (C), 119.0 (CH), 122.3 (C), 122.9 (CH), 124.6 (CH), 127.4 (CH), 128.9 (2CH), 129.5 (C), 132.2 (C), 150.3 (C), 166.4 (C), 194.5 (C). HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{21}O_3$ $[M + H]^+$: 333.1491, found: 333.1486.

9,9,11,11-Tetramethyl-7*a*,9-dihydro-10*H*,14*H*-benzo[*f*]chromeno[2,3-*b*]chromene-10,12(11*H*)-dione (3aj). A mixture of 1*H*-benzo[*f*]chromene-2-carbaldehyde **1a** (210 mg, 1 mmol), syncarpic acid **2j** (182 mg, 1 mmol) and ammonium acetate (77 mg, 1 mmol) in acetic acid (4 mL) was heated under reflux for 1 min. The resulting solution was slowly cooled to room temperature, the formed precipitate was collected, washed with AcOH and water. The crude product was purified by recrystallization from AcOH. Yield: 40%, 150 mg. Colorless solid, mp 203–205 °C. IR ν_{max}: 1722, 1690, 1628, 1601, 1566, 1512, 1472, 1456, 1435, 1354, 1327, 1296, 1273, 1105, 1040, 989, 808, 745, 681. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.24 (s, 3H, CH_3–C-11), 1.26 (s, 3H, CH_3–C-11), 1.44 (s, 3H, CH_3–C-9), 1.47 (s, 3H, CH_3–C-9), 4.00 (s, 2H, CH_2-14), 6.76 (s, 1H, H-13), 6.78 (s, 1H, H-7a), 7.07 (d, J = 8.9 Hz, 1H, H-6), 7.40 (t, J = 7.4 Hz, 1H, H-3), 7.54 (t, J = 7.3 Hz, 1H, H-2), 7.73 (d, J = 9.0 Hz, 1H, H-5), 7.81–7.85 (m, 2H, H-1,4). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 24.56 ($\underline{C}H_3$–C-11), 24.60 ($\underline{C}H_3$–C-11), 25.21 ($\underline{C}H_3$–C-9), 25.23 ($\underline{C}H_3$–C-9), 29.7 (CH_2-14), 47.2 (C-9), 55.4 (C-11), 96.7 (CH-7a), 106.3 (C-12a), 113.0 (CH-13), 115.7 (C-14a), 119.0 (CH-6), 122.9 (CH-1), 123.7 (C-13a), 124.7 (CH-3), 127.5 (CH-2), 128.89 (CH-5), 128.92 (CH-4), 129.5 (C-4a), 132.2 (C-14b), 150.2 (C-6a), 167.4 (C-8a), 195.0 (C-12), 211.6 (C-10). HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{23}O_4$ $[M + H]^+$: 375.1596, found: 375.1602.

3-[(2-Hydroxynaphthalen-1-yl)methyl]-7,7-dimethyl-7,8-dihydroquinolin-5(6*H*)-one (4ai) and 3-[(2-hydroxynaphthalen-1-yl)methyl]-6,6,8,8-tetramethylquinoline-5,7(6*H*,8*H*)-dione (4aj). A mixture of 1*H*-benzo[*f*]chromene-2-carbaldehyde **1a** (210 mg, 1 mmol), dimedone **2i** (140 mg, 1 mmol) or syncarpic acid **2j** (182 mg, 1 mmol) and ammonium acetate (77 mg, 1 mmol) in acetic acid (4 mL) was heated under reflux for 20 min. Afterward, the mixture was poured into 10 mL of a saturated water solution of sodium chloride to yield a solid product, which was filtered, washed with water, and dried. The crude product was purified by recrystallization from ethanol. Yields of **4ai** and **4aj** were 60 (199 mg) and 67% (250 mg), respectively. Products were identical in spectral characteristics to samples prepared previously.[5a]

Compound **4ai** was also prepared from 1*H*-benzo[*f*]chromene-2-carbaldehyde **1a** (210 mg, 1 mmol), 3-(benzylamino)-5,5-dimethylcyclohex-2-enone **2m** and ammonium acetate (385 mg, 5 mmol) in acetic acid (4 mL) after refluxing for 10 min in 70% yield (232 mg).

2-[(1*H*-Benzo[*f*]chromen-2-yl)methylene]-1*H*-indene-1,3(2*H*)-dione (5ak). A mixture of 1*H*-benzo[*f*]chromene-2-carbaldehyde **1a** (210 mg, 1 mmol), 1,3-indandione **2k** (146 mg, 1 mmol) and ammonium acetate (77 mg, 1 mmol) in acetic acid (3 mL) was heated under reflux for 5 min. The mixture was slowly cooled to room temperature, the formed precipitate was collected and washed with ice-cold methanol. The crude product was purified by recrystallization from DMF. Yield: 21%, 71 mg. Bright-yellow solid, mp 204–207 °C (dec.). IR ν_{max}: 1726, 1678, 1601, 1564, 1518, 1468, 1439, 1389, 1352, 1312, 1227, 1213, 1180, 1157, 989, 974, 800, 766, 727. ^{1}H NMR (400 MHz, DMSO-d_6) (at 100 °C) δ: 4.38 (s, 2H), 7.19 (d, J = 9.0 Hz, 1H), 7.47–7.51 (m, 2H), 7.66 (t, J = 7.7 Hz, 1H), 7.79 (d, J = 8.9 Hz, 1H), 7.83–7.92 (m, 6H), 8.01 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (at 100 °C) δ: 24.1 (CH_2), 113.5 (C), 115.0 (C), 117.4 (CH), 123.05 (CH), 123.07 (CH), 123.2 (CH), 125.7 (CH), 127.1 (C), 127.8 (CH), 128.9 (CH), 129.1 (CH), 131.5 (C), 132.0 (C), 135.7 (CH), 135.8 (CH), 140.0 (C), 142.4 (C), 145.4 (CH), 146.6 (C), 157.7 (CH), 189.1 (C), 189.7 (C). HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{15}O_3$ $[M + H]^+$: 339.1021, found: 339.1016.

3-[(2-Hydroxynaphthalen-1-yl)methyl]-5*H*-indeno[1,2-*b*]pyridin-5-one (6ak). A mixture of 1*H*-benzo[*f*]chromene-2-carbaldehyde **1a** (210 mg, 1 mmol), 1,3-indandione **2k** (146 mg, 1 mmol) and ammonium acetate (385 mg, 5 mmol) in acetic acid (4 mL) was heated under reflux for 5 h and cooled to room temperature. The precipitate was filtered off, washed with methanol and purified by recrystallization from DMF. Yield: 71%, 239 mg. Orange solid, mp 299–300 °C (DMF). IR ν_{max}: 3200–2400, 1722, 1612, 1574, 1508, 1464, 1445, 1356, 1294, 1279, 1233, 1173, 995, 980, 810, 752. ^{1}H NMR (400 MHz, DMSO-d_6) (at 120 °C) δ: 4.42 (s, 2H), 7.23–7.27 (m, 2H), 7.38–7.44 (m, 2H), 7.58–7.64 (m, 3H), 7.68–7.72 (m, 2H), 7.76 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 8.5 Hz, 1H), 8.60 (s, 1H), 9.47 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (at 120 °C) δ: 27.9 (CH_2), 117.4 (C), 119.0 (CH), 120.8 (CH), 123.0 (CH), 123.1 (CH), 124.2 (CH), 127.0 (CH), 128.2 (C), 128.9 (CH), 129.0 (CH), 129.2 (C), 131.16 (CH), 131.23 (CH), 133.7 (C), 135.1 (C), 136.0 (CH), 138.2 (C), 143.8 (C), 153.4 (C), 154.6 (CH), 162.6 (C), 191.7 (C). HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{16}NO_2$ $[M + H]^+$: 338.1181, found: 338.1189.

(*E*)-3-[(1*H*-Benzo[*f*]chromen-2-yl)methylene]indolin-2-one (5al). A mixture of 1*H*-benzo[*f*]chromene-2-carbaldehyde **1a**

(420 mg, 2 mmol), oxindole **2l** (266 mg, 2 mmol) and ammonium acetate (154 mg, 2 mmol) in acetic acid (6 mL) was heated under reflux for 2 h and cooled to room temperature. The precipitate was filtered off and washed with methanol. The product was obtained as a mixture of *E*- and *Z*-isomers in ratio 3.5 : 1 in 78% yield (507 mg). After three-fold recrystallization from DMF, the pure *E*-isomer was isolated in 38% yield (247 mg). Bright-yellow solid, mp 264–265 °C. IR ν_{max}: 3400–2700, 1705, 1639, 1574, 1462, 1437, 1400, 1331, 1308, 1298, 1231, 1215, 1204, 1132, 1086, 874, 854, 808, 781. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.17 (s, 2H), 6.85 (d, J = 7.6 Hz, 1H), 7.00 (t, J = 7.4 Hz, 1H), 7.16–7.25 (m, 3H), 7.50 (t, J = 7.3 Hz, 1H), 7.61–7.66 (m, 2H), 7.80 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 8.9 Hz, 1H), 7.92 (d, J = 7.6 Hz, 2H), 10.50 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 24.7 (CH_2), 110.5 (CH), 112.1 (C), 117.8 (CH), 121.87 (CH), 121.92 (C), 123.3 (CH), 124.3 (CH), 124.9 (C), 125.5 (CH), 127.8 (CH), 128.9 (CH), 129.2 (CH, C), 129.6 (CH), 131.0 (C), 131.9 (C), 135.4 (CH), 143.0 (C), 147.1 (C), 148.1 (CH), 169.6 (C). HRMS (ESI, m/z) calcd for $C_{22}H_{16}NO_2$ $[M + H]^+$: 326.1181, found: 326.1175.

Conflicts of interest

There are no conflicts to declare.

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