

Three-Component Condensation of Meldrum's Acid with 2-Naphthylamine and Esters Derived from Vanillin

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Abstract—Three-component condensation of Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) with 2-naphthylamine and esters derived from vanillin involves intermediate formation of *N*-arylmethylidene-2-naphthylamines which are cleaved with Meldrum's acid to give 5-arylmethylidene-2,2-dimethyl-1,3-dioxane-4,6-diones and arylmethylideneketenes. Reaction of the latter with 2-naphthylamine leads to formation of 2-methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[*f*]quinolin-1-yl)phenyl carboxylates.

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We previously [1] described reactions of *N*-arylmethylidene-2-naphthylamines with 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid) and presumed that the final products, 3-aryl-1,2,3,4-tetrahydrobenzo[*f*]quinolin-1-ones, are formed via heterocyclization of intermediate 2-arylaminoenol, the latter resulting from addition of Meldrum's acid to the Schiff base, followed by decarboxylation. Our further studies [2] showed that three-component condensation of 2-naphthylamine with substituted benzaldehydes and Meldrum's acid involves addition of the latter to 2-naphthylamine with formation of enamine which then reacts with benzaldehyde. The formation of cyclic condensation products is accompanied by cleavage of the 1,3-dioxane ring in Meldrum's acid, which leads to 1-aryl-1,2,3,4-tetrahydrobenzo[*f*]quinolin-3-ones.

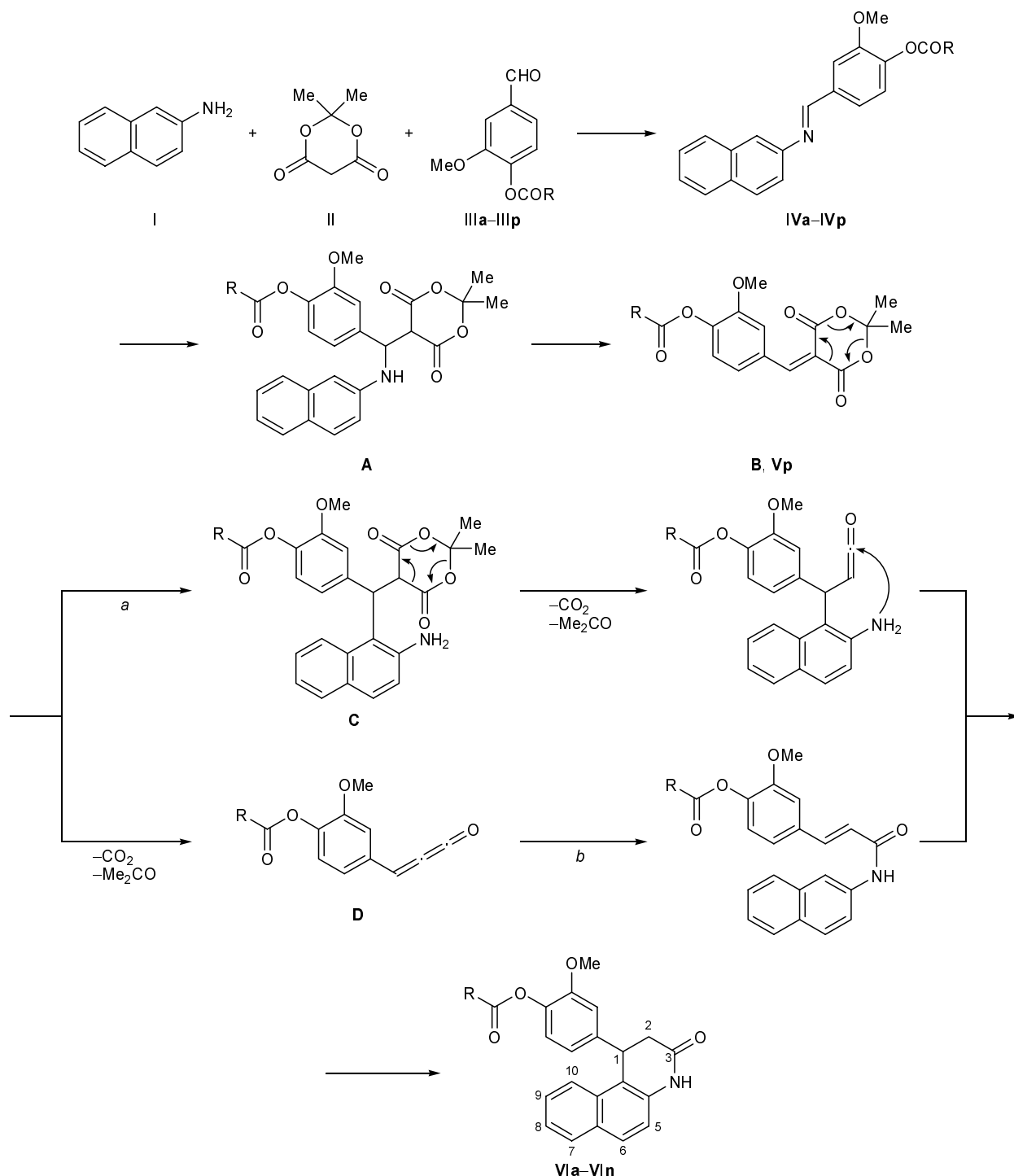
In the present work we examined three-component condensation of 2-naphthylamine (**I**) with Meldrum's acid (**II**) and esters **IIIa–IIIp** derived from vanillin. Insofar as molecules **IIIa–IIIp** contain a highly reactive aldehyde group, these compounds may be used as building blocks in the synthesis of fused nitrogen-containing heterocycles of the benzophenanthridine and benzoacridine series via condensation with 2-naphthylamine and CH acids [3, 4]. Insofar as compounds **IIIa–IIIp** act as source of acyloxy and methoxyphenyl fragments in the resulting aza heterocycles, they are very important for the synthesis of biologically active representatives of the above classes, such as cardioprotectors, enzyme inhibitors, analgetics,

antitumor agents [5, 6], and analogs of plant alkaloids of the acridinone series [7].

The reactions were carried out by heating equimolar amounts of the reactants in boiling alcohol over a period of 0.5–3 h. The products were identified as 2-methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[*f*]quinolin-1-yl)phenyl carboxylates **VIa–VIIn** (Scheme 1). According to published data [8], 5-arylmethylidene-2,2-dimethyl-1,3-dioxane-4,6-diones could give rise to diketene; therefore, we believe that two path of formation of tetrahydrobenzo[*f*]quinolines are possible. Here, condensation of 2-naphthylamine (**I**) with aldehydes **IIIa–IIIp** to give Schiff bases **IVa–IVp** is a common stage for both paths. Next follows nucleophilic addition of Meldrum's acid at the CH=N carbon atom of Schiff base, which possesses a partial positive charge. The addition is favored by protonation of the nitrogen atom with a proton abstracted from diketone **II** (as a result, electrophilic properties of the CH=N carbon atom increase). 2-Arylamino-diketone **A** thus formed decomposes to 2-naphthylamine (**I**) and 5-arylmethylidene-2,2-dimethyl-1,3-dioxane-4,6-dione **B** [9].

The exocyclic carbon atom of the double Ar–C=C bond in intermediate **B** possesses a positive charge; therefore, nucleophilic addition of 2-naphthylamine at the α -carbon atom in **B** to form intermediate **C** (path *a*) is possible. The subsequent transformation of intermediate **C** is accompanied by elimination of carbon dioxide and acetone and heterocyclization, leading to the final product, tetrahydrobenzo[*f*]quinoline derivative

Scheme 1.



VIa–VIIn. In keeping with the data of [8], ketene intermediate **D** generated from arylmethylidenedioxanedione **B** is also capable of taking up naphthylamine **II** [10], and cyclization of the adduct gives

tetrahydrobenzo[*f*]quinolines **VIa–VIIn** (path *b*). Liberation of carbon dioxide (which was identified by passing through a solution of barium hydroxide) and acetone (which was isolated from the reaction mixture

and identified as 2,4-dinitrophenylhydrazone) indicates cleavage of the dioxanedione ring (cf. [11]). On the other hand, stability of the ester group under the given conditions must be noted.

The yield of 2-methoxy-4-(tetrahydrobenzo[*f*]quinolin-1-yl)phenyl carboxylates **VIa–VIh** depends on the length of the radical in the acid fragment. As the length of that radical increases, the yield of the final product decreases from 80 to 52%, while hexanoic acid ester **IIIp** fails to react at all. In the series of benzoic acid esters, substituent in the benzene ring is fairly distant from the reaction center, and it almost does not affect the charge on the exocyclic double-bonded carbon atom. Presumably, the role of steric factor on the product yield is more significant; thus the yields of 2-methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[*f*]quinolin-1-yl)phenyl esters **VIa–VIh** derived from aliphatic carboxylic acids are greater than the yields of benzoates **VIg–VIh**.

Unexpectedly, by heating a mixture of 2-naphthylamine (**I**), Meldrum's acid (**II**), and 2-methoxy-4-formylphenyl 3,4,4-trichlorobut-3-enoate (**IIIp**) for 1 h we obtained 4-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidenemethyl)-2-methoxyphenyl 3,4,4-trichlorobut-3-enoate (**Vp**) as the only product. No tetrahydrobenzo[*f*]quinoline derivative was formed even when the reaction time was prolonged to 6 h. By contrast, Strods *et al.* [12] previously reported on the formation of benzoquinolines on prolonged heating of 5-arylmethylidene-2,2-dimethyl-1,3-dioxane-4,6-diones obtained by reaction of *N*-arylmethylidenenaphthylamines with Meldrum's acid. Presumably, steric effect of the acid fragment in ester **IIIp** hampers addition of 2-naphthylamine at the double bond of **Vp**.

The structure of products **Vp** and **VIa–VIh** was confirmed by the ¹H NMR, IR, and mass spectra. The ¹H NMR spectra of 2-methoxy-4-(tetrahydrobenzo[*f*]quinolin-1-yl)phenyl carboxylates **VIa–VIh** contained a doublet at δ 4.92–5.09 ppm from the 1-H proton, a singlet at δ 10.20–10.48 ppm from the NH proton, and two doublets of doublets at δ 2.70–3.06 and 3.06–3.15 ppm from protons on C². The aromatic part of the ¹H NMR spectra of **VIa–VIh** was typical of their benzoquinoline structure [13]. In the IR spectra of **VIa–VIh** we observed absorption bands at 3197–2962 (NH), 1756–1603 (C=O, amide I), 1525–1465 cm⁻¹ (δNH, amide II). Esters **VIa–VIh** showed in the mass spectra the molecular ion peaks with a relative intensity of 20–50% and [M – MeO – RCOOC₆H₃]⁺ ion

peaks (*m/z* 195, *I*_{rel} 18–60%); further fragmentation of the latter gave rise to [RCO]⁺ ions which were the most abundant in the spectra (*I*_{rel} 100%).

EXPERIMENTAL

The IR spectra were recorded on a Nicolet Protege-460 Fourier spectrometer. The ¹H and ¹³C NMR spectra were measured on Tesla BS-567A (100 MHz for ¹H) and Bruker AC-500 instruments (500 MHz for ¹H) from 2–5% solutions in DMSO-*d*₆; the chemical shifts were referenced to tetramethylsilane as internal standard. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT INCOS 50 mass spectrometer and on a Hewlett–Packard HP 5890/5972 GC–MS system (HP-5MS capillary column, 5% of phenylmethylsilicone, 30 m × 0.25 mm, film thickness 0.25 μm; injector temperature 250°C).

Initial esters **IIIa–IIIp** were synthesized from vanillin and the corresponding carboxylic acid chloride according to the procedure described in [14]. Meldrum's acid (**II**) was prepared by condensation of malonic acid with acetone in the presence of acetic anhydride [15].

4-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene-methyl)-2-methoxyphenyl 3,4,4-trichlorobut-3-enoate (Vp) and 2-methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[*f*]quinolin-1-yl)phenyl carboxylates VIa–VIh (general procedure). A mixture of 0.01 mol of 2-naphthylamine (**I**), 0.01 mol of Meldrum's acid (**II**), and ester **IIIa–IIIp** in 30 ml of ethanol was heated for 0.5–3 h under reflux. The precipitate was filtered off, washed with diethyl ether to remove unreacted initial compounds, and recrystallized from ethanol–benzene (2:1) (compounds **VIh**, **Vli**, **Vll**, and **Vlm** were recrystallized from dioxane, and compounds **Vlk** and **Vln**, from acetic acid) until a purity of no less than 95%.

4-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene-methyl)-2-methoxyphenyl 3,4,4-trichlorobut-3-enoate (Vp). Yield 60%, light yellow crystals, mp 216°C. IR spectrum, ν, cm⁻¹: 3480, 1771, 1728, 1614, 1599, 1510, 1392, 1370, 1341, 1282, 1268, 1250, 1227, 1203, 1142, 1024, 928, 876, 802, 762. ¹H NMR spectrum, δ, ppm: 1.78 s (6H, Me), 3.84 s (3H, OMe), 4.10 s (2H, CH₂), 7.30 d (1H, H_{arom}, *J* = 6.9 Hz), 7.70 d (1H, H_{arom}, *J* = 7.0 Hz), 7.95 s (1H, H_{arom}), 8.40 s (1H, CH). Mass spectrum, *m/z* (*I*_{rel}, %): [M]⁺ 421 (30), 172 (100), 139 (43). Found, %: C 51.28; H 3.60; Cl 25.16. C₁₈H₁₅Cl₃O₇. Calculated, %: C 51.31; H 3.56; Cl 25.18.

2-Methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[*f*]-quinolin-1-yl)phenyl acetate (VIa). Yield 80%, colorless crystals, mp 207°C. IR spectrum, ν , cm^{-1} : 3197, 3042, 2933, 1756, 1682, 1626, 1604, 1525, 1510, 1473, 1429, 1391, 1324, 1285, 1248, 1221, 1205, 1140, 1116, 1032, 905, 854, 820, 751. ^1H NMR spectrum, δ , ppm: 2.20 s (3H, Me), 3.05 d (1H, CH_2 , $J = 9.8$ Hz), 3.10 d (1H, CH_2 , $J = 9.6$ Hz), 3.72 s (3H, OMe), 4.94 d (1H, CH, $J = 6.9$ Hz), 6.50 d (1H, H_{arom} , $J = 8.0$ Hz), 6.79 d (1H, H_{arom} , $J = 7.6$ Hz), 6.95 s (1H, H_{arom}), 7.20–7.30 m (2H, H_{arom}), 7.40 m (1H, H_{arom}), 7.70–7.80 m (3H, H_{arom}), 10.25 s (1H, NH). Mass spectrum, m/z (I_{rel} , %): $[M]^+$ 361 (22), 195 (60), 43 (100). Found, %: C 73.10; H 5.28; N 3.90. $\text{C}_{22}\text{H}_{19}\text{NO}_4$. Calculated, %: C 73.13; H 5.26; N 3.88.

2-Methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[*f*]-quinolin-1-yl)phenyl propionate (VIb). Yield 74%, colorless crystals, mp 215–216°C. IR spectrum, ν , cm^{-1} : 3190, 3045, 2937, 1752, 1679, 1614, 1523, 1511, 1476, 1432, 1324, 1281, 1242, 1210, 1147, 1110, 1035, 906, 854, 820, 750. ^1H NMR spectrum, δ , ppm: 1.10 t (3H, CH_2CH_3), 1.30 q (2H, CH_2CH_3), 3.07 d (1H, CH_2 , $J = 9.8$ Hz), 3.15 d (1H, CH_2 , $J = 9.6$ Hz), 3.70 s (3H, OMe), 4.97 d (1H, CH, $J = 7.0$ Hz), 6.30 d (1H, H_{arom} , $J = 8.0$ Hz), 6.80 d (1H, H_{arom} , $J = 7.9$ Hz), 7.10 m (1H, H_{arom}), 7.35–7.50 m (3H, H_{arom}), 7.80–7.97 m (3H, H_{arom}), 10.30 s (1H, NH). Mass spectrum, m/z (I_{rel} , %): $[M]^+$ 375 (32), 195 (23), 57 (100). Found, %: C 73.61; H 5.64; N 3.70. $\text{C}_{23}\text{H}_{21}\text{NO}_4$. Calculated, %: C 73.60; H 5.60; N 3.73.

2-Methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[*f*]-quinolin-1-yl)phenyl butanoate (VIc). Yield 70%, colorless crystals, mp 186–187°C. IR spectrum, ν , cm^{-1} : 2962, 2933, 1752, 1689, 1624, 1517, 1478, 1376, 1280, 1242, 1227, 1179, 1043, 908, 857, 822. ^1H NMR spectrum, δ , ppm: 1.00 t (3H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.70 m (2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.50 m (2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.09 d (1H, CH_2 , $J = 10.0$ Hz), 3.04 (1H, CH_2 , $J = 9.6$ Hz), 3.71 s (3H, OMe), 4.95 d (1H, CH, $J = 7.0$ Hz), 6.55 d (1H, H_{arom} , $J = 8.6$ Hz), 6.78 d (1H, H_{arom} , $J = 7.4$ Hz), 6.80 s (1H, H_{arom}), 7.25–7.34 m (2H, H_{arom}), 7.38–7.46 m (1H, H_{arom}), 7.74–7.86 m (3H, H_{arom}), 10.20 s (1H, NH). Mass spectrum, m/z (I_{rel} , %): $[M]^+$ 389 (43), 195 (18), 71 (100). Found, %: C 74.06; H 5.89; N 3.61. $\text{C}_{24}\text{H}_{23}\text{NO}_4$. Calculated, %: C 74.04; H 5.91; N 3.59.

2-Methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[*f*]-quinolin-1-yl)phenyl 2-methylpropanoate (VIId). Yield 70%, colorless crystals, mp 197°C. IR spectrum, ν , cm^{-1} : 2967, 2940, 1744, 1684, 1625, 1603, 1513, 1466, 1386, 1319, 1289, 1270, 1240, 1184, 1147,

1029, 862, 819. ^1H NMR spectrum, δ , ppm: 1.29 d [6H, $\text{CH}(\text{CH}_3)_2$, $J = 7.4$ Hz], 2.80 m [1H, $\text{CH}(\text{CH}_3)_2$], 3.06 d (1H, CH_2 , $J = 9.7$ Hz), 3.10 (1H, CH_2 , $J = 9.6$ Hz), 3.70 s (3H, OMe), 4.96 d (1H, CH, $J = 6.8$ Hz), 6.53 d (1H, H_{arom} , $J = 8.7$ Hz), 6.78 d (1H, H_{arom} , $J = 7.7$ Hz), 6.96 s (1H, H_{arom}), 7.20–7.30 m (2H, H_{arom}), 7.40 m (1H, H_{arom}), 7.70–7.85 m (3H, H_{arom}), 10.25 s (1H, NH). Mass spectrum, m/z (I_{rel} , %): $[M]^+$ 389 (45), 195 (19), 71 (100). Found, %: C 74.02; H 5.90; N 3.57. $\text{C}_{24}\text{H}_{23}\text{NO}_4$. Calculated, %: C 74.04; H 5.91; N 3.59.

2-Methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[*f*]-quinolin-1-yl)phenyl pentanoate (VIe). Yield 60%, colorless crystals, mp 193°C. IR spectrum, ν , cm^{-1} : 3160, 3026, 2904, 1757, 1694, 1646, 1535, 1518, 1472, 1436, 1340, 1287, 1245, 1229, 1205, 1149, 1035, 911, 852, 817, 746. ^1H NMR spectrum, δ , ppm: 0.95 t (3H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.42 m (2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.65 m (2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.40 t (2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.00 d (1H, CH_2 , $J = 9.2$ Hz), 3.08 (1H, CH_2 , $J = 8.9$ Hz), 3.68 s (3H, OMe), 4.92 d (1H, CH, $J = 6.7$ Hz), 6.50 d (1H, H_{arom} , $J = 8.2$ Hz), 6.72 d (1H, H_{arom} , $J = 7.5$ Hz), 6.92 s (1H, H_{arom}), 7.25–7.35 m (2H, H_{arom}), 7.43 m (1H, H_{arom}), 7.60–7.75 m (3H, H_{arom}), 10.30 s (1H, NH). Mass spectrum, m/z (I_{rel} , %): $[M]^+$ 403 (38), 195 (34), 85 (100). Found, %: C 74.46; H 6.19; N 3.47. $\text{C}_{25}\text{H}_{25}\text{NO}_4$. Calculated, %: C 74.44; H 6.20; N 3.46.

2-Methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[*f*]-quinolin-1-yl)phenyl 2-methylprop-2-enoate (VIIf). Yield 52%, colorless crystals, mp 222–223°C. IR spectrum, ν , cm^{-1} : 3073, 2908, 1752, 1691, 1646, 1539, 1465, 1335, 1280, 1253, 1232, 1211, 1142, 1038, 917, 850, 823, 741. ^1H NMR spectrum, δ , ppm: 1.90 s (3H, Me), 2.70 d (1H, CH_2 , $J = 9.0$ Hz), 3.14 (1H, CH_2 , $J = 8.4$ Hz), 3.70 s (3H, OMe), 5.03 d (1H, CH, $J = 6.9$ Hz), 5.80 s (1H, CH_2), 6.15 s (1H, CH_2), 6.42 d (1H, H_{arom} , $J = 8.0$ Hz), 6.90 d (1H, H_{arom} , $J = 7.6$ Hz), 7.10 s (1H, H_{arom}), 7.24–7.28 m (1H, H_{arom}), 7.32–7.38 m (1H, H_{arom}), 7.41–7.50 m (1H, H_{arom}), 7.85 m (3H, H_{arom}), 10.30 s (1H, NH). Mass spectrum, m/z (I_{rel} , %): $[M]^+$ 387 (43), 195 (60), 69 (100). Found, %: C 74.42; H 5.43; N 3.59. $\text{C}_{24}\text{H}_{21}\text{NO}_4$. Calculated, %: C 74.41; H 5.42; N 3.61.

2-Methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[*f*]-quinolin-1-yl)phenyl benzoate (VIg). Yield 50%, colorless crystals, mp 258°C. IR spectrum, ν , cm^{-1} : 3018, 1730, 1672, 1630, 1517, 1389, 1281, 1270, 1236, 1173, 1137, 1120, 1071, 1038, 815, 750. ^1H NMR spectrum, δ , ppm: 2.84 d (1H, CH_2 , $J = 9.0$ Hz),

3.10 (1H, CH₂, *J* = 8.2 Hz), 3.74 s (3H, OMe), 5.00 d (1H, CH, *J* = 7.0 Hz), 6.60 d (1H, H_{arom}, *J* = 8.0 Hz), 6.90 d (1H, H_{arom}, *J* = 7.6 Hz), 7.00 s (1H, H_{arom}), 7.29–7.32 m (2H, H_{arom}), 7.40–7.54 m (2H, H_{arom}), 7.60–7.64 m (2H, H_{arom}), 7.80–7.88 m (3H, H_{arom}), 8.10 m (2H, H_{arom}), 10.29 s (1H, NH). Mass spectrum, *m/z* (*I*_{rel}, %): [*M*]⁺ 423 (27), 228 (13), 195 (52), 105 (100). Found, %: C 76.57; H 4.98; N 3.33. C₂₇H₂₁NO₄. Calculated, %: C 76.59; H 4.96; N 3.31.

2-Methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[*f*]-quinolin-1-yl)phenyl 4-chlorobenzoate (VIh). Yield 45%, colorless crystals, mp 229–230°C. IR spectrum, *v*, cm⁻¹: 3080, 2910, 1736, 1685, 1625, 1603, 1588, 1512, 1466, 1449, 1420, 1394, 1316, 1289, 1246, 1201, 1183, 1164, 1139, 1119, 1091, 1033, 908, 863, 815, 744. ¹H NMR spectrum, *δ*, ppm: 2.80 d (1H, CH₂, *J* = 8.8 Hz), 3.10 (1H, CH₂, *J* = 8.0 Hz), 3.79 s (3H, OMe), 5.00 d (1H, CH, *J* = 6.4 Hz), 6.60 d (1H, H_{arom}, *J* = 7.6 Hz), 6.90 d (1H, H_{arom}, *J* = 7.9 Hz), 7.06 s (1H, H_{arom}), 7.30 m (2H, H_{arom}), 7.46 m (2H, H_{arom}), 7.50–7.54 m (2H, H_{arom}), 7.72–7.80 m (2H, H_{arom}), 7.87 d (1H, H_{arom}, *J* = 7.2 Hz), 8.00 d (1H, H_{arom}, *J* = 7.6 Hz), 10.25 s (1H, NH). Mass spectrum, *m/z* (*I*_{rel}, %): [*M*]⁺ 457 (32), 262 (21), 195 (37), 139 (100). Found, %: C 70.90; H 4.38; Cl 7.69; N 3.07. C₂₇H₂₀ClNO₄. Calculated, %: C 70.89; H 4.38; Cl 7.66; N 3.06.

2-Methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[*f*]-quinolin-1-yl)phenyl 4-bromobenzoate (VIi). Yield 43%, colorless crystals, mp 249°C. IR spectrum, *v*, cm⁻¹: 3080, 1729, 1690, 1621, 1607, 1582, 1512, 1464, 1443, 1411, 1327, 1275, 1242, 1200, 1157, 1133, 1117, 1095, 1032, 910, 864, 749. ¹H NMR spectrum, *δ*, ppm: 2.85 d (1H, CH₂, *J* = 8.4 Hz), 3.09 (1H, CH₂, *J* = 8.1 Hz), 3.78 s (3H, OMe), 5.00 d (1H, CH, *J* = 6.7 Hz), 6.60 d (1H, H_{arom}, *J* = 7.9 Hz), 6.94 d (1H, H_{arom}, *J* = 8.0 Hz), 7.00–7.10 m (1H, H_{arom}), 7.28–7.34 m (1H, H_{arom}), 7.40–7.50 m (1H, H_{arom}), 7.65–7.70 m (2H, H_{arom}), 7.74–7.80 m (2H, H_{arom}), 7.90 m (2H, H_{arom}), 8.00 m (2H, H_{arom}), 10.30 s (1H, NH). Mass spectrum, *m/z* (*I*_{rel}, %): [*M*]⁺ 502 (43), 307 (29), 195 (54), 184 (100). Found, %: C 65.54; H 4.00; Br 15.97; N 2.76. C₂₇H₂₀BrNO₄. Calculated, %: C 65.54; H 3.98; Br 15.94; N 2.79.

2-Methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[*f*]-quinolin-1-yl)phenyl 4-methylbenzoate (VIj). Yield 40%, colorless crystals, mp 276–277°C. IR spectrum, *v*, cm⁻¹: 3020, 2980, 1734, 1676, 1624, 1603, 1514, 1389, 1285, 1271, 1239, 1204, 1177, 1137, 1122, 1073, 1035, 818, 749. ¹H NMR spectrum, *δ*, ppm: 2.79 d (1H, CH₂, *J* = 8.2 Hz), 3.09 (1H, CH₂, *J* = 8.0 Hz),

3.76 s (3H, OMe), 5.00 d (1H, CH, *J* = 6.5 Hz), 6.59 d (1H, H_{arom}, *J* = 7.3 Hz), 6.90 d (1H, H_{arom}, *J* = 7.8 Hz), 7.00 s (1H, H_{arom}), 7.28–7.34 m (3H, H_{arom}), 7.40–7.50 m (2H, H_{arom}), 7.72–7.86 m (3H, H_{arom}), 7.90 m (2H, H_{arom}), 10.26 s (1H, NH). Mass spectrum, *m/z* (*I*_{rel}, %): [*M*]⁺ 438 (47), 243 (31), 195 (19), 119 (100). Found, %: C 76.73; H 5.49; N 3.24. C₂₈H₂₄NO₄. Calculated, %: C 76.71; H 5.48; N 3.20.

2-Methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[*f*]-quinolin-1-yl)phenyl 3-nitrobenzoate (VIk). Yield 38%, colorless crystals, mp 223°C. IR spectrum, *v*, cm⁻¹: 3070, 2906, 1746, 1683, 1625, 1603, 1532, 1509, 1464, 1350, 1291, 1254, 1201, 1125, 1057, 1031, 814, 715. ¹H NMR spectrum, *δ*, ppm: 2.80 d (1H, CH₂, *J* = 8.0 Hz), 3.12 (1H, CH₂, *J* = 8.4 Hz), 3.79 s (3H, OMe), 5.10 d (1H, CH, *J* = 6.9 Hz), 6.53 d (1H, H_{arom}, *J* = 7.5 Hz), 6.80 d (1H, H_{arom}, *J* = 7.4 Hz), 7.00–7.50 m (4H, H_{arom}), 7.80–8.00 m (3H, H_{arom}), 8.40–8.70 m (4H, H_{arom}), 10.48 (1H, NH). Mass spectrum, *m/z* (*I*_{rel}, %): [*M*]⁺ 468 (50), 273 (54), 195 (37), 150 (100). Found, %: C 70.25; H 4.29; N 5.97. C₂₇H₂₀N₂O₆. Calculated, %: C 70.23; H 4.27; N 5.98.

2-Methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[*f*]-quinolin-1-yl)phenyl 2-chlorobenzoate (VII). Yield 25%, colorless crystals, mp 225°C. IR spectrum, *v*, cm⁻¹: 3075, 2907, 1732, 1681, 1625, 1607, 1594, 1517, 1462, 1448, 1420, 1388, 1311, 1242, 1207, 1184, 1162, 1131, 1119, 1086, 1035, 907, 859, 823, 742. ¹H NMR spectrum, *δ*, ppm: 2.70 d (1H, CH₂, *J* = 8.0 Hz), 3.06 (1H, CH₂, *J* = 7.8 Hz), 3.70 s (3H, OMe), 4.98 d (1H, CH, *J* = 6.3 Hz), 6.50 d (1H, H_{arom}, *J* = 8.0 Hz), 7.10–7.40 m (5H, H_{arom}), 7.60–7.85 m (5H, H_{arom}), 7.95–8.10 m (2H, H_{arom}), 10.42 s (1H, NH). Mass spectrum, *m/z* (*I*_{rel}, %): [*M*]⁺ 457 (35), 262 (41), 195 (28), 139 (100). Found, %: C 70.88; H 4.41; Cl 7.68; N 3.04. C₂₇H₂₀ClNO₄. Calculated, %: C 70.89; H 4.38; Cl 7.66; N 3.06.

2-Methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[*f*]-quinolin-1-yl)phenyl 2,4-dichlorobenzoate (VIIm). Yield 30%, colorless crystals, mp 207°C. IR spectrum, *v*, cm⁻¹: 3080, 2910, 1734, 1682, 1625, 1603, 1572, 1510, 1464, 1442, 1427, 1398, 1312, 1285, 1248, 1203, 1187, 1162, 1135, 1114, 1096, 1031, 908, 865, 817, 744. ¹H NMR spectrum, *δ*, ppm: 2.76 d (1H, CH₂, *J* = 8.0 Hz), 3.18 (1H, CH₂, *J* = 8.0 Hz), 3.80 s (3H, OMe), 5.00 d (1H, CH, *J* = 7.0 Hz), 6.50 d (1H, H_{arom}, *J* = 7.9 Hz), 7.00–7.30 m (4H, H_{arom}), 7.40–7.80 m (5H, H_{arom}), 7.90–8.00 m (2H, H_{arom}), 10.39 (1H, NH). Mass spectrum, *m/z* (*I*_{rel}, %): [*M*]⁺ 491 (27), 296 (47), 195 (22), 173 (100). Found, %: C 66.00; H 3.84;

Cl 14.23; N 2.88. $C_{27}H_{19}Cl_2N_2O_4$. Calculated, %: C 65.99; H 3.87; Cl 14.26; N 2.85.

2-Methoxy-4-(3-oxo-1,2,3,4-tetrahydrobenzo[f]-quinolin-1-yl)phenyl 1-phenylprop-2-enoate (VIa). Yield 18%, colorless crystals, mp 235–236°C. IR spectrum, ν , cm^{-1} : 3079, 2910, 1753, 1691, 1653, 1543, 1462, 1338, 1274, 1250, 1237, 1219, 1146, 1043, 919, 854, 828, 741. 1H NMR spectrum, δ , ppm: 2.85 d (1H, CH_2 , $J = 7.4$ Hz), 3.14 d (1H, CH_2 , $J = 7.9$ Hz), 3.78 s (3H, OMe), 5.09 d (1H, CH, $J = 7.2$ Hz), 6.40 d (1H, H_{arom} , $J = 7.9$ Hz), 6.80 d (1H, H_{arom} , $J = 7.5$ Hz), 6.90–7.00 m (3H, H_{arom}), 7.30–7.60 m (5H, H_{arom}), 7.80–7.95 m (2H, CH), 8.05–8.20 m (4H, H_{arom}), 10.35 (1H, NH). Mass spectrum, m/z (I_{rel} , %): $[M]^+$ 449 (42), 254 (38), 195 (53), 131 (100). Found, %: C 77.53; H 5.10; N 3.11. $C_{29}H_{23}NO_4$. Calculated, %: C 77.50; H 5.12; N 3.12.

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