Studies on the Biginelli Reactions of Salicylaldehyde and 2-Hydroxy-l-naphthaldehyde

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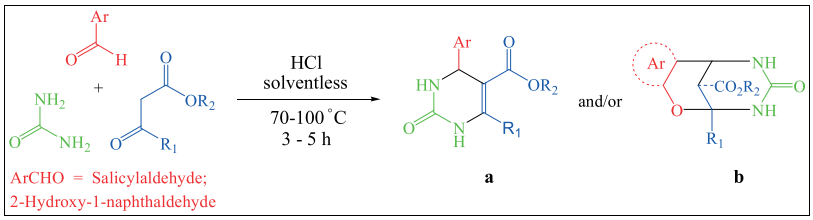

The Biginelli reactions of salicylaldehyde and 2-hydroxy-l-naphthaldehyde with ethyl or methyl acetoacetate, ethyl benzoylacetate, and urea have been reinvestigated both in the structures of the reaction products and in the reaction conditions. Salicylaldehyde with ethyl and methyl acetoacetate resulted in oxygen-bridged tricyclic tetrahydro pyrimidines, whereas with ethyl benzoylacetate afforded the only normal 3,4-dihydropyrimidin-2-one. 2-Hydroxy-l-naphthaldehyde with ethyl and methyl acetoacetate formed the tricyclic compounds. Steric effect is likely to be the principal determinant in governing the formation of product dichotomy. Previous controversial results as to the structure of the Biginelli products have been discussed and settled. The molecular structures of the dihydropyrimidinones and bridged tricyclic products have been fully characterized and confirmed unambiguously by single crystal X-ray diffraction.

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INTRODUCTION

Recently, 3,4-dihydropyrimidin-2-ones (DHPMs) and the derivatives have attracted considerable attention in natural and synthetic organic chemistry because of their wide range of biological activities and pharmacological properties, such as antiviral, antibacterial, antitumour, calcium channel blockers, antihypertensive agents, α-1a-antagonists, and neuropeptide Y antagonists.[1] Among the biologically important compounds, notably, *monastrol* **1**, a recently highlighted DHPM compound, is the only cell-permeable molecule currently known to specifically inhibit mitotic kinesis Eg5 and is considered to be a lead for the development of new anticancer drugs, [2] whereas the (*R*)-*SQ 32926* **2** has been identified as a potent orally active antihypertensive agent.[3] Moreover, several alkaloids containing the dihydropyrimidione core unit have been isolated from marine source, which also shows interesting biological properties. Most notably among these are the batzelladine alkaloids, which have been found to be potent HIV gp-120-CD4 inhibitors.[4]

Thus, formation of this heterocyclic nucleus has gained prime importance in synthetic organic chemistry. The well-known preparation is the Biginelli reaction, which involves three components and one-pot condensation of an aldehyde, β-ketoester, and urea catalyzed by hydrochloric acid in ethanol.[5] A number of more efficient and green synthetic modifications and improved procedures have been developed.[6,7]

As to the Biginelli reaction of *ortho*-hydroxy aromatic aldehydes such as salicylaldehyde with ethyl or methyl acetoacetate and urea or thiourea, the product structure was dihydropyrimidinones as Folkers [8] reported, but was later disproved firstly in 1991 by Světlík [9] as oxygen-bridged tricycle, and then Kettmann,[10] Fu,[11] Bose,[12] and Kumar [13] also obtained the tricyclic compound, respectively. Světlík *et al.*[14] recently reported the product dichotomy of dimethyl and diethyl 3-oxoglutarate with salicylaldehyde. Dimethyl 3-oxoglutarate gave rise to a tricyclic structure, but diethyl 3-oxoglutarate afforded the normal dihydropyrimidinones, to which the steric effect of ethoxycarbonyl was attributed. Two different monastrol products, 4-(2-hydroxyphenyl)pyrimidines and 9-methyl-11-oxo (or thioxo)-8-oxa-10,12-diazatricyclotrideca derivatives were synthesized by Cheng and the coauthors under solvent-free conditions catalyzed by $NaHSO_4$. [15]

In continuation of our interest in the green synthesis of DHPMs and derivatives, we have made the studies on the Biginelli reactions of *ortho*-hydroxy aromatic aldehydes including salicylaldehyde and β-hydroxy-α-naphthaldehyde with β-ketoesters, such as methyl and ethyl acetoacetate and

ethyl benzoylacetate, and urea both in the molecular structures of the products and the reaction conditions (Scheme 1).

RESULTS AND DISCUSSION

The results of the Biginelli reactions of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with ethyl acetoacetate, methyl acetoacetate, ethyl benzoylacetate, and urea under solvent-free conditions are summarized in Table 1.

Ethyl acetoacetate with salicylaldehyde under solvent-free conditions produced oxygen-bridged tricyclic compound **3b** and then converted to DHPM **3a** after being refluxed in ethanol catalyzed with HCl (Scheme 2).

The ^{1}H-NMR signal at δ_H 9.58 ppm in **3a** indicates the presence of the phenolic hydroxyl, which reveals that **3a** is the normal Biginelli DHPM product. In the ^{1}H-NMR spectrum of **3b**, δ_H 9.58 ppm is replaced with δ_H 3.24 ppm assigned to C_9—H. In addition, the ^{13}C-NMR of **3b** at δ_C 83.6 ppm attributed to sp^3 C_1 provides convincing evidence of tricyclic structure resulted from the intramolecular conjugate addition of the phenolic hydroxyl to C_5═C_6—C═O of the dihydropyrimidine. Under solvent-free or low-temperature conditions, **3b** is the main product (solvent-free at 70°C for 3 h is the optimum conditions for **3b**, and in ethanol at refluxed temperature is the optimum conditions for **3a**). Extending the reaction time, the amount of **3b** decreases and that of **3a** increases contrastively. This suggests that **3b** is initially formed and is isomerized to **3a** via tricycle opening. In addition, **3b** cannot be transformed into **3a** in ethanol refluxed in the absence of hydrochloric acid, which shows that acidic catalysis is indispensable for the ring opening transformation.

Similarly, methyl acetoacetate with salicylaldehyde in refluxed ethanol also afforded bridged tricyclic **4b** and then transformed into DHPM **4a** after being refluxed but for prolonged time in ethanol with HCl catalyzed. Their structures are characterized by ^{1}H-NMR and ^{13}C-NMR spectra and confirmed unambiguously by single crystal X-ray diffraction (Fig. 1 and Fig. 2).

Experiments show that ring transformation of **3b** to **3a** is much easier than that of **4b** to **4a**, indicating that tricyclic tetrahydropyrimidine **4b** is more stable than **3b**, to which less steric effect of methoxycarbonyl CO_2CH_3 is attributed. Obviously, the C-6 position is considerably hindered by the adjacent ethoxycarbonyl $CO_2C_2H_5$ of C-5, as compared with the less bulkier methoxycarbonyl CO_2CH_3 group. Consequently, the ring opening of **3b** is easier to occur than that of **4b** (Fig. 3).

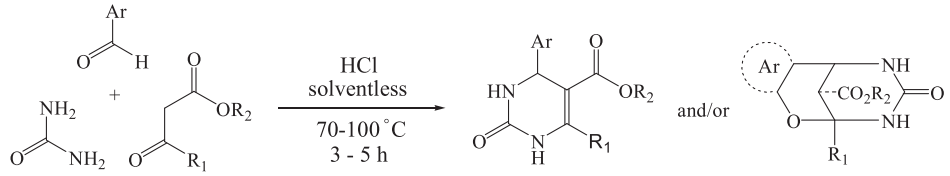
The Biginelli reaction of 2-hydroxy-l-naphthaldehyde with ethyl acetoacetate and urea under different reaction conditions, including solvent-free with HCl catalyzed at 70°C for 3 h, in refluxed ethanol catalyzed by HCl for 3 and 14 h, all gave rise to tricyclic product **5b** and failed to be converted to DHPM (Scheme 3). Such a result is also found in the Biginelli reaction of 2-hydroxy-l-naphthaldehyde with methyl acetoacetate and urea under the same conditions. This can be rationalized by the stabilization effect of cyclization of bulker naphthalyl.

In contrast to the reactions of 2-hydroxy-l-naphthaldehyde with methyl or ethyl acetoacetate, ethyl benzoylacetate with salicylaldehyde afforded only DHPM **7a**, which is governed by both electronic and steric effects of conjugate and bulkier phenyl group bounded to C_6. Phenyl substituent pushes the *ortho*-hydroxy of C_4—Ph away from its bonding contact, and the conjugate effect of phenyl decreased the addition reactivity with phenolic hydroxy. Moreover, the π-π conjugate system formed with phenyl and C═C makes the DHPM structure **7a** much more stable.

CONCLUSION

In summary, we have re-examined the Biginelli reactions of *ortho*-hydroxy aromatic aldehydes, including salicylaldehyde and 2-hydroxy-l-naphthaldehyde, with ethyl or methyl acetoacetate, ethyl benzoylacetate, and urea both in the structures of the reaction products and the reaction conditions. Salicylaldehyde with ethyl or methyl acetoacetate and urea under solvent-free conditions resulted in oxygen-bridged tricyclic products

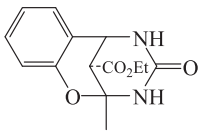
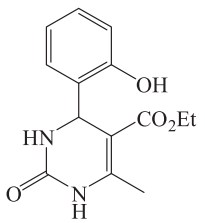
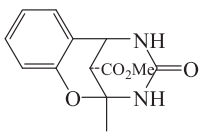
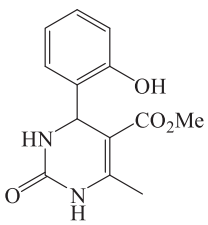
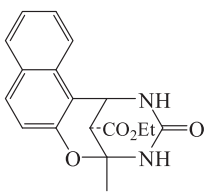
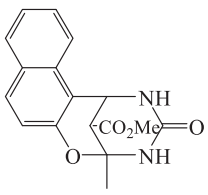
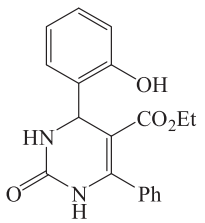
Scheme 1. The Biginelli reactions of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with β-ketoesters and urea under solvent-free conditions.



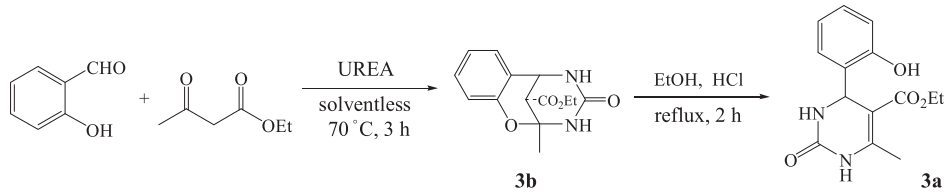
3a: Ar = 2-HOC$_6$H$_4$, R_1 = Me, R_2 = Et; **3b**: Ar = 2-HOC$_6$H$_4$, R_1 = Me, R_2 = Et
4a: Ar = 2-HOC$_6$H$_4$, R_1 = Me, R_2 = Me; **4b**: Ar = 2-HOC$_6$H$_4$, R_1 = Me, R_2 = Me
5b: Ar = 2-HOC$_{10}$H$_6$, R_1 = Me, R_2 = Et; **6b**: Ar = 2-HOC$_{10}$H$_6$, R_1 = Me, R_2 = Me
7a: Ar = 2-HOC$_6$H$_4$, R_1 = Ph, R_2 = Et

Table 1

The Biginelli reactions of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with β-ketoesters and urea under solvent-free conditions.

No.	Ar	R_1	R_2	Product structure	Yield (%)[a]	Time (h)	T (°C)	mp [c] (lit) (°C)
3b	2-HOC_6H_4	Me	Et		98	2.5	70	198.2–200.3 (200–202)[13]
3a	2-HOC_6H_4	Me	Et		80	3	Reflux	216.4–217.2 (217)
4b	2-HOC_6H_4	Me	Me		92	3	70	209.1–210.3 (195–197)
4a	2-HOC_6H_4	Me	Me		78	3	Reflux	231.0–232.9
5b	2-$HOC_{10}H_6$	Me	Et		61.6	3	70	231.4–232.7
6b	2-$HOC_{10}H_6$	Me	Me		88.5	3	70	215.3–215.8
7a	2-HOC_6H_4	Ph	Et		45	5	70	240.1–241.8

Scheme 2. The Biginelli reactions of salicylaldehyde with ethyl acetoacetate and urea under solvent-free conditions.



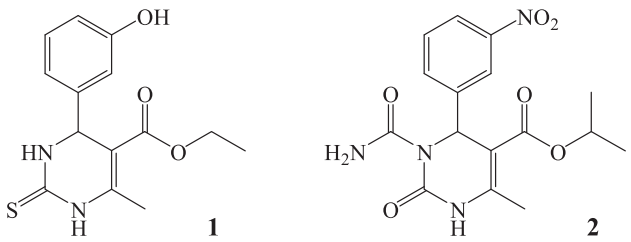


Figure 1. Dihydropyrimidine antagonists.

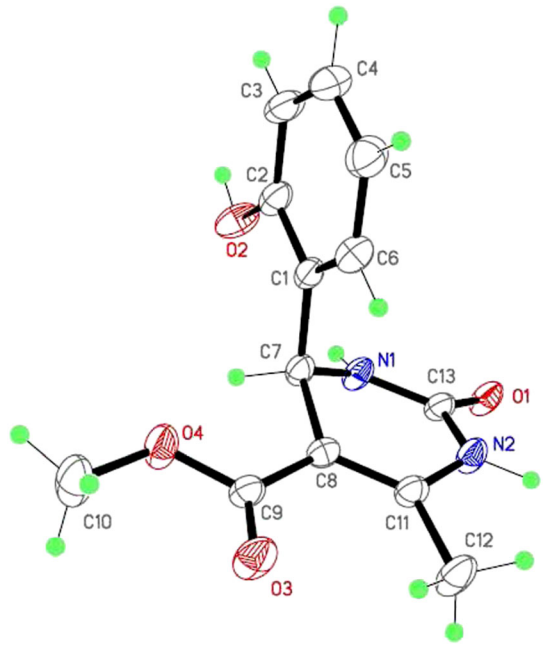


Figure 2. Crystal structure ORTEP of **4a**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

3b and **4b**, whereas salicylaldehyde with ethyl benzoylacetate and urea afforded DHPM **7a**. 2-Hydroxy-l-naphthaldehyde with ethyl or methyl acetoacetate and urea under solvent-free conditions formed tricyclic compounds **5b** and **6b**. Benzoylacetic ethyl ester with salicylaldehyde resulted in only DHPM **7a**. Steric effect is likely to be the principal determinant in governing the formation of reaction product dichotomy. Previous controversial results as to the structure of the Biginelli products have been discussed and settled.

EXPERIMENTAL

General. ^{1}H-NMR and ^{13}C-NMR spectra were determined on a Bruker Advance 300 spectrometer (Bruker AXS, Germany) in DMSO-d_6 with TMS as internal reference (300 MHz for ^{1}H and 75 MHz for ^{13}C). IR spectra were recorded on a Bruker Tensor 27 spectrometer (Bruker AXS, Germany) in KBr plates. Mass spectra were determined with an Agilent 5973N Mass Selective Detector spectrometer in EI mode at 70 eV. Elemental analyses were carried out with a Perkin Elmer PE 2400 II HONS analyzer (Perkin-Elmer Corporation, USA). Single crystal X-ray diffraction was performed on a Bruker SMART APEX CCD Diffractometer (Bruker AXS, Germany). Melting points are uncorrected. Salicylaldehyde, ethyl and methyl acetoacetate, and ethyl benzoylacetate were all reagent grade and were redistilled *in vacuo* unless otherwise stated. 2-Hydroxy-l-naphthaldehyde was prepared from 2-naphthol according to the literature procedure.

General procedures. ***General procedure for the synthesis of 3a and 4a.*** A mixture of salicylaldehyde (5 mmol), ethyl or methyl acetoacetate (5.5 mmol), urea (5.5 mmol), and hydrochloric acid (2 drops) was refluxed for 3 h. Upon cooling to RT, the precipitates were filtered off and recrystallized from isopropyl alcohol to afford **3a** and **4a**, respectively.

General procedure for the synthesis of all other compounds. A mixture of aldehyde (5 mmol), β-ketoester (5.5 mmol), urea (5.5 mmol), and hydrochloric acid (2 drops) was heated at 70°C for 2.5–3 h (monitored by TLC). Upon cooling to RT, the reaction mixture was poured into water. The solids were filtered off, washed with water and 95% ethanol, and recrystallized from ethanol to afford **3b**, **4b**, **5b**, **6b**, and **7a**, respectively.

Structural characterization. ***Ethyl 4-(2-hydroxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one-9-carboxylate 3a.*** Colorless solid, mp 216.4–217.2°C (lit.[14] 217°C). ^{1}H-NMR: δ_H 9.58 (s, 1H), 9.10 (s, 1H), 7.10–6.68 (m, 5H), 5.46 (s, 1H), 3.92 (q, J = 7.0 Hz, 2H), 2.27 (s, 3H), 1.03 (t, J = 7.0 Hz, 3H) ppm. IR: ν_{max} 3414, 3349, 2938, 1699, 1651 cm^{-1}. Elemental *Anal.*: Calcd for $C_{14}H_{16}N_2O_4$: C 60.86, H 5.84, N 10.14; found: C 61.05, H 5.84, N 10.10.

Ethyl 1-methyl-2-oxa-7-oxo-6,8-diazabenzo[c]bicyclo[3.3.1]nonane-9-car-boxylate 3b. Colorless solid, mp199.8–200.3°C (lit.[13] 200–202°C); ^{1}H-NMR: δ_H 7.58 (s, 1H), 7.18 (t, J = 7.1 Hz, 3H), 6.89 (t, J = 7.1 Hz, 1H), 6.77 (d, J = 8.2 Hz, 1H), 4.46 (s, 1H), 4.16 (m, J = 7.0 Hz, 2H), 3.24 (s, 1H), 1.72 (s, 3H), 1.22 (t, J = 7.0 Hz, 3H) ppm. ^{13}C-NMR: δ_C 168.8, 155.0, 151.1, 129.7, 129.0, 125.9, 120.9, 117.0, 83.6, 61.0, 48.2, 44.4, 24.4, 14.4 ppm. IR: ν_{max} 3216, 3078, 1748, 1684 cm^{-1}. Elemental *Anal.*: Calcd for $C_{14}H_{16}N_2O_4$: C 60.86, H 5.84, N 10.14; found: C 60.53, H 5.87, N 9.84.

Methyl 4-(2-hydroxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one-9-carboxylate 4a. Colorless solid, mp 231.0–232.9°C. ^{1}H-NMR: δ_H 9.62 (s, 1H), 9.12 (s, 1H), 7.06–6.68 (m, 5H), 5.44 (s, 1H), 3.47 (s, 3H), 2.27 (s, 3H) ppm. IR: ν_{max} 3416, 3228, 2952, 2361, 1683, 1645 cm^{-1}. Elemental *Anal.*:

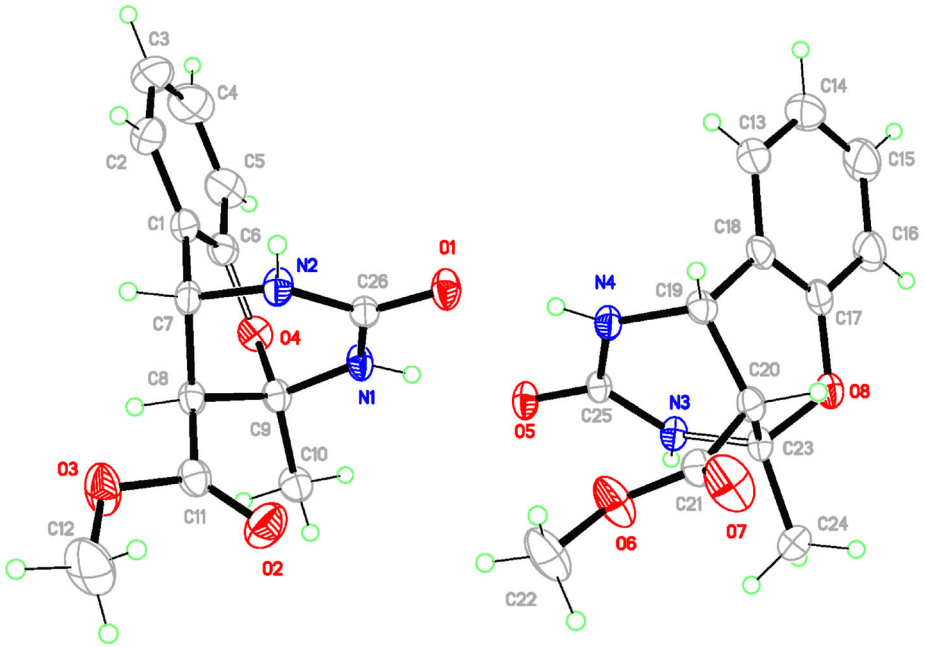
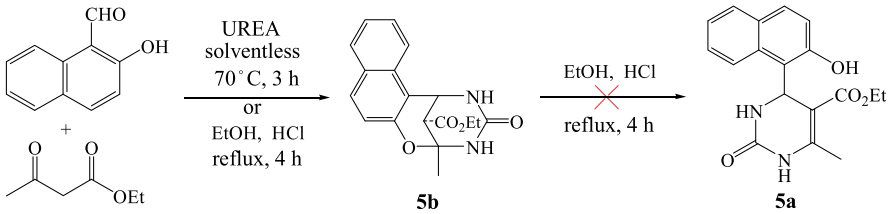


Figure 3. Crystal structure ORTEP of **4b**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

Scheme 3. The Biginelli reaction of 2-hydroxy-1-naphthaldehyde with ethyl acetoacetate and urea under solvent-free conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]



Calcd for $C_{13}H_{14}N_2O_4$: C 59.54, H 5.38, N 10.68; found: C 60.04, H 5.30, N 10.60.

Methyl 1-methyl-2-oxa-7-oxo-6,8-diazabenzo[c]bicyclo[3.3.1]nonane-9-car-boxylate 4b. Colorless solid, mp 209.1–210.3°C (lit.[13] 195–197°C). ^{1}H-NMR: δ_H 7.62 (s, 1H), 7.19 (q, J = 7.2 Hz, 3H), 6.89 (t, J = 7.2 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 4.47 (s, 1H), 3.69 (s, 3H), 3.30 (s, 1H), 1.72 (s, 3H) ppm. ^{13}C-NMR: δ_C 169.3, 154.9, 151.1, 129.8, 129.1, 125.8, 120.9, 116.0, 83.5, 52.3, 48.1, 44.3, 24.5 ppm. IR: ν_{max} 3225, 3085, 1749, 1698 cm^{-1}. Elemental *Anal.*: Calcd for $C_{13}H_{14}N_2O_4$: C 59.54, H 5.38, N 10.68; found: C 59.11, H 5.43, N 10.50.

Ethyl 1-methyl-2-oxa-7-oxo-6,8-diazanaphtho[2,1-c]bicyclo[3.3.1]nonane-9-carboxylate 5b. Colorless solid, mp 231.4–232.7°C. ^{1}H-NMR: δ_H 8.04 (d, J = 8.4 Hz, 1H), 7.83 (q, J = 8.9 Hz, 2H), 7.55 (t, J = 7.5 Hz, 3H), 7.39 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 8.9 Hz, 1H), 5.07 (s, 1H), 4.20 (t, J = 7.0 Hz, 2H), 3.32 (s, 1H), 1.80 (s, 3H), 1.27 (t, J = 7.0 Hz, 3H) ppm. ^{13}C-NMR: δ_C 169.0, 154.8, 148.8, 131.2, 130.2, 129.0, 128.8, 127.3, 124.1, 122.2, 118.9, 117.2, 83.6, 61.1, 44.6, 44.2, 24.3, 14.5 ppm. IR: ν_{max} 3261, 1747, 1698, 1624, 1600 cm^{-1}; MS: *m/z* (%) 326 (M$^+$, 100), 297 (40), 280 (61), 253 (50), 235 (57), 183 (71), 144 (71), 115 (59). Elemental *Anal.*: Calcd for $C_{18}H_{18}N_2O_4$: C 66.25, H 5.56, N 8.58; found: C 65.95, H 5.67, N 8.11.

Methyl 1-methyl-2-oxa-7-oxo-6,8-diazanaphtho[2,1-c]bicyclo[3.3.1]nonane-9-carboxylate 6b. Colorless solid, mp 215.3–215.8°C. ^{1}H-NMR: δ_H 8.04 (d, J = 8.3 Hz, 1H), 7.84 (q, J = 8.8 Hz, 2H), 7.63 (s, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 8.8 Hz, 1H), 5.09 (s, 1H), 3.75 (s, 3H), 1.81 (s, 3H) ppm. ^{13}C-NMR: δ_C 169.5, 154.9, 148.7, 131.2, 130.2, 129.1, 128.8, 127.3, 124.1, 122.2, 118.9, 117.2, 83.6, 52.4, 44.6, 44.1, 24.3 ppm. IR: ν_{max} 3247, 1745, 1690, 1627 cm^{-1}. MS: *m/z* (%) 312 (M$^+$, 54), 169 (56), 144 (100), 115 (92). Elemental *Anal.*: Calcd for $C_{17}H_{16}N_2O_4$: C 65.38, H 5.16, N 8.97; found: C 65.65, H 5.37, N 8.91.

Ethyl 4-(2-hydroxyphenyl)-6-phenyl-3,4-dihydropyrimidin-2(1H)-one-9-carboxylate 7a. Colorless solid, mp 240.1–241.8°C. ^{1}H-NMR: δ_H 9.68 (s, 1H), 9.17 (s, 1H), 7.43–6.77 (m, 10H), 5.54 (d, J = 3.0 Hz, 1H), 3.68 (q, J = 7.1 Hz, 2H), 0.71 (t, J = 7.1 Hz, 3H) ppm. ^{13}C-NMR: δ_C 165.6, 155.3, 152.7, 149.6, 135.8, 130.0, 129.2, 128.9, 128.8, 128.2, 127.6, 119.4, 116.0, 99.6, 59.4, 50.0, 13.8 ppm. IR: ν_{max} 3407, 3241, 2985, 2361, 1661, 1598 cm^{-1}. MS: *m/z* (%) 338 (M$^+$, 38), 309 (57), 291 (55), 265 (100), 245 (59), 104 (49). Elemental *Anal.*: Calcd for $C_{19}H_{18}N_2O_4$: C 67.44, H 5.36, N 8.28; found: C 66.97, H 5.64, N 7.89.

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