One-pot Combinatorial Synthesis of Benzo[4,5]imidazo-[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one Derivatives

Shen, Shide[a](沈士德) Zhang, Honghong[b](张红红) Yang, Weihua[b](杨伟华)
Yu, Chenxia[b,c](于晨侠) Yao, Changsheng*[,b,c](姚昌盛)

[a] *Xuzhou Institute of Architectural Technology, Xuzhou, Jiangsu 221116, China*
[b] *School of Chemistry & Chemical Engineering, Xuzhou Normal University, Xuzhou, Jiangsu 221116, China*
[c] *Key Laboratory of Biotechnology for Medicinal Plants, Xuzhou Normal University, Xuzhou, Jiangsu 221116, China*

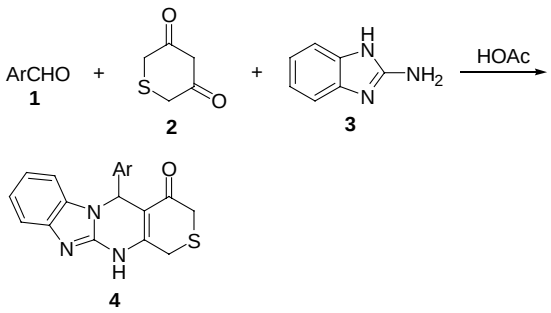
A series of novel fused tetracyclic benzo[4,5]imidazo[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one derivatives were synthesized via the reaction of aryl aldehyde, 2*H*-thiopyran-3,5(4*H*,6*H*)-dione, and 1*H*-benzo[*d*]imidazol-2-amine in glacial acetic acid. This protocol features mild reaction conditions, high yields and short reaction time.

Keywords benzo[4,5]imidazo[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one, multicomponent reactions, combinatorial chemistry

Introduction

Thiopyran and fused thiopyran derivatives belong to the most common heterocyclic compounds. They play an important role in the field of medicinal chemistry and argrochemistry because of their potential biological activities, such as weed control and antitumor activity.[1,2] Benzo[4,5]imidazo[1,2-*a*]pyrimidine derivatives can be used as inhibitor of cell proliferation,[3] lymphocyte specific kinase,[4] DNA-topoisomerase and protein kinase.[5,6] The compounds with thiopyran and pyrimidine core unit have important biological activities, such as anti-HIV virus, antibacterial and fungicidal activity,[7] neuroleptic activity.[8] However, to the best of our knowledge, there has been no report on the synthesis of imidazo[1,2-*a*]-thiopyrano[3,4-*d*]pyrimidine derivatives. Considering the biological significance of scaffolds of thiopyran and imidazo[1,2-*a*]pyrimidine, developing a simple and convenient approach for the synthesis of these fused S,N-containing compounds is still desirable. In recent years, multi-component reactions (MCRs) are very useful for the combinatorial chemistry as powerful tools due to their valuable features such as atom-economy, environmental friendliness, straightforward reaction condition, and the opportunity to construct target compounds by the introduction of several diversity elements in a single chemical operation.[9] By now, many organic transformations have been reported to proceed efficiently by multi-component reactions. To continue our work on the synthesis of heterocyclic compounds via MCR,[10] herein we shall report an efficient and easy method to synthesize benzo[4,5]imidazo[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one derivatives **4** via a three-component reaction of aryl aldehyde **1**, 2*H*-thiopyran-3,5(4*H*,6*H*)-dione (**2**), and 1*H*-benzo[*d*]-imidazol-2-amine (**3**) in glacial acetic acid (Scheme 1).

Scheme 1



Results and discussion

The effect of solvent on the reaction was initially examined using the reaction of **2** (1 mmol), **3** (1 mmol) with phenyl aldehyde **1a** (1 mmol) as a model reaction at 50 ℃. It was found that the reaction in glacial acetic acid (Table 1, Entry 1) gave higher yield than those in other solvents. So glacial acetic acid was used as the optimal solvent to synthesize the target compounds.

To screen the optimal temperature in glacial acetic acid, the previous reaction was performed at 20, 40, 50, 60, and 70 ℃, resulting in the isolation of **4a** in 40%,

* E-mail: csyao@xznu.edu.cn; Tel.: 0086-0516-83403165; Fax: 0086-0516-83403165
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Table 1 Solvent effect on the synthesis of **4a**

Entry	Solvent	Time/h	Yield[a]/%
1	HOAc	8	82
2	$CHCl_3$	8	50
3	EtOH	8	73
4	CH_3CN	8	70
5	DMF	8	60
6	Solvent-free	8	70

[a] Isolated yield.

78%, 82%, 75% and 56% yields (Table 2, Entries 1—5), respectively. As shown in Table 2, 50 ℃ was the suitable temperature for this reaction from the viewpoint of yield.

Table 2 Temperature optimization for synthesis of **4a**

Entry	Temp./℃	Time/h	Yield[a]/%
1	20	20	40
2	40	10	78
3	50	8	82
4	60	8	75
5	70	6	56

[a] Isolated yield.

Based on the optimized reaction conditions, a series of benzo[4,5]imidazo[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one derivatives were synthesized successfully. As shown in Table 3, the reactions at 50 ℃ in glacial acetic acid gave the corresponding products in moderate to good yields. The results revealed that not only electron-rich aryl aldehyde (such as a methoxy group), but also electron-deficient aryl aldehyde (such as a nitro group, halogen) in the multi-component reaction afforded the corresponding product efficiently under the same conditions. However, when the aliphatic and heteroaromatic aldehydes were used to this reaction, no expected product was obtained.

Table 3 Synthesis of compound **4**

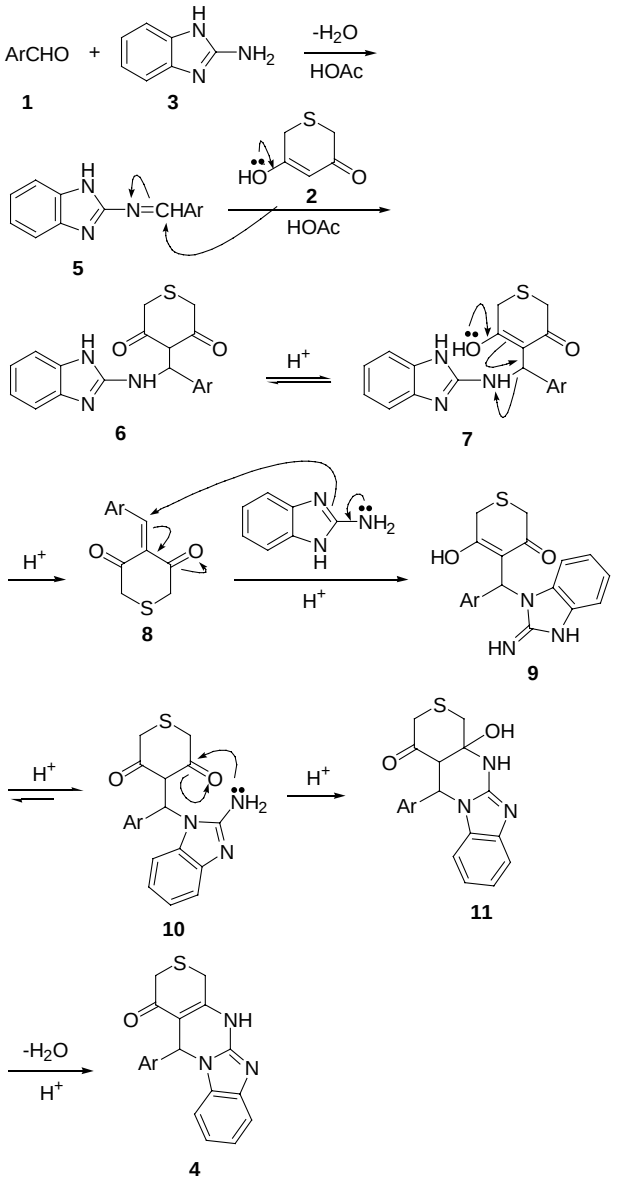
Entry	Compd.	Ar	Time/h	Yield[a]/%	m.p./℃
1	**4a**	C_6H_5	8	82	295—297
2	**4b**	4-BrC_6H_4	8	82	292—294
3	**4c**	2-FC_6H_4	7	77	＞300
4	**4d**	4-FC_6H_4	7	80	＞300
5	**4e**	2-ClC_6H_4	8	73	193—295
6	**4f**	3-ClC_6H_4	8	75	292—293
7	**4g**	3,4-$Cl_2C_6H_3$	7	84	283—285
8	**4h**	3-$NO_2C_6H_4$	6	85	292—293
9	**4i**	4-$NO_2C_6H_4$	7	85	293—296
10	**4j**	4-$CH_3C_6H_4$	10	84	＞300
11	**4k**	3-$CH_3OC_6H_4$	10	76	273—274
12	**4l**	4-$CH_3OC_6H_4$	9	80	280—282
13	**4m**	3,4,5-$(CH_3O)_3C_6H_2$	10	85	284—286

[a] Isolated yield.

All of the products were characterized by FTIR, ^{1}H NMR, and HRMS.

A possible mechanism for the formation of the products **4** was outlined in Scheme 2. In the initial step, the condensation of aryl aldehyde **1** and 1*H*-benzo[*d*]-imidazol-2-amine (**3**) gave Schiff base **5**. The addition of **2** to Schiff base **5**, followed by elimination, furnished the intermediate **8**. Michael addition between 1*H*-benzo[*d*]-imidazol-2-amine (**3**) and **8** afforded the intermediate product **9**, which upon isomerization, intramolecular cyclization and dehydration gave the final product **4**.

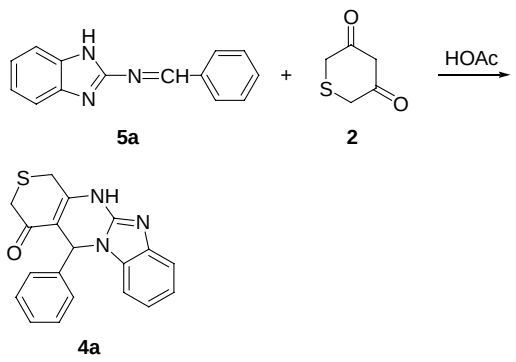
Scheme 2



To test the proposed mechanism, the intermediate **5a**, *N*-benzylidene-1*H*-benzo[*d*]imidazol-2-amine was pre-

pared via the condensation of benzaldehyde and 1*H*-benzo[*d*]imidazol-2-amine under the same conditions. It could react with **2** to give the expected product **4a** with slightly lower yield (76%) than the one-pot reaction (82%). The fact supported the supposed reaction pathway (Scheme 3).

Scheme 3



Conclusion

In summary, we have developed a simple and efficient method for synthesis of a series of benzo[4,5]-imidazo[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one derivatives via a one-pot multi-component reaction in acidic media. This procedure features short reaction time, generally good to excellent yields, easily available starting materials, and operational simplicity (only one pot).

Experimental

Reaction progress was monitored with analytical TLC on 0.25 mm silica gel precoated glass plates with a fluorescent indicator UV254. Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a TENSOR 27 spectrometer in KBr. ^{1}H NMR spectra were measured on a DPX 400 spectrometer operating at 400 MHz, using $CDCl_3$ or DMSO-d_6 as solvent and TMS as an internal standard. HRMS (ESI) were determined by using micro-TOF-QIIHRMS/MS instrument (Bruker). Solvents and commercial reagents of analytical reagent grade were purchased and used without any further purification.

General procedure for the synthesis of 5-aryl-5,12-dihydro-1*H*-benzo[4,5]imidazo[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one

Aryl aldehyde **1** (1 mmol), 2*H*-thiopyran-3,5-(4*H*,6*H*)-dione (**2**, 1 mmol), 1*H*-benzo[*d*]imidazol-2-amine (**3**, 1 mmol) and HOAc (10 mL) were mixed and then stirred at 50 ℃ for 6—10 h. After completion of the reaction (monitored by TLC), the reaction mixture was poured into water. After filtration, the solid product was recrystallized from ethanol (95%) to give pure product **4**.

5-Phenyl-5,12-dihydro-1*H*-benzo-[4,5]imidazo[1,2-*a*]-thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one (**4a**): ^{1}H NMR ($CDCl_3$) δ: 11.47 (s, 1H, NH), 7.38 (d, J=7.6 Hz, 1H, ArH), 7.34 (d, J=7.2 Hz, 2H, ArH), 7.30 (d, J=8.0 Hz, 1H, ArH), 7.26 (t, J=7.6 Hz, 2H, ArH), 7.17 (t, J=7.2 Hz, 1H, ArH), 7.07 (t, J=7.6 Hz, 1H, ArH), 6.99 (t, J=7.6 Hz, 1H, ArH), 6.50 (s, 1H, CH), 3.96 (d, J=17.2 Hz, 1H, CH_2), 3.60 (d, J=17.2 Hz, 1H, CH_2), 3.54 (d, J=16.0 Hz, 1H, CH_2), 3.14 (d, J=16.0 Hz, 1H, CH_2); IR (KBr) v: 3200, 2847, 1639, 1616, 1592, 1567, 1350, 1273, 742, 512 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{16}N_3OS$ $[M+H]^+$ 334.1014, found 334.1012.

5-(4-Bromophenyl)-5,12-dihydro-1*H*-benzo[4,5]imidazo[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one (**4b**): ^{1}H NMR (DMSO-d_6) δ: 11.50 (s, 1H, NH), 7.46 (d, J=8.0 Hz, 2H, ArH), 7.39 (d, J=8.0 Hz, 1H, ArH), 7.31—7.28 (m, 3H, ArH), 7.08 (d, J=7.6 Hz, 1H, ArH), 7.00 (d, J=7.6 Hz, 1H, ArH), 6.51 (s, 1H, CH), 3.94 (d, J=16.8 Hz, 1H, CH_2), 3.59 (d, J=17.2 Hz, 1H, CH_2), 3.53 (d, J=16.0 Hz, 1H, CH_2), 3.14 (d, J=16.0 Hz, 1H, CH_2); IR (KBr) v: 3211, 1636, 1602, 1555, 1357, 1270, 1010, 747, 513 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{15}BrN_3OS$ $[M+H]^+$ 412.0119, found 412.0115.

5-(2-Fluorophenyl)-5,12-dihydro-1*H*-benzo[4,5]imidazo[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one (**4c**): ^{1}H NMR ($CDCl_3$) δ: 11.55 (s, 1H, NH), 7.47 (s, 1H, ArH), 7.41 (d, J=8.0 Hz, 1H, ArH), 7.35 (d, J=7.6 Hz, 1H, ArH), 7.31—7.22 (m, 3H, ArH), 7.09 (t, J=8.0 Hz, 1H, ArH), 7.02 (t, J=7.6 Hz, 1H, ArH), 6.55 (s, 1H, CH), 3.95 (d, J=16.8 Hz, 1H, CH_2), 3.63 (d, J=17.2 Hz, 1H, CH_2), 3.54 (d, J=16.0 Hz, 1H, CH_2), 3.16 (d, J=16.4 Hz, 1H, CH_2); IR (KBr) v: 3399, 2872, 1638, 1616, 1592, 1570, 1359, 1268, 1206, 757, 510 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{15}FN_3OS$ $[M+H]^+$ 352.0920, found 352.0917.

5-(4-Fluorophenyl)-5,12-dihydro-1*H*-benzo[4,5]imidazo[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one (**4d**): ^{1}H NMR ($CDCl_3$) δ: 11.49 (s, 1H, NH), 7.41—7.38 (m, 3H, ArH), 7.31 (d, J=7.6 Hz, 1H, ArH), 7.09 (t, J=8.8 Hz, 3H, ArH), 7.00 (t, J=7.6 Hz, 1H, ArH), 6.53 (s, 1H, CH), 3.95 (d, J=16.8 Hz, 1H, CH_2), 3.61 (dd, J_1=1.2 Hz, J_2=16.8 Hz, 1H, CH_2), 3.54 (dd, J_1=0.8 Hz, J_2=16.0 Hz, 1H, CH_2), 3.15 (dd, J_1=1.2 Hz, J_2=16.0 Hz, 1H, CH_2); IR (KBr) v: 3210, 3024, 2843, 1641, 1618 1593, 1572, 1512, 1348, 1273, 1229, 744, 527 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{15}FN_3OS$ $[M+H]^+$ 352.0920, found 352.0917.

5-(2-Chlorophenyl)-5,12-dihydro-1*H*-benzo[4,5]imidazo[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one (**4e**): ^{1}H NMR ($CDCl_3$) δ: 11.63 (s, 1H, NH), 7.54 (s, 1H, ArH), 7.39 (d, J=7.6 Hz, 1H, ArH), 7.35 (t, J=8.0 Hz, 1H, ArH), 7.29 (t, J=7.2 Hz, 1H, ArH), 7.23 (t, J=7.6 Hz, 1H, ArH), 7.14 (d, J=7.6 Hz, 1H, ArH), 7.08 (t, J=7.2 Hz, 1H, ArH), 6.99 (t, J=7.2 Hz, 1H, ArH), 6.72 (s, 1H, CH), 3.93 (d, J=16.8 Hz, 1H, CH_2), 3.62 (d, J=16.8 Hz, 1H, CH_2), 3.49 (d, J=16.4 Hz, 1H, CH_2), 3.13 (d, J=16.0 Hz, 1H, CH_2); IR (KBr) v: 3216, 2899, 1638, 1615, 1565, 1350, 1268, 738, 524 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{15}ClN_3OS$ $[M+H]^+$

368.0624, found 368.0612.

5-(3-Chlorophenyl)-5,12-dihydro-1*H*-benzo[4,5]-imidazo[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one (**4f**): ^{1}H NMR ($CDCl_3$) δ: 11.57 (s, 1H, NH), 7.56 (t, J=7.2 Hz, 1H, ArH), 7.39 (d, J=8.0 Hz, 1H, ArH), 7.28—7.23 (m, 1H, ArH), 7.16—7.14 (m, 2H, ArH), 7.11—7.06 (m, 2H, ArH), 7.00 (t, J=7.2 Hz, 1H, ArH), 6.63 (s, 1H, CH), 3.95 (d, J=17.6 Hz, 1H, CH_2), 3.62 (d, J=17.2 Hz, 1H, CH_2), 3.52 (d, J=16.0 Hz, 1H, CH_2), 3.14 (d, J=16.0 Hz, 1H, CH_2); IR (KBr) v: 3243, 3047, 1589, 1636, 1589, 1556, 1353, 1266, 794, 745, 517 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{15}ClN_3OS$ $[M+H]^+$ 368.0624, found 368.0617.

5-(3,4-Dichlorophenyl)-5,12-dihydro-1*H*-benzo-[4,5]-imidazo[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one (**4g**): ^{1}H NMR ($CDCl_3$) δ: 11.60 (s, 1H, NH), 7.74 (s, 1H, ArH), 7.53 (d, J=8.4 Hz, 1H, ArH), 7.41 (d, J=8.0 Hz, 1H, ArH), 7.36 (d, J=8.0 Hz, 1H, ArH), 7.22 (d, J=8.4 Hz, 1H, ArH), 7.11 (t, J=7.6 Hz, 1H, ArH), 7.03 (t, J=7.6 Hz, 1H, ArH), 6.57 (s, 1H, CH), 3.94 (d, J=16.8 Hz, 1H, CH_2), 3.63 (d, J=17.2 Hz, 1H, CH_2), 3.54 (d, J=16.0 Hz, 1H, CH_2), 3.15 (d, J=16.0 Hz, 1H, CH_2); IR (KBr) v: 3293, 2886, 1635, 1604, 1560, 1353, 1264, 1031, 746, 512 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{14}Cl_2N_3OS$ $[M+H]^+$ 402.0235, found 402.0209.

5-(3-Nitrophenyl)-5,12-dihydro-1*H*-benzo[4,5]imidazo[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one (**4h**): ^{1}H NMR ($CDCl_3$) δ: 11.65 (s, 1H, NH), 8.29 (s, 1H, ArH), 8.06 (d, J=8.0 Hz, 1H, ArH), 7.72 (d, J=7.6 Hz, 1H, ArH), 7.57 (t, J=8.0 Hz, 1H, ArH), 7.41 (d, J=8.0 Hz, 1H, ArH), 7.34 (d, J=7.6 Hz, 1H, ArH), 7.09 (t, J=8.0 Hz, 1H, ArH), 7.00 (t, J=7.6 Hz, 1H, ArH), 6.74 (s, 1H, CH), 3.96 (d, J=16.8 Hz, 1H, CH_2), 3.64 (d, J=16.8 Hz, 1H, CH_2), 3.54 (d, J=16.0 Hz, 1H, CH_2), 3.16 (d, J=16.0 Hz, 1H, CH_2); IR (KBr) v: 3228, 3053, 2915, 1638, 1589, 1556, 1348, 1271, 1212, 748, 730 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{15}N_4O_3S$ $[M+H]^+$ 379.0865, found 379.0824.

5-(4-Nitrophenyl)-5,12-dihydro-1*H*-benzo[4,5]imidazo[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one (**4i**): ^{1}H NMR ($CDCl_3$) δ: 11.62 (s, 1H, NH), 8.14 (d, J=8.8 Hz, 2H, ArH), 7.62 (d, J=8.4 Hz, 2H, ArH), 7.41 (d, J=8.0 Hz, 1H, ArH), 7.29 (d, J=8.0 Hz, 1H, ArH), 7.10 (d, J=7.6 Hz, 1H, ArH), 7.00 (t, J=7.6 Hz, 1H, ArH), 6.69 (s, 1H, CH), 3.97 (d, J=16.8 Hz, 1H, CH_2), 3.62 (d, J=17.2 Hz, 1H, CH_2), 3.55 (d, J=16.0 Hz, 1H, CH_2), 3.15 (dd, J_1=1.2 Hz, J_2=16.0 Hz, 1H, CH_2); IR (KBr) v: 3217, 1637, 1603, 1589, 1556, 1520, 1349, 1272, 828, 745, 511 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{15}N_4O_3S$ $[M+H]^+$ 379.0865, found 379.0833.

5-(*p*-Tolyl)-5,12-dihydro-1*H*-benzo-[4,5]imidazo-[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one (**4j**): ^{1}H NMR ($CDCl_3$) δ: 11.40 (s, 1H, NH), 7.37 (d, J=8.0 Hz, 1H, ArH), 7.28 (d, J=7.6 Hz, 1H, ArH), 7.22 (d, J=8.0 Hz, 2H, ArH), 708—7.04 (m, 3H, ArH), 6.98 (t, J=7.6 Hz, 1H, ArH), 6.45 (s, 1H, CH), 3.94 (d, J=16.8 Hz, 1H, CH_2), 3.59 (d, J=17.2 Hz, 1H, CH_2), 3.53 (d, J=16.0 Hz, 1H, CH_2), 3.12 (d, J=16.0 Hz, 1H, CH_2), 2.18 (s, 3H, CH_3); IR (KBr) v: 3200, 3099, 2751, 1639, 1556, 1515, 1456, 1355, 1269, 736, 515 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{18}N_3OS$ $[M+H]^+$ 348.1171, found 348.1160.

5-(3-Methoxyphenyl)-5,12-dihydro-1*H*-benzo[4,5]-imidazo[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one (**4k**): ^{1}H NMR ($CDCl_3$) δ: 11.47 (s, 1H, NH), 7.38 (t, J=7.6 Hz, 2H, ArH), 7.16 (t, J=8.0 Hz, 1H, ArH), 7.08 (t, J=7.6 Hz, 1H, ArH), 7.00 (t, J=7.6 Hz, 1H, ArH), 6.94 (s, 1H, ArH), 6.83 (d, J=8.0 Hz, 1H, ArH), 6.75 (d, J=8.0 Hz, 1H, ArH), 6.49 (s, 1H, CH), 3.95 (d, J=16.8 Hz, 1H, CH_2), 3.69 (s, 3H, OCH_3), 3.60 (d, J=17.2 Hz, 1H, CH_2), 3.54 (d, J=16.4 Hz, 1H, CH_2), 3.14 (d, J=16.0 Hz, 1H, CH_2); IR (KBr) v: 3396, 2836, 1637, 1611, 1593, 1571, 1455, 1349, 1257, 745, 694, 515 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{18}N_3O_2S$ $[M+H]^+$ 364.1120, found 364.1112.

5-(4-Methoxyphenyl)-5,12-dihydro-1*H*-benzo[4,5]-imidazo[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one (**4l**): ^{1}H NMR ($CDCl_3$) δ: 11.37 (s, 1H, NH), 7.38 (t, J=8.0 Hz, 1H, ArH), 7.31 (d, J=8.0 Hz, 1H, ArH), 7.26 (d, J=8.4 Hz, 2H, ArH), 7.07 (t, J=7.6 Hz, 1H, ArH), 6.99 (t, J=7.6 Hz, 1H, ArH), 6.80 (d, J=8.8 Hz, 2H, ArH), 6.45 (s, 1H, CH), 3.95 (d, J=16.8 Hz, 1H, CH_2), 3.66 (s, 3H, OCH_3), 3.59 (d, J=16.0 Hz, 1H, CH_2), 3.53 (d, J=16.0 Hz, 1H, CH_2), 3.13 (d, J=16.0 Hz, 1H, CH_2); IR (KBr) v: 3320, 2905, 1638, 1614, 1567, 1512, 1351, 1253, 1178, 1031, 839, 744, 531 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{18}N_3O_2S$ $[M+H]^+$ 364.1120, found 364.1117.

5-(3,4,5-Trimethoxyphenyl)-5,12-dihydro-1*H*-benzo-[4,5]imidazo[1,2-*a*]thiopyrano[3,4-*d*]pyrimidin-4(3*H*)-one (**4m**): ^{1}H NMR ($CDCl_3$) δ: 11.45 (s, 1H, NH), 7.53 (d, J=7.6 Hz, 1H, ArH), 7.39 (d, J=8.0 Hz, 1H, ArH), 7.09 (t, J=7.6 Hz, 1H, ArH), 7.04 (t, J=7.6 Hz, 1H, ArH), 6.67 (s, 2H, ArH), 6.48 (s, 1H, CH), 3.95 (d, J=16.8 Hz, 1H, CH_2), 3.69 (s, 6H, 2OCH_3), 3.65 (d, J=17.2 Hz, 1H, CH_2), 3.57 (s, 3H, OCH_3), 3.55 (d, J=16.0 Hz, 1H, CH_2), 3.19 (d, J=16.0 Hz, 1H, CH_2); IR (KBr) v: 3350, 2942, 2838, 1645, 1614, 1593, 1573, 1349, 1241, 1127, 1006, 736, 510 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{22}N_3O_4S$ $[M+H]^+$ 424.1331, found 424.1325.

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