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DIRECT OXIDATIVE CONVERSION OF ALDEHYDES INTO 2-SUBSTITUTED 1,4,5,6-TETRAHYDROPYRIMIDINES USING MOLECULAR IODINE OR 1,3-DIIODO-5,5-DIMETHYLHYDANTOIN

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Abstract **-** Various aromatic and aliphatic aldehydes were efficiently converted into the corresponding 1,4,5,6-tetrahydro-2-arylpyrimidines and 1,4,5,6-tetrahydro-2-alkylpyrimidines in good yields by the reaction with 1,3-propanediamine in the presence of molecular iodine•K_2CO_3 or 1,3-diiodo-5,5-dimethylhydantoin. Those 1,4,5,6-tetrahydropyrimidines were oxidized to the corresponding 2-aryl- and 2-alkylpyrimidines in moderate yields using MnO_2.

Dedicated to Professor Dr. A. Eschenmoser on the occasion of his 85th birthday.

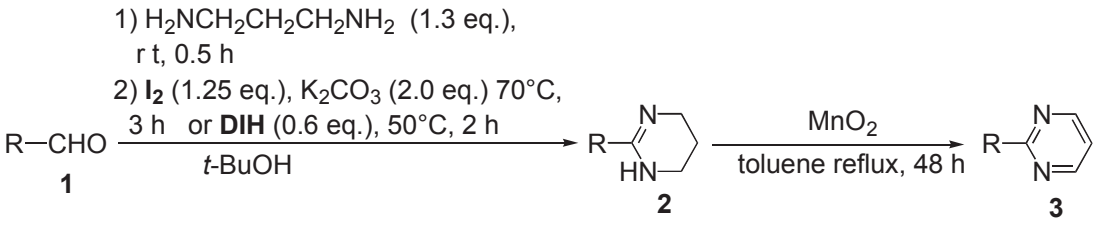
1. INTRODUCTION

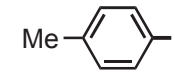
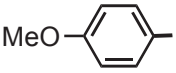
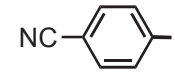
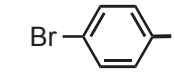
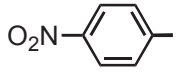
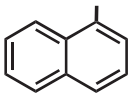
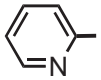
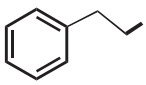
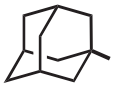
The preparation of 2-substituted 1,4,5,6-tetrahydropyrimidines and pyrimidines[1] has become of great interest and importance because of their pharmaceutical utility, *i.e.*, potent biological activities against inflammatory diseases, pain, type II diabetes, and cancer were reported for 1,4,5,6-tetrahydropyrimidines,[2] and antitumor, antibacterial, antifungal, antimalarial, and anticonvulsant activities were noted for pyrimidines.[3] Several synthetic methods are available for the preparation of 2-substituted 1,4,5,6-tetrahydropyrimidines from nitriles, esters, orthoesters, thioamides, amidines, and carboxylic acids with 1,3-propanediamine.[1,4,5]

On the other hand, aldehydes can be also used for the preparation of 2-substituted 1,4,5,6-tetrahydropyrimidines by the reaction with 1,3-propanediamine under oxidative conditions. To the best of our knowledge, synthetic studies for the preparation of 2-substituted 1,4,5,6-tetrahydropyrimidines from aldehydes are extremely limited, and recently the one-pot preparation of 2-(*p*-iodophenyl)- and 2-(*p*-bromophenyl)-1,4,5,6-tetrahydropyrimidines by the reaction of

p-iodobenzaldehyde and *p*-bromobenzaldehyde with 1,3-propanediamine and the successive treatment with NBS was reported.[5]

Table 1. Formation of 2-Substituted 1,4,5,6-Tetrahydropyrimidines and Pyrimidines



Entry	1 R–	Yields **2** (%)[a] I_2	 DIH	Yield **3** (%)[a]
1	Me– 	99	99	48
2		77	78	69
3	MeO– 	99	94	35
4	NC– 	52	67	31
5	Br– 	99	94	52
6	O_2N– 	99	82	46
7		100	97	57
8		82	74[b]	-
9		69	76	-
10		57	62	<5
11	$Me(CH_2)_6$–	83	82	<5
12		50	87[c]	<5
13		95	96	51

[a] Isolated yield.

[b] Reaction time was 8 h at the second step.

[c] K_2CO_3 (2.0 equiv.) was added.

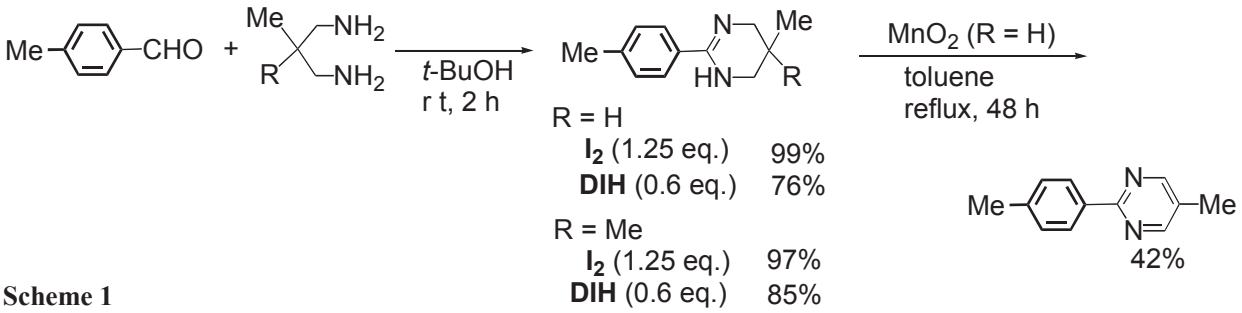
Here, as part of our basic study of molecular iodine and related iodine reagents for organic synthesis,[6] we would like to report the preparation of 1,4,5,6-tetrahydro-2-arylpyrimidines and 1,4,5,6-tetrahydro-2-alkylpyrimidines **2** by the reaction of aromatic and aliphatic aldehydes **1** with 1,3-propanediamine in the presence of molecular iodine•K_2CO_3 or 1,3-diiodo-5,5-dimethylhydantoin (DIH).

First, *p*-tolualdehyde was treated with 1,3-propanediamine (1.3 eq.) in *t*-BuOH at rt. After 0.5 h, molecular iodine (1.25 eq.) and K_2CO_3 (2.0 eq.) were added to the mixture and the whole was warmed at 70 °C for 3 h to provide 1,4,5,6-tetrahydro-2-(4'-methylphenyl)pyrimidine in 99% yield, as shown in Table 1 (entry 1, left side). Then, *p*-tolualdehyde was treated with 1,3-propanediamine (1.3 eq.) in *t*-BuOH at rt. After 0.5 h, 1,3-diiodo-5,5-dimethylhydantoin (DIH, 0.6 eq.) was added to the mixture and the whole was warmed at 50 °C for 2 h to provide 1,4,5,6-tetrahydro-2-(4'-methylphenyl)pyrimidine in 99% yield (entry 1, right side). Based on these results, other aromatic aldehydes **1**, such as benzaldehyde, *p*-methoxybenzaldehyde, *p*-cyanobenzaldehyde, *p*-bromobenzaldehyde, *p*-nitrobenzaldehyde, 1-naphthaldehyde, 2-thiophenaldehyde, and 2-pyridinecarboxaldehyde, were treated with 1,3-propanediamine in the presence of molecular iodine•K_2CO_3 or DIH to give the corresponding 1,4,5,6-tetrahydro-2-arylpyrimidines **2** in good yields (entries 2~9). The reactivity of molecular iodine and DIH was almost the same to provide the corresponding 2-substituted 1,4,5,6-tetrahydropyrimidines **2** in good yields. The same treatment of aliphatic aldehydes **1**, such as 3-phenylpropanal, octanal, cyclohexanecarboxaldehyde, and 1-adamantanecarboxaldehyde with 1,3-propanediamine in the presence of molecular iodine•K_2CO_3 or DIH provided the corresponding 1,4,5,6-tetrahydro-2-alkylpyrimidines **2** in good yields (entries 10~13).

Then, the oxidation of 2-substituted 1,4,5,6-tetrahydropyrimidines **2** to the corresponding 2-substituted pyrimidines **3** was carried out using MnO_2, Pd-C under oxygen, DDQ, and *N*-bromosuccinimide (NBS), respectively, and MnO_2 showed the best results to give the corresponding 2-substituted pyrimidines **3** in moderate yields except for entries 8~12, as shown in Table 1 (right column).

Finally, as an extension of the present method, *p*-tolualdehyde was treated with 2-methyl-1,3-propanediamine and 2,2-dimethyl-1,3-propanediamine in the presence of molecular iodine•K_2CO_3 or DIH to provide 1,4,5,6-tetrahydro-2-(4'-methylphenyl)-5-methylpyrimidine and 1,4,5,6-tetrahydro-2-(4'-methylphenyl)-5,5-dimethylpyrimidine, respectively, in good yields, as shown in Scheme 1.

1,4,5,6-Tetrahydro-2-(4'-methylphenyl)-5-methylpyrimidine was then oxidized by MnO_2 in toluene to give 2-(4'-methylphenyl)-5-methylpyrimidine in moderate yield. Thus, the present method can be used for the preparation of various kinds of 2-substituted 1,4,5,6-tetrahydropyrimidine and pyrimidine derivatives with aldehydes and 1,3-propanediamines.



Scheme 1

In summary, 1,4,5,6-tetrahydro-2-arylpyrimidines and 1,4,5,6-tetrahydro-2-alkylpyrimidines **2** were efficiently obtained by the reaction of various aromatic and aliphatic aldehydes **1** with 1,3-propanediamine in the presence of molecular iodine•K_2CO_3 or DIH. 1,4,5,6-Tetrahydro-2-arylpyrimidines **2** were smoothly oxidized to 2-arylpyrimidines **2** in moderate yields. Moreover, using 2-substituted 1,3-propanediamines and aldehydes, 2,5-disubstituted 1,4,5,6-tetrahydropyrimidines and pyrimidines can be prepared by the present method. Therefore, the present method is a simple and efficient tool for the preparation of various 2-substituted and 2,5-disubstituted 1,4,5,6-tetrahydropyrimidines and pyrimidines.

EXPERIMENTAL

General: ^{1}H and ^{13}C NMR spectra were obtained with JEOL-JNM-LA-400, JEOL-JNM-LA-400s, and JEOL-JNM-LA-500 spectrometers. Chemical shifts are expressed in ppm downfield from tetramethylsilane (TMS) in δ units. IR spectra were measured with JASCO FT/IR-810 and FT/IR-4100 spectrometers. Mass spectra were recorded on JEOL-HX-110 and JEOL-JMS-ATII15 spectrometers. Melting points were determined with a Yamato Melting Point Apparatus Model MP-21. Silica gel 60 (Kanto Kagaku Co.) was used for column chromatography and Wakogel B-5F was used for preparative TLC. DIH is commercially available from Tokyo Kasei Co.

Typical Procedure for Preparation of 2-Substituted 1,4,5,6-Tetrahydropyrimidines from Aldehydes

To a solution of *p*-tolualdehyde (120.2 mg, 1 mmol) in *t*-butyl alcohol (10 mL) was added 1,3-diaminopropane (96.4 mg 1.3 mmol). The obtained mixture was stirred at room temperature under an argon atmosphere for 30 min, and then DIH (228.0 mg, 0.6 mmol) was added to the mixture and stirred at 50 °C. After 2 h, the mixture was quenched with sat. aq Na_2SO_3 until the iodine color almost disappeared, and was extracted with $CHCl_3$. The organic layer was washed with aq. K_2CO_3 and brine, and dried over Na_2SO_4. After filtration, the mixture was evaporated in vacuo to provide 172.4 mg of 1,4,5,6-tetrahydro-2-(4'-methylphenyl)pyrimidine in 99% yield as an almost pure state.

2-Substituted 1,4,5,6-tetrahydropyrimidines and pyrimidines were recrystallized from a mixture ethyl acetate and hexane.

1,4,5,6-Tetrahydro-2-(4'-methylphenyl)pyrimidine. mp 161-162 °C; IR (KBr): 3130, 1635, 1430, 1320, 1205, 825, 725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.85 (quintet, *J* = 5.8 Hz, 2H), 2.36 (s, 3H), 3.49 (t, *J* = 5.8 Hz, 4H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H); HRMS (FAB); Obsd M+H = 175.1232. Calcd for $C_{11}H_{15}N_2$ M+H = 175.1230.

1,4,5,6-Tetrahydro-2-phenylpyrimidine. syrup; IR (paraffin): 3249, 2943, 2897, 1614, 1418, 1312, 1187, 781, 696 cm^{-1}; ^1H NMR (400MHz, $CDCl_3$): δ = 1.86 (quintet, *J* = 5.8 Hz, 2H), 3.51 (t, *J* = 5.8 Hz, 4H), 7.34-7.41 (m, 3H), 7.66 (d, *J* = 8.2 Hz, 2H); HRMS (FAB); Obsd M+H = 161.1077. Calcd for $C_{10}H_{13}N_2$ M+H = 161.1073.

1,4,5,6-Tetrahydro-2-(4'-methoxyphenyl)pyrimidine. syrup; IR (paraffin): 3145, 2938, 1633, 1504, 1442, 1373, 1311, 1261, 1191, 1024, 838, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.83 (quintet, *J* = 5.8 Hz, 2H), 3.47 (t, *J* = 5.8 Hz, 4H), 3.81 (s, 3H), 6.86 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.7 (s), 42.2 (s), 55.2 (p), 113.4 (t), 127.3 (t), 129.7 (q), 154.1 (q), 160.6 (q).

1,4,5,6-Tetrahydro-2-(4'-nitrophenyl)pyrimidine. mp 138-142 °C; IR (paraffin): 3144, 1623, 1463, 1341, 860, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.87 (quintet, *J* = 5.8 Hz, 2H), 3.53 (t, *J* = 5.8 Hz, 4H), 7.83 (d, *J* = 8.9 Hz, 2H), 8.21 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.4 (s), 42.4 (s), 123.7 (t), 127.3 (t), 142.8 (q), 148.7 (q), 153.2 (q); HRMS (FAB); Obsd M+H = 206.0929. Calcd for $C_{10}H_{12}N_3O_2$ M+H = 206.0924.

1,4,5,6-Tetrahydro-2-(4'-cyanophenyl)pyrimidine. syrup; IR (paraffin): 3259, 2951, 2857, 2230, 1615, 1465, 1364, 1305, 853 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.88 (quintet, *J* = 5.8 Hz, 2H), 3.54 (t, *J* = 5.8 Hz, 4H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H); HRMS (FAB); Obsd M+H = 186.1031. Calcd for $C_{11}H_{12}N_3$ M+H = 186.1026.

1,4,5,6-Tetrahydro-2-(4'-bromophenyl)pyrimidine. mp 148-150 °C; IR (paraffin): 3133, 2955, 2853, 1621, 1539, 1484, 1309, 1008, 835 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.86 (quintet, *J* = 5.8 Hz, 2H), 3.50 (t, *J* = 5.8 Hz, 4H), 7.49 (d, *J* = 8.9 Hz, 2H), 7.54 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.4 (s), 42.1 (s), 123.7 (q), 127.6 (t), 131.2 (t), 135.9 (q), 153.8 (q); HRMS (FAB); Obsd M+H = 239.0181. Calcd for $C_{10}H_{12}N_2Br$ M+H = 239.0178.

1,4,5,6-Tetrahydro-2-(2'-pyridyl)pyrimidine. oil; IR (neat): 3404, 3054, 2930, 2854, 1634, 1509, 1463, 1363, 1320, 802, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.87 (quintet, *J* = 5.8 Hz, 2H), 3.55 (t, *J* = 5.8 Hz, 4H), 7.36 (dd, *J* = 4.8 and 1.2 Hz, 1H), 7.77 (td, *J* = 7.7 and 0.7 Hz, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 8.57 (dt, *J* = 4.8 and 0.7 Hz, 1H); HRMS (FAB); Obsd M+H.162.1032. Calcd for $C_9H_{12}N_3$ M+H.162.1026.

1,4,5,6-Tetrahydro-2-(1'-naphthyl)pyrimidine. mp 139-140 °C; IR (paraffin): 3142, 2922, 2853, 1615, 1462, 1376, 772 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.88 (quintet, *J* = 5.8 Hz, 2H), 3.44 (t, *J* = 5.8 Hz,

4H), 7.45–7.57 (m, 3H), 7.75 (dd, *J* = 7.3 and 1.2 Hz, 1H), 7.85–7.91 (m, 2H), 8.68 (d, *J* = 8.5 Hz, 1H) ; HRMS (FAB); Obsd M+H 211.1236. Calcd for $C_{14}H_{15}N_2$ M+H.211.1230.

1,4,5,6-Tetrahydro-2-(2'-thienyl)pyrimidine. mp 167-171 °C; IR (paraffin): 3186, 2923, 2853, 1605, 1463, 1362, 862, 718 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.87 (quintet, *J* = 5.8 Hz, 2H), 3.50 (t, *J* = 5.8 Hz, 4H), 7.00 (dd, *J* = 3.6 and 5.1 Hz, 1H), 7.20 (dd, *J* = 1.2 and 3.6 Hz, 1H), 7.30 (dd, *J* = 1.2 and 5.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9 (s), 42.3 (s), 123.6 (t), 127.1 (t), 127.3 (t), 141.9 (q), 149.9 (q); HRMS (FAB); Obsd M+H = 167.0643. Calcd for $C_8H_{11}N_2S$ M+H = 167.0637.

1,4,5,6-Tetrahydro-2-(2'-phenylethyl)pyrimidine. oil; IR (neat): 3154, 2938, 1654, 1454, 1319, 1205, 752, 700 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$): δ = 1.72 (quintet, *J* = 5.8 Hz, 2H), 2.45 (t, *J* = 8.0 Hz, 2H), 2.93 (t, *J* = 8.0 Hz, 2H), 3.24 (t, *J* = 5.8 Hz, 4H), 7.10-7.24 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.0 (s), 32.8 (s), 34.4 (s), 38.5 (s), 126.0 (t), 127.9 (t), 128.0 (t), 138.8 (q), 161.5 (q) ; HRMS (FAB); Obsd M+H = 188.1386. Calcd for $C_{12}H_{17}N_2$ M+H = 188.1386.

1,4,5,6-Tetrahydro-2-heptylpyrimidine. oil; IR (neat): 3178, 2927, 2856, 1650, 1558, 1466, 1319, 1205 cm^{-1}; ^1H NMR (400MHz, $CDCl_3$): δ = 0.87 (t, *J* = 8.0 Hz, 3H), 1.27-1.32 (m, 10H), 1.61 (quintet, *J* = 5.8 Hz, 2H), 2.22 (t, *J* = 8.1 Hz, 2H), 3.57 (t, *J* = 5.8 Hz, 4H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9 (p), 19.1 (s), 22.5 (s), 27.4 (s), 28.9 (s), 29.0 (s), 31.6 (s), 34.0 (s), 39.5 (s), 161.8 (q); HRMS (FAB); Obsd M+H = 183.1863. Calcd for $C_{11}H_{23}N_2$ M+H = 183.1856.

1,4,5,6-Tetrahydro-2-cyclohexylpyrimidine. mp 116-118 °C; IR (paraffin): 3163, 3046, 2936, 2877, 1652, 1317, 1203 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.20-1.33 (m, 5H), 1.58-1.89 (m, 7H), 2.49 (tt, *J* = 11.5 and 3.4 Hz, 1H), 3.39 (t, *J* = 5.8 Hz, 4H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0 (s), 25.2 (s), 25.7 (s), 30.2 (s), 39.4 (s), 43.4 (t), 165.6 (q) ; HRMS (FAB); Obsd M+H.167.1542. Calcd for $C_{10}H_{19}N_2$ M+H.167.1543.

1,4,5,6-Tetrahydro-2-(1'-adamantyl)pyrimidine. mp 225-228 °C; IR (paraffin): 3181, 2924, 2853, 1634, 1456, 1376, 1308, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.70-1.74 (m, 6H), 1.79 (quintet, *J* = 5.8 Hz, 2H), 1.80-2.00 (m, 6H), 2.04-2.07 (m, 3H), 3.40 (t, *J* = 5.8 Hz, 4H); HRMS (FAB); Obsd M+H = 219.1865. Calcd for $C_{14}H_{23}N_2$ M+H = 219.1856.

1,4,5,6-Tetrahydro-2-(4'-methylphenyl)-5,5-dimethylpyrimidine. mp 170.5-171.5 °C; IR (paraffin): 3194, 1618, 1506, 1359, 1282, 1041, 974, 832, 725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.98 (s, 6H), 2.35 (s, 3H), 3.11 (s, 4H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2 (p), 24.9 (p), 26.2 (q), 54.1 (s), 126.0 (t), 129.0 (t), 133.5 (q), 139.8 (q), 153.7 (q) ; HRMS (FAB); Obsd M+H = 203.1541. Calcd for $C_{13}H_{19}N_2$ M+H = 203.1543.

1,4,5,6-Tetrahydro-2-(4'-methylphenyl)-5-methylpyrimidine. mp 149-151 °C; IR (paraffin): 3150, 1617, 1540, 1507, 1378, 1333, 1281, 1267, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.99 (d, *J* = 6.8 Hz, 3H), 1.93 (m, 1H), 2.35 (s, 3H), 3.03 (dd, *J* = 12.7 and 9.6 Hz, 2H), 3.50 (dd, *J* = 13.2 and 4.6 Hz,

2H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.7 (p), 21.3 (p), 25.2 (t), 49.3 (s), 125.9 (t), 129.0 (t), 133.8 (q), 139.8 (q), 154.4 (q); HRMS (FAB); Obsd M+H = 189.1381. Calcd for $C_{12}H_{17}N_2$ M+H =189.1386.

Typical Procedure for Oxidation of 2-Substituted 1,4,5,6-Tetrahydropyrimidines to 2-Substituted Pyrimidines

To a solution of 1,4,5,6-tetrahydro-2-(4'-methylphenyl)pyrimidine (87.1 mg, 0.5 mmol) in toluene (3 mL) was added manganese dioxide (434.7 mg, 5 mmol). The obtained mixture was stirred at refluxing conditions under air. After 48 h, the mixture was filtered and evaporated in vacuo. The residue was chromatographed on silica gel (AcOEt) to give 40.9 mg of 2-(4'-methylphenyl)pyrimidine in 48% yield.

2-(4'-Methylphenyl)pyrimidine. mp 92-94 °C (lit.,[7] mp 89-89.5 °C); IR (paraffin): 2960, 2861, 1609, 1565, 1463, 1417, 1376, 1177, 788 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ = 2.43 (s, 3H), 7.16 (t, *J* = 5.0 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 2H), 8.33 (d, *J* = 8.6 Hz, 2H), 8.79 (d, *J* = 5.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5 (p), 118.8 (t), 128.1 (t), 129.4 (t), 134.8 (q), 141.0 (q), 157.2 (t), 164.8 (q); HRMS (FAB); Obsd M+H = 171.0915. Calcd for $C_{11}H_{11}N_2$ M+H = 171.0917.

2-Phenylpyrimidine. mp 38-39 °C (lit.,[8] mp 37-38 °C); IR (paraffin): 2936, 2911, 1567, 1418, 745, 691 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.15 (t, *J* = 4.9 Hz, 1H), 7.74-7.50 (m, 3H), 8.45 (d, *J* = 8.2 Hz, 2H), 8.79 (d, *J* = 4.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.0 (t), 128.1 (t), 128.5 (t), 130.7 (t), 137.5 (q), 157.2 (t), 164.7 (q); HRMS (FAB); Obsd M+H = 157.0760. Calcd for $C_{10}H_9N_2$ M+H = 157.0760.

2-(4'-Methoxyphenyl)pyrimidine. mp 60-64 °C (lit.,[8] mp 66.1-67 °C); IR (paraffin): 2963, 2861, 1603, 1565, 1415, 1167, 1024, 799 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ = 3.87 (s, 3H), 7.00 (d, *J* = 9.0 Hz, 2H), 7.10 (t, *J* = 5.0 Hz, 1H), 8.40 (d, *J* = 9.0 Hz, 2H), 8.74 (d, *J* = 5.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3 (p), 113.9 (t), 118.3 (t), 129.7 (t), 130.2 (q), 157.1 (t), 161.8 (q), 164.4 (q).

2-(4'-Nitrophenyl)pyrimidine. mp 192-194 °C (lit.,[9] mp 198-199 °C); IR (paraffin): 2966, 2877, 1561, 1514, 1419, 1348, 807, 739 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.31 (t, *J* = 4.8 Hz, 1H), 8.34 (d, *J* = 9.1 Hz, 2H), 8.65 (d, *J* = 9.1 Hz, 2H), 8.88 (d, *J* = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.3 (t), 123.8 (t), 129.1 (t), 143.4 (q), 149.4 (q), 157.6 (t), 162.7 (q).

2-(4'-Cyanophenyl)pyrimidine. mp 164-166 °C; IR (paraffin): 2974, 2222, 1552, 1416, 806 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.28 (t, *J* = 4.8 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 2H), 8.58 (d, *J* = 8.7 Hz, 2H), 8.86 (d, *J* = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 114.2 (q), 118.9 (q), 120.2 (t), 128.8 (t), 132.6 (t), 141.8 (q), 157.6 (t), 163.1 (q); HRMS (FAB); Obsd M+H = 182.0712. Calcd for $C_{11}H_8N_3$ M+H = 182.0713.

2-(4'-Bromophenyl)pyrimidine. mp 126-127 °C; IR (paraffin): 2924, 2854, 1565, 1463, 1414, 1172, 1066, 1008, 789 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.21 (t, *J* = 5.1 Hz, 1H), 7.63 (d, *J* = 8.7 Hz, 2H),

8.33 (d, *J* = 8.7 Hz, 2H), 8.80 (d, *J* = 5.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.4 (t), 125.7 (q), 129.8 (t), 131.9 (t), 136.6 (q), 157.4 (t), 164.0 (q); HRMS (FAB); Obsd M+H = 234.9862. Calcd for $C_{10}H_8N_2Br$ M+H = 234.9865.

2-(1'-Naphthyl)pyrimidine. syrup; IR (neat): 3046, 1566, 1420, 1390, 1254, 909, 798, cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.26 (q, *J* = 3.3 Hz, 1H), 7.49-7.61 (m, 3H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 8.06 (d, *J* = 7.3 Hz, 1H), 8.63 (d, *J* = 7.7 Hz, 1H), 8.92 (dd, *J* = 5.0 and 3.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.9 (t), 125.3 (t), 125.8 (t), 126.0 (t), 127.0 (t), 128.6 (t), 129.5 (t), 130.6 (t), 131.0 (q), 134.2 (q), 136.0 (q), 157.3 (t), 167.4 (q); HRMS (FAB); Obsd M+H = 207.0925. Calcd for $C_{14}H_{11}N_2$ M+H = 207.0917.

2-(1'-Adamantyl)pyrimidine. mp 73-75 °C (lit.,[10] mp 74-75 °C); IR (paraffin): 3032, 2901, 2848, 2656, 1643, 1557, 1418, 1342, 790 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ = 1.78-2.00 (m, 6H), 2.06-2.10 (m, 6H), 2.10-2.13 (m, 3H), 7.09 (t, *J* = 4.8 Hz 1H), 8.70 (d, *J* = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.6 (t), 36.7 (s), 41.2 (s), 118.1 (t), 156.7 (t), 161.5 (q), 176.7 (q); HRMS (FAB); Obsd M+H = 215.1542. Calcd for $C_{14}H_{19}N_2$ M+H = 215.1543.

2-(4'-Methylphenyl)-5-methylpyrimidine. mp 123.5-124.5 °C; IR (paraffin): 1588, 1550, 1429, 1176, 1017, 839, 785 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ =2.33 (s, 3H), 2.41 (s, 3H), 7.29 (d, *J* = 8.2 Hz, 2H), 8.29 (d, *J* = 8.2 Hz, 2H), 8.61 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.5 (p), 21.4 (p), 127.7 (t), 127.9 (q), 129.3 (t), 134.9 (q), 140.5 (q), 157.3 (t), 162.5 (q); HRMS (FAB); Obsd M+H =185.1071. Calcd for $C_{12}H_{13}N_2$ M+H = 185.1079.

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