# Convenient and Efficient Method for the Synthesis of *N*-Heteroaryl Aminonaphthols under Solvent-Free Conditions

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A convenient, efficient and green synthesis of *N*-heteroaryl aminonaphthols has been developed by one-pot, three-component condensation of *β*-naphthol, heteroaryl amines and substituted benzaldehydes under solvent-free conditions at elevated temperature. The advantages of these reactions are simplicity of the reaction procedure, short reaction times, simple work-up, catalyst-free conditions and pure products in good to excellent yields.

**Keywords** *β*-naphthol, Betti base, solvent-free, heteroaryl amine, aminonaphthol

## Introduction

Organic reactions under solvent-free or so-called solventless conditions have gained in popularity in recent years. The solid-state reaction has many advantages: reduced pollution, shorter reaction time, simpler reactors, low cost, simplicity in process and efficient work up procedures. Moreover, these factors are especially important in industry.

The Mannich reaction (aminoalkylation) is an example of multi-component condensation between a non-enolizable aldehyde, an amine (**1** or **2**) and an enolizable carbonyl compound.[1] Direct aminoalkylation has great interest in synthetic organic chemistry and considerable importance for the synthesis of drugs, pesticides and natural products.[2]

Many methods of aminoalkylation of electron rich aromatic compounds have been studied to date. Katritzky *et al*.[3] have reported an improved aminoalkylation of 2-naphthol and phenol derivatives with prefor med iminium salts derived from aromatic aldehydes, in a two-step sequence with 26%—92% yields. Moreover, aminoalkylation of electron rich aromatic compounds such as 2-naphthol for the synthesis of Betti base derivatives[4-14] in the presence of $LiClO_4$, $Sc(OTf)_3$, $Yb(OTf)_3$, $La(OTf)_3$, $YbCl_3$, $TiCl_4$ and $Me_3SiCl$ as catalysts has been reported.[15-17]

The racemic aminonaphthols (Betti bases) have been used for transformation into products with anti bacterial activity. Betti base derivatives have also provided convenient access to many useful synthetic building blocks via the amino and phenolic hydroxy functional groups.[18,19] Optical active Betti bases have been used as ligands complexed to dialkyl zinc for enantioselective addition to aryl aldehydes. These ligands show highly efficient asymmetric induction to give the corresponding alcohols up to 99% *ee* yields.[20-22] We now wish to describe the synthesis of Betti base derivatives via a facile three-component and one-pot method for aminoalkylation of 2-naphthol using aromatic aldehydes and heteroaryl amines in the absence of catalyst, short reaction time and solvent-free conditions. As such, utilization of environmental friendly (absence of organic solvent) not only provides the product in an easy work-up procedure, but also is in accord with green sustainable chemistry principles.

## Results and discussion

We have previously reported a facile synthesis of aminonaphthols (Betti bases) with heteroaryl amines in water at ambient temperature[23] and 50 ℃[24] in almost quantitative yields. In this paper, we decided to synthesize these aminonaphthols cleanly and efficiently under solventless conditions.

As the model reaction, we initially examined the one-pot, three-component, Mannich reaction of 2-naphthol, 2-aminopyrimidine and benzaldehyde in solvent-free conditions at 100—150 ℃ in the absence of acid catalyst. Our investigation demonstrated that the best result was obtained when temperature was fixed at 125 ℃ at which the reaction was completed in 1 min. Under the optimized reaction conditions, we decided to examine the other reactions in catalyst and solvent-free conditions at 125 ℃.

One-pot, three-component reaction of 2-naphthol, aromatic aldehydes **1a**—**1h** (benzaldehyde, 4-chlorobenzaldehyde, 3-chlorobenzaldehyde, 4-methyl benzal-

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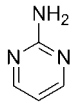
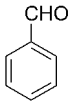
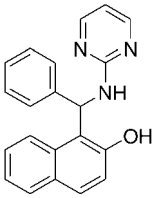
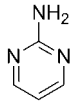
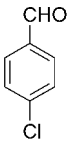
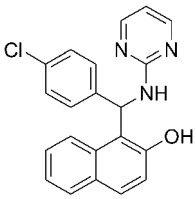
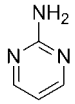
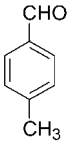
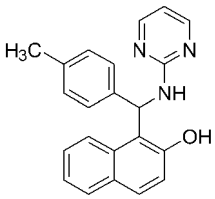
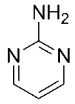
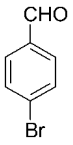
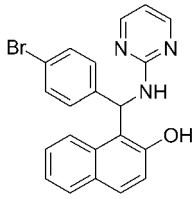
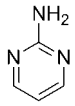
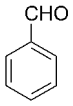
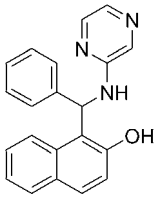
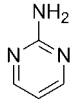
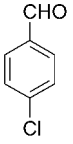
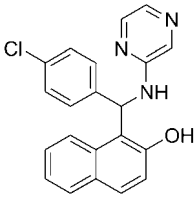
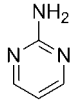
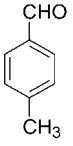
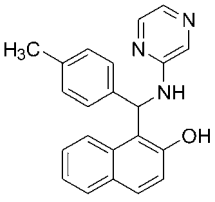
dehyde, 4-bromobenzaldehyde, 3-bromobenzaldehyde, 4-nitrobenzaldehyde and 3-nitrobenzaldehyde) and heteroaryl amines **2a**—**2d** (2-aminopyrimidine, 2-aminopyrazine, 2-aminopyridine and 3-aminopyridine) in solvent-free conditions at 125 ℃ in appropriate time (Table 1) directly afforded aminonaphthols **3a**—**3s** in good to excellent yields (Scheme 1).

These reactions require neither solvent nor inert atmosphere conditions. Each compound was isolated by the addition of ethanol to the reaction mixture and filtration of the resulting precipitate. The results of the above mentioned reactions are shown in Table 1. As indicated in Table 1, the reactions proceeded slowly with 3-aminopyridine with respect to the previously mentioned

**Table 1** Synthesis of *N*-heteroaryl aminonaphthols under solvent-free conditions at 125 ℃

| Entry | Amine | Aldehyde | Product | **3** | Time/min | Yield/% |
|---|---|---|---|---|---|---|
| 1 |  |  |  | **3a** | 1 | 90 |
| 2 |  |  |  | **3b** | 2 | 92 |
| 3 |  |  |  | **3c** | 3 | 92 |
| 4 |  |  |  | **3d** | 2 | 91 |
| 5 |  |  |  | **3e** | 3 | 94 |
| 6 |  |  |  | **3f** | 4 | 90 |
| 7 |  |  |  | **3g** | 4 | 89 |

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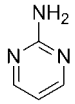
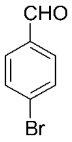
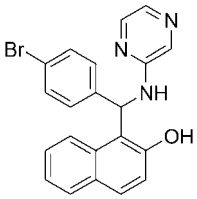
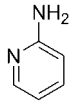
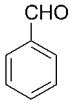
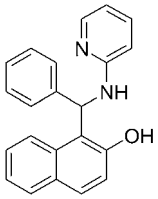
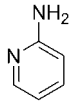
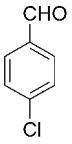
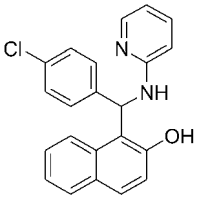
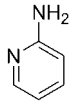
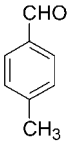
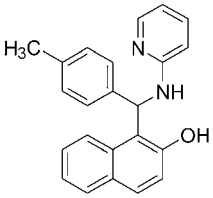
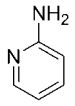
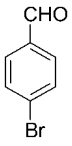
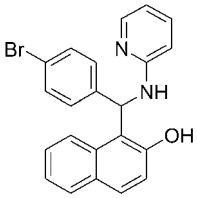
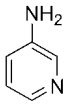
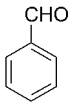
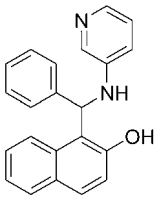
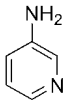
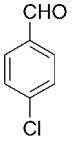
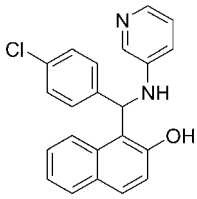
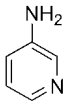
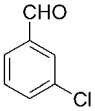
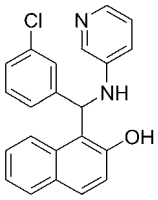
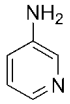
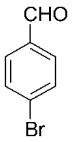
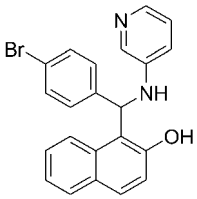
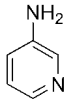
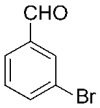
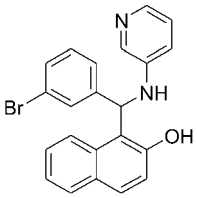
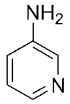
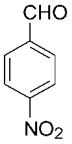
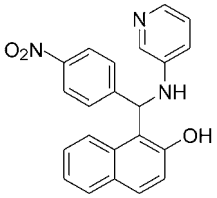
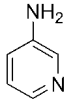
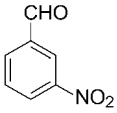
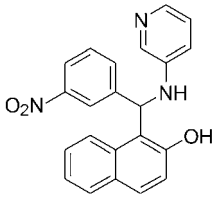
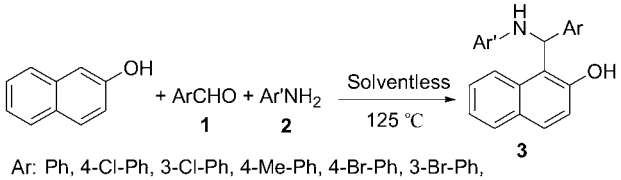
| Entry | Amine | Aldehyde | Product | **3** | Time/min | Yield/% |
|---|---|---|---|---|---|---|
| 8 |  |  |  | **3h** | 6 | 93 |
| 9 |  |  |  | **3i** | 6 | 91 |
| 10 |  |  |  | **3j** | 5 | 90 |
| 11 |  |  |  | **3k** | 5 | 93 |
| 12 |  |  |  | **3l** | 4 | 87 |
| 13 |  |  |  | **3m** | 15 | 90 |
| 14 |  |  |  | **3n** | 20 | 92 |
| 15 |  |  |  | **3o** | 15 | 89 |

Continued

| Entry | Amine | Aldehyde | Product | **3** | Time/min | Yield/% |
|---|---|---|---|---|---|---|
| 16 |  |  |  | **3p** | 20 | 91 |
| 17 |  |  |  | **3q** | 25 | 89 |
| 18 |  |  |  | **3r** | 20 | 94 |
| 19 |  |  |  | **3s** | 25 | 90 |

**Scheme 1** Synthesis of *N*-heteroaryl aminonaphthols **3**

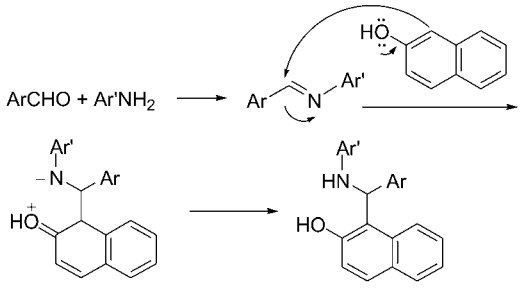



Ar: Ph, 4-Cl-Ph, 3-Cl-Ph, 4-Me-Ph, 4-Br-Ph, 3-Br-Ph, 4-$NO_2$-Ph, 3-$NO_2$-Ph

Ar': 2-pyrimidinyl, 2-pyrazinyl, 2-pyridinyl, 3-pyridinyl

heteroaryl amines. However, we proposed the mechanism for the formation of 1-[substituted phenyl (heteroarylamino)methyl] naphthalene-2-ols in Scheme 2.

**Scheme 2** Proposed reaction mechanism




In this mechanism, imine generated *in situ* from reaction of amine and aldehyde in the first step. Then, in the second step imine reacts with 2-naphthol affording the corresponding aminonaphthol. As a result, negative charge on the nitrogen in the intermediate, was stabilized with 2-aminopyrimidine, 2-aminopyrazine and 2-aminopyridine with very electron poor nature, whereas 3-aminopyridine with partially less electron deficiency was not able to stabilize the negative charge.

To make insight into the reaction mechanism, we initially studied the reaction of 2-naphthol with aldehyde. No reaction progress was observed during several hours. When the Schiff base product obtained from amine condensation with aldehyde was treated with 2-naphthol under the reaction conditions, the corresponding Betti base derivative was obtained.

## Conclusion

In conclusion, we have successfully developed a quick, convenient, efficient and uncatalyzed method for the synthesis of *N*-heteroaryl aminonaphthols (Betti bases) by condensation reaction of 2-naphthol, aldehydes and heteroaryl amines in catalyst and solvent-free conditions. The present method has advantages such as no organic solvent, generality and simplicity of procedure, lower reaction time, simple work-up, catalyst-free conditions and low cost procedure for the synthesis of these products in good to excellent yields.

CHINESE JOURNAL OF CHEMISTRY

## Experimental

All commercially available chemicals and reagents were used without further purification. Melting points (uncorrected) were determined by an Electrothermal engineering LTD 9100 apparatus. IR spectra were recorded on a Perkin-Elmer model 543, the $^1$H NMR and $^{13}$C NMR spectra were obtained using BRUKER AVANCE DRX 300 apparatus at 298 K. Chemical shifts ($\delta$) are referenced to the NMR solvent peak. Progress of the reactions was monitored by TLC using precoated sheets of silica gel Merck 60 F254 on aluminium. Mass spectra of the products were obtained with a HP (Agilent technologies) 5937 Mass Selective Detector. Elemental analyses were carried out by a CHN-O-Rapid Heraeus elemental analyzer (Wellesley, MA).

**1-(Phenyl(2-pyrimidinylamino)methyl)naphthalene-2-ol (3a)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 6.63 (t, $J$=4.8 Hz, 1H, pyrimidine-H5), 7.14—7.49 (m, 10H, Ph-H, NPh-H, methine-H and NH), 7.77—8.12 (m, 3H, NPh-H), 8.33 (d, $J$=4.8 Hz, 2H, pyrimidine-H4 and H6), 10.24 (s, 1H, OH); $^1$H NMR (DMSO-$d_6$+$D_2O$, 500 MHz) $\delta$: 6.62 (t, $J$=4.8 Hz, 1H, pyrimidine-H5), 7.12—8.08 (m, 9H, Ph-H, NPh-H and methine-H), 7.75—8.08 (m, 3H, NPh-H), 8.30 (d, $J$=4.8 Hz, 2H, pyrimidine-H4 and H6); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 51.02, 111.77, 119.61, 120.38, 123.49, 123.52, 126.95, 127.10, 127.67, 128.93, 129.24, 129.51, 130.07, 133.16, 143.95, 153.92, 153.10, 162.76; IR (KBr) $v$: 3400, 3080, 1625, 1566, 1269, 1055, 813 cm$^{-1}$; MS (EI) $m/z$: 327 ($M^+$), 231, 202, 166, 115, 97. Anal. calcd for $C_{21}H_{17}N_3O$: C 77.06, H 5.19, N 12.84; found C 69.98, H 5.17, N 12.80.

**1-[*p*-Chlorophenyl(2-pyrimidinylamino)methyl]naphthalene-2-ol (3b)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 6.65 (t, $J$=4.8 Hz, 1H, pyrimidine-H5), 7.22—7.50 (m, 9H, Ph-H, NPh-H, methine-H and NH), 7.78—8.09 (m, 3H, NPh-H), 8.33 (d, $J$=4.8 Hz, 2H, pyrimidine-H4 and H6), 10.27 (s, 1H, OH); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 50.59, 111.94, 119.57, 119.93, 123.39, 123.55, 127.77, 128.83, 128.88, 129.26, 129.55, 130.30, 131.73, 133.05, 143.05, 153.97, 159.11, 162.68; IR (KBr) $v$: 3425, 3022, 1631, 1595, 1271, 1174, 808 cm$^{-1}$; MS (EI) $m/z$: 361 ($M^+$), 265, 231, 202, 144, 115, 95. Anal. calcd for $C_{21}H_{16}ClN_3O$: C 69.71, H 4.42, N 11.61; found C 69.75, H 4.40, N 11.63.

**1-(*p*-Methylphenyl(2-pyrimidinylamino)methyl)naphthalene-2-ol (3c)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 3.05 (s, 3H, $CH_3$), 6.62 (t, $J$ = 4.7 Hz, 1H, pyrimidine-H5), 7.04 (d, $J$=7.9 Hz, 2H, Ph-H), 7.16 (d, $J$=7.9 Hz, 2H, Ph-H), 7.21—8.09 (m, 8H, NPh-H, NH and methine-H), 8.32 (d, $J$=4.7 Hz, 2H, pyrimidine-H4 and H6), 10.22 (s, 1H, OH); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 21.39, 50.82, 111.70, 119.60, 120.45, 123.45, 126.90, 127.60, 129.22, 129.46, 129.48 129.50, 129.97, 133.120, 136.11, 140.89, 153.86, 159.08, 162.73; IR (KBr) $v$: 3415, 3053, 1629, 1595, 1566, 1460, 1358, 1170, 1058, 850 cm$^{-1}$; MS (EI) $m/z$: 341 ($M^+$), 245, 231, 202, 144, 115. Anal. calcd for $C_{22}H_{19}N_3O$: C 77.42, H 5.57, N 12.31; found C 77.39, H 5.60, N 12.30.

**1-[*p*-Bromophenyl(2-pyrimidinylamino)methyl]naphthalene-2-ol (3d)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 6.65 (t, $J$=4.8 Hz, 1H, pyrimidine-H5), 7.22 (d, 2H, $J$=8.5 Hz, Ph-H) 7.44 (d, 2H, $J$=8.5 Hz, Ph-H), 7.24, 7.33, 7.45—7.50 (m, 5H, NPh-H, methine-H and NH), 7.78—8.09 (m, 3H, NPh-H), 8.33 (d, $J$=4.8 Hz, 2H, pyrimidine-H4 and H6), 10.27 (s, 1H, OH); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 50.63, 111.95, 119.55, 119.87, 120.17, 123.38, 123.55, 127.78, 129.22, 129.25, 129.55, 130.31, 131.80, 133.03, 143.51, 153.97, 159.12, 162.66; IR (KBr) $v$: 3425, 3053, 1629, 1593, 1568, 1269, 1176, 806 cm$^{-1}$; MS (EI) $m/z$: 405 ($M^+$), 407 ($M^+$), 311, 231, 202, 144, 115, 95. Anal. calcd for $C_{21}H_{16}BrN_3O$: C 62.06, H 3.94, N 10.34; found C 61.98, H 3.97, N 10.31.

**1-[Phenyl(2-pyrazinylamino)methyl]naphthalene-2-ol (3e)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 7.13—7.98, (m, 12H, Ph-H, NPh-H and methine-H), 7.67 (br, 1H, NH), 7.68 (d, $J$=2.8 Hz, 1H, pyrazine-H5), 7.92 (dd, $J$=1.3, 2.8 Hz, 1H, pyrazine-H6), 8.27 (d, $J$= 1.3 Hz, 1H, pyrazine-H3), 10.05 (s, 1H, OH); $^1$H NMR (DMSO-$d_6$+$D_2O$, 500 MHz) $\delta$: 7.12—7.34, 7.73—7.78, 7.94 (m, 12H, Ph-H, NPh-H and methine-H), 7.65 (d, $J$=2.8 Hz, 1H, pyrazine-H5), 7.90 (dd, $J$=1.3, 2.8 Hz, 1H, pyrazine-H6), 8.19 (d, $J$=1.3 Hz, 1H, pyrazine-H3); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 50.19, 119.37, 120.30, 123.27, 124.52, 126.87, 127.09, 127.13, 128.85, 129.44, 129.51, 130.12, 132.43, 133.28, 134.83, 142.25, 143.96, 153.97, 155.67; IR (KBr) $v$: 3390, 3080, 1629, 1593, 1433, 1295, 1205, 810 cm$^{-1}$; MS (EI) $m/z$: 327 ($M^+$), 231, 202, 182, 144, 115, 95. Anal. calcd for $C_{21}H_{17}N_3O$: C 77.06, H 5.19, N 12.84; found C 69.95, H 5.18, N 12.78.

**1-[*p*-Chlorophenyl(2-pyrazinylamino)methyl]naphthalene-2-ol (3f)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 7.22—7.93 (m, 12H, Ph-H, NPh-H, methine-H and NH), 7.71 (d, $J$=2.8 Hz, 1H, pyrazine-H5), 7.94 (dd, $J$=1.3, 2.8 Hz, 1H, pyrazine-H6), 8.28 (d, $J$=1.3 Hz, 1H, pyrazine-H3), 10.10 (s, 1H, OH); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 49.77, 119.33, 119.86, 123.35, 124.33, 127.30, 128.76, 128.78, 128.93, 129.50, 130.36, 131.41, 132.60, 133.15, 134.93, 142.23, 143.18, 153.98, 155.57; IR (KBr) $v$: 3251, 3047, 1627, 1591, 1431, 1292, 1203, 817 cm$^{-1}$; MS (EI) $m/z$: 361 ($M^+$), 265, 231, 202, 144, 115, 95. Anal. calcd for $C_{21}H_{16}ClN_3O$: C 69.71, H 4.42, N 11.61; found C 69.70, H 4.45, N 11.59.

**1-[*p*-Methylphenyl(2-pyrazinylamino)methyl]naphthalene-2-ol (3g)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 2.26 (s, 3H, $CH_3$), 7.04 (d, 2H, $J$=8.0 Hz, Ph-H), 7.13 (d, 2H, $J$=8.0 Hz, Ph-H), 7.22—7.98 (m, 8H, NPh-H, methine-H and NH), 7.68 (d, $J$ = 2.8 Hz, 1H, pyrazine-H5), 7.92 (dd, $J$=1.3, 2.8 Hz, 1H, pyrazine-H6), 8.26 (d, $J$=1.3 Hz, 1H, pyrazine-H3), 10.02 (s, 1H, OH); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 21.41, 50.00, 119.36, 120.38, 123.22, 124.57, 127.02, 127.05, 129.41, 129.43, 129.51, 130.01, 132.35, 133.25, 134.76, 135.80, 140.87, 142.23, 153.89, 155.65; IR (KBr) $v$: 3300, 3085, 1627, 1591, 1431, 1305, 1203, 806 cm$^{-1}$; MS (EI) $m/z$: 341 ($M^+$), 245, 231, 202, 144, 115, 95. Anal. calcd for $C_{22}H_{19}N_3O$: C 77.42, H 5.57, N 12.31; found C 77.46, H 5.59, N 12.28.

**1-[*p*-Bromophenyl(2-pyrazinylamino)methyl]naphthalene-2-ol (3h)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 7.16 (d, 2H, $J$=8.5 Hz, Ph-H), 7.43 (d, 2H, $J$=8.5 Hz, Ph-H), 7.20—7.92 (m, 8H, NPh-H, methine-H and NH), 7.71 (d, $J$=2.8 Hz, 1H, pyrazine-H5), 7.94 (dd, $J$=1.3, 2.8 Hz, 1H, pyrazine-H6), 8.28 (d, $J$=1.3 Hz, 1H, pyrazine-H3), 10.09 (s, 1H, OH); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 49.76, 119.30, 119.79, 119.82, 123.35, 124.30, 127.30, 129.32, 129.49, 130.37, 130.40, 131.68, 132.59, 133.12, 134.92, 142.22, 143.64, 153.96, 155.54,; IR (KBr) $v$: 3240, 3120, 1625, 1591, 1429, 1309, 1203, 1068, 806 cm$^{-1}$; MS (EI) $m/z$: 405 ($M^+$), 407 ($M^+$), 311, 231, 202, 144, 115. Anal. calcd for $C_{21}H_{16}BrN_3O$: C 62.06, H 3.94, N 10.34; found C 62.01, H 3.92, N 10.38.

**1-[Phenyl(2-pyridinylamino)methyl]naphthalene-2-ol (3i)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 6.52—6.50 (m, 1H, pyridine-H), 6.82 (d, $J$=8.4 Hz, 1H, pyridine-H), 7.12—7.41 (m, 11H, Ph-H, NPh-H, pyridine-H, methine-H and NH), 7.74 — 8.01 (m, 4H, NPh-H), 10.23 (s, 1H, OH); $^1$H NMR (DMSO-$d_6$+$D_2O$, 500 MHz) $\delta$: 6.53—6.51 (m, 1H, pyridine-H), 6.73 (d, $J$=8.4 Hz, 1H, pyridine-H), 7.11—7.40 (m, 10H, Ph-H, NPh-H, pyridine-H and methine-H), 7.72—7.99 (m, 4H, NPh-H); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 50.57, 109.77, 113.02, 119.62, 121.14, 123.22, 124.64, 126.71, 126.99, 127.08, 128.75, 129.36, 129.55, 129.89, 133.24, 137.73, 144.55, 148.09, 153.99, 159.27; IR (KBr) $v$: 3365, 3020, 1606, 1568, 1512, 1274, 1160, 810 cm$^{-1}$; MS (EI) $m/z$: 326 ($M^+$), 284, 157,101, 144, 88. Anal. calcd for $C_{22}H_{18}N_2O$: C 80.98, H 5.52, N 8.58; found C 80.94, H 5.55, N 8.61.

**1-[*p*-Chlorophenyl(2-pyridinylamino)methyl]naphthalene-2-ol (3j)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 6.53—6.51 (m, 1H, pyridine-H), 6.82 (d, $J$=8.4 Hz, 1H, pyridine-H), 7.19—7.41 (m, 10H, Ph-H, NPh-H, pyridine-H, methine-H and NH), 7.75 — 7.98 (m, 4H, NPh-H), 10.21 (s, 1H, OH); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 50.12, 109.91, 113.18, 119.55, 120.68, 123.31, 124.47, 127.17, 128.67, 128.96, 129.43, 129.54, 130.13, 131.22, 133.16, 137.70, 143.88, 148.13, 153.99, 159.18; IR (KBr) $v$: 3408, 3060, 1614, 1568, 1515, 1274, 1155, 819 cm$^{-1}$; MS (EI) $m/z$: 360 ($M^+$), 265, 231, 202, 144, 115, 94, 79. Anal. calcd for $C_{22}H_{17}ClN_2O$: C 73.23, H 4.71, N 7.76; found C 73.27, H 4..65, N 7.78.

**1-[*p*-Methylphenyl(2-pyridinylamino)methyl]naphthalene-2-ol (3k)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 2.22 (s, 3H, $CH_3$), 6.51—6.49 (m, 1H, pyridine-H), 6.80 (d, $J$=8.4 Hz, 1H, pyridine-H), 7.03 (d, 2H, $J$=8.0 Hz, Ph-H) 7.14 (d, 2H, $J$=8.0 Hz, *Ph-H*), 7.19—7.40 (m, 6H, NPh-H, pyridine-H, methine-H and NH), 7.73—7.99 (m, 4H, NPh-H), 10.25 (s, 1H, OH); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 21.42, 50.51, 109.74, 113.00, 119.72, 121.28, 123.21, 124.73, 126.95, 127.06, 129.37, 129.40, 129.61, 129.84, 133.25, 135.68, 137.76, 141.43, 148.07, 154.02, 159.29; IR (KBr) $v$: 3490, 3018, 1614, 1565, 1515, 1271, 1155, 811 cm$^{-1}$; MS (EI) $m/z$: 340 ($M^+$), 245, 231, 202, 195, 144, 115, 94, 79. Anal. calcd for $C_{23}H_{20}N_2O$: C 81.17, H 5.88, N 8.23; found C 81.12, H 5.59, N 8.20.

**1-[*p*-Bromophenyl(2-pyridinylamino)methyl]naphthalene-2-ol (3l)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 6.53—6.51 (m, 1H, pyridine-H), 6.82 (d, $J$=8.4 Hz, 1H, pyridine-H), 7.17 (d, 2H, $J$=8.5 Hz, Ph-H), 7.42 (d, 2H, $J$ = 8.5 Hz, Ph-H), 7.20 — 7.40 (m, 6H, NPh-H, pyridine-H, methine-H and NH), 7.75—7.98 (m, 4H, NPh-H), 10.20 (s, 1H, OH); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 50.16, 109.91, 113.18, 119.52, 119.65, 120.63, 123.30, 124.46, 127.18, 129.37, 129.42, 129.53, 130.13, 131.57, 133.15, 137.67, 144.36, 148.13, 153.97, 159.17; IR (KBr) $v$: 3400, 3057, 1614, 1568, 1515, 1272, 1155, 817 cm$^{-1}$; MS (EI) $m/z$: 404 ($M^+$), 406 ($M^+$), 311, 231, 202, 144, 115, 94, 79. Anal. calcd for $C_{22}H_{17}BrN_2O$: C 65.18, H 4.19, N 6.91; found C 65.14, H 4.22, N 6.88.

**1-[Phenyl(3-pyrimidinylamino)methyl]naphthalene-2-ol (3m)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 6.55 (d, $J$=6.6 Hz, 1H, methine-H), 6.72 (d, $J$=6.6 Hz, 1H, NH), 7.00—8.15 (m, 15H, NPh-H, Ph-H and Pyridine-H), 10.25 (s, 1H, OH); $^1$H NMR (DMSO-$d_6$+$D_2O$, 500 MHz) $\delta$: 6.57 (s, 1H, methine-H), 7.01—8.09 (m, 15H, NPh-H, Ph-H and Pyridine-H); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 53.39, 119.08, 119.17, 119.56, 123.26, 124.34, 124.94, 126.91, 127.32, 127.59, 129.06, 129.45, 129.70, 130.19, 133.08, 136.73, 138.11, 143.11, 145.44, 153.88; IR (KBr) $v$: 3394, 3068, 2900, 1625, 1240, 804 cm$^{-1}$; MS (EI) $m/z$: 326 [$M^+$], 231, 202, 94. Anal. calcd for $C_{22}H_{18}N_2O$: C 80.98, H 5.52, N 8.58; found C 80.87, H 5.60, N 8.49.

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**1-[4-Chlorophenyl(3-pyrimidinylamino)methyl]naphthalene-2-ol (3n)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 6.60 (d, $J$=6.6 Hz, 1H, methine-H), 6.72 (d, $J$=6.6 Hz, 1H, NH), 7.02—8.12 (m, 14H, NPh-H, Ph-H and Pyridine-H), 10.25 (s, 1H, OH); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 52.86, 119.07, 119.21, 119.26, 123.33, 124.36, 124.69, 127.08, 128.99, 129.42, 129.51, 129.66, 130.39 131.83, 132.95, 136.76, 138.26, 142.27, 145.27, 153.85; IR (KBr) $v$: 3373, 3051, 2917, 1627, 1299, 806 cm$^{-1}$; MS (EI) $m/z$: 360 [M+], 265, 231, 202, 144, 94. Anal. calcd for $C_{22}H_{17}ClN_2O$: C 73.23, H 4.71, N 7.76; found C 73.19, H 4.64, N 7.80.

**1-[3-Chlorophenyl(3-pyrimidinylamino)methyl]naphthalene-2-ol (3o)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 6.57 (d, $J$=6.8 Hz, 1H, methine-H), 6.74 (d, $J$=6.8 Hz, 1H, NH), 7.02—8.13 (m, 14H, NPh-H, Ph-H and Pyridine-H), 10.28 (s, 1H, OH); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 52.97, 119.10, 119.17, 119.24, 123.39, 124.37, 124.52, 126.29, 127.15, 127.23, 127.32, 129.55, 129.61, 130.48, 130.96, 132.93, 133.81, 136.77, 138.35, 145.16, 145.95, 153.90; IR (KBr) $v$: 3404, 3051, 2906, 1625, 1292, 815 cm$^{-1}$; MS (EI) $m/z$: 360, [M$^+$], 265, 231, 216, 202, 144, 94. Anal. calcd for $C_{22}H_{17}ClN_2O$: C 73.23, H 4.71, N 7.76; found C 73.16, H 4.68, N 7.72.

**1-[4-Bromophenyl(3-pyrimidinylamino)methyl]naphthalene-2-ol (3p)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 6.53 (d, $J$=6.3 Hz, 1H, methine-H), 6.71 (d, $J$=6.3 Hz, 1H, NH), 7.02—8.12 (m, 14H, NPh-H, Ph-H and Pyridine-H), 10.26 (s, 1H, OH); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 52.93, 119.10, 119.25, 120.33, 123.35, 124.38, 124.60, 124.72, 127.10, 129.52, 129.67, 129.82, 130.41, 131.91, 132.96, 136.78, 138.28, 142.75, 145.29, 153.87; IR (KBr) $v$: 3373, 3051, 2915, 1627, 1249, 806 cm$^{-1}$; MS (EI) $m/z$: 404 [M$^+$], 406 [M$^+$], 311, 231, 202, 144, 94. Anal. calcd for $C_{22}H_{17}BrN_2O$: C 65.18, H 4.19, N 6.91; found C 65.21, H 4.11, N 6.89.

**1-[3-Bromophenyl(3-pyrimidinylamino)methyl]naphthalene-2-ol (3q)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 6.59 (d, $J$=6.3 Hz, 1H, methine-H), 6.75 (d, $J$=6.3 Hz, 1H, NH), 7.02—8.15 (m, 14H, NPh-H, Ph-H and Pyridine-H), 10.32 (s, 1H, OH); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 52.96, 119.10, 119.15, 119.25, 122.51, 123.39, 124.37, 126.67, 127.21, 129.55, 129.60, 130.13, 130.21, 130.48, 131.25, 131.90, 132.94, 136.78, 138.36, 145.16, 146.19, 153.94; IR (KBr) $v$: 3394, 3053, 2923, 1625, 1238, 817 cm$^{-1}$; MS (EI) $m/z$: (%) 404 [M$^+$], 406 [M$^+$], 311, 231, 202, 144, 95. Anal. calcd for $C_{22}H_{17}BrN_2O$: C 65.18, H 4.19, N 6.91; found C 65.14, H 4.16, N 6.97.

**1-[4-Nitrophenyl(3-pyrimidinylamino)methyl]naphthalene-2-ol (3r)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 6.68 (d, $J$=6.3 Hz, 1H, methine-H), 6.81 (d, $J$=6.3 Hz, 1H, NH), 7.06—8.19 (m, 14H, NPh-H, Ph-H and Pyridine-H), 10.35 (s, 1H, OH); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 53.29, 119.08, 119.11, 119.14, 119.37, 123.47, 124.28, 124.44, 127.37, 128.69, 129.58, 129.64, 130.76, 132.92, 136.86, 138.53, 145.17, 147.01, 151.70, 153.93; IR (KBr) $v$: 3406, 3087, 2916, 1627, 1514, 1346, 1244, 827 cm$^{-1}$; MS (EI) $m/z$: 371 [M$^+$], 260, 231, 202, 144, 94. Anal. calcd for $C_{22}H_{17}N_3O_3$: C 71.16, H 4.58, N 11.32; found C 71.20, H 4.57, N 11.22.

**1-[3-Nitrophenyl(3-pyrimidinylamino)methyl]naphthalene-2-ol (3s)**

Colorless crystals; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 6.71 (d, $J$=6.7 Hz, 1H, methine-H), 6.93 (d, $J$=6.7 Hz, 1H, NH), 7.10—8.23 (m, 14H, NPh-H, Ph-H and Pyridine-H), 10.40 (s, 1H, OH); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 53.01, 118.75, 119.21, 120.07, 122.09, 122.46, 123.49, 124.22, 124.71, 127.45, 129.59, 129.64, 130.60, 130.80, 132.91, 134.32, 136.07, 137.90, 145.28, 145.81, 148.71, 154.10; IR (KBr) $v$: 3390, 3078, 2925, 1622, 1527, 1348, 1236, 804 cm$^{-1}$; MS (EI) $m/z$: 371 [M$^+$], 276, 260, 231, 202, 144, 94. Anal. calcd for $C_{22}H_{17}N_3O_3$: C 71.16, H 4.58, N 11.32; found C 71.11, H 4.50, N 11.25.

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