Mol Divers (2015) 19:87–101
DOI 10.1007/s11030-014-9559-x

FULL-LENGTH PAPER

Synthesis of a new class of Betti bases by the Mannich-type reaction: efficient, facile, solvent-free and one-pot protocol

Aziz Shahrisa · Reza Teimuri-Mofrad · Mahdi Gholamhosseini-Nazari

Received: 28 April 2014 / Accepted: 25 November 2014 / Published online: 21 December 2014

Abstract A variety of organocatalysts has been screened for the synthesis of arylaminonaphthols. It has been shown that (*N,N*-dimethylethanolamine) is a highly efficient organocatalyst for the direct synthesis of a novel class of arylaminonaphthols via three-component condensation of 2-naphthol, aldehydes, and arylamines under solvent-free conditions. Mild, one-pot, and green reaction conditions, relatively short reaction times and good yields make this protocol highly significant. 25 new compounds have been synthesized by this method.

Keywords 1-Aminoalkyl-2-naphthol · Betti base · Organocatalyst · Solvent-free reaction · One-pot · *N*,*N*-dimethylethanolamine · MCRs

Introduction

Compounds bearing 1,3-amino-oxygenated functional groups are frequently found in various biologically active natural products [1] and are used as drugs [1–3]. One important class of such compounds is the aminonaphthols, so-called 'Betti bases' [4]. In light of these compounds possesing beneficial biological properties, such as antipain, antibacterial, hypotensive, and bradycardiac activities [5–8] (Fig. 1), the catalytic and synthetic applications of Betti bases, as well as the synthesis of substituted Betti base derivatives have become an important area in synthetic organic chemistry [4,9].

Since Betti's first report in 1900, several methods for the synthesis of aminonaphthols have been developed. The most popular method for the preparation of aminonaphthols is the reaction of an aldehyde, 2-naphthol and an aliphatic amine (Scheme 1) [4]. Another approach is the hydrolysis of preformed amidoalkyl naphthols. For this reason, the synthesis of amidoalkyl naphthols has received a lot of attention (Scheme 1) [10–19]. A literature survey shows that most of the reported methods suffer from disadvantages, such as low product yields, expensive catalysts, long-reaction times and laborious workup [4,9]. Furthermore, most of these methods are unsuccessful [20–22] or inefficient [23,24] for the synthesis of arylaminonaphthols. However, some hetroarylaminonaphthols have been synthesized when using electron-rich hetroaromatic amines as amine sources [25–27].

Organocatalysts have shown immense promise in multicomponent reactions [28]. The choice of organic catalyst has some advantages including (i) easy preparation or availability, (ii) performing reactions under milder reaction conditions, (iii) selectivity, and (iv) compatibility with numerous functional groups [29]. Recently, various organocatalysts including derivatives of *N*,*N*-dialkylethanolamine have been used to catalyze Michael addition [30] and Friedel–Crafts alkylation reactions [31,32]. Nevertheless, to the best of our knowledge, there are no reports for the synthesis of Betti bases using organocatalysts. Therefore, we selected several commercially available amines and aminoalcohols to catalyze the Betti reaction, taking advantage of their hydrogen bond donor and/or acceptor attributes.

As a part of our ongoing interest in the study of MCRs [33–37], herein we describe the use of bifunctional organocatalysts as catalysts for the direct and efficient synthesis of alkyl- and arylaminonaphthol derivatives via the one-pot and

Electronic supplementary material The online version of this article (doi:10.1007/s11030-014-9559-x) contains supplementary material, which is available to authorized users.

A. Shahrisa (✉) · R. Teimuri-Mofrad · M. Gholamhosseini-Nazari
Department of Organic and Biochemistry, Faculty of Chemistry, University of Tabriz, 5166614766 Tabriz, Iran
e-mail: ashahrisa@yahoo.com

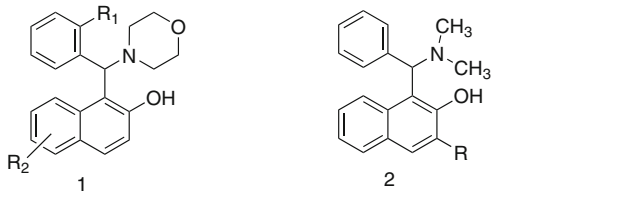


Fig. 1 A selection of aminonaphthols with antipain and antibacterial activities

solvent-free three-component condensation of β-naphthol, aldehydes, and arylamines.

Results and discussion

As a starting point for our studies, the reaction of 2-naphthol (**3a**) with benzaldehyde (**12a**) and aniline (**13a**) was chosen as our model reaction to investigate. For this, a variety of organocatalysts (Fig. 2) was tested using various organic solvents and solvent-free condition. The results are summarized in Table 1.

As shown in Table 1, different conventional organic solvents, such as EtOH, $CHCl_3$ and CH_2Cl_2 afforded low to moderate yields at r.t. (15–50 %, entries 1–15). Interestingly, the best results were achieved under solvent-free conditions. Organocatalyst IX, with one H-bond donor and one H-bond acceptor gave a promising result (70 % yield, entry 26). Although organocatalysts V, VI, and VII possess two or three H-bond donors and one H-bond acceptor, they produced lower yields (55–62 %, entries 22–24), and organocatalysts without a H-bond donor (I–IV) provided poor results (15–25 % yield, entries 18–21). These results show the importance of H-bond donor and H-bond acceptor interactions of the catalyst with substrates in these reactions. Notably, there was no need to carry out the reactions in an inert atmosphere.

To optimize the reaction conditions, the model reaction was exposed to different quantities of organocatalyst IX (5, 7.5, and 10 mol %) at various temperatures. As shown in Table 2, the best result (90 % yield) was obtained

Scheme 1 Methods for synthesis of aminonaphthols

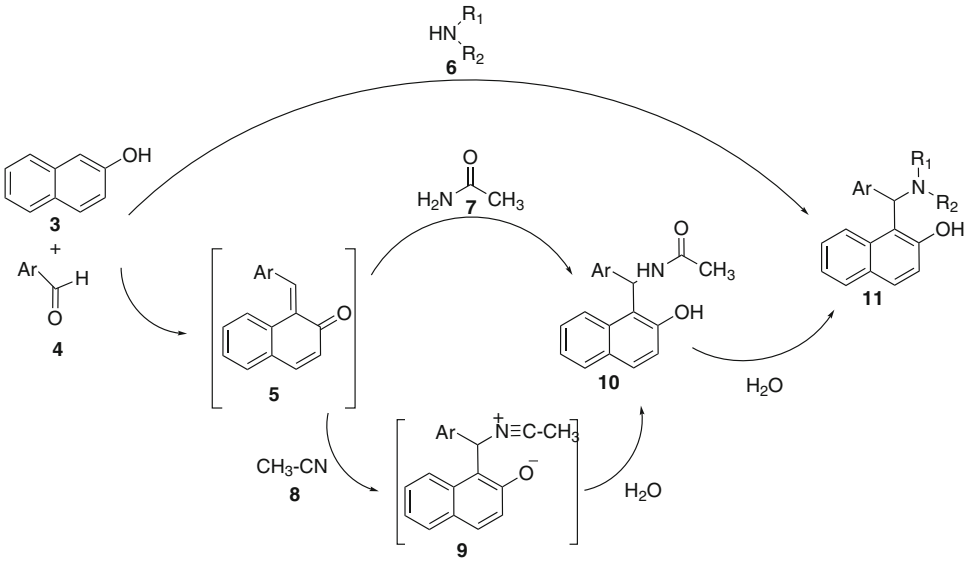


Fig. 2 Organocatalysts I–IX

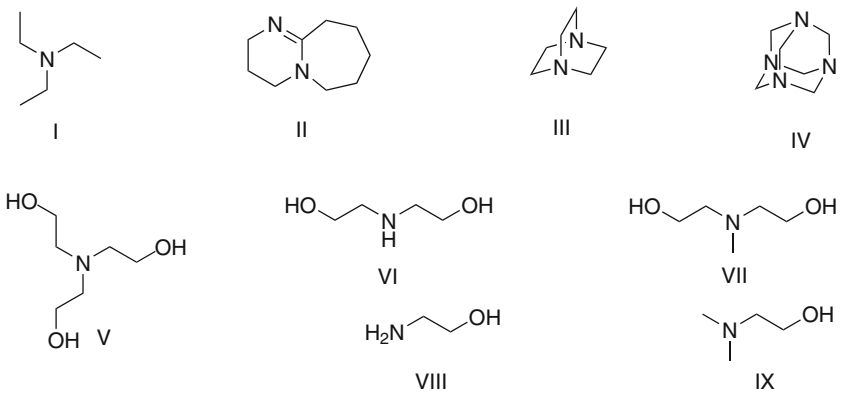
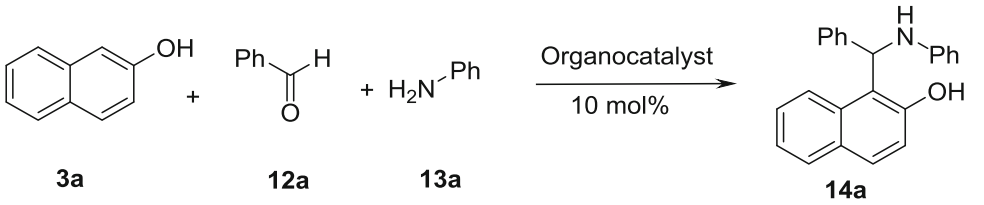


Table 1 Optimization of organocatalytic synthesis of arylaminonaphthol under various conditions



3a **12a** **13a** **14a**

Entry	Catalyst (10 mol%)	Solvent	Time (h)	Yield (%)[a]
1[b]	I	$CHCl_3$	24	20
2[b]	I	CH_2Cl_2	26	15
3[b]	I	EtOH	20	25
4[b]	II	$CHCl_3$	24	20
5[b]	III	$CHCl_3$	24	25
6[b]	IV	$CHCl_3$	24	20
7[b]	V	$CHCl_3$	24	40
8[b]	V	CH_2Cl_2	24	35
9[b]	V	EtOH	24	40
10[b]	VI	$CHCl_3$	24	45
11[b]	VII	$CHCl_3$	24	40
12[b]	VIII	$CHCl_3$	24	40
13[b]	IX	$CHCl_3$	24	45
14[b]	IX	CH_2Cl_2	24	45
15[b]	IX	EtOH	24	45
16[b]	–	EtOH	48	11
17[c]	–	EtOH	18	65
18[d]	I	–	2	25
19[d]	II	–	2	20
20[d]	III	–	2	15
21[d]	IV	–	2	20
22[d]	V	–	2	55
23[d]	VI	–	2	60
24[d]	VII	–	2	62
25[d]	VIII	–	2	50
26[d]	IX	–	2	70

[a] Isolated yield
[b] Reaction was carried out at r.t.
[c] Reaction was run at reflux condition
[d] Reaction carried out at 40 °C under solvent-free conditions

when the reaction was performed using 7.5 mol% of *N*,*N*-dimethylethanolamine (DMEA) at 50 °C (entry 6).

To explore the scope and generality of this procedure, the condensation of 2-naphthols with a variety of aromatic aldehydes and aromatic amines (Fig. 3) was examined in the presence of DMEA (7.5 mol%) at 50 °C under solvent-free condition (Table 3).

As shown in Table 3, the reactions were carried out efficiently within 30–45 min, and the desired products were produced in good to excellent yields (Fig. 4). Different substituted benzaldehydes successfully reacted with aniline and 2-naphthol giving the corresponding products **14a–i** in 81–95 % yields. Reacting substituted anilines with benzaldehyde

Table 2 Optimization of temperature and amount of DMEA in the model reaction under solvent-free condition

Entry	Catalyst amount (mol%)	Temperature (°C)	Time (min)	Yield (%)[a]
1	10	25	55	50
2	10	40	45	68
3	10	50	40	85
4	10	60	45	80
5	5.0	50	45	71
6	7.5	50	40	90

Reaction conditions 2-naphthol/benzaldehyde/morpholine/ = 1:1:1.2
[a] Isolated yield

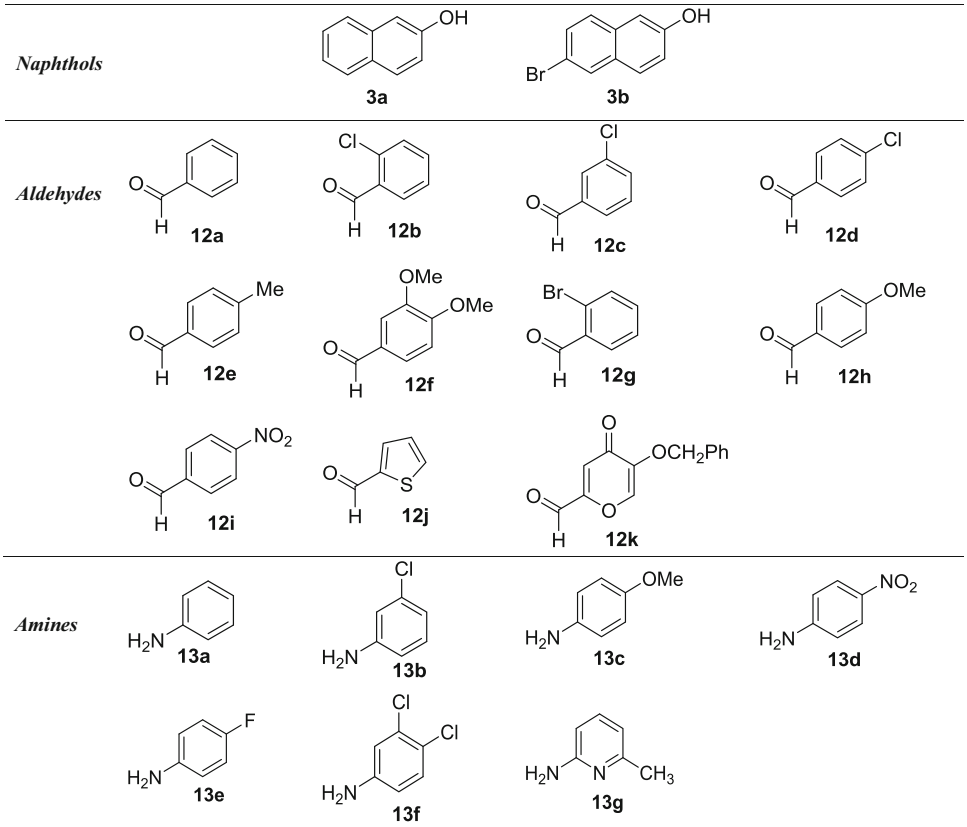


Fig. 3 Diversity of reactants used

and 2-naphthol afforded their corresponding products **14j–n** in 80–95 % yields. Also, when both of benzaldehyde and aniline were substituted the desired products **14o–q** obtained in 92–95 % yields.

The reaction of heteroaromatic aldehydes with heteroarylamines in the presence of catalytic amounts of DMEA also afforded desired products **14r–14t** in high yields (92–95 %).

To rationalize the beneficial role of DMEA, we offer two plausible interactions of bifunctional organocatalyst in this transformation (Fig. 5).

After obtaining satisfactory results for the formation of arylaminonaphthols (Fig. 4), we extended this method to the synthesis of the corresponding alkylaminonaphthol analogs under similar conditions and, as expected, the products were also obtained in good to high yields (Table 4).

A plausible mechanistic rationalization of the DMEA-catalyzed reaction is shown in Scheme 2. It is expected that the reaction proceeds via an iminium salt intermediate which is generated by the condensation of a secondary aliphatic amine with aldehyde followed by dehydration. In the next step, the nucleophilic attack of 2-naphthol to the iminium salt generates an alkylaminonaphthol. In a similar manner, corresponding arylaminonaphthols are synthesized via imine intermediates when using primary aromatic amines.

To highlight the applicability and the efficiency of our methodology, we compared the results of two DMEA-catalyzed reactions with other recently reported methodologies. As shown in Table 5, DMEA has a significant impact in the performance of the reaction proving to be convincingly superior to other catalytic methods.

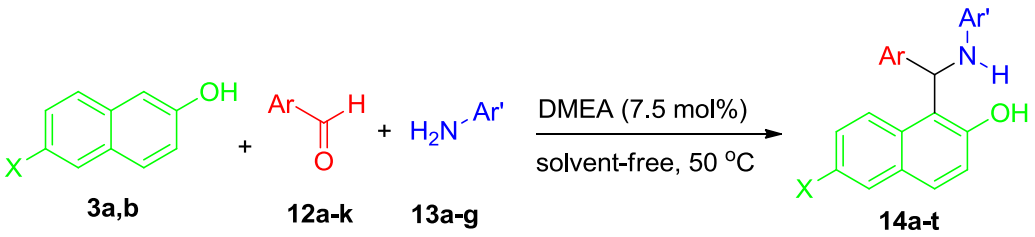
Conclusions

In conclusion, we have developed a high-yielding protocol for the synthesis of aminonaphthols using DMEA as organocatalyst. A novel series of arylaminonaphthols were synthesized via the one-pot three-component reaction of an aldehyde, an aromatic amine, and 2-naphthol in the presence of DMEA under solvent-free conditions. Our methodology proved to also be useful for the synthesis of alkylaminonaphthols. The operational simplicity of our procedure, short-reaction times, easy workup, extremely mild reaction conditions, and environmental friendliness (non-corrosive catalyst) make our method very attractive.

Experimental

All chemicals were purchased from Merck or Aldrich chemical companies and used without further purification. Melting points were determined on a MEL-TEMP model 1202D and

Table 3 Synthesis of arylaminonaphthols using DMEA under solvent-free conditions



Entry	Reactant	Product	Time (min)	Yield (%)[a]
1	3a/12a/13a	**14a**	40	90
2	3a/12b/13a	**14b**	45	90
3	3a/12c/13a	**14c**	45	90
4	3a/12d/13a	**14d**	40	92
5	3a/12e/13a	**14e**	40	92
6	3a/12f/13a	**14f**	40	95
7	3a/12g/13a	**14g**	45	81
8	3b/12g/13a	**14h**	45	85
9	3a/12h/13a	**14i**	40	92
10	3a/12a/13b	**14j**	45	90
11	3a/12a/13c	**14k**	45	80
12	3a/12a/13d	**14l**	35	95
13	3a/12a/13e	**14m**	40	90
14	3a/12a/13f	**14n**	40	90
15	3a/12d/13b	**14o**	40	92
16	3a/12e/13c	**14p**	38	95
17	3a/12d/13e	**14q**	40	92
18	3a/12i/13g	**14r**	30	93
19	3a/12j/13a	**14s**	30	92
20	3a/12k/13a	**14t**	30	95

Reaction conditions 2-naphthol/aldehyde/amine = 1:1:1.2 and DMEA (7.5 mol%) at 50 °C under solvent free condition
[a] Isolated yield

are uncorrected. FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer as KBr disks. The ^{1}H NMR spectra were recorded on a Bruker Spectrospin Advance 400 spectrometer. ^{13}C NMR spectra were also recorded on the same instrument at 100 MHz. All chemical shifts were reported as δ (ppm) relative to solvent's signals as internal standards and coupling constants (J) are given in Hz. Multiplicities are indicated as the following: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doubled doublet. Preparative layer chromatography was done using silica gel (Merk Kieselgel 60 HF254, no. 7739).

General procedure for the synthesis of aminonaphthols

To a mixture of 2-naphthol (1 mmol), aldehyde (1 mmol) and amine (1.2 mmol) was added DMEA (7.5 mol%). The mixture was stirred at 50 °C under solvent-free conditions in an oil bath for an appropriate time (Tables 3, 4), and the reaction was monitored by TLC (acetone/chloroform/*n*-hexane: 1/2/5). After completion of the reaction, the mixture was cooled to room temperature, ethanol (10 mL) was added, and the mixture was stirred for 10 min. The resulting solid was collected by filtration. Crude products (**14l**, **14m**, **14q**, **14r**, and **14t**) were purified by preparative layer chromatography on silica gel using (EtOAc / *n*-hexane, 1:5). Compounds (**14a-k**, **14n**, **14o**, **14p**, **14s**, and **16a-j**) were purified by recrystallization (EtOH/acetone, 4:1). All compounds were characterized by melting point (mp), IR, ^{1}H NMR, ^{13}C NMR and elemental (C, H, N) analysis (Fig. 5).

1-[Phenyl(phenylamino)methyl]naphthalen-2-ol (**14a**)

White solid; Yield 90 %; mp: 132–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.15 (1H, bs, N–H, disappeared in

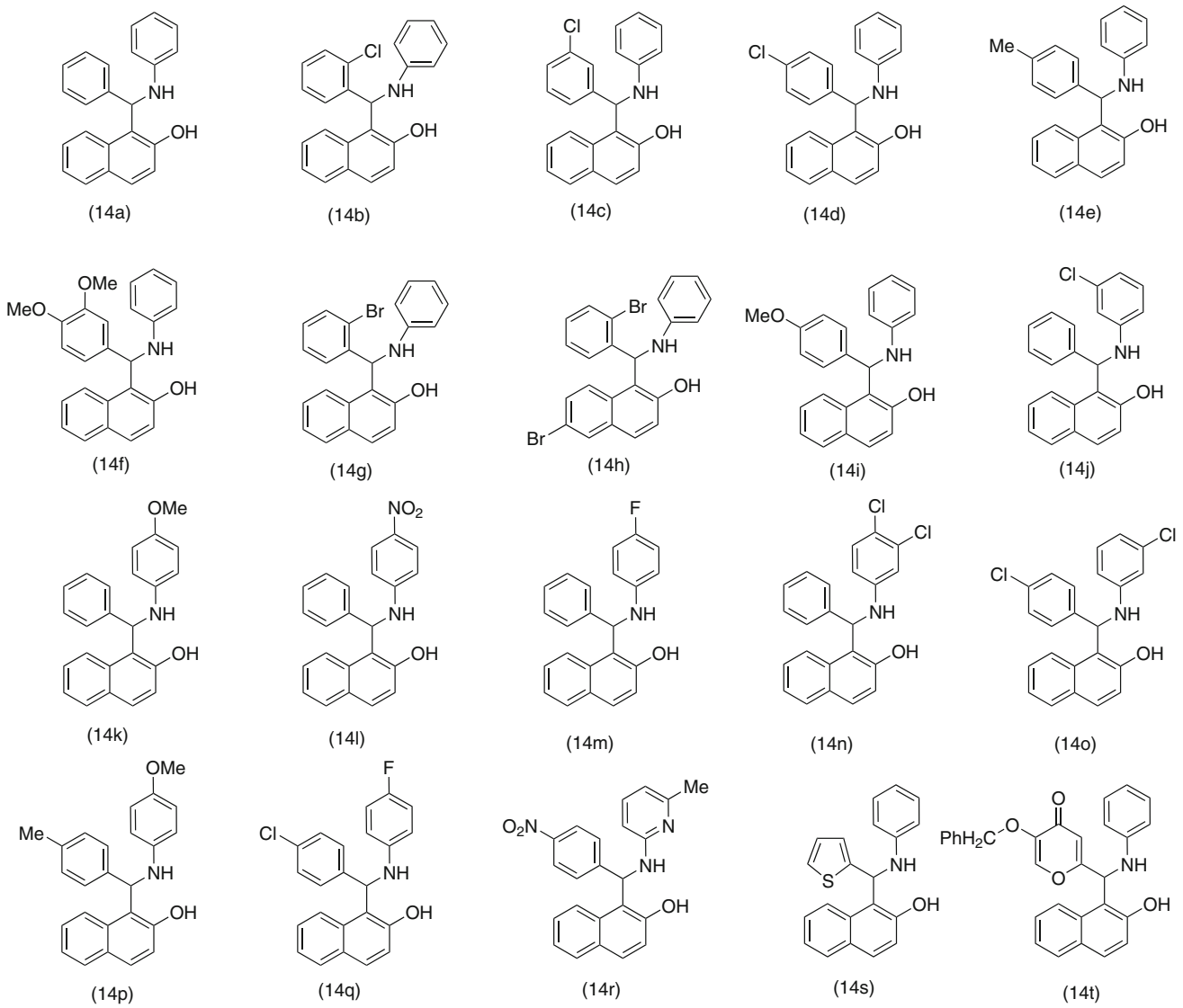


Fig. 4 Products **14a–14t**

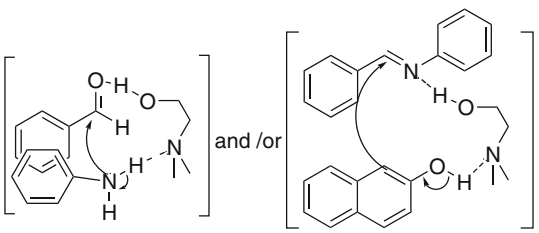


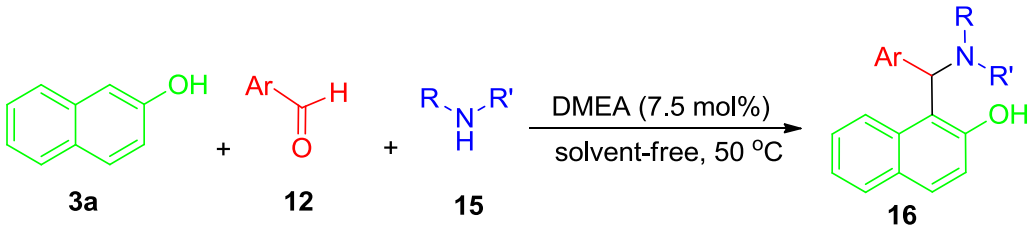
Fig. 5 Two plausible interactions for catalytic activity of bifunctional DMEA

the presence of D_2O), 6.17 (1H, s, methine-H), 6.76 (2H, d, J = 7.6 Hz, Ar–H), 6.92 (1H, t, J = 7.3 Hz, Ar–H), 7.13–7.49 (10H, m, Ar–H), 7.76–7.82 (3H, m, Ar–H), 11.54 (1H, bs, OH, disappeared in the presence of D_2O) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 61.7, 115.2, 118.9, 120.4, 120.8, 121.8, 125.5, 125.8, 126.9, 127.0, 127.6, 127.9, 128.2, 128.3, 128.4, 128.9, 139.9, 145.6, 156.7 ppm.

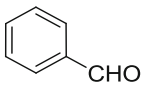
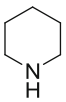
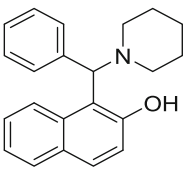
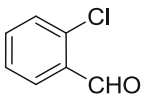
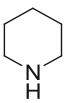
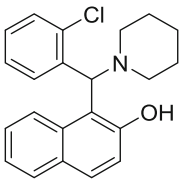
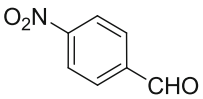
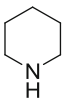
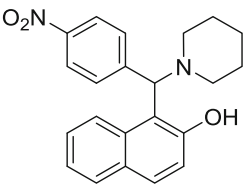
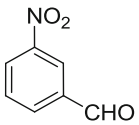
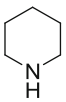
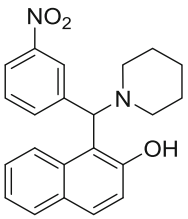
*1-[(2-Chlorophenyl)(phenylamino)methyl]naphthalen-2-ol (**14b**)*

Colorless crystals; Yield 90 %; mp: 150–152 °C; FT-IR (KBr) ν 3418, 3301, 3059, 2906, 1604, 1490, 1229, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.07 (1H, bs, N–H), 6.54 (1H, s, methine-H), 6.80 (2H, d, J = 8 Hz, Ar–H), 6.93 (1H, t, J = 7.3 Hz, Ar–H), 7.08–7.18 (5H, m, Ar–H), 7.22–7.38 (3H, m, Ar–H), 7.49 (1H, d, J = 8 Hz, Ar–H), 7.58 (1H, d, J = 8.4 Hz, Ar–H), 7.77–7.79 (2H, m, Ar–H), 11.64 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 58.4, 111.7, 115.5, 118.9, 120.3, 121.1, 121.9, 126.0, 126.7, 127.9, 128.0, 128.3, 129.0, 129.1, 129.2, 129.3, 130.4, 132.8,

Table 4 Synthesis of alkylaminonaphthols with DMEA as organocatalyst



3a 12 15 16

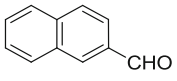
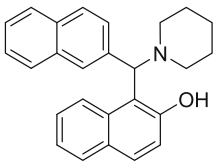
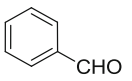
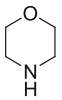
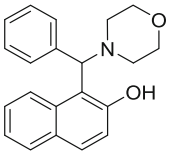
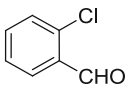
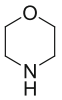
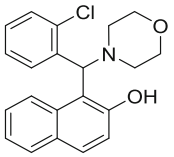
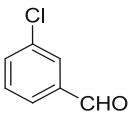
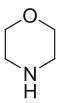
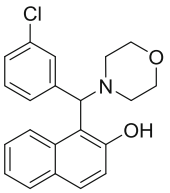
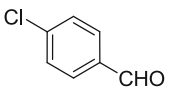
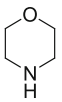
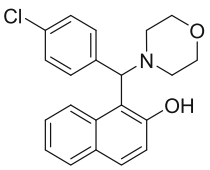
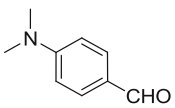
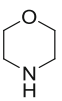
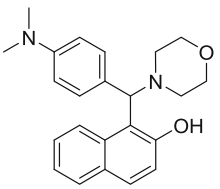
Entry	Aldehyde	Amine	Product	Time (min)	Yield (%)[a]	Obs.mp (°C)	Lit.mp (°C)
1			 (16a)	40	87	192–194	193–195 [38]
2			 (16b)	37	87	150–152	-
3			 (16c)	40	88	177–179	-
4			 (16d)	40	85	169–171	-

136.4, 145.9, 156.0 ppm. Anal. Calcd. For $C_{23}H_{18}ClNO$: C, 76.77; H, 5.04; N, 3.89; Found: C, 76.51; H, 5.12; N, 3.75 %.

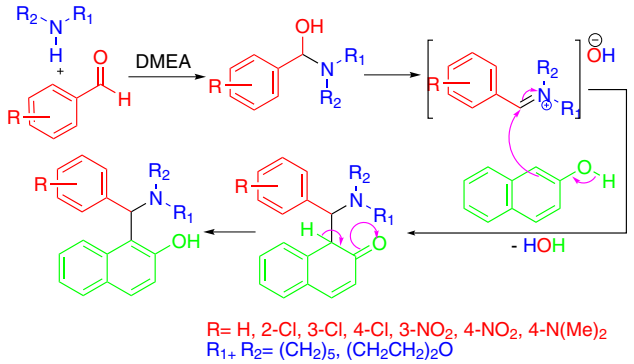
1-[(3-Chlorophenyl)(phenylamino)methyl]naphthalen-2-ol (**14c**)

Colorless crystals; Yield 90 %; mp: 138–140 °C; FT-IR (KBr) ν 3378, 3337, 3054, 2902, 1601, 1496, 1231, 754 cm^{-1};[1] H NMR (400 MHz, $CDCl_3$): δ 4.12 (1H, bs, N–H), 6.12 (1H, s, methine-H), 6.74 (2H, d, J = 8 Hz, Ar–H), 6.92 (1H, t, J = 7.3 Hz, Ar–H), 7.12–7.20 (4H, m, Ar–H), 7.31 (1H, t, J = 7.3 Hz, Ar–H), 7.37–7.43 (3H, m, Ar–H), 7.64 (1H, s, Ar–H), 7.73–7.79 (3H, m, Ar–H), 11.36 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 60.9, 112.1, 115.2, 119.0, 120.1, 120.9, 121.9, 122.2, 125.6, 125.9, 128.1, 128.4, 129.3, 129.9, 130.0, 130.3, 130.7, 142.1, 145.3, 155.1

Table 4 continued

Entry	Aldehyde	Amine	Product	Time (min)	Yield (%)[a]	Obs.mp (°C)	Lit.mp (°C)
5			 **(16e)**	34	88	240 °C (dec.)	-
6			 **(16f)**	45	92	174–176	175–177 [39]
7			 **(16g)**	40	83	163–165	-
8			 **(16h)**	45	82	160–162	-
9			 **(16i)**	35	89	155–157	160–162 [38]
10			 **(16j)**	35	83	135–137	-

Reaction conditions 2-naphthol/aldehyde/amine = 1:1:1.2 and DMEA (7.5 mol%) at 50 °C under solvent free condition
[a] Isolated yield



Scheme 2 Proposed mechanism for the synthesis of alkylaminonaphthols via reaction of aliphatic amines, aromatic aldehydes, and 2-naphthol catalized by DMEA

ppm. Anal. Calcd. For $C_{23}H_{18}ClNO$: C, 76.77; H, 5.04; N, 3.89; Found: C, 76.48; H, 5.14; N, 3.78 %.

1-[(4-Chlorophenyl)(phenylamino)methyl]naphthalen-2-ol (**14d**)

Colorless crystals; Yield 92 %; mp: 121–123 °C; FT-IR (KBr) ν 3412, 3348, 3060, 2962, 1623, 1599, 1491, 1220, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.04 (1H, bs, N–H), 6.11 (1H, s, methine-H), 6.75 (1H, d, J = 8 Hz, Ar–H), 6.85–6.92 (1H, m, Ar–H), 7.05 (1H, t, J = 8 Hz, Ar–H), 7.13–7.21 (3H, m, Ar–H), 7.29–7.46 (7H, m, Ar–H), 7.72–7.83 (2H, m, Ar–H), 11.41 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 60.9, 111.7, 115.2, 118.0, 121.8, 122.7, 123.2, 124.6, 125.8, 127.2, 127.6, 128.4, 128.5, 129.6, 132.5, 140.1, 145.5, 151.6, 155.0 ppm. Anal. Calcd. For $C_{23}H_{18}ClNO$: C, 76.77; H, 5.04; N, 3.89; Found: C, 76.54; H, 5.09; N, 3.81 %.

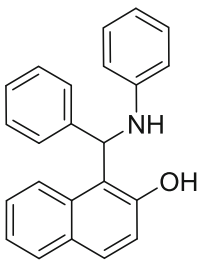
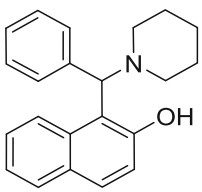
1-[(Phenylamino)(p-tolyl)methyl]naphthalen-2-ol (**14e**)

Colorless crystals; Yield 92 %; mp: 130–132 °C; FT-IR (KBr) ν 3419, 3342, 3052, 2966, 1602, 1497, 1230 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (3H, s, –CH_3), 4.17 (1H, bs, N–H), 6.12 (1H, s, methine-H), 6.73 (2H, d, J = 8 Hz, Ar–H), 6.89 (1H, t, J = 7.2 Hz, Ar–H), 7.11–7.13 (5H, m, Ar–H), 7.25–7.38 (4H, m, Ar–H), 7.71–7.78 (3H, m, Ar–H), 11.61 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.1, 61.4, 112.9, 115.2, 118.9, 120.4, 120.7, 121.7, 125.7, 126.8, 127.9, 128.0, 128.4, 128.8, 128.9, 130.4, 137.0, 137.3, 145.7, 155.0 ppm. Anal. Calcd. For $C_{24}H_{21}NO$: C, 84.92; H, 6.24; N, 4.13; Found: C, 84.64; H, 6.31; N, 4.06 %.

1-[(3,4-Dimethoxyphenyl)(phenylamino)methyl]naphthalen-2-ol (**14f**)

Light brown solid; Yield 95 %; mp: 139–141 °C; FT-IR (KBr) ν 3398, 3318, 3016, 2959, 1598, 1510, 1227, 1027 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.79 (3H, s, –OCH_3),

Table 5 Comparison of the present method with the recently reported methods

Aminonaphthols	Catalyst/solvent/condition	Time	Yield (%)	Ref.
 **14a**	$HClO_4$-SiO_2/solvent-free/125 °C	–	–[a]	[21]
	$Fe(HSO_4)_3$/solvent-free/85 °C	–	–[a]	[22]
	Zeolite H-BEA/solvent-free/125 °C	–	–[a]	[20]
	nanocrystallineMgO/water/rt	4 hr	20	[23]
	–/EtOH/reflux[b]	12 hr	75	[24]
	DMEA/solvent-free/50 °C	40 min	90	–[c]
 **16a**	$LiClO_4$/Et_2O/r.t.	60 min	70	[40]
	18-crown-6/$PhCH_3$/reflux[d]	12 hr	87	[41]
	–/EtOH/reflux[e]	12 hr	90	[24]
	non-ionic surfactant/water/rt	2.5 hr	90	[42]
	nanocrystallineMgO/water/rt	2 hr	90	[23]
	DMEA/solvent-free/50 °C	40 min	87	–[c]

[a] In this methodology desired product was not obtained
[b] In this methodology catalyst not used and the intermediate (oxazine derivatives) was hydrolyzed with acidic/basic solutions
[c] Our work
[d] One of the most valuable methodology which reported by Katritzky et al. and benzotriazole moiety from *N*-[α-(dialkylamino)alkyl]benzotriazoles used instead of preformed iminium salts and the reaction was done in two steps under refluxing toluene
[e] In this methodology catalyst was not used

3.81 (3H, s, –OCH_3), 4.19 (1H, bs, N–H), 6.11 (1H, s, methine-H), 6.75–6.79 (3H, m, Ar–H), 6.90 (1H, t, J = 7.3 Hz, Ar–H), 6.98–7.00 (2H, m, Ar–H), 7.10-7.16 (3H, m, Ar–H), 7.29 (1H, t, J = 7.3 Hz, Ar–H), 7.39 (1H, m, Ar–H), 7.72–7.81 (3H, m, Ar–H), 11.55 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.8, 61.5, 109.7, 110.4, 113.0, 115.2, 118.9, 119.3, 120.4, 120.7, 121.8, 125.7, 127.9, 128.1, 128.4, 128.9, 130.4, 132.5, 145.7, 148.1, 148.5, 155.0 ppm. Anal. Calcd. For $C_{25}H_{23}NO_3$: C, 77.90; H, 6.01; N, 3.63; Found: C, 77.63; H, 6.07; N, 3.58 %.

*1- [(2-Bromophenyl)(phenylamino)methyl]naphthalen-2-ol (***14g***)*

Light brown crystals; Yield 81 %; mp: 150–152 °C; FT-IR (KBr) ν 3425, 3344, 3057, 3018, 2960, 1621, 1601, 1494, 1224, 694 cm^{-1};[1] H NMR (400 MHz, $CDCl_3$): δ 4.07 (1H, bs, N–H), 6.49 (1H, s, methine-H), 6.79 (2H, d,J = 8.0 Hz, Ar–H), 6.91 (1H, t, J = 8.0 Hz, Ar–H), 7.12–7.17 (6H, m, Ar–H), 7.27–7.38 (2H, m, Ar–H), 7.57 (1H, d, J = 8.4 Hz, Ar–H), 7.66–7.69 (1H, m, Ar–H), 7.78 (2H, d, J = 8.8 Hz, Ar–H), 11.62 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 60.8, 111.8, 115.4, 118.9, 120.4, 121.0, 121.9, 123.5, 126.0, 127.3, 127.9, 128.0, 128.3, 129.3, 129.4, 130.4, 132.4, 138.0, 145.9, 155.9 ppm. Anal. Calcd. For $C_{23}H_{18}BrNO$: C, 68.33; H, 4.49; N, 3.46; Found: C, 68.06; H, 4.54; N, 3.51 %.

*6-Bromo-1-[(2-bromophenyl)(phenylamino)methyl] naphthalen-2-ol (***14h***)*

Pale yellow solid; Yield 85 %; mp: 163–165 °C; FT-IR (KBr) ν 3391, 3343, 3053, 2950, 1649, 1597, 1494, 1027, 755 cm^{-1};[1] H NMR (400 MHz, $CDCl_3$): δ 4.06 (1H, bs, N–H), 6.42 (1H, s, methine-H), 6.79 (2H, d, J = 8.0 Hz, Ar–H), 6.95 (1H, t, J = 8.0 Hz, Ar–H), 7.12–7.22 (6H, m, Ar–H), 7.43 (2H, m, Ar–H), 7.68–7.71 (2H, m, Ar–H), 7.94 (1H, s, Ar–H), 11.66 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 60.9, 112.3, 115.5, 115.7, 120.1, 121.3, 122.2, 123.4, 127.4, 128.4, 129.0, 129.23, 129.27, 129.4, 129.5, 129.8, 132.6, 137.8, 145.8, 156.3 ppm. Anal. Calcd. For $C_{23}H_{17}Br_2NO$: C, 57.17; H, 3.55; N, 2.90; Found: C, 56.91; H, 3.61; N, 2.94 %.

*1-[(4-Methoxyphenyl)(phenylamino)methyl]naphthalen-2-ol (***14i***)*

Light brown solid; Yield 92 %; mp: 270 °C (dec.); FT-IR (KBr) ν 3412, 3337, 3008, 2951, 1619, 1508, 1241, 821 cm^{-1};[1] H NMR (400 MHz, $CDCl_3$): δ 3.68 (3H, s, –OCH_3), 4.12 (1H, bs, N–H), 6.10 (1H, s, methine-H), 6.71 (2H, d, J = 8.2 Hz, Ar–H), 6.80 (2H, d, J = 8.5 Hz, Ar–H), 6.88 (1H, t, J = 7.3 Hz, Ar–H), 7.08–7.14 (3H, m, Ar–H), 7.24–7.37 (4H, m, Ar–H), 7.69–7.77 (3H, m, Ar–H), 11.54 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.2, 61.0, 113.1, 113.5, 115.2, 118.9, 120.4, 120.7, 121.7, 125.7, 127.9, 128.0, 128.2, 128.3, 128.8, 130.4, 132.1, 145.7, 154.9, 158.5 ppm. Anal. Calcd. For $C_{24}H_{21}NO_2$: C, 81.10; H, 5.96; N, 3.94; Found: C, 80.87; H, 5.98; N, 3.90 %.

*1-[(3-Chlorophenylamino)(phenyl)methyl]naphthalen-2-ol (***14j***)*

Colorless crystals; Yield 90 %; mp: 112–114 °C; FT-IR (KBr) ν 3375, 3337, 3062, 2925, 1595, 1476, 752 cm^{-1};[1] H NMR (400 MHz, $CDCl_3$): δ 4.13 (1H, bs, N–H), 6.16 (1H, s, methine-H), 6.62 (1H, dd, J = 8.0 Hz, J = 1.2Hz, Ar–H), 6.78 (1H, s, Ar–H), 6.88 (1H, d, J = 8.0 Hz, Ar–H), 7.05 (1H, t, J = 8.0 Hz, Ar–H), 7.14 (1H, d, J = 8.8 Hz, Ar–H), 7.29–7.41 (5H, m, Ar–H), 7.45 (2H, d, J = 7.0 Hz, Ar–H), 7.75–7.80 (3H, m, Ar–H), 10.88 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 61.4, 112.3, 113.0, 115.6, 118.9, 120.4, 120.8, 122.0, 125.9, 126.9, 127.7, 128.1, 128.2, 128.5, 129.2, 129.6, 130.4, 134.0, 139.6, 146.9, 154.8 ppm. Anal. Calcd. For $C_{23}H_{18}ClNO$: C, 76.77; H, 5.04; N, 3.89; Found: C 76.52; H, 5.11; N, 3.85 %.

*1-[(4-Methoxyphenylamino)(phenyl)methyl]naphthalen-2-ol (***14k***)*

Light Brown solid; Yield 80 %; mp: 117–119 °C; FT-IR (KBr) ν 3397, 3327, 3025, 2927, 1621, 1509, 1235, 821 cm^{-1};[1] H NMR (400 MHz, $CDCl_3$): δ 3.70 (3H, s, OCH_3), 4.23 (1H, bs, N–H), 6.11 (1H, s, methine-H), 6.70–6.76 (4H, m, Ar–H), 7.15 (1H, d, J = 8.8Hz, Ar–H), 7.28–7.39 (5H, m, Ar–H), 7.48 (2H, d, J = 7.2 Hz, Ar–H), 7.73–7.78 (3H, m, Ar–H), 11.98 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.5, 62.5, 112.7, 113.8, 116.8, 119.1, 120.3, 121.7, 125.7, 126.9, 127.5, 127.9, 128.0, 128.4, 128.9, 130.5, 139.1, 140.1, 153.9, 155.3 ppm. Anal. Calcd. For $C_{24}H_{21}NO_2$: C, 81.10; H, 5.96; N, 3.94; Found: C, 80.91; H, 5.92; N, 3.89 %.

*1-[(4-Nitrophenylamino)(phenyl)methyl]naphthalen-2-ol (***14l***)*

Yellow solid; Yield 95 %; mp: 154–156 °C; FT-IR (KBr) ν 3396, 3354, 3024, 2955, 1597, 1509, 1308, 1112, 768 cm^{-1};[1] H NMR (400 MHz, $CDCl_3$): δ 5.07 (1H, bs, N–H, disappeared in the presence of D_2O), 6.41 (1H, s, methine-H), 6.71 (2H, d, J = 8.8 Hz, Ar–H), 7.10 (1H, d, J = 8.8 Hz, Ar–H), 7.29–7.37 (4H, m, Ar–H), 7.43–7.46 (3H, m, Ar–H), 7.76–7.86 (3H, m, Ar–H), 8.02 (2H, d, J = 8.8 Hz, Ar–H), 11.67 (1H, bs, OH, disappeared in the presence of D_2O) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 58.1, 113.1, 113.7, 118.4, 120.6, 122.5, 125.0, 126.3, 126.5, 127.5, 128.2, 128.4, 128.5, 129.6, 130.6, 138.9, 139.7, 151.4, 153.1 ppm. Anal.

Calcd. For $C_{23}H_{18}N_2O_3$: C, 74.58; H, 4.90; N, 7.56; Found: C, 74.32; H, 4.95; N, 7.49 %.

*1-[(4-Fluorophenylamino)(phenyl)methyl]naphthalen-2-ol (***14m***)*

White solid; Yield 90 %; mp: 110–112 °C; FT-IR (KBr) ν 3397, 3339, 3023, 2962, 1602, 1503, 1229, 815, 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.14 (1H, bs, N–H), 6.11 (1H, s, methine-H), 6.69–6.72 (2H, m, Ar–H), 6.80–6.85 (2H, m, Ar–H), 7.14 (1H, d, J = 8.8 Hz, Ar–H), 7.27–7.39 (5H, m, Ar–H), 7.46–7.48 (2H, m, Ar–H), 7.73–7.78 (3H, m, Ar–H), 11.68 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 61.5, 112.9, 114.9, 115.3, 118.9, 120.4, 120.8, 121.8, 125.7, 126.9, 127.2, 127.4, 127.9, 128.1, 128.4, 128.9, 129.0, 130.5, 137.1, 137.4, 145.7, 155.1, 157.1, 159.6 ppm. Anal. Calcd. For $C_{23}H_{18}FNO$: C, 80.45; H, 5.28; N, 4.08; Found: C, 80.24; H, 5.26; N, 4.05 %.

*1-[(3,4-Dichlorophenylamino)(phenyl)methyl]naphthalen-2-ol (***14n***)*

Brown solid; Yield 90 %; mp: 123–125 °C; FT-IR (KBr) ν 3402, 3352, 3061, 2953, 1596, 1474, 1024, 749 cm^{-1};[1] H NMR (400 MHz, $CDCl_3$): δ 4.27 (1H, bs, N–H), 6.13 (1H, s, methine-H), 6.52 (1H, dd, J = 8.8 Hz, J = 2.4 Hz, Ar–H), 6.82 (1H, d, J = 2.4 Hz, Ar–H), 7.09–7.13 (2H, m, Ar–H), 7.29–7.33 (4H, m, Ar–H), 7.35–7.43 (3H, m, Ar–H), 7.72–7.77 (3H, m, Ar–H), 10.54 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 60.9, 114.2, 116.9, 118.7, 120.3, 122.1, 122.4, 126.0, 126.7, 126.8, 127.7, 128.1, 128.2, 128.4, 129.3, 129.9, 130.4, 131.9, 139.3, 145.2, 154.4 ppm. Anal. Calcd. For $C_{23}H_{17}Cl_2NO$: C, 70.06; H, 4.35; N, 3.55; Found: C, 69.85; H, 4.38; N, 3.53 %.

*1-[(4-Chlorophenyl)(3-chlorophenylamino)methyl]naphthalen-2-ol (***14o***)*

Brown solid; Yield 92 %; mp: 121–123 °C; FT-IR (KBr) ν 3398, 3345, 3063, 2964, 1597, 1484, 750 cm^{-1};[1] H NMR (400 MHz, $CDCl_3$): δ 4.25 (1H, bs, N–H), 6.12 (1H, s, methine-H), 6.56 (1H, d, J = 8.0 Hz, Ar–H), 6.72 (1H, s, Ar–H), 6.84 (1H, d, J = 8.0 Hz, Ar–H), 6.97 (1H, t, J = 8.0 Hz, Ar–H), 7.10 (1H, d, J = 8.8 Hz, Ar–H), 7.24 (2H, d, J = 8.4 Hz, Ar–H), 7.28–7.40 (4H, m, Ar–H), 7.71 (2H, d, J = 8.4 Hz, Ar–H), 7.75 (1H, d, J = 8.0 Hz, Ar–H), 10.69 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.9, 112.8, 115.3, 118.7, 120.2, 120.7, 122.1, 122.3, 126.0, 128.0, 128.1, 128.2, 128.4, 128.6, 129.4, 129.5, 130.2, 133.3, 133.9, 137.9, 146.6, 154.4 ppm. Anal. Calcd. For $C_{23}H_{17}Cl_2NO$: C, 70.06; H, 4.35; N, 3.55; Found: C, 69.81; H, 4.39; N, 3.53 %.

*1-[(4-Methoxyphenylamino)(p-tolyl)methyl]naphthalen-2-ol (***14p***)*

Brown solid; Yield 95 %; mp: 114–116 °C; FT-IR (KBr) ν 3400, 3338, 3012, 2958, 1604, 1508, 1251, 753 cm^{-1};[1] H NMR (400 MHz, $CDCl_3$): δ 2.40 (3H, s, $–CH_3$), 3.82 (3H, s, $–OCH_3$), 4.10 (1H, bs, N–H), 6.07 (1H, s, methine-H), 6.69–6.75 (2H, m, Ar–H), 6.92 (2H, d, J = 8.8 Hz, Ar–H), 7.14 (2H, d, J = 8.0 Hz, Ar–H), 7.24–7.27 (3H, m, Ar–H), 7.35 (2H, d, J = 8.0 Hz, Ar–H), 7.74–7.79 (3H, m, Ar–H), 11.67 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.6, 64.3, 83.4, 112.3, 115.3, 118.1, 122.1, 122.4, 124.3, 125.6, 126.9, 127.3, 128.1, 128.2, 128.4, 131.3, 132.1, 136.4, 141.8, 143.5, 151.9 ppm. Anal. Calcd. For $C_{25}H_{23}NO_2$: C, 81.27; H, 6.27; N, 3.79; Found: C, 81.09; H, 6.29; N, 3.75 %.

*1-[(4-Chlorophenyl)(4-fluorophenylamino)methyl]naphthalen-2-ol (***14q***)*

Colorless crystals; Yield 92 %; mp: 163–165 °C; FT-IR (KBr) ν 3431, 3354, 3060, 2960, 1623, 1505, 1220, 815, 771 cm^{-1};[1] H NMR (400 MHz, $CDCl_3$): δ 4.11 (1H, bs, N–H), 6.07 (1H, s, methine-H), 6.73 (2H, t, J = 8.4 Hz, Ar–H), 7.04–7.08 (2H, m, Ar–H), 7.21 (2H, d, J = 8.4 Hz, Ar–H), 7.31–7.35 (3H, m, Ar–H), 7.41 (2H, d, J = 8.4 Hz, Ar–H), 7.88 (3H, d, J = 8.8 Hz, Ar–H), 11.51 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 63.3, 111.5, 114.2, 114.5, 117.9, 121.8, 122.8, 125.9, 126.7, 127.1, 127.2, 127.7, 128.4, 128.6, 128.9, 129.5, 132.6, 132.7, 134.4, 140.0, 151.6, 155.0, 157.4, 159.9 ppm. Anal. Calcd. For $C_{23}H_{17}ClFNO$: C, 73.11; H, 4.54; N, 3.71; Found: C, 72.93; H, 4.57; N, 3.70 %.

*1-[(6-Methyl-2-pyridinylamino)(4-nitrophenyl)methyl]naphthalen-2-ol (***14r***)*

Pale yellow solid; Yield 93 %; mp: 160–162 °C; FT-IR (KBr) ν 3441, 3333, 3064, 2962, 1576, 1514, 1340, 1261, 1098, 802 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (3H, s, CH_3), 5.97 (1H, s, NH, disappeared in the presence of D_2O), 6.46 (1H, d, J = 8.4 Hz, Ar–H), 6.51 (1H, d, J = 7.2 Hz, Ar–H), 7.04 (1H, s, methine-H), 7.22–7.26 (3H, m, Ar–H), 7.34–7.40 (2H, m, Ar–H), 7.54 (2H, d, J = 8.4 Hz, Ar–H), 7.70 (1H, d, J = 8.4 Hz, Ar–H), 7.75–7.77 (1H, m, Ar–H), 8.09 (2H, d, J = 8.4 Hz, Ar–H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.7, 50.4, 105.6, 112.5, 118.1, 119.5, 121.8, 121.9, 122.6, 125.4, 126.2, 128.3, 128.8, 129.3, 130.5, 138.0, 145.7, 148.9, 153.9, 154.7, 156.0 ppm; Anal. Calcd. For $C_{23}H_{19}N_3O_3$: C, 71.67; H, 4.97; N, 10.90; Found: C, 71.48; H, 4.99; N, 10.87 %.

*1-[2-Furyl(phenylamino)methyl]naphthalen-2-ol (***14s***)*

White solid; Yield 92 %; mp: 161–163 °C; FT-IR (KBr) ν 3412, 3364, 3010, 2949, 1509, 1029, 760 cm^{-1}; ^{1}H NMR

(400 MHz, $CDCl_3$): δ 4.05 (1H, bs, N–H), 6.81 (1H, s, methine-H), 6.91–6.94 (1H, m, Ar–H), 7.08 (2H, d, J = 8.4 Hz, Ar–H), 7.20 (1H, m, Ar–H), 7.31–7.42 (4H, m, Ar–H), 7.73 (2H, d, J = 8.4 Hz, Ar–H), 7.80 (2H, d, J = 8.0Hz, Ar–H), 7.91 (2H, d, J = 8.4 Hz, Ar–H), 11.08 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 58.3, 112.9, 115.4, 119.0, 121.2, 122.4, 125.7, 126.2, 126.4, 127.9, 128.1, 128.6, 129.1, 130.3, 134.7, 139.3, 147.5, 152.1 ppm. Anal. Calcd. For $C_{21}H_{17}NOS$: C, 76.10; H, 5.17; N, 4.23; Found: C, 75.88; H, 5.16; N, 4.18 %.

*1-[(5-(Benzyloxy)-4-oxo-4H-pyran-2-yl)(phenylamino) methyl]naphthalen-2-ol (***14t***)*

Pale yellow solid; Yield 95 %; mp 123–125 °C; FT-IR (KBr) ν 3391, 3324, 3061, 2925, 1637, 1601, 1506, 1209, 751 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.90 (1H, bs, N–H), 5.03 (2H, s, benzylic-H), 6.16 (1H, s, methine-H), 6.48 (1H, s, pyrone-H), 6.74 (2H, d,J = 8.0 Hz, Ar–H), 6.88 (1H, t, J = 7.2 Hz, Ar–H), 7.14–7.18 (3H, m, Ar–H), 7.33–7.38 (6H, m, Ar–H), 7.50 (1H, t, J = 8.0 Hz, Ar–H), 7.58 (1H, s, pyrone-H), 7.72 (1H, d, J = 8.8 Hz, Ar–H), 7.80 (1H, d, J = 8.0 Hz, Ar–H), 7.86 (1H, d, J = 8.8 Hz, Ar–H), 10.24 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 70.8, 112.9, 114.4, 118.6, 119.8, 120.1, 122.2, 126.5, 126.6, 127.5, 127.8, 128.0, 128.3, 128.5, 130.1, 130.7, 134.4, 136.2, 140.2, 144.7, 146.2, 154.5, 174.1 ppm. Anal. Calcd. For $C_{29}H_{23}NO_4$: C, 77.49; H, 5.16; N, 3.12; Found: C, 77.28; H, 5.20; N, 3.10 %.

*1-(Phenyl(pipyridin-1-yl)methyl)naphthalen-2-ol (***16a***)*

White solid; Yield 87 %; mp: 192–194 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21–1.65 (6H, m, CH_2), 1.89–2.07 (2H, m, –NCH), 2.65 (1H, m, –NCH), 3.29 (1H, m, –NCH), 5.06 (1H, s, methine-H), 7.14–7.25 (5H, m, Ar–H), 7.34 (1H, t,J = 7.6 Hz, Ar–H), 7.54 (2H, m, Ar–H), 7.64 (1H, d, J = 8.8 Hz, Ar–H), 7.67 (1H, d, J = 8.8 Hz, Ar–H), 7.82 (1H, d, J = 8.4 Hz, Ar–H), 14.06 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.1, 25.0, 50.8, 53.7, 71.0, 115.1, 118.9, 119.9, 121.2, 122.1, 125.3, 126.6, 126.8, 127.5, 127.8, 128.1, 128.3, 131.3, 138.6, 154.4 ppm; Anal. Calcd. For $C_{22}H_{23}NO$: C, 83.24; H, 7.30; N, 4.41; Found: C, 83.08; H, 7.35; N, 4.36 %.

*1-[(2-Chlorophenyl)(pipyridin-1-yl)methyl]naphthalen-2-ol (***16b***)*

White solid; Yield 87 %; mp: 150–152 °C; FT-IR (KBr) ν 3415, 3059, 3011, 2935, 1622, 1470, 1034, 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21–1.76 (6H, m, CH_2), 2.26–2.36 (2H, m, –NCH), 2.62 (1H, m, –NCH), 3.32 (1H, m, –NCH), 5.83 (1H, s, methine-H), 7.09–7.16 (3H, m, Ar–H), 7.19–7.23 (1H, m, Ar–H), 7.34–7.38 (2H, m, Ar–H), 7.59–7.61 (1H, m, Ar–H), 7.66–7.69 (2H, m, Ar–H), 7.78 (1H, d, J = 8.4 Hz, Ar–H), 14.30 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.9, 24.9, 25.3, 48.3, 53.8, 65.2, 114.8, 119.1, 120.2, 121.5, 125.6, 127.0, 127.4, 127.7, 128.1, 128.4, 128.5, 129.9, 131.7, 133.2, 135.8, 155.5 ppm; Anal. Calcd. For $C_{22}H_{22}ClNO$: C, 75.09; H, 6.30; N, 3.98; Found: C, 74.86; H, 6.32; N, 3.93 %.

*1-[(4-Nitrophenyl)(pipyridin-1-yl)methyl]naphthalen-2-ol (***16c***)*

Yellow solid; Yield 88 %; mp: 177–179 °C; FT-IR (KBr) ν 3387, 3068, 3017, 2937, 1622, 1529, 1349, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23–1.69 (6H, m, CH_2), 2.00–2.16 (2H, m, –NCH), 2.61 (1H, m, –NCH), 3.33 (1H, m, –NCH), 5.19 (1H, s, methine-H), 7.15 (1H, d, J = 8.8 Hz, Ar–H), 7.21–7.25 (1H, m, Ar–H), 7.38 (1H, t, J = 8.0 Hz, Ar–H), 7.66–7.78 (5H, m, Ar–H), 8.09 (2H, d, J = 8.0Hz, Ar–H), 13.57 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.9, 24.9, 51.4, 53.4, 70.1, 113.9, 119.0, 119.4, 121.7, 123.0, 125.7, 127.7, 128.1, 128.7, 129.1, 130.9, 146.2, 146.4, 154.4 ppm; Anal. Calcd. For $C_{22}H_{22}N_2O_3$: C, 72.91; H, 6.12; N, 7.73; Found: C, 72.68; H, 6.15; N, 7.66 %.

*1-[(3-Nitrophenyl)(pipyridin-1-yl)methyl]naphthalen-2-ol (***16d***)*

Yellow solid; Yield 85 %; mp: 169–171 °C; FT-IR (KBr) ν 3362, 3061, 3013, 2937, 1619, 1525, 1349, 767 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22–1.69 (6H, m, CH_2), 2.13 (2H, m, –NCH), 2.62 (1H, m, –NCH), 3.66 (1H, m, –NCH), 5.19 (1H, s, methine-H), 7.16 (1H, d, J = 8.8Hz, Ar–H), 7.23 (1H, t, J = 7.2 Hz, Ar–H), 7.38 (1H, d, J = 7.2 Hz, Ar–H), 7.42 (1H, d, J = 7.2 Hz, Ar–H), 7.69 (2H, t, J = 8.8 Hz, Ar–H), 7.78 (1H, d, J = 8.8 Hz, Ar–H), 7.93 (1H, m, Ar–H), 8.04 (1H, d, J = 8.0 Hz, Ar–H), 8.40 (1H, s, Ar–H), 13.57 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.9, 24.9, 51.3, 53.6, 70.1, 114.0, 119.1, 119.4, 121.7, 122.0, 122.9, 125.8, 127.7, 128.1, 129.0, 130.9, 133.9, 141.0, 154.5 ppm; Anal. Calcd. For $C_{22}H_{22}N_2O_3$: C, 72.91; H, 6.12; N, 7.73; Found: C, 72.73; H, 6.16; N, 7.68 %.

*1-[(Naphthalen-2-yl)(pipyridin-1-yl)methyl]naphthalen-2-ol (***16e***)*

Light brown solid; Yield 88 %; mp 240 °C (dec.); FT-IR (KBr) ν 3443, 3014, 2950, 1619, 1384, 1021, 760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25–1.69 (6H, m, CH_2), 2.00 (1H, m, –NCH), 2.21 (1H, m, –NCH), 2.66 (1H, m, –NCH), 3.42 (1H, m, –NCH), 5.26 (1H, s, methine-H), 7.17–7.20 (2H, m, Ar–H), 7.34 (1H, t, J = 7.6 Hz, Ar–H), 7.41–7.43 (2H, m, Ar–H), 7.65–7.68 (2H, m, Ar–H), 7.73 (3H,

m, Ar–H), 7.82 (1H, m, Ar–H), 7.91–7.96 (2H, m, Ar–H), 14.14 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.1, 25.0, 50.2, 52.9, 70.5, 114.7, 118.7, 120.2, 121.4, 122.3, 124.8, 125.2, 125.4, 126.1, 127.5, 127.6, 127.8, 128.3, 128.7, 128.9, 131.3, 133.6, 134.3, 136.3, 153.9 ppm; Anal. Calcd. For $C_{26}H_{25}NO$: C, 84.98; H, 6.86; N, 3.81; Found: C, 84.72; H, 6.87; N, 3.77 %.

*1-[Morpholino(phenyl)methyl]naphthalen-2-ol (**16f**)*

White solid; Yield 92 %; mp: 174–1766 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.24–2.41 (3H, m, –NCH), 3.09 (1H, m, –NCH), 3.58–3.81 (4H, m, –OCH), 5.09 (1H, s, methine-H), 7.14–7.27 (5H, m, Ar–H), 7.37 (1H, t, J = 7.2 Hz, Ar–H), 7.55 (2H, m, Ar–H), 7.65–7.69 (2H, m, Ar–H), 7.83 (1H, d, J = 8.4Hz, Ar–H), 13.18 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 50.4, 52.8, 65.8, 70.8, 114.0, 118.7, 199.9, 121.5, 125.5, 127.1, 127.6, 127.8, 128.7, 131.2, 137.5, 153.6 ppm; Anal. Calcd. For $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39; Found: C, 78.71; H, 6.67; N, 4.36 %.

*1-[(2-Chlorophenyl)(morpholino)methyl]naphthalen-2-ol (**16g**)*

White solid; Yield 83 %; mp: 163–165 °C; FT-IR (KBr) ν 3421, 3054, 2966, 1619, 1460, 1114, 748 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (1H, m, –NCH), 2.56–2.74 (2H, m, –NCH), 3.12 (1H, m, –NCH), 3.54-3.89 (4H, m, –OCH), 5.89 (1H, s, methine-H), 7.11–7.17 (3H, m, Ar–H), 7.24 (1H, t, J = 7.2 Hz, Ar–H), 7.37–7.41 (2H, m, Ar–H), 7.61–7.65 (1H, m, Ar–H), 7.68–7.71 (2H, m, Ar–H), 7.81 (1H, d, J = 8.4 Hz, Ar–H), 13.38 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 48.1, 52.9, 65.1, 65.7, 66.3, 113.9, 118.9, 120.3, 121.8, 125.8, 127.1, 127.7, 127.8, 128.5, 128.6, 129.0, 129.9, 131.7, 133.4, 134.9, 154.7 ppm; Anal. Calcd. For $C_{21}H_{20}ClNO_2$: C, 71.28; H, 5.70; N, 3.96; Found: C, 71.10; H, 5.73; N, 3.90 %.

*1-[(3-Chlorophenyl)(morpholino)methyl]naphthalen-2-ol (**16h**)*

Colorless crystals; Yield 82 %; mp: 160–162 °C; FT-IR (KBr) ν 3430, 3060, 3014, 2964, 1622, 1469, 1119, 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26–2.44 (3H, m, –NCH), 3.07 (1H, m, –NCH), 3.61-3.82 (4H, m, –OCH), 5.05 (1H, s, methine-H), 7.09-7.16 (2H, m, Ar–H), 7.24 (1H, t, J = 7.6 Hz, Ar–H), 7.32 (1H, d, J = 8.0 Hz, Ar–H), 7.39 (1H, d, J = 8.0 Hz, Ar–H), 7.49 (1H, m, Ar–H), 7.67–7.71 (3H, m, Ar–H), 7.78 (1H, d, J = 8.4 Hz, Ar–H), 12.98 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 50.5, 52.7, 65.7, 70.2, 113.3, 118.8, 119.6, 121.7, 125.7, 126.6, 127.7, 127.9, 129.0, 129.5, 130.3, 130.7, 131.0, 139.8, 153.6 ppm; Anal. Calcd. For $C_{21}H_{20}ClNO_2$: C, 71.28; H, 5.70; N, 3.96; Found: C, 71.06; H, 5.75; N, 3.94 %.

*1-[(4-Chlorophenyl)(morpholino)methyl]naphthalen-2-ol (**16i**)*

Brown solid; Yield 89 %; mp: 155–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.16–2.49 (3H, m, –NCH), 3.09 (1H, m, –NCH), 3.61–3.84 (4H, m, –OCH), 5.09 (1H, s, methine-H), 7.14 (1H, d, J = 8.8 Hz, Ar–H), 7.23–7.27 (3H, m, Ar–H), 7.39 (1H, t, J = 7.6 Hz, Ar–H), 7.49–7.51 (2H, m, Ar–H), 7.67–7.74 (2H, m, Ar–H), 7.77 (1H, d, J = 8.8 Hz, Ar–H), 13.05 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 50.4, 52.8, 65.7, 70.1, 113.6, 118.7, 119.7, 121.7, 125.7, 127.7, 127.9, 128.7, 128.9, 129.3, 131.0, 132.9, 136.1, 153.5 ppm; Anal. Calcd. For $C_{21}H_{20}ClNO_2$: C, 71.28; H, 5.70; N, 3.96; Found: C, 71.02; H, 5.76; N, 3.92 %.

*1-[(4-(Dimethylamino)phenyl)(morpholino)methyl]naphthalen-2-ol (**16j**)*

White solid; Yield 83 %; mp: 135–137 °C; FT-IR (KBr) ν 3479, 3052, 3006, 2960, 1615, 1521, 1117, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.25-2.51 (3H, m, –NCH), 2.86 (6H, s, $-CH_3$), 3.06 (1H, m, –NCH), 3.61–3.82 (4H, m, –OCH), 5.03 (1H, s, methine-H), 6.59 (2H, d, J = 8.4 Hz, Ar–H), 7.13 (1H, d,J = 8.8 Hz, Ar–H), 7.19–7.24 (1H, m, Ar–H), 7.34–7.39 (3H, m, Ar–H), 7.64–7.69 (2H, m, Ar–H), 7.83 (1H, d, J = 8.8 Hz, Ar–H), 13.30 (1H, bs, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.3, 50.2, 52.9, 65.9, 70.3, 111.3, 114.7, 118.6, 120.2, 121.4, 122.3, 124.8, 125.4, 127.8, 128.3, 128.9, 131.3, 149.1, 153.5 ppm; Anal. Calcd. For $C_{23}H_{26}N_2O_2$: C, 76.21; H, 7.23; N, 7.73; Found: C, 76.03; H, 7.28; N, 7.69 %.

Acknowledgments We thank research affairs of the University of Tabriz for financial support.

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